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THE AROMATIC DIAZO-COMPOUNDS AND THEIR TECHNICAL APPLICATIONS

BY

K. H. SAUNDERS

M.C., M.A.(Cantab.), B.Sc.(Lond.), F.R.I.C.

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PREFACE TO THE SECOND EDITION

In preparing this edition the author has attempted a compromise between the needs of students and professional chemists, and hence the work cannot be entirely satisfactory to either. Such is the nature of compromises. For the unconventional arrangement of the references the author makes no apology, though the chronological form is in fact a by-product of the late war, since these lists of literature references and tables of patents were prepared in 1939 in duplicate and dispersed, so that should the author's home be destroyed the means to reconstruct his files would remain. In this form the lists were found so useful for reference that the form has been preserved at the expense of breaking the sequence of reference numbers in the text. Nor are all the references used in the text, since this would have made the work too unwieldy, but chemists interested in detail can rapidly check off the references in any scientific library for information they need. Papers with good references to yet earlier literature are specially marked, but chemists are warned that these lists are NOT complete, for it is impossible to include all references to diazo-compounds in the literature. It is hoped that no key reference has been omitted.

The author acknowledges communications on diazo chemistry from a number of correspondents, and some of the information so received has been embodied in this edition. Also he has been much helped to a better knowledge of the work of Italian chemists by the fortune of war that brought Dr. Jolles to the same laboratory in I.C.I., Dyestuffs Division, Blackley.

Finally, the author is indebted to the Directors of the Dyestuffs Division of Imperial Chemical Industries, Ltd., for the use of the facilities of the library at Blackley, without which the labour of marshalling the literature would have been enormously increased, and to the library staff, who have taken great pains to procure copies of publications which are scarce in Great Britain. He also wishes to record the assistance received from his colleague, Mr. H. Swann, B.Sc., A.R.C.S., who kindly volunteered to read the page proofs.

Hale, Altrincham,
Cheshire.

December, 1947.

CONTENTS

CHAP. PAGE

I. INTRODUCTION—THE FORMATION OF DIAZO-COMPOUNDS, THE DIRECT AND INDIRECT METHODS, DIAZOTISATION IN CONCENTRATED ACIDS, THE METHODS OF WITT, GRIESS, AND KNOEVENAGEL—DIAZOTISATION AND TETRAZOTISATION OF DIAMINES—DIAZO-OXIDES, DIAZOIMINES, AND NITROSOACYLARYLAMIDES — DIAZONIUM SALTS — FAILURE OF THE DIAZOTISATION REACTION—THEORIES OF THE DIAZOTISATION REACTION—OTHER REACTIONS PRODUCING DIAZO-COMPOUNDS—HETEROCYCLIC DIAZO-COMPOUNDS 1

II. THE STABILITY OF DIAZO-COMPOUNDS IN THE SOLID STATE AND IN SOLUTION—STABILITY OF DIAZO-COMPOUNDS—STABILISED DIAZO-COMPOUNDS—VARIATION OF STABILITY WITH pH—RELATION BETWEEN pH AND CONSTITUTION OF DIAZO-COMPOUNDS—CONSTITUTIONS OF COMMERCIAL ICE COLOUR BASES 61

III. REACTIONS OF THE DIAZO-COMPOUNDS. INTRODUCTION—CLASSIFICATION AND GENERAL DISCUSSION OF REACTION MECHANISMS. REACTIONS OF CLASS A—HALOGENATION, NITRATION, SULPHONATION—EXCHANGE OF SUBSTITUENTS BETWEEN ARYL NUCLEUS AND SOLVENT—EXCHANGE OF ANIONS WITH SUBSTITUENTS OF THE ARYL NUCLEUS 105

IV. REACTIONS OF THE DIAZO-COMPOUNDS, CLASS B—METALLIC DIAZOTATES AND DIAZOANHYDRIDES—DIAZO ETHERS—DIAZOCYANIDES—DIAZOSULPHONATES—DIAZOPERHALIDES—DIAZOSULPHIDES . . . 126

V. REACTIONS OF THE DIAZO-COMPOUNDS, CLASS C—TRIAZENS—OXIDATION PRODUCTS—REDUCTION PRODUCTS—ARYLAZIDES, AND OTHER PRODUCTS OF INTERACTION WITH NITROGEN-CONTAINING BASES—S-AZO-COMPOUNDS 157

VI. REACTIONS OF THE DIAZO-COMPOUNDS, CLASS C (*contd.*)—THE FORMATION OF AZO-COMPOUNDS BY THE COUPLING REACTION. INTRODUCTION—COUPLING OF PHENOLS, NAPHTHOLS, AMINO-COMPOUNDS, PROTEINS, *m*-AMINO-*p*-CRESOL, AMINONAPHTHOLSULPHONIC ACIDS—PREVENTION OF MIXED COUPLINGS—COUPLING OF SUBSTANCES HAVING REACTIVE METHYLENE GROUPS, NITROPARAFFINS, PHENOL ETHERS, HYDROCARBONS—ELIMINATION OF SUBSTITUENTS—MIGRATION OF THE DIAZO-GROUP—EFFECT OF PYRIDINE—CONFIGURATION OF AZO-COMPOUNDS—KINETICS OF THE COUPLING REACTION—MECHANISM OF THE COUPLING REACTION 194

VII. REACTIONS OF THE DIAZO-COMPOUNDS, CLASS D. FORMATION OF RING COMPOUNDS—CINNOLINE—INDAZOLE—BENZTRIAZOLE—BENZTRIAZINE — THIODIAZOLE — PHENANTHRENE — FLUORENE AND FLUORENONE — DIBENZFURAN, DIBENZTHIOPHEN — CARBAZOLE — OTHER RING COMPOUNDS 241

CHAP. PAGE

VIII. REACTIONS OF THE DIAZO-COMPOUNDS, CLASS E. DERIVATIVES FORMED BY REPLACEMENT OF THE DIAZO-GROUP. REPLACEMENT BY HYDROGEN — HALOGENS — NITROGEN-CONTAINING GROUPS — OXYGEN—CARBON-CONTAINING GROUPS—SULPHUR, SELENIUM, TELLURIUM—ARSENIC, ANTIMONY, BISMUTH, PHOSPHORUS—METALS 268

IX. THE ANALYTICAL DETERMINATION OF DIAZO-COMPOUNDS—DETERMINATION OF ARYLAMINES BY DIAZOTISATION—DETERMINATIONS WITH DIAZO-COMPOUNDS, GENERAL, BIOCHEMICAL—DETERMINATION OF NITROUS ACID—THERMOCHEMISTRY OF DIAZO-COMPOUNDS—DIAZO-COMPOUNDS AS EXPLOSIVES—MISCELLANEOUS APPLICATIONS OF DIAZO-COMPOUNDS 339

X. THE ACTION OF LIGHT ON DIAZO-COMPOUNDS—DIAZOTYPES . . 357

XI. THEORIES OF THE CONSTITUTION OF THE DIAZO-COMPOUNDS . . 378

AUTHOR INDEX 403

PATENT INDEX (BRITISH, UNITED STATES, GERMAN) . . . 417

SUBJECT INDEX 423

LIST OF ABBREVIATIONS

A	British Chemical Abstracts A.
Agfa	Aktiengesellschaft für Anilinfabrikation in Berlin.*
Amer. Cyanamid	American Cyanamid Co.
Am. J. Pharm.	American Journal of Pharmacy.
Anales Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Angew. Chem.	Angewandte Chemie. Changed from Z. angew. Chem. in 1932.
Anilinokras. Prom.	Anilinokrasotschnaja Promischlennosti.
Anm.	Deutsches Reichs-Patent Anmeldung.
Ann.	Justus Liebig's Annalen der Chemie.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Trop. Med. & Parasitol.	Annals of Tropical Medicine and Parasitology.
Arch. Pharm.	Archiv der Pharmazie.
B	British Chemical Abstracts B.
B.A.S.F.	Badische Anilin-und Soda-Fabrik, Ludwigshaven a Rhein.*
Bayer	Farbenfabriken vorm. Frich. Bayer & Co., Elberfeld.*
Ber.	Berichte der Deutschen Chemischen Gesellschaft. All references are to the B series unless otherwise stated.
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
B.I.O.S.	British Intelligence Objectives Sub-Committee. H.M. Stationery Office.
Boll. Soc. Ital. Biol. sper.	Bolletino della Società Italiana di Biologia sperimentalla.
B.P.	British Patent.
Brit. J. Expt. Med.	British Journal of Experimental Medicine.
Brit. Med. J.	British Medical Journal.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chemie biologique.
Bull. Soc. chim.	Bulletin de la Société Chimique de France.
Bull. Soc. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Cain	The Chemistry and Technology of the Diazo-compounds. Arnold, London, 1920.
Can. J. Res.	Canadian Journal of Research.
Can. Med. Assoc. J.	Canadian Medical Association Journal.
Cassella	Cassella & Co., Mainkur.*
Cent.	Centralblatt.
C.A.	Chemical Abstracts.
Chem. & Ind.	Chemistry & Industry.
Chem. Listy	Chemické Listy pro Vědu a Průmysl.
Chem. News	Chemical News.
Chem. Revs.	Chemical Reviews.
Chem. Wkbld.	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
C.I.	Colour Index of the Society of Dyers & Colourists (1st ed.).
C.I.O.S.	Combined Intelligence Objectives Sub.-Committee. H.M. Stationery Office.
C.r.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Deut. Arch. klin. Med.	Deutsches Archiv für klinische Medizin.
D.R.P.	Deutsches Reichs-Patent.

Du Pont	E.I. Du Pont de Nemours & Co.
F.I.A.T.	Field Information Agency, Technical. U.S. Group Control Council for Germany.
F.P.	French Patent.
Fr.	Friedländer's Forschritte der Teerfarbenfabrikation.
Gazz.	Gazzetta chimica italiana.
Gen. Aniline	General Aniline Works.
Griesheim	Farbwerk Griesheim-Electron, Offenbach am Main.*
Helv. Chim. Acta	Helvetica Chimica Acta.
Heyden	Chemische Fabrik von Heyden, Dresden.
I.C.I.	Imperial Chemical Industries, Ltd., London.
I.G.	Interessen Gemeinschaft A.-G., Frankfort.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
I.R.I.	Institute of the Rubber Industry.
J. Am. C.S.	Journal of the American Chemical Society.
J. appl. Chem. Russ.	Journal of Applied Chemistry, Russia.
J. Austral. Chem. Inst.	Journal of the Australian Chemical Institute.
J. Biol. Chem.	Journal of Biological Chemistry.
J.C.S.	Journal of the Chemical Society of London.
J. Exp. Med.	Journal of Experimental Medicine.
J. Indian C.S.	Journal of the Indian Chemical Society.
J. Infect. Diseases	Journal of Infectious Diseases.
J. Org. Chem.	Journal of Organic Chemistry.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Tech. Coll.	Journal of the Royal Technical College, Glasgow.
J.S.C.I.	Journal of the Society of Chemical Industry.
J.S.D. & C.	Journal of the Society of Dyers & Colourists.
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences.
Klin. Wochschr.	Klinische Wochenschrift.
Kuhlmann	Compagnie National de Matières Colourantes et Manufacture de Produits chimiques du Nord Reunis Établissements Kuhlmann.
Lectures	Sir Robert Robinson, Two Lectures on an " Outline of an Electrochemical Theory of the Course of Organic Reactions." Institute of Chemistry of Great Britain and Ireland, London, 1932.
Mellor	Comprehensive Treatise on Inorganic Chemistry.
M.L.B.	Farbwerke Höchst, vorm. Meister, Lucius, and Bruning.*
Monats.	Monatshefte für Chemie.
Nat. Aniline	National Aniline Co., U.S.A.
Org. Synth.	Organic Syntheses.
Pharma.	Pharma Chemical Corp., U.S.A.
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. Journ.	Photographic Journal.
Proc.	Proceedings of the Chemical Society.
R.A.L.	Atti della Reale Accademia dei Lincei.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Russ. P.	Russian Patent.
S.C.I.	Society of Chemical Industry in Basle.
Sidgwick	Organic Chemistry of Nitrogen. Taylor and Baker. Oxford, 1936.
St. Denis	Société anonyme des Matière Colorantes et Produits Chimiques de Saint-Denis.
Sw.P.	Swiss Patent.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Textilber.	Melliand's Textilberichte.
U.S.P.	United States Patent.
Weiler-ter-Meer	Weiler-ter-Meer & Co., Uerdingen.*

Zavod Lab. . . .	Zavodskaja Laboratorija.
Z. anal. Chem. . .	Zeitschrift für analytische Chemie.
Z. angew. Chem. . .	,, angewandte Chemie
Z. anorg, Chem. . .	,, anorganische und allegemeine Chemie.
Z. Elektrochem. . .	,, Elektrochemie.
Z. Farb. Ind. . . .	,, Farben-Industrie.
Z. Immunitäts forsch. und exp. Therap. . .	,, Immunitäts forschung und experimentell Therapie.
Z. für klin. Med. . .	,, klinische Medizin.
Z. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. wiss. Phot. . . .	Zeitschrift für wissenschaftliche Photographie.

* Firms marked with an asterisk became members of the I.G.

NOMENCLATURE

Ac $COCH_3$.
AQ the anthraquinone nucleus, which may be substituted.
Ar any aromatic nucleus which may or may not be substituted.
Bz COC_6H_5.
Et C_2H_5.
Me CH_3
Ph C_6H_5

* denotes a free radical, *e.g.*, Ar* is a free aryl radical.

† References marked thus are summary papers or papers containing useful lists of references to the earlier literature.

The name " diazo " or " diazo-compound " is used as a generic name to cover all forms in which these compounds can exist.

" Diazonium " and " diazonium salts " refers to the cations of strong salt-forming bases.

" Diazotate " refers to acidic forms of which the free acids are the diazohydroxides.

The evolution of the system of nomenclature and the structures by which the various forms are differentiated is explained in Chapter XI.

The somewhat obsolescent terms " positive " and " negative " are retained for substituents which are electron-repelling and electron-attracting respectively.

GENERAL REFERENCES TO THE LITERATURE OF THE DIAZO-COMPOUNDS

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CHAPTER I

THE FORMATION OF DIAZO-COMPOUNDS

INTRODUCTION—THE FORMATION OF DIAZO-COMPOUNDS BY THE DIRECT AND INVERTED METHODS, DIAZOTISATION IN CONCENTRATED ACIDS, THE METHODS OF WITT, GRIESS, AND KNOEVENAGEL—DIAZOTISATION AND TETRAZOTISATION OF DIAMINES—DIAZO-OXIDES, DIAZO-IMINES, AND NITROSOACYLARYLAMIDES—DIAZONIUM SALTS—FAILURE OF THE DIAZOTISATION REACTION—THEORIES OF THE DIAZOTISATION REACTION—OTHER REACTIONS PRODUCING DIAZO-COMPOUNDS—HETEROCYCLIC DIAZO-COMPOUNDS.

Introductory. In the whole realm of Organic Chemistry there is no reaction the occurrence of which can be relied upon with more certainty than the formation of a diazo-compound by the action of nitrous acid on a primary aromatic amine. The certainty and smoothness with which this reaction can be accomplished under appropriate conditions, coupled with the high reactivity of the resulting diazo-compound, make it one of the utmost value, alike to the manufacturer of chemicals on a large scale and to the chemist engaged in research. The initiating ripple of the whole tide of human energy which has since been expended in the study of these compounds was released at Marburg in the year 1858, when Peter Griess first had in hand a specimen of diazotised picramic acid and recognised it as a member of a hitherto unknown class of chemical compounds.

This discovery, like all others, did not arise by spontaneous generation from the loom of time. Some knowledge of the reaction of nitrous acid with the amino-group was already in existence, and it was known that aminobenzoic acid could be converted into hydroxybenzoic acid by the action of warm aqueous nitrous acid, for which reason Kolbe had suggested to Griess that in like manner picramic acid might be converted into a hydroxy-derivative. Griess, however, altered the experimental conditions slightly by using nitrous acid in the cold in alcoholic solution, and so obtained a substance which had none of the properties to be expected from the substance sought, and by acting on other primary arylamines in the same way he was soon convinced that he had discovered a reaction of general applicability. Griess thought that the previous investigators had failed to detect the new substances because they had worked in aqueous solutions, whereas he, thanks to the use of alcohol as a solvent, had isolated them in the crystalline state.

At the time of Griess's discovery the labours of organic chemists were directed towards elucidating the nature of radicals and the effect of

substitution on such entities, and he gave to his new compounds the name "diazo," because he believed that they owed their genesis to the replacement of two hydrogen atoms by two atoms of nitrogen in the aromatic radicals from which they were derived. Griess soon laid down the main lines of the chemistry of the diazo-compounds, but as his method of performing the operation of diazotisation was cumbersome (cf. p. 16), and as his view as to the constitution of the diazo-compounds was erroneous, it is not expedient to describe the early work in detail at this point. Instead, the more profitable course will be followed of setting out the various means now known by which the diazo-compounds may be formed, and in the course of so doing the contribution made by Griess will be seen in its proper relationship to the chemistry of the aromatic diazo-compounds, which will alone be the theme of this book.

A number of distinct ways of producing the diazo-compounds are known, but one of them so dominates the others that they are of trifling importance by comparison, and they are discussed later (cf. p. 50). The dominant reaction by which the diazo-compounds are formed is expressed in its simplest and most general way as follows :—

$$ArNH_2 + HX + HNO_2 = ArN_2X + 2H_2O$$

where Ar is a mono- or poly-nuclear aromatic radical which may be substituted and HX is a strong monobasic acid or its equivalent.

The exigencies arising from the differing properties of arylamines and the purposes to which the reaction products are to be put have caused the evolution of a number of variations in the operating technique. The nitrous acid may arise from different sources, the association of amine and acid may be altered, while the reaction may be carried out in aqueous solution or in solution or suspension in mineral acids or organic solvents. But whatever device may be employed the fundamental sequence of chemical changes will be found to be expressed by the above equation.

In Table I is brought into a small compass a survey of methods of diazotisation which will afterwards be enlarged in detail, but it will be realised that the size of this volume forbids any attempt to cover even a small fraction of the examples of diazotisation mentioned in the literature. For that purpose such works as that of Beilstein must be consulted. Nor will any attempt be made to discuss or describe special details in the conduct of diazotisation on the manufacturing scale. Suffice it to remark that this is effected substantially in the same manner as in the laboratory, except that wooden vessels or vessels having linings such as tiles or rubber are employed. The high pitch of efficiency necessary in technical working is reached by attention in the case of each amine to the details of temperature, speed of agitation, rate of addition of nitrite, presence of metals, and so forth. A number of works dealing with this aspect of the matter are included in the list of general references (p. xi).

TABLE I

Methods of Producing Diazo-Compounds Based on the Fundamental Reaction :—$ArNH_2 + HX + HNO_2 = ArN_2X + 2H_2O$

Reaction technique.	Sphere of employment.
1. A solution of a metallic nitrite is added to a cold solution of the arylamine in aqueous mineral acid :— $ArNH_2 + 2HX + NaNO_2 = ArN_2X + NaX + 2H_2O$ The " Direct Method ".	(i) Strongly basic amines giving salts readily soluble in aqueous mineral acid. (ii) Amines sulphonated sufficiently to be soluble in acid solution.
2. Mixed alkaline solutions of a metallic nitrite and a salt of a sulphonated or carboxylated arylamine are run into excess of cold mineral acid :— $Ar(NH_2)(SO_3Na) + NaNO_2 + 3HX = Ar(N_2X)(SO_3H) + 2NaX + 2H_2O$ The " Inverted Method ".	(i) Amino-acids, *e.g.*, sulphanilic, naphthionic, aminobenzoic acid. (ii) Some weakly basic amines.
3. The arylamine is dissolved in a concentrated acid (sulphuric acid, phosphoric acid, glacial acetic acid) and diazotised with nitrosylsulphuric acid :— $ArNH_2 + NO{\cdot}SO_4H = ArN_2{\cdot}SO_4H + H_2O$	For weakly basic amines.
4. The arylamine is dissolved in nitric acid and meta-bisulphite is added, thus producing nitrous acid which diazotises the amine. The method of Witt.	For weakly basic amines not easily nitrated or oxidised.
5. The arylamine salt is suspended or dissolved in water or alcohol and treated with gaseous nitrogen trioxide. The method of Griess.	Now rarely used; allows solid diazonium salts to be isolated from alcohol.
6. The arylamine salt is dissolved in water, or suspended in alcohol or inert solvent and treated with an alkyl nitrite or an ester of nitrous acid, *e.g.*, nitrosyl chloride :— $ArNH_2,HX + Alkyl{\cdot}O{\cdot}NO = ArN_2X + Alkyl{\cdot}OH + H_2O$ The method of Knoevenagel.	For effecting diazotisation so that the solid diazonium salt may be isolated.

METHOD I. THE "DIRECT METHOD"

The selection of this method to occupy the foremost place and the bestowal upon it of the name " direct " are both entirely arbitrary, but may be justified by the consideration that this is the method which it is always preferable to employ if the basicity of the arylamine is sufficient. The use of the method is limited by the basicity of the amine because at least a proportion of the amine present must be in solution as salt in the aqueous acid, since the nitrous acid reacts only with the dissolved amine.

Simplicity, speed, and cheapness are the advantages to be gained by its use, but it is not suitable when isolation of the diazo-compound in the solid state is in view, except when stable diazo-compounds (cf. p. 69) are to be made. This is the method, therefore, on which extensive manufacturing processes are based, and in which, on account of the instability of the diazo-compounds, their isolation is neither desirable nor necessary, as the synthetic reactions for which they are employed are carried out in the same solution in which diazotisation has previously taken place. Of the scores of tons of diazo-compounds manufactured daily by this reaction, not one solid particle is seen by the workers.

Martius [1] was the chemist to whom the introduction of sodium nitrite as the source of nitrous acid was due. The liberation of nitrous acid by the action of mineral acid and its attack on the arylamine salt occur with great rapidity (cf. p. 45). If the basicity of the amine salt is insufficient for all to be dissolved at the commencement of the reaction, then it is important that the portion remaining as a solid phase should be as finely divided as possible, so that it can be dissolved as fast as that in solution is converted into the diazo-salt. The fine grinding of α-naphthylamine sulphate for this purpose has been patented,[5] but usually the necessary fineness can be attained by dissolving the base in one equivalent of hot dilute acid, then cooling and adding the remainder of the acid with agitation, when the amine salt is precipitated in a sufficiently fine form. The use of dispersing agents which do not interfere with the reaction has been patented for the purpose of obtaining amines, ordinarily difficult to diazotise, in the finest possible state of division.[19, 27] The base can also be dissolved in an amide inert to nitrous acid, such as dimethylformamide, $HCO{\cdot}NMe_2$.[26]

There is nothing to be gained by conducting the diazo-reaction any slower than the maximum rate at which the amine is found to react with nitrous acid. The reaction takes place with liberation of heat, and this may prevent the reaction speed being utilised to the full, as it may not be possible to withdraw heat quickly enough to prevent undue rise in temperature. On the other hand, to proceed too slowly is to run the risk of a diazo-solution contaminated with decomposition products. There are cases, too, where delay results in the appearance of diazoamino-compounds due to combination of the diazo-compound first formed with unchanged amine. When once formed some diazoamino-compounds cannot be split back to diazo-compound and amine, even by the addition of much extra acid, and to prevent their formation the nitrite is added all at once to the amine solution, which is cooled by floating ice. Cooling by ice in this manner is often known as internal cooling. *p*-Nitroaniline is an example where retarded diazotisation by the slow addition of nitrite results in the formation of a diazoamino-compound.

Diazotisation can rarely, if ever, be brought about with only the theoretical two equivalents of acid indicated by the above equation,

because there is always risk that diazoamino-compounds may appear unless the solution remains fully acid until completion of the reaction, and also because diazonium salts are particularly unstable in solutions which are not fully acid. Two and a quarter to two and a half equivalents is the minimum amount usually allowed, and more is required as the amine diminishes in basicity. If an organic acid is used, more is necessary than the amount which will suffice if a highly ionised mineral acid is employed in the same reaction. Altschul [4] examined this point, and found that in diazotising aniline eleven equivalents of acetic acid are needed before diazotisation becomes complete. He also discovered that if only one equivalent of mineral acid is used the amount of diazo-compound is related to the concentration of the amine salt and increases rapidly as the concentration of the latter becomes greater, but a 10% solution of aniline hydrochloride affords only 32% of benzenediazonium chloride and the remainder is diazoaminobenzene.

The above remarks may be better appreciated by a few examples.

Diazotisation of 4-*Chloro*-o-*toluidine.* (2 : 4 : 1-$NH_2 \cdot C_6H_3ClMe$; "*Fast Red KB Base.*")

The hydrochloride of the base (17·7 g. = 0·1 mol.) is dissolved in hot water (50 c.c.) and the contents of the beaker are allowed to cool with stirring. Concentrated hydrochloric acid (12 c.c.) is then added, and precipitates the hydrochloride as a sludge. The beaker is surrounded by ice and water and stirring continued until the temperature falls below 5°. Then a solution made by dissolving dry technical sodium nitrite (7 g. = 0·1 mol.) in water (12 c.c.) is run in slowly either down the side or under the surface, at such speed that the temperature does not rise above 5°. The hydrochloride passes smoothly into solution as diazotisation proceeds. When all the nitrite has been added, a drop of the pale yellow solution should still show mineral acidity on Congo paper and a pale blue spot on starch-iodide paper. If the spot on starch-iodide is negative, extra nitrite solution must be added drop by drop until the test is positive; if so strong as to indicate an excess of nitrous acid, a solution of the hydrochloride of the base must be added until the reaction on starch-iodide is just positive. This final operation is frequently spoken of as "balancing". The chlorodiazotoluene solution so obtained should be clear, pale yellow, though the technical product may be darker and need filtering from flocculent impurities.

The following points should be noted :—

1. The molecular weight of sodium nitrite is 69, but analysis of good-quality material usually shows its molecular weight to lie between 70 and 71. It should be dried in a steam oven, ground, and kept in a stoppered bottle. All metallic nitrites are slightly deliquescent.

2. The end-point of the reaction is detected with starch-iodide paper, which shows the appearance of an excess of nitrous acid. Cadmium iodide is usually considered to be the iodide which affords the most sensitive papers. It must not be forgotten that mineral acid in moderate concentration also causes the paper to turn blue, and when diazotising in strongly acid solution, care must be taken not to confound the mark left by acid with that left by nitrous acid. The colour left by the latter develops more sharply and is richer than that left by acid, but a few blanks will soon give a working comparison in any case where doubt has

arisen. Spotting the paper through a pinch of salt is a device sometimes used to ensure a clear mark; a better mark is sometimes shown on paper which has been wetted.

While starch iodide is universally used to detect the end-point of the diazotisation reaction almost any means of detecting nitrous acid could be made to serve (cf. p. 349), and the end-point can also be determined potentiometrically (cf. p. 342). In a method described by Chervinskaya [21] a dilute solution of a dye containing a secondary amino-group is added to a solution of a strongly basic amine dissolved in aqueous acid. Metanil Yellow (C.I. 138) will serve the purpose. Excess of sodium nitrite is then added and the excess of nitrous acid is back-titrated with more amine solution until the indicator turns pink. Bucherer and Schmidt [12] detected the end-point in the diazotisation of naphthionic acid by adding a drop to a solution of sodium acetate; on completion of diazotisation no red colour is formed due to coupling with unchanged naphthionic acid. On the face of it such methods have no advantage over direct determination of the end-point with starch-iodide paper.

Excess of nitrous acid may be destroyed instead of removing by balancing. Urea was for long used for this purpose, but sulphamic acid, $NH_2 \cdot SO_2 \cdot OH$, is now an article of commerce, reacts far more rapidly than urea, and is generally used in the laboratory. It has been used in leather dyeing where improved results are obtained if every trace of nitrous acid is removed before developing a diazotised dye.[25]

The procedure described above is the standard process for the simple strongly basic monoamines such as aniline, the toluidines, xylidines, aminophenol ethers, and also the monochloroanilines. The diamines of the benzidine series also belong to this group, as do α- and β-naphthylamine. The optimum temperature is 0—2° for the simple bases, 0—5° for the *m*-halogenated bases, 10—12° for benzidine bases, naphthylamines, and *o*- and *p*-halogeno bases.

p-Nitroaniline is a representative of those bases in which diazotisation by the direct method is made more difficult by negative groups in the *ortho* or *para* positions to the amino-group and, owing to the importance which it had for dyeing Para Red, a considerable literature relating to its diazotisation exists.[8, 10] For diazotising this amine both the direct method and the inverted method, to be described later, can be used. The process published by Schwalbe is as follows :—

p-Nitroaniline (21·0 g. = 0·15 mol.) is dissolved by warming with 10N-hydrochloric acid (50 c.c.) diluted with water (50 c.c.). When dissolved the solution is cooled to 5—10° by pouring on ice (200 g.). A solution of sodium nitrite (11·5 g.) in water (80 c.c.) is then poured in all at once and the mixed solutions are stirred until a clear solution is obtained.

Amines which can be dealt with in the above way are those having *ortho*- or *para*-nitro-groups and the various chloronitroamines used in ice

colour dyeing. As the basicity becomes less the amount of hydrochloric acid must be increased, until just that concentration can be found at which the amine will dissolve in the hot acid. If that point is overshot, then the acid salts out the hydrochloride, and lumps very resistant to the action of nitrous acid are formed. 2 : 5-Dichloroaniline, which falls in this category, can be smoothly diazotised as follows [7, 9] :—

10N-Hydrochloric acid (50 c.c.) is diluted to 210 c.c. and brought to the boil when 2 : 5-dichloroaniline (16·5 g. = 0·1 mol.) is added and boiling continued until the molten base has dissolved. The solution is cooled with stirring until the temperature of the thick white mass of crystals has fallen to 10°. A solution of sodium nitrite (7 g.) is then added over thirty seconds with strong stirring, when almost all the solid passes into solution. A slight permanent reaction on starch-iodide paper must remain or the stable diazoamino-compound will form. After five minutes the pale yellow solution is filtered from a little flocculent matter, and is ready for use.

Bases such as the above can also be diazotised by grinding with concentrated hydrochloric acid in a stone edge-runner mill and adding solid nitrite in portions to the thick slurry which liquefies as diazotisation proceeds and finally provides a concentrated solution of the diazo-compound. A specification [14] of meagre detail broadly claims the production of dry benzenediazonium sulphate by pushing the above procedure to the limit; solid sodium nitrite is added to a paste of aniline sulphate made from the base and a mixture of 93% sulphuric acid and aqueous hydrochloric acid (98 : 2 parts), and the sodium sulphate formed takes up the water produced in the reaction, thus leaving a dry mass on completion of diazotisation. An inert liquid can be used as a diluent.

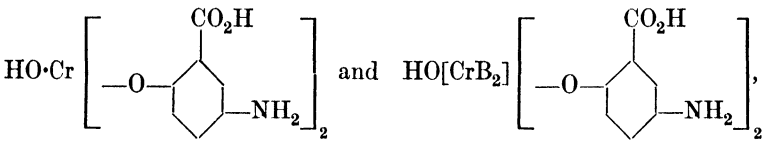
When the diazo-compound is sparingly soluble as well as the amine, a circumstance which sometimes occurs among the aminoazo-bases, then there is no avoidance of a prolonged reaction time. *p*-Aminoazobenzene is typical of this group and its diazotisation is described by Erban and Mebus [10] :—

Aminoazobenzene (19·7 g. = 0·1 mol.) is ground in a warm mortar with boiling water (40 c.c.), and then with the addition of 10N-sulphuric acid (40 c.c.) until the mass is Bordeaux red. 50 c.c. more of water can be added before dissociation of the salt sets in. The contents are washed out of the mortar with water (200 c.c.) which cools the suspension to 28°, and diazotisation is then performed with sodium nitrite (7·8 g.) dissolved on water (50 c.c.) and dropped in so slowly that no nitrous acid is lost. After twenty hours' stirring the vessel is filled with a red crystalline mass of the diazonium sulphate. (For directions for the diazotisation of *o*-aminoazotoluene in hydrochloric acid, cf. p. 74.)

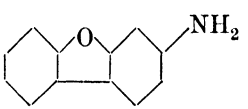
Griess [2] diazotised *p*-aminoazobenzene sulphonic acid by the direct method in aqueous hydrochloric acid, and noted that the resultant sparingly soluble brick-red diazo-compound is free from chlorine ions on account of internal salt formation. The *o*-aminoazo-bases in which the amino-group is *ortho* to the azo link are often difficult to diazotise because they are oxidised by the nitrous acid to a triazole. Nevertheless, Zincke and Lawson [3] diazotised 2-amino-5 : 4-dimethylazobenzene by the direct method, whilst the same method has been used for bases like 2'-chloro-

4′-nitro-2-amino-4-methoxy-5-methylazobenzene, which afford brown ice colours with 2 : 3-hydroxynaphthoic arylamides.[18]

The literature abounds with examples of diazotisation by the direct method, but before passing on, a few random examples of special cases may be noted. Acylation of the amino-group usually prevents diazotisation, but sulphamic acids, $ArNH{\cdot}SO_3H$, and nitramic acids, $ArNH{\cdot}NO_2$, suffer scission by aqueous nitrous acid and are diazotised,[13, 20] as are also phosphamic acids, $ArNH{\cdot}PO_3H_2$. The disulphuric ester of leuco-β-aminoanthraquinonesulphamic acid is diazotised with scission of the sulphamic acid, but without hydrolysis of the ester,[15] as is also the corresponding free amino-compound.[23] Aminoleucoindigotin sulphuric esters can also be diazotised.[24] Co-ordinated chromium compounds,



where B is a non-diazotisable organic base, can be tetrazotised without breaking down the complex,[16] and aminoaryl lead compounds of the type $Ph_3Pb{\cdot}C_6H_4{\cdot}NH_2$ can be diazotised without damage.[28] Aminostyrene-maleic anhydride resins are diazotisable.[29] There is usually no advantage to be gained by the presence of additional metal salts during direct diazotisation, but 3-amino-4-methoxyphenyl-1-trifluoromethylsulphone [3 : 4 : 1-$NH_2{\cdot}C_6H_3(OMe){\cdot}SO_2{\cdot}CF_3$] is diazotised by dissolution in acetone with zinc chloride and aqueous hydrochloric acid; ice is added to the solution followed by nitrite solution.[22] A few diazonium salts are so stable that they can be diazotised at a raised temperature. One such is 2-aminodibenzfuran,



The amine (38·6 g.) is boiled with water (300 c.c.) and 20% sulphuric acid (150 c.c.), cooled to 50—60°, and diazotised with aqueous nitrite added dropwise. The solution is filtered, and conc. sulphuric acid (~250 c.c.) is added, and on cooling the diazonium sulphate separates in yellow needles.[17]

While it is the amine on which interest is usually fixed in diazotisation, it must not be forgotten that both the acid and nitrite are variables which can sometimes be employed to effect. Instead of sodium nitrite, both calcium nitrite and barium nitrite [6] have been used, the latter because by diazotising with the exact amount of sulphuric acid the barium and sulphuric acid are both removed from the solution as barium sulphate, leaving only the diazonium salt. Lastly, Wallach [11] made *m*-xylidine nitrite, 1 : 3 : 4-$C_6H_3Me{\cdot}NH_2,HNO_2$, by acting on the amine hydrochloride

with sodium nitrite, and on dissolving in water and adding acid he obtained diazoxylene.

When one equivalent of nitrite is added to an acid solution of *p*-aminobenzylamine or 1-*p*-aminophenyl-2-aminopropane

(p-NH_2·C_6H_4·CH_2·CHMe·NH_2)

the aromatic amino-group is diazotised while the aliphatic amino-group remains intact [3a, 30].

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METHOD 2. THE "INVERTED METHOD"

Since many of the monoaminoarylcarboxylic and -sulphonic acids are sparingly soluble in water, and so can be acted on but slowly by nitrous acid, whilst the derived diazo salts are also sparingly soluble, diazotisation by the direct method may soon come to a halt. The reactivity of the amino-acid may be increased by precipitating it in a fine state of division by adding mineral acid to a solution of one of its soluble salts, but a better alternative is to add the nitrite to the alkaline solution of the amino-acid and then run the mixture steadily into the chilled acid. Hence arises the name

" inverted method." Diazotisation usually takes place instantly, and the insoluble substance which separates is the diazo-compound.

Diazotisation of sulphanilic acid :—

Sodium sulphanilate (23 g. = 0·1 mol.) and sodium nitrite (7 g.) are dissolved in water (120 c.c.), cooled with ice, and then poured with stirring into sulphuric acid (sp. gr. 1·81, 17 c.c.) diluted with water (100 c.c.). The diazo-compound is precipitated, and reaction is complete almost as soon as the last of the solution is added to the acid.[2]

Another convenient method of diazotising sulphanilic acid is to stir the ground acid into a solution of one equivalent of sodium nitrite, when it dissolves almost completely. Upon addition of one equivalent of hydrochloric acid the diazo-compound is precipitated.

Reumuth [5] dissolves sulphanilic acid (50 g.) and caustic potash (25 g.) in water (250 c.c.), cools, and mixes with a solution of sodium nitrite (20 g.) in water (200 c.c.); to this is added drop by drop an ice-cooled mixture of water (40 c.c.) and hydrochloric acid (sp. gr. 1·16, 80 c.c.) when the diazo-compound is precipitated.

The diazobenzene-*p*-sulphonic acid can be collected and dried, but it is a dangerous substance (cf. p. 61).

The aminobenzoic acids and aniline disulphonic acids can be diazotised in the same way, as can also naphthylaminesulphonic acids such as naphthionic acid.

The inverted method is also serviceable for weakly basic amines. Erban and Mebus [1] used it for a number of such amines, including the nitroanilines, *o*-nitro-*p*-phenetidine, *o*-nitro-*p*-toluidine, aminoazobenzene, and aminoazotoluene. They called the method " Diazotisation as nitrite paste," since they ground the amine to a paste with the nitrite solution.

Diazotisation of p-*nitroaniline* [3, 4] :—

p-Nitroaniline (14 g. = 0·10 mol.) is pasted with water (28 c.c.) and sodium nitrite (7·5 g.) to a smooth slurry and poured on ice (30 g.) and concentrated hydrochloric acid (30 c.c.). The whole is stirred vigorously and filtered after ten minutes. If sulphuric acid is used diazotisation is slower.[1]

This method has the advantage over the direct one that it gives a more concentrated solution, and can be carried out more quickly, as no heating is required, while the acid requirement can be cut down 0·1 mol. excess over the theoretical.[3]

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METHOD 3. DIAZOTISATION OF WEAKLY BASIC AMINES IN CONCENTRATED ACIDS

When the basicity of an amine is so much reduced that it is no longer soluble in aqueous acids because its salts suffer complete hydrolytic dissociation, the use of such media for diazotisation becomes impossible.

Weakly basic amines are soluble only in concentrated or anhydrous acids, and diazotisation must perforce be carried out in such solutions. Concentrated sulphuric acid is the solvent which is most commonly employed both in the laboratory and on the large scale. The nitrous acid is introduced either by powdering in the solid nitrite with stirring or as a nearly saturated aqueous solution, or it may be first dissolved in the concentrated sulphuric acid, thus forming a solution containing nitrosylsulphuric acid, into which the amine may be stirred in the dry state or which may be added to a solution of the amine in concentrated sulphuric acid. The progress of diazotisation can be followed by allowing drops of the reaction solution to fall into water, the reaction being complete when flocks of the free base no longer appear. Starch-iodide paper is rarely useful in these cases. The reaction mixture is finally diluted either by pouring on ice or by adding lumps of ice until sufficiently diluted to pour into water without undue rise in temperature.

Diazotisation of 2 : 4-*Dinitroaniline* :—

Dry sodium nitrite (7·0 g.) is slowly added with stirring to sulphuric acid (sp. gr. 1·80, 150 c.c.), allowing the temperature to rise, and if necessary raising it to 70° to ensure complete dissolution. The dinitroaniline (16·7 g. = 0·1 mol.) is added over about twenty minutes at 30—35°, and then the solution is stirred for two hours while the temperature is allowed to fall. When a test drop with water shows only a slight precipitate of base the mixture is poured on ice, allowed to stand for impurities to settle, and filtered.

The same process can be used for 2 : 6-dichloro-4-nitroaniline [22] and for 4-nitro-2-cyanoaniline.[24]

This technique required several decades for its evolution. Thus Friedländer [2] dissolved 2 : 4-dinitro-1-naphthylamine in concentrated sulphuric acid, added a little water and diazotised by passing in nitrous gases. Claus and his co-workers [1, 4] dissolved the amine in concentrated sulphuric acid, then added water or ice until precipitation of the base just commenced and diazotised with a solution of nitrite, finally diluting with ice or water. Up to 30% of unchanged base may remain for filtration, but in this way they successfully diazotised 3 : 5-dinitro-*p*-toluidine [3 : 5 : 1 : 4-$(NO_2)_2{\cdot}C_6H_2Me{\cdot}NH_2$], and 2 : 4-dibromo-6-nitroaniline (6 : 2 : 4 : 1-$NO_2{\cdot}C_6H_2Br_2{\cdot}NH_2$); this method has also been used for diazotising aposafranine,[3] 1-aminoanthraquinone,[9] and 3- and 4-amino-1 : 2-dihydroxyanthraquinone ("α-", and "β-aminoalizarine").[12] Jacobson[13] found that pentabromoaniline diazotised as a precipitate of the sulphate in 70% sulphuric acid with excess of nitrous acid gives pentabromobenzenediazonium nitrate (cf. also p. 24).

The method given above for 2 : 4-dinitroaniline is now often used for amines of the anthraquinone series, for which purpose it was introduced by Gattermann,[15] who dropped nitrosylsulphuric acid into the solution of the amine in concentrated sulphuric acid, but he also used a method, previously outlined by Lauth [7] for the diazotisation of 1-aminoanthraquinone, in which ice is added to the solution of the base in concentrated

sulphuric acid until the sulphate is precipitated. This is then collected, suspended in water and, after adding nitrite, stirred until all the salt has dissolved, which requires about twenty hours for 1-aminoanthraquinone sulphate.

Schoutissen [20] failed to diazotise *p*-aminobenzaldehyde in concentrated sulphuric acid and came to the conclusion that the nitrosylsulphuric acid does not liberate nitrous acid with sufficient ease, and in order to weaken the link he diluted the solution with a weaker acid, such as phosphoric acid. This is an improvement which has rendered possible the smooth diazotisation of the most intractable amines, including *p*-amino benzaldehyde.[23]

Diazotisation of 2 : 6-*Dibromo*-4-*nitroaniline* (Schoutissen) :—

The base (3 g.) is dissolved in sulphuric acid (sp. gr. 1·84, 15 c.c.) and cooled to 0°. To this is added nitrosylsulphuric acid made by dissolving sodium nitrite (0·99 g.) in sulphuric acid (15 c.c.). Then with stirring there is run in phosphoric acid (60 c.c., sp. gr. 1·70) at 0°. After half an hour urea (2 g.) is added and the reaction mixture is poured on ice, when a clear diazo-solution is obtained directly.

2 : 6-Dichloro-4-nitroaniline and 2 : 4 : 6-trinitro-5-amino-anisol and -phenetol can be diazotised in the same way.

There is collateral evidence for the soundness of Schoutissen's modification, which has the same effect as adding water, but without precipitating the amine salt. When diazotisation is performed in completely anhydrous sulphuric acid the indications are that reaction proceeds only slowly; for example, Blangy [18] required twenty-four hours for the diazotisation of picramide [2 : 4 : 6 : 1-$(NO_2)_3C_6H_2 \cdot NH_2$]. As Witt [14] first pointed out, the greater part of the diazotisation takes place while the sulphuric acid is being diluted by ice or water, and nitrous acid makes its presence evident if the dilution is carried out too quickly or too soon after mixing the components. Schoutissen found that after aniline and nitrosylsulphuric acid have been allowed to remain in contact for some time, the addition of concentrated nitric acid causes the product on dilution to be *m*-nitrobenzenediazonium sulphate. But, as Griess discovered, benzenediazonium salts cannot be nitrated in the cold, and therefore Schoutissen argues that aniline must be present unchanged in the sulphuric acid solution with the nitrosylsulphuric acid, and therefore that it nitrates normally in the *meta* position, whilst diazotisation does not occur until the subsequent dilution. This method of diazotising by diluting the solution of the amine in nitrosylsulphuric acid was used by Reverdin and Dresel [10] to diazotise 3 : 5-dinitro-4-aminophenol [3 : 5 : 4 : 1-$(NO_2)_2C_6H_2(NH_2) \cdot OH$], and anthraquinone-1 : 2-*iso*oxazoles are also diazotised by diluting the solution in nitrosylsulphuric acid with water so as to keep the temperature at 40—60°, thus producing a solution of 1-diazoanthraquinone-2-carboxylic acid.[19]

Misslin,[17] in a study of methods of diazotising weakly basic amines, dissolved the base in glacial acetic acid and added nitrosylsulphuric acid

to the solution, noting that diazotisation does not commence until all the base has been converted into sulphate.

Diazotisation of 2 : 6-*dinitro*-4-*chloroaniline* [2 : 6 : 4 : 1-$(NO_2)_2C_6H_2Cl{\cdot}NH_2$] :—

To a solution of the amine (6·6 g.) in glacial acetic acid (250 g.) at 15° is added dropwise a solution of sodium nitrite (2·1 g.) in sulphuric acid (sp. gr. 1·84, 160 g.). As the nitrosylsulphuric acid is added the temperature may be lowered, and finally a clear yellow syrup at 3° is obtained. It can be diluted with ice and used for synthetic reactions.

Hodgson and Walker [21] also diazotised weakly basic amines, such as 2- and 4-nitro-1-naphthylamine and 2 : 4-dinitro-1-naphthylamine, by dissolving the base in glacial acetic acid and adding the solution to nitrosylsulphuric acid, the reversal of Misslin's process.

General Method for Diazotising Weakly Basic Amines :—

A solution of the base in hot glacial acetic acid (12 c.c. for each 1 g. of base) is rapidly cooled to room temperature and gradually stirred into a solution of sodium nitrite in sulphuric acid (sp. gr. 1·84, 7 c.c. for each 1 g. of $NaNO_2$). This solution is made by adding finely powdered nitrite to the acid with vigorous stirring, raising the temperature to 70° until dissolution is complete and cooling to room temperature. The removal of the precipitate of sodium hydrogen sulphate is optional. The addition of the acetic acid solution is carried out below 20° with 10% excess of nitrosylsulphuric acid.

In a further variation of the method Hodgson and Turner [29] hydrolysed 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide with concentrated sulphuric acid, then mixed with nitrosylsulphuric acid and poured the whole into glacial acetic acid, thus obtaining a solution of 1 : 6-dinitronaphthalene-2-diazonium sulphate.

Solid diazonium sulphate can be precipitated from a solution prepared by the Hodgson–Walker method by adding ether.[30]

Since it is sometimes desirable to have the diazonium chloride or bromide rather than the sulphate, recourse must be had to diazotisation in concentrated hydrochloric acid or hydrobromic acid, and if the amine in question is not of too low basicity, this operation can be carried out. Claus and Wallbaum [4] diazotised 2 : 3 : 5 : 6-tetrabromoaniline in 40% aqueous hydrochloric acid at — 10° and 2 : 5 : 6-tribromo-4-nitroaniline and 4 : 5 : 6-tribromo-2-nitroaniline in 42% hydrobromic acid; they also used mixtures of these acids with glacial acetic acid for diazotising 2 : 3 : 4 : 6-tetrabromoaniline and 2 : 3 : 6-tribromo-4-nitroaniline respectively. Because diazotisation may be slow and nitrous acid may be lost as gas during the long period of stirring, Seidler [6] proposed to carry out the reaction under pressure, but there is nothing to be gained in doing this. The amines of the anthraquinone series can be diazotised in hydrochloric acid,[5, 8, 11] and Schaarschmidt [16] took advantage of the fact that the anthraquinone diazonium salts are of good stability, and so carried out the reaction with increased speed at a raised temperature.

Diazotisation of 1-*Aminoanthraquinone* :—

The amine is obtained first in a finely-divided state by dissolution in concentrated sulphuric acid, pouring into water, collecting, and washing the base (liberated by

hydrolysis of the sulphate) free from acid. By mixing with concentrated hydrochloric acid it is converted into the greyish-white hydrochloride, and diazotised by running an equivalent of sodium nitrite solution under the surface with stirring at 30—40°. Completion of the reaction is detected by diluting a drop of the reaction solution with water, all the amine being diazotised when red flocks, due to hydrolysis of the unchanged amine hydrochloride, no longer appear. The crude diazonium chloride is poured into fifteen times its volume of water at 85—90°, the solution is filtered, and salt is added to throw out the pure anthraquinone-1-diazonium chloride in shining, pale brownish-yellow plates.

A convenient test-tube method for converting weakly basic amines into the diazonium chloride consists in first preparing a solution of cold nitrous acid by adding concentrated hydrochloric acid (about 3 c.c.) to ice (10 g.) in a stout boiling tube; the temperature falls to below — 10°, and on adding 2N-sodium nitrite solution (1 c.c.) the transient blue solution becomes a pale brown from which very little nitrous acid escapes. To this the amine (0·05—0·1 g.) dissolved in hot glacial acetic acid or formic acid (at most 5 c.c. should suffice) is added all at once and the tube is shaken strongly. Diazotisation is usually immediate and complete because the amine is precipitated in finely-divided form in the presence of excess of nitrous acid. This method is not easy to carry out on a much larger scale without special apparatus, because of the difficulty of obtaining sufficiently good mixing of the acetic acid solution with the nitrous acid and ice.

Dissolution in organic bases is another way which has been tried to overcome the solubility difficulties of weakly basic amines. Battegay and Boehler [26] dissolved β-anthramine in pyridine, added hydrochloric acid followed by nitrite, which slowly converts the precipitated β-anthramine hydrochloride into anthracene-β-diazonium chloride. de Milt and Van Zandt [25] dissolved the bases in pyridine, quinoline, or *iso*quinoline, and added the solution to nitrosylsulphuric acid; among other bases they thus diazotised 2 : 6-dichloro-4-nitroaniline, 3-nitro-4-aminodiphenyl, and 3-aminophenanthrene (pyridine) and 4 : 6-dibromo-2-nitroaniline (quinoline). Lothrop [28] queried their diazotisation of picramide in *iso*quinoline.

Diazotisation in concentrated sulphuric acid can follow another operation in the same solvent. Thus 2-chloro- or 2-bromo-4-nitroaniline can be nitrated in mixed acid, then diazotised, and on dilution there is obtained a solution of 6-chloro- or -bromo-2 : 4-dinitrodiazobenzene.[27]

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METHOD 4. THE METHOD OF WITT

The principle of this method is to use concentrated nitric acid as the solvent for the amine, and at the same time by the action of a reducing agent to derive from it the nitrous acid necessary for diazotisation.[3] The reducing agent most appropriate for this purpose is a metabisulphite, the requisite quantity of the sodium salt being derived from the equation :—

$$Na_2S_2O_5 + 2HNO_3 = Na_2S_2O_7 + 2HNO_2$$

The metabisulphite may be either added to the nitric acid solution of the amine, or the amine and metabisulphite may be mixed and slowly stirred into the nitric acid.

Diazotisation of 3 : 5-*dinitro*-o-*toluidine* [3 : 5 : 1 : 2-$(NO_2)_2C_6H_2Me{\cdot}NH_2$] :—

The dinitrotoluidine (9·8 g. = 0·05 mol.) is mixed with sodium metabisulphite (5·9 g.) and added with cooling to fuming nitric acid (sp. gr. 1·5, 50 c.c.). The solution is set aside for at least half an hour, and then poured into water (100 c.c.) mixed with ice (200 g.). The solution is filtered, and is ready for use.

The method is not suitable for technical purposes, but it is sometimes useful for experimental purposes, and it has been studied from that viewpoint. It is useless for easily-oxidised amines, while there is, of course, danger of nitration, which Elion[4] encountered when diazotising 3 : 5-dibromo-4-amino-benzoic acid, -benzaldehyde, and -acetophenone. In each case the carboxyl, aldehyde, or ketone group at 1 was replaced by a nitro-group, so that the product was 2 : 6-dibromo-4-nitrobenzenediazonium nitrate. In 3 : 5-dibromo-2-aminobenzoic acid the bromine atom at 5 is replaced by the nitro-group, so that the product is 3-bromo-5-nitro-2-diazobenzoic acid. Fuchs[5] said that such results are due to departure from the rigid conditions laid down by Witt, but Elion[6] replied that the determining factor is the concentration of the nitric acid.

The amino-compound itself can act as reducing agent for the nitric

acid, being thus in part destroyed and in part diazotised. Thus Stenhouse [1] obtained a good yield of the diazo-derivative of picramic acid by acting on it with concentrated nitric acid alone.

Mention should also be made that Möhlau [2] showed that benzenediazonium chloride can be made by reducing aniline nitrate with zinc and hydrochloric acid :—

$$PhNH_2,HNO_3 + Zn + 3HCl = PhN_2Cl + ZnCl_2 + 3H_2O$$

Knecht [7] brought about diazotisation in a similar way, using titanous chloride as the reducing agent :—

$$ArNH_2,HCl + HNO_3 + 2HCl + 2TiCl_3 = ArN_2Cl + 2TiCl_4 + 3H_2O$$

The latter reaction fails when reducible groups, such as the nitro-group, are present in the aromatic nucleus.

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METHOD 5. THE METHOD OF GRIESS

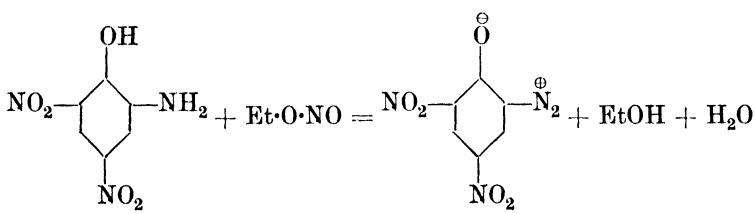
In the method of diazotisation due to Griess the nitrous acid is supplied in gaseous form as " nitrous acid gases " generated by reducing nitric acid of specific gravity 1·35 with starch or arsenic trioxide. This mixture of gases behaves as if composed of nitrous anhydride, and therefore it dissolves in water to form two molecules of nitrous acid :—

$$N_2O_3 + H_2O = 2HNO_2$$

and in ethanol to form two molecules of ethyl nitrite :—

$$N_2O_3 + 2EtOH = 2Et{\cdot}O{\cdot}NO + H_2O$$

By passing nitrous acid gases into a solution of picramic acid in ethanol, Griess [1, 4] obtained as a precipitate the first diazo-compound to be recognised as such and as the representative of a new class of organic compounds :—



He also diazotised nitroaminophenol and chloronitroaminophenol in the same way.[4, 8]

When he passed the nitrous acid gases into neutral solutions of other arylamines, *e.g.*, aniline, in ethanol he obtained diazoamino-compounds,[2, 5] since there is no acidic centre within such molecules capable of combining with the diazo anion which is formed. Griess perceived the nature of these compounds on finding that treatment with acid splits them into a diazo-compound and a salt of the original amine, and he thereupon completely diazotised aminobenzoic acid by adding dilute nitric acid to the ethanol solution before passing nitrous gases, or by passing the gases into a concentrated solution of aminobenzoic acid in dilute aqueous nitric acid; in either method a white precipitate of carboxybenzenediazonium nitrate was formed.[6]

About the same time Schmitt [3, 7] diazotised sulphanilic acid by the method of Griess as a neutral suspension in water and, as in Griess's original experiment, was successful because the molecule contains within itself the necessary anion :—

$$C_6H_4\begin{cases}NH_2\\SO_3H\end{cases} + HNO_2 = C_6H_4\begin{cases}N_2\\|\\SO_3\end{cases} + 2H_2O$$

His method of diazotisation served Griess well, for his object was usually to isolate, analyse, and characterise the diazo-compounds as such, rather than to use them for intermediates in a synthesis. Thus he started with a solution or suspension of an amine salt in ethanol or water, and passed nitrous acid gases until a drop of the reaction mixture added to dilute alkali no longer showed unchanged base. The diazonium salt then sometimes crystallised, or could be precipitated by adding ether to an ethanol solution, or by adding sufficient ethanol to an aqueous solution to ensure homogeneity on subsequently adding ether as a precipitant. By this method he was the first to obtain many of the common diazonium salts in the solid state and, indeed, but for this method the diazo-compounds, owing to their extreme solubility in water, might have remained longer unknown. The method is applicable to weakly basic amines, and Böttger and Petersen [9] early obtained anthraquinone-1-diazonium nitrate by diazotising 1-aminoanthraquinone nitrate in ether suspension. The method can also be carried out in concentrated sulphuric acid, and Scholl [11] diazotised 2 : 3-nitroaminoanthraquinone in this way. A variant of the method is to dissolve nitrous acid gases in chilled ethanol and then add the amine salt.

At the present time the method is not much used, as the generating apparatus for the nitrous acid gases is cumbersome, and there are more convenient ways of producing diazonium salts in the solid state, especially the method of Knoevenagel.

A few experiments have been recorded on the action of liquid nitrogen trioxide on arylamines. Bamberger [10] excluded water and acids in the

expectation that the first product of reaction would be the nitrosamine, ArNH·NO, which under the action of acid would rearrange through a *n*-diazotate to a diazonium salt. He added liquid nitrogen trioxide dropwise to *p*-nitroaniline dissolved in a mixture of ether and ethyl acetate and obtained a yellow precipitate soluble in water and coupling with R-salt, but he could not be sure that the reaction had not produced *p*-nitrobenzenediazonium nitrite or nitrate. Briner and Jonas,[12] noting that nitrous acid exists as part of the system $3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$, carried out diazotisation with nitrogen trioxide under pressure so as to drive the equilibrium to the left. They distilled the nitrogen trioxide into a cooled tube containing the amine and hydrochloric acid, and, after sealing, allowed the temperature to rise. Thus they obtained the corresponding diazonium chloride from dinitroaniline, tribromoanilines, and *p*-sulphobenzeneazo-α-naphthylamine, but the method failed with picramide.

If the conditions of Griess's method of diazotisation are made too drastic, replacement of the diazonium group by hydroxyl and nuclear nitration may occur. Varma and Krishnamurthy [13] passed nitrous acid gases into aqueous solutions of amine hydrochlorides below 0°, then warmed after half an hour, and thus obtained 2 : 4-dinitrophenol from aniline and from *p*-nitroaniline.

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METHOD 6. THE METHOD OF KNOEVENAGEL

Thirty-two years elapsed before Knoevenagel [4] modified the original method of Griess by replacing the nitrous acid gases by the more accurately controllable alkyl nitrites as the source of nitrous acid. This method is now commonly employed when a water-soluble diazonium salt is to be prepared pure in the solid state. Knoevenagel did not discover the use of alkyl nitrites, for Griess [1] had already noted that ethyl or amyl nitrite can be used to make diazoaminobenzoic acid. Knoevenagel, however, established the general utility of the reagent, and he suspended the dry amine salt in alcohol, and so brought it into reaction with the alkyl

rite, afterwards precipitating the diazonium salt with ether. Other dia can replace alcohol. Hantzsch and Jochem [9] used glacial acetic d as being more suitable for working on a larger scale, whilst Smith and aring [18] used a mixture of glacial acetic acid and dioxan. Amyl nitrite he usual source of nitrous acid, as ethyl nitrite is somewhat too volatile convenience, but octyl nitrite [17] has also been used. Hirsch [8] phasised that excess of acid must be avoided in the preparation of logenated benzenediazonium chlorides, such as *p*-chlorobenzene-azonium chloride,[7] since excess of acid causes the diazonium salt to be cky, due to the formation of a double compound with the acid (Ref. , p. 81).

Diazotisation can be expeditiously carried out if the amine is dissolved alcohol and the salt prepared immediately before adding the alkyl rite.

Diazotisation of Aniline Sulphate (Schoutissen [11]) :—
Aniline (15 g.) is dissolved in 96% ethanol (140 c.c.). The solution is cooled to ow 10°, and enough sulphuric acid, sp. gr. 1·84, added to redissolve the precipitated line sulphate at 0—10°. This requires about 30 g. Amyl nitrite (20 g.) is then led drop by drop while the solution is stirred at 0—5°. After 15—30 minutes the drogen benzenediazonium sulphate crystallises in white needles. An equal volume ether is added and the diazonium salt is collected, washed with ethanol-ether 1), and dried *in vacuo*.

Weakly basic amines, such as 2-aminoanthraquinone,[10] can be azotised by this method so long as their salts are not dissociated in ohols.

Diazotisation of 2-aminoanthraquinone (Kaufler [10]) :—
2-Aminoanthraquinone (5 g.) is boiled in glacial acetic acid (100 g.) with aqueous drochloric acid (3·0—4·0 c.c., sp. gr. 1·175) until the precipitate is yellow to yish-yellow (5—10 minutes). The crystal mass formed on cooling is diazotised at om temperature with amyl nitrite (4·1 c.c.; 30% excess); all the crystals dissolve. e filtered solution is poured in ether (300 c.c.), when the diazonium chloride parates in granular form; it is collected, washed with ether, and dried on a tile. eld 5·2 g.

It will be noted from the equation given in Table I that a molecule of ater is produced in the reaction, and therefore a solvent should be em-oyed with which this water is miscible, or the diazonium salt will be cky. Technically it is not possible to use the great quantities of ether cessary to bring about the separation of diazonium salts from hydroxylic lvents, and hence attempts have been made to use non-hydroxylic lvents, such as carbon tetrachloride, benzene, ethyl acetate, and others, d to remove the water produced in the reaction by adding a water-nding salt, such as calcined sodium sulphate.[13] According to a later tent, a better granulating effect is obtained by adding the water-nding reagent at the commencement of the reaction.[14]

The alkyl nitrites are not the only derivatives of nitrous acid which n be used to bring about diazotisation. Pabst and Girard [3] made

general claims as early as 1879 for nitrosyl chloride and bromide, and nitrosylsulphuric acid used in conjunction with glacial acetic acid, whilst Konink [2] had already converted aniline into diazoaminobenzene with nitrosyl bromide. Pabst and Girard also claimed nitrogen tetroxide, which they recognised as being able to react as nitrosyl nitrate, $NO_2 \cdot O \cdot NO$. Hence it is logical to review under the method Knoevenagel the few experiments which have been made to bring about diazotisation with these reagents, excepting nitrosylsulphuric acid, which occupies a special position and has already been discussed.

Both Bamberger [5] and Kastle and Keiser [6] found that nitrosyl chloride fails to give isolable benzenediazonium chloride from aniline dissolved in ether, the former obtaining diazoaminobenzene and the latter a double salt of the constitution PhN_2Cl,NH_2Ph,HCl. In a patented process [16] the arylamine is dispersed in water, and then diazotised with nitrosyl chloride at below 5°.

Houston and Johnson [12] distilled a weighed amount of nitrogen tetroxide into a solution of one of the mononitroanilines in benzene. The supposed overall reaction is: $ArNH_2 + ON \cdot O \cdot NO_2 = ArN_2 \cdot NO_3 + H_2O$. In fact, *m*-nitroaniline and nitrogen tetroxide in equal molecular proportions give 3 : 3′-dinitrodiazoaminobenzene, and three molecular proportions of nitrogen tetroxide are necessary to obtain *m*-nitrobenzenediazonium nitrate in 69% yield. *p*-Nitroaniline gives *p*-nitrobenzenediazonium nitrate in 84% yield with two molecular proportions of nitrogen tetroxide. Russian investigators [15] find that nitrogen tetroxide reacts with aniline in chloroform at 0° as a nitrating agent, the diazotised amino-group being replaced by hydroxyl, so that the isolable product is 2 : 4-dinitrophenol in 23% yield, with a little *p*-nitroaniline (compare the reaction of nitrogen trioxide, p. 18).

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THE ACTION OF NITROUS ACID ON DIAMINES

Mention of diamines has been purposely avoided up to the present point because they are best discussed as a group distinct from the simple monoamines. The following sub-headings are distinguishable :—

1. The diazotisation of diamino-compounds, including *p*-phenylenediamine.
2. The diazotisation of nuclear-substituted *p*-phenylenediamine.
3. The diazotisation of *N*-aryl- and -alkyl-*p*-phenylenediamines.
4. The tetrazotisation of the phenylenediamines and their congeners.

1. The Diazotisation of Diamino-compounds, including *p*-Phenylenediamine.—When two or more amino-groups are attached to different aromatic nuclei forming part of the same molecule, the whole can be considered for purposes of diazotisation as an assemblage of two or more different aromatic amines, in which it may nevertheless be possible to diazotise one group preferentially to the others. If both groups are attached to the same benzene ring, then their orientation can be determined by the action of one equivalent of nitrous acid, for, as Nietzki [1] pointed out, *o*-phenylenediamine affords a triazole (cf. p. 247), *m*-phenylenediamine is converted into the dye Bismarck Brown by diazotisation and self-coupling, whilst a monodiazo derivative can be obtained from *p*-phenylenediamine (see below).

Two methods have been described for the monodiazotisation of benzidine. In the first [3, 7] benzidine hydrochloride is treated with one equivalent of nitrite, thus forming a diazoamino-compound as a reddish-brown precipitate, which on stirring with more hydrochloric acid at room temperature for 12 to 18 hours passes into solution as 4-aminodiphenyl-4′-diazonium chloride. The same compound can be made by adding one equivalent of nitrite to benzidine dissolved in more than one equivalent of hydrochloric acid.[11] Tolidine, dianisidine and analogous compounds and 4 : 4′-diaminostilbene can also be monodiazotised through their diazoamino-compounds.[7] The second method, due to Täuber,[6] is interesting, and consists in mixing one equivalent of benzidine hydrochloride with a solution of tetrazotised benzidine in dilute hydrochloric acid and allowing the solution to stand for 2 to 3 days, during which time interchange of a diazo-group occurs, producing 4-aminodiphenyl-4′-diazonium chloride in 80—90% yield. This interchange lends support to those who have pointed out that diazo-compounds behave in some respects as anilides of nitrous acid which in aqueous solution are in equilibrium with a small concentration of base and nitrous acid. The isomeric 2 : 2′-diaminodiphenyl [15] cannot be diazotised in only one amino-group, but 2 : 4′-diaminodiphenyl [16] is singly diazotised at 2.

Other diamines which are diazotisable in one amino-group are

1 : 4-[12, 13] and 1 : 5-diaminoanthraquinone,[12] diazotised in nitrosylsulphuric acid, 2 : 7-diaminonaphthalene hydrobromide,[9] when diazotised by the method of Knoevenagel, 4 : 4′-diaminobenzeneazo-1-naphthalene,[5] and 1 : 4 : 5 : 8-tetra-aminoanthraquinone,[17] diazotised in formic acid.

Griess [2] obtained a solution of *p*-aminobenzenediazonium chloride by acting on *p*-phenylenediamine dissolved in hydrochloric acid with one equivalent of nitrite and precipitated it as the auric chloride double salt, $p\text{-}NH_2\cdot C_6H_4\cdot N_2Cl,2AuCl_3$. *p*-Aminobenzenediazonium chloride [8, 10] is so stable that it can also be made by diazotising *p*-aminoacetanilide, then removing the acetyl-group by hydrolysis with hydrochloric acid at 70°, or it crystallises when a concentrated aqueous solution of *p*-acetamidobenzenediazonium chloride is saturated with gaseous hydrochloric acid and allowed to stand.[18]

By the action of chlorosulphonic acid on *o*-, *m*-, or *p*-phenylenediamine there are formed disulphamic acids, $C_6H_4(NH\cdot SO_3H)_2$, and these when treated with nitrous acid in hydrochloric acid are singly diazotised with the ejection of one molecule of sulphuric acid from one amino-group giving *o*-, *m*-, or *p*-sulphamidobenzenediazonium chloride, $HO_3S\cdot NH\cdot C_6H_4\cdot N_2Cl$.[14]

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2. The Diazotisation of Nuclear-substituted *p*-Phenylenediamine.—The diamines mentioned in the previous section can be tetrazotised if desired, but a negative substituent in *p*-phenylenediamine often prevents diazotisation of one amino-group, usually, but not always, that to which it stands *ortho*, except under drastic conditions (cf. Section 4 below). If the diazo-compound so obtained is coupled it may be possible to diazotise the other amino-group in the resultant aminoazo-compound, whilst acetylation of the diazotisable amino-group may permit diazotisation of the one previously obstructed.

Griess [1] discovered that only one amino-group can be diazotised in

2 : 5-diaminobenzoic acid, and Bülow [2] could only diazotise the amino-group at 4 in 2-nitro-*p*-phenylenediamine, no matter how great the excess of nitrous acid, but after coupling with R-salt the amino-group at 1 could be diazotised in the azo-compound. On the other hand, if the amino-group at 4 is acetylated, that at 1 can be diazotised.[3] Similarly, in 2 : 6-dichloro-*p*-phenylenediamine and in *p*-phenylenediamine-2-sulphonic acid,[6] only the amino-group at 4 can be diazotised, and in the homologous 1 : 4-diaminonaphthalene-2-sulphonic acid it is only the amino-group at 4 that can be diazotised, but after it has been coupled that at 1 can be diazotised.[4] The arsonic acid group has the reverse effect to the above, for in *p*-phenylenediamine-2-arsonic acid it is the amino-group at 1 which is diazotisable.[7]

In the anthraquinone series the amino-group at 1 cannot be diazotised in 1 : 4-diaminoanthraquinone-2 : 6- or -2 : 7-disulphonic acid [8] or in 2-chloro- or -bromo-1 : 4-diaminoanthraquinone,[9] but with halogen atoms at both 2 and 3 one of the amino-groups remains diazotisable.[9]

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3. The Diazotisation of *N*-Aryl- and -Alkyl-*p*-Phenylenediamines.—From these amines are derived diazo-compounds which comprise a group whose characteristics mark them off clearly from other diazo-compounds. The effect of the substituted amino-group is to weaken the positive charge on the diazo-group, and so make it sluggish in reaction, especially in coupling, which takes place only under narrowly defined conditions. On the other hand, their sluggishness to react with surrounding molecules is reflected in stability to heat, but they are among the most sensitive of the diazo-compounds to light and many of the diazo-components used for diazotypes (cf. Chapter X) are drawn from this group. Diazonium salts derived from singly diazotised *p*-phenylenediamine, already discussed under section 1 (cf. p. 22), also belong to this group.

NN-Dimethyl-*p*-phenylenediamine (p-$NH_2 \cdot C_6H_4 \cdot NMe_2$), commonly called *p*-aminodimethylaniline, can be diazotised by the direct method [1, 2, 9]; the diazo-solution is coloured reddish-yellow,[9] but small amounts of impurities in the technical base usually cause the solution to be purple.

p-Aminodiethylaniline is diazotised in the same way.[9] Solid diazonium salts can also be made by the method of Knoevenagel :—

Diazotisation of p-*Aminodimethylaniline* (Koenigs, Ruppelt [11]) :—

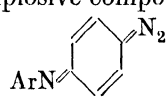
p-Aminodimethylaniline (20·0 g.) dissolved in ethanol (150 c.c.) is converted into the hydrochloride by passing in gaseous hydrochloric acid until the solution is acid to Congo. Amyl nitrite (13·0 g.) dissolved in ethanol (20 c.c.) is added, and the diazonium chloride is precipitated as a free-flowing white powder with ether (800 c.c.).

Hantzsch [4] said that *N*-methyl-*p*-phenylenediamine cannot be diazotised, but Hodgson and Marsden [12] have diazotised this base by the direct method, the diazonium salts showing the expected properties.

p-Aminodiphenylamine was first diazotised by Ikuta [3] by the direct method in dilute sulphuric acid. The yellow diazonium sulphate crystallised in hair-like crystals, and, to his astonishment, Ikuta found that it can be crystallised from hot water and is stable to 120°. He also noted how rapidly it is decomposed by light. Various *p*-arylaminobenzenediazonium salts have become of technical importance, not only for diazotypes, but because they afford beautiful blue shades of good fastness on cellulosic fibres by the ice-colour process (cf. p. 102).

Diazotisation of 4-*Amino*-4′-*ethoxydiphenylamine* (Rowe [8]) :—

The base (11·4 g. = 0·05 mol.) is dissolved at the boil in water (150 c.c.) and 10N-hydrochloric acid (6 c.c.). On cooling to 80° further acid (25 c.c.) is added, and at 45° a solution of sodium nitrite (3·5 g.) in water (25 c.c.). Diazotisation is immediate and, after filtering from some dark flocculent material, a clear orange-yellow solution of the diazonium chloride is obtained.

Caustic soda converts these diazonium salts into explosive compounds which Hantzsch [4] considered to be quinone diazides,  but treatment with acid does not regenerate the diazonium salt.

Jacobson [5] found that diazotisation of halogenated *p*-aminodiphenylamines in 70% sulphuric acid with excess of nitrite produces the diazonium nitrate.

Diazotisation of pentabromo-p-*aminodiphenylamine* :—

The base (1 g.) is dissolved or suspended in a mixture of water (40 c.c.) and sulphuric acid (40 c.c., sp. gr. 1·84), sodium nitrite (2 g.) dissolved in water (20 c.c.) is added, and the whole is boiled; on cooling yellow pentabromo-*p*-aminophenylbenzenediazonium nitrate crystallises.

For commercial purposes, where yield is of paramount importance, care must be taken to control the acidity of the reaction medium, or oxidation may occur with scission of the diphenylamine molecule into a quinone and another diazonium salt.[10] The optimum pH lies between 1 and 4, and is controlled by using aqueous solutions of salts, such as zinc chloride or aluminium sulphate, the base being prepared in finely divided form either by grinding or by dissolution in an inert solvent and pouring into the reaction medium.[10]

Carbazole-3-diazonium salts,[7] produced by diazotisation of 3-amino-

carbazole by the direct method, closely resemble those of *p*-arylaminodiazobenzene, for they may be regarded as derived from the latter by a link joining the *ortho* positions to the imino-group in the two benzene rings. Hence the carbazole-3-diazonium salts are coloured, usually yellow to red, can be crystallised from hot water, and are sensitive to light.

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4. The Tetrazotisation of the Phenylenediamines and their Congeners.—The attempt to tetrazotise *m*-phenylenediamine by the direct method without special precautions produces the brown basic dye Bismarck Brown (C.I. 331), benzene-*m*-disazo-bis-*m*-phenylenediamine, which is formed by the coupling of unchanged diamine with that already tetrazotised. Nevertheless, *m*-phenylenediamine can be tetrazotised by the direct method in small quantity by thorough cooling and sudden mixing of the two solutions (but see also p. 44). Schoutissen [11] has also used the direct method with strong stirring at − 5°, and it was the subject of an early patent.[41] Heertjes, Kolb, and Waterman [15] allow an acid solution of *m*-phenylenediamine to flow down a cooled inclined surface and mix it near the top with nitrite solution. They say that this method produces only 1% of Bismarck Brown, whereas Griess's recipe produces 51% and the stirring method 17%. Griess,[1] who first achieved the tetrazotisation, suppressed the formation of the unwanted dye by keeping nitrous acid in excess of the diamine, and this principle is now often adopted for dealing with such compounds. It is said that the titrazotisation is improved by the presence of polyhydric alcohols.[20]

Tetrazotisation of m-*Phenylenediamine* (Täuber, Walder [4]):—

Fuming hydrochloric acid (80 c.c., sp. gr. 1·2) is poured on ice (400 g.) and the whole is cooled in a freezing mixture; to this is added a cold solution of sodium nitrite (15 g.). Into the solution of nitrous acid thus prepared is immediately poured an already prepared solution of *m*-phenylenediamine (9 g.) acidified with hydrochloric acid (10 c.c., sp. gr. 1·18). A yellow solution of the tetrazo-compound is produced forthwith.

Epstein [45] added a mixture of *m*-phenylenediamine (2 mols.) and nitrite (3 mols.) or *m*-tolylenediamine (3 mols.) and nitrite (4 mols.) to acid, and so obtained diazotised Bismarck Brown by the inverted method.

When *m*-phenylenediamine is substituted, tetrazotisation is so much facilitated that it can be brought about by the direct method, and the examples cited here are drawn from various patents for the manufacture of azo dyes. Thus 2 : 4-diaminophenol [2 : 4 : 1-$(NH_2)_2C_6H_3$·OH] can be tetrazotised direct,[50] as can a number of its derivatives, which include 2 : 4-diaminophenol ethers,[52] diaminosalicylic acid [2 : 4 : 1 : 6-$(NH_2)_2C_6H_2(OH)$·CO_2H],[43] and 4-chloro-1 : 3-diaminobenzene-5-sulphonic acid [51]; the 4-sulphonic acid of the isomeric 2 : 6-diaminophenol [2 : 6 : 1 : 4-$(NH_2)_2C_6H_2(OH)$·SO_3H] [46] can also be tetrazotised direct. *m*-Phenylenediamine-4-sulphonic acid [49] and tolylenediaminesulphonic acid [2 : 6 : 1 : 4-$(NH_2)_2C_6H_2Me$·SO_3H] [42] can be diazotised in one amino-group without self-coupling, whilst *m*-phenylenediamine-4 : 6-disulphonic acid [47] on direct tetrazotisation replaces one sulphonic acid group by hydroxyl, and similarly the alkyl-group is removed on tetrazotisation of 2 : 6-diaminoalkoxybenzene-4-sulphonic acids.[48]

Griess [1] tetrazotised *p*-phenylenediamine by the same method that he used for the *m*-isomer, and Schoutissen [10] has applied his technique of phosphoric acid and nitrosylsulphuric acid to *p*-diamines, and so succeeded in tetrazotising not only *p*-phenylenediamine but also 2 : 5-dichloro-, 2 : 6-dichloro-, and -dibromo-, and trichloro-*p*-phenylenediamine, as well as the nitro- and sulpho-*p*-phenylenediamine—in fact, all those diamines which have been mentioned in Section 2 as refusing to pass beyond the monodiazo stage by the direct method. The fluoboric acid method of Ruggli and Caspar, (Ref. 58, p. 81), is also an efficient method of producing tetrazonium salts (cf. p. 283), but they are not very stable, and Hantzsch and Borghaus [3] made an important contribution when they showed that the solid tetrazosulphate is much more stable than the hydrochloride in the case of both *m*- and *p*-tetrazobenzene. The art of manufacturing solid benzene-*p*-tetrazonium sulphate by tetrazotising in nitrosylsulphuric acid has been patented.

*Preparation of Solid Benzene-*p*-tetrazonium Sulphate* [52] :—

p-Phenylenediamine (108 g.) is charged into a solution of nitrosylsulphuric acid (265 g.) in 78% sulphuric acid (800 g.) at 20—25°. The solution is stirred at 25° until tetrazotisation is complete, after which the tetrazonium sulphate may be isolated :—

1. By cooling to −15° and collecting on an acid-proof filter.
2. By pouring on ice (600 g.) with strong cooling and collecting at −15°.
3. By pouring into methanol, ethanol, or acetone (1600 g.) and collecting at a low temperature.

Tetrazotisation can also be carried out by the glacial acetic acid–nitrosylsulphuric acid method. Misslin [8] tetrazotised 1 : 3 : 5-trinitro-2 : 6-diaminobenzene by pouring a solution of sodium nitrite (0·7 g.) in sulphuric acid (600 g.) into one of the diamine (1·3 g.) in glacial acetic acid (600 g.). Hodgson and Walker,[12, 18] utilising the principle of Griess, reversed the procedure, and so succeeded in tetrazotising *o*-phenylene-

diamine which had been previously tetrazotised by Schoutissen [10, 17, 19] in small yield by the phosphoric acid-nitrosylsulphuric acid method.

Tetrazotisation of o-*Phenylenediamine* (Hodgson, Walker [12]) :—

The base (21·6 g.) is dissolved in glacial acetic acid (150 c.c.) and added below 30° to well-stirred nitrosylsulphuric acid made by dissolving sodium nitrite (32 g.) in sulphuric acid (320 c.c. = 580 g., sp. gr. 1·84) at 70° and cooling. A test portion dissolves clear in water, and treatment with cuprous chloride gives *o*-dichlorobenzene in 70% yield.

Morgan and Davies [9] made experiments to discover how many diazo-groups can be attached to one benzene ring, and concluded that two is the limit, while Hein and Wagner [13] failed to obtain a hexakisazo derivative of 2 : 4 : 6-triaminotoluene.

The naphthylenediamines in which the two amino-groups are in different nuclei are comparatively easy to tetrazotise,[2] and 1 : 5-naphthylene diamine [21, 40] was tetrazotised by the direct method in the same year that Griess tetrazotised *m*-phenylenediamine; the 1 : 5-, 2 : 5-, and 2 : 8-naphthylenediaminesulphonic acids [44] are also tetrazotised by the direct method. As already noted, 2 : 7-naphthylenediamine is only diazotised by Knoevenagel's method (cf. p. 18), but it can be tetrazotised with nitrosylsulphuric acid.

Tetrazotisation of 2 : 7-*Naphthylenediamine* (Morgan, Micklethwait [5]) :—

The base (0·5 g.) dissolved in sulphuric acid (2 c.c., sp. gr. 1·84) is mixed with ice (1 g.) and diazotised with nitrosylsulphate (2 g.), the mixture being cooled with more ice (1 g.). The cold filtered solution is slowly added to a mixture of ether (2 pt.) and ethanol (7 pt.), more ethanol being added if the precipitate is viscid. The light yellow crystals are washed with ether-ethanol and finally with ether. The yield is 86% of naphthalene-2 : 7-bisdiazonium sulphate, 2 : 7-$C_{10}H_6(N_2 \cdot HSO_4)_2, \frac{1}{2}EtOH$.

1 : 8-Naphthylenediamine can form an internal diazoamino-compound if nitrous acid is not kept in excess and/or the concentration of acid is too low; Hodgson and Whitehurst [21] tetrazotise this diamine by dissolution in glacial acetic acid and pouring into nitrosylsulphuric acid.

If both amino-groups are in the same ring of naphthalene, tetrazotisation is very difficult, because of the ease with which the diamines are oxidised; nitrous acid oxidises 1 : 4-naphthylenediamine to 1 : 4-naphthaquinone. In attempting to tetrazotise 2-chloro-1 : 4-naphthylenediamine Hodgson and Elliott [16] found that the tetrazo-compound first produced couples with the unchanged diamine with elimination of the chlorine atom.

In the anthraquinone series tetrazotisation presents few difficulties; 1 : 5-diaminoanthraquinone [6] is tetrazotised in nitrosylsulphuric acid, and the 1 : 4-isomer [7] by the method of Knoevenagel.

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		B.P.	U.S.P.	D.R.P.		F.P.
40	B.A.S.F.	—	—	39,954	*Fr.*, **1**, 525	—
41	R. G. Williams	1,593/88	—	—	—	—
42	Oehler	17,546/92	516,380	65,863	*Fr.*, **3**, 740	—
43	Cassella	—	—	68,303	*Fr.*, **3**, 638	—
44	Holliday	26,020/96	—	—	—	—
45	Epstein	—	—	103,660 103,685	*Fr.*, **5**, 634	—
46	M.L.B.	18,624/00	693,670	128,619	*Fr.*, **6**, 916	313,748
47	M.L.B.	18,283/03	—	—	—	—
48	M.L.B.	—	—	148,085	*Fr.*, **7**, 98	—
49	M.L.B.	—	—	152,879	*Fr.*, **7**, 75	—
50	S.C.I.	82/05	823,793	168,299	*Fr.*, **8**, 629	358,844
51	B.A.S.F.	—	—	156,828	*Fr.*, **8**, 632	—
52	I.G.	440,424	2,053,745	611,463	*Fr.*, **21**, 967	775,038

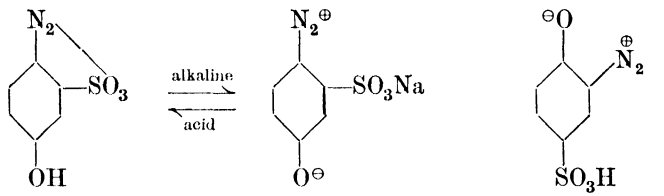
DIAZO-OXIDES, DIAZOIMINES, AND NITROSO-ACYLARYLAMIDES

By virtue of their properties, the diazo-oxides, diazoimines, and nitrosoacylarylamides occupy special places in the chemistry of the diazo-compounds. They may require methods of preparation different from those already described, and on account of their constitution their reactivity differs from diazonium salts, chiefly because they can exist in forms which are internally compensated and do not ionise in aqueous solution.

Diazo-oxides.—The diazotisation of compounds having hydroxyl *ortho* or *para* to the amino-group leads to products having properties quite different from those of other diazonium salts. The true water-soluble *o*- or *p*-hydroxybenzene diazonium salts can be prepared from *o*- and *p*-aminophenol,[6] but they are stable only in acid solution, and many of their congeners give a precipitate directly on diazotisation, often increased in amount by dilution with water or the addition of alkali, providing groups imparting solubility in water are absent. The same compounds appear when halogen atoms or nitro-groups *ortho* or *para* to the diazonium

group are eliminated by the action of water and replaced by hydroxyl (cf. Chapter III). On examination of such a precipitate it is found that the diazonium cation and its equivalent anion are no longer present, and that the molecule is internally satisfied by loss of acid or water between the diazonium and hydroxyl groups which are now in some way linked; hence the name diazo-oxide. The compounds are also called quinone diazides and diazo-anhydrides, the latter especially in German writings, though the context usually leaves no doubt that Bamberger's substances of the same name (cf. p. 133) are not in question. The name diazo-oxide has also been used for the O-azo compounds, which can sometimes be isolated as an intermediate step in the coupling reaction.[19]

The internal interaction of a diazo-group with hydroxyl is quite general, being manifested in the benzene, naphthalene, and anthraquinone series as well as among heterocyclic compounds having fused aromatic rings. When an acid group is also present in the molecule there may be competition between it and the hydroxyl to satisfy the diazo-group. Thus, 1 : 4-diazophenol-3-sulphonic acid is colourless in acid solution, being an internal sulphonate, but is yellow in alkaline solution, being then the sulphonic acid salt of the diazo-oxide :—



I.

In contrast, 2 : 1-diazophenol-4-sulphonic acid (I) is yellow in acid solution, showing that here affinity between phenolic hydroxyl and the diazo group is the greater.[17]

The diazo-oxides of the benzene series can usually be prepared without difficulty by any of the known methods and, as already mentioned, the first diazo-compound to be observed by Griess, 4 : 6-dinitrobenzene-2 : 1-diazo-oxide belongs to this group.

Preparation of 2-*Nitro*-p-*diazophenol* (Morgan, Porter [16]) :—

Aqueous sodium nitrite is added slowly to an ice-cold solution of 2-nitro-*p*-aminophenol [2 : 4 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OH$] dissolved in dilute sulphuric acid whereupon a yellow crystalline precipitate of 2-nitro-*p*-diazophenol is thrown down, collected, and is purified by crystallisation from hot water affording yellow leaflets, exploding at 168°; the substance is soluble in acetone or ethyl acetate, sparingly soluble in methanol and ethanol, and insoluble in benzene or chloroform. It couples readily with alkaline β-naphthol.

So strong can be the tendency to diazo-oxide formation that when 2 : 6-dinitro-*p*-anisidine [2 : 6 : 4 : 1-$(NO_2)_2C_6H_2(NH_2) \cdot OMe$] is diazotised the ethereal methyl-group is split off and the *p*-diazo-oxide is formed.[13] At the other end of the scale of tendency to diazo-oxide formation is 3-nitro-*p*-hydroxybenzenediazonium chloride [3 : 4 : 1-$NO_2 \cdot C_6H_3(N_2Cl) \cdot OH$],

which does not form a diazo-oxide even in alkaline solution; the oxide is, however, obtained when 3-nitro-4-aminophenol is diazotised in ether by the method of Griess.[16]

In the naphthalene series, however, conditions are different because the 1 : 2-, 2 : 1-, and 1 : 4-aminonaphthols are easily oxidised by nitrous acid to 1 : 2-,[4] or 1 : 4-naphthaquinone. 1 : 2-Aminonaphthol-4-sulphonic acid is particularly valuable as a chrome dye component and a variety of ways of minimising oxidation have been described. The earliest method was to diazotise with acetic or oxalic acid,[9] or to acetylate the hydroxy-group and remove the acetyl-group after diazotisation,[11] but the direct method became possible when it was discovered that the oxidising effect of nitrous acid is diminished in the presence of copper sulphate. Thus, in the presence of this salt it is possible to diazotise 1 : 2- and 2 : 1-aminonaphthol,[10] 1 : 2-aminonaphthol-4-sulphonic acid,[10] 1 : 2-aminonaphthol-8-sulphonic acid,[25] and 1 : 2-aminonaphthol-4-carboxylic acid.[22]

Diazotisation of 1 : 2-*aminonaphthol*-4-*sulphonic acid* :—

The acid (30 g.) is pasted with water (200 c.c.) and cooled to 5°; then in sequence there are added solutions of copper sulphate (2·5 g.) and sodium nitrite (9·0 g.). After diazotisation has taken place the solution is filtered, and concentrated hydrochloric acid is added to the orange-yellow filtrate. The naphthalene-1 : 2-diazo-oxide-4-sulphonic acid separates as yellow needles, which are collected, washed with dilute hydrochloric acid, and dried in the air. The yield is 30 g.

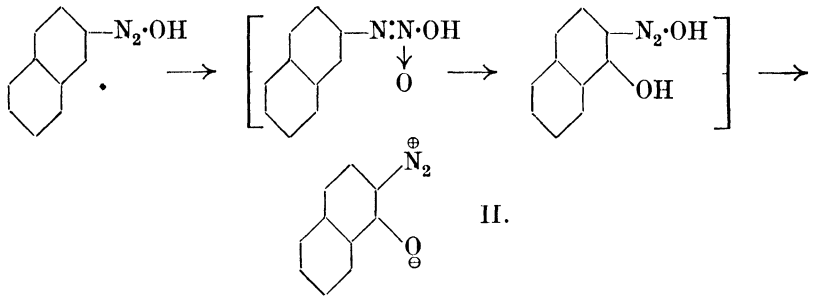
The diazo-oxide can be further purified by crystallising quickly from hot water. The salts have been described by Schmidt and Maier,[24] who report that the free acid affords a green solution in concentrated sulphuric acid.

Claims have also been made for diazotising 1 : 2-aminonaphthol-4-sulphonic acid in presence of salts of zinc or heavy metals,[12] salts of alkali or alkali-earth metals,[14] whilst Kozlov [27] diazotises *o*- and *p*-aminophenols in presence of stannous chloride, or manganous or ferrous salts. 2 : 3-Aminonaphthol-6-sulphonic acid [7] does not require copper salts, but diazotises smoothly, like the substituted *o*-aminophenols of the benzene series, but copper sulphate does not prevent oxidation of 1-amino-2-hydroxy-4-cyanonaphthalene to 4-cyano-1 : 2-naphthaquinone by excess of nitrosylsulphuric acid, though by adding powdered nitrite to the amine dissolved in glacial acetic acid it is converted into 4-cyanonaphthalene-1 : 2-diazo-oxide.[34]

Hodgson and Birtwell [30] have described four methods of preparation of diazo-oxides from the negatively-substituted naphthylamines. Thus, if 2 : 4-dinitro-1-naphthylamine is diazotised in : (*a*) glacial acetic acid, it affords the diazonium salt, which is converted into 4-nitronaphthalene-1 : 2-diazo-oxide on dilution, (*b*) glacial acetic acid in the presence of copper carbonate, when the diazo-oxide is produced immediately, as it is also by, (*c*) diazotisation in sulphuric acid, followed by partial neutralisation with ammonia, and (*d*) diazotisation in warm glacial acetic acid; 4-iodonaphthalene-1 : 2-diazo-oxide can only be obtained in this latter way. Hodgson and Hathway [33] report that in general diazo-oxide

formation is minimised by working with the least possible quantity of water, as in (*a*) above.

There is also a totally different method of limited application discovered by Bamberger and his co-workers [20, 21] for preparing diazo-oxides. They oxidised α- and β-diazonaphthalene with alkaline ferricyanide and obtained naphthalene-1 : 2- and -2 : 1-diazo-oxide. β-Diazonaphthalene is oxidised thus :—



II.

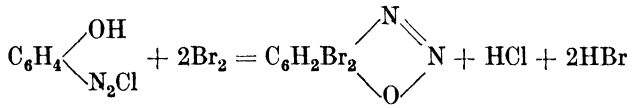
The yield from β-diazonaphthalene [8 g. of (II) from 10 g. of β-$C_{10}H_7 \cdot NH_2$] is much better than that from α-diazonaphthalene or that obtainable by the action of nitrous acid on 1 : 2- or 2 : 1-aminonaphthol.

Diazo-oxides are never formed from *m*-aminophenols,[16] and Anderson and Roedel [35] said that they could not prepare naphthalene*peri*diazo-oxide from 1 : 8-aminonaphthol, but the orange colour of 1-diazo-8-naphthol-4-sulphonic acid indicates that there is probably some interaction between the diazo- and the hydroxy-group in this compound.

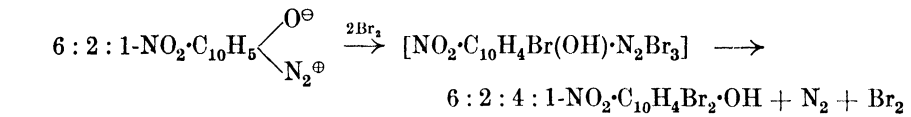
The diazo-oxides are nearly always coloured, ranging from very pale yellow to orange, and they may exhibit characteristic colours when dissolved in concentrated sulphuric acid. They may be explosive, especially if heated suddenly, and if several nitro-groups are present they can be detonated (cf. p. 354). Naturally substituents and their position affect the stability and the reactivity; for naphthalene-1 : 2-diazo-oxide Hodgson and Birtwell [31] put substituents at 4 in the following descending order of stabilising effect : $NO_2 > Cl > Br > 1 > SO_3H$.

The diazo-oxides are not associated in aqueous solution [5], they have the simple molecular weight, and nearly always have water of crystallisation. They are often sensitive to light, and are used for diazo-type emulsions (cf. p. 365). As a class they are somewhat inert towards reagents compared with the diazonium ion, the distinctive reactions of which are absent or weak. Thus, the vigour of the coupling reaction is often much diminished, and coupling is only rapid in strong couplers like resorcinol; they sometimes couple best in quite strong acid because in acid medium the link between the diazo-group and hydroxyl has been broken.[17] Another characteristic of the diazonium ion—that of forming well-defined solid crystalline double salts—is absent, as is the capacity to form

perhalogeno compounds. The action of bromine is to attack and substitute the aryl nucleus. Böhmer [3] early discovered that the addition of bromine to aqueous solutions of *p*-hydroxybenezenediazonium salts at once gives a bright yellow precipitate of 2 : 6-dibromo-4-diazophenol. He represented the reaction as :—

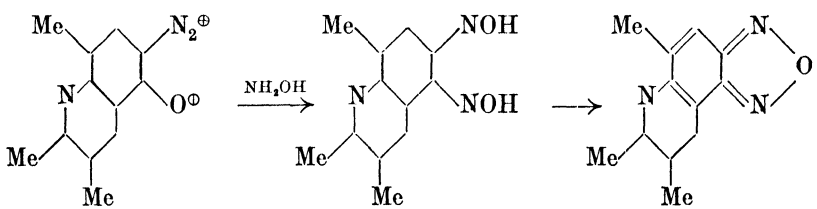


Böhmer also acted on *p*-hydroxybenzenediazonium nitrate with hydrobromic acid, and describes how, after a short induction period, the nitrate ion oxidises the hydrobromic acid, and the free bromine at once gives the yellow precipitate of the dibromodiazophenol and the *p*-hydroxybenzenediazonium bromide in equal molecular proportions. Replacement of the diazo-nitrogen and substitution can both occur; for example, 6-nitronaphthalene-2 : 1-diazo-oxide affords 2 : 4-dibromo-6-nitro-1-naphthol when treated with bromine [32] :—



No hydrobromic acid appears in this reaction, being apparently used up to convert the diazo-oxide into diazonium bromide, which then takes up more bromine to form the diazonium perbromide (in brackets above), which at once decomposes into bromonaphthol, nitrogen, and bromine.

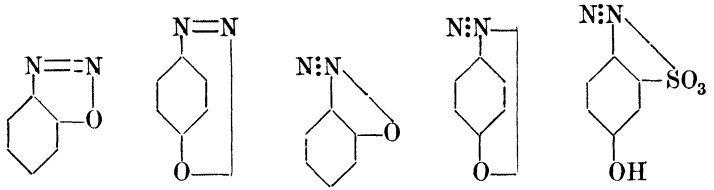
So inert is the nitrogen in the diazo-oxides that the oxygen can react without loss of the diazo-nitrogen; for example, naphthalene-2 : 1- and -1 : 2-diazo-oxide treated with phosphorus pentasulphide afford the naphthathiodiazole [20, 21] (cf. p. 253), the oxygen being replaced by sulphur, whereupon the thiodiazole ring closes. Modlin and Burger [28] attempted to demonstrate the presence of the keto-group in 5-hydroxy-6-diazo-2 : 3 : 8-trimethylquinoline with hydroxylamine, but obtained instead the 5 : 6-quinonedioxime which can be dehydrated to the furazane :—



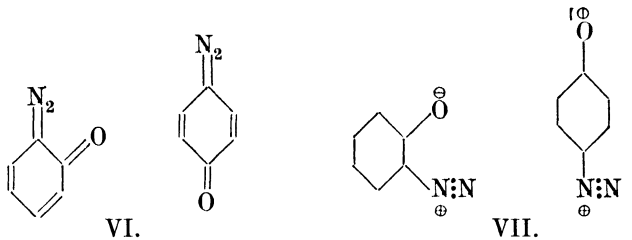
The constitution of the diazo-oxides will be discussed here, since it is distinct from the controversies as to the constitution of the more closely-

related diazo-compounds, the problems of which are considered in Chapter XI.

Five different constitutions have been proposed for the diazo-oxides :—



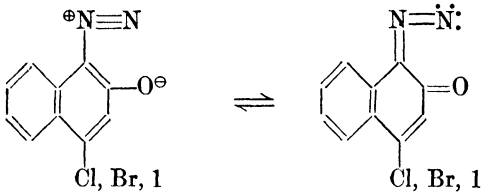
III. IV. V.



VI. VII.

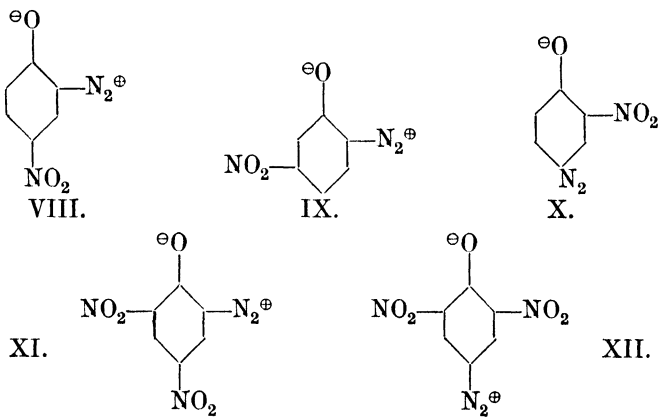
(V) is an example of the special case already mentioned where an acidic group competes with the hydroxyl as anion to the diazonium cation, and though it has been suggested [23] as a possible constitution, it can be discarded at the start, as it does not in fact represent a diazo-oxide in which an association must exist between the diazo-group and the hydroxyl. Klemenc [15] was the chief protagonist of the diazonium constitution (IV) originally mooted by Bamberger,[5] who thought that normal and *iso*-diazo-oxides might exist. It can be ruled out because it contains penta-covalent nitrogen, and because a diazonium constitution does not account for the colour, most simple diazonium salts being colourless. The constitution (III) having a definite link between the diazo-nitrogen atoms and the oxygen was the first proposed, being suggested by Kekulé [1] as long ago as 1867; the azo link and the readily broken ring explain the colour and the loss of the diazonium ion reactions. Hantzsch and Davidson [6] thought that there might be oscillation between (III) and (IV), but to many chemists the bridge link of (III) for the *p*-diazo-oxides must have been an offence. Nevertheless, it was favoured by Morgan and his co-workers [66, 17, 18] and also be Battegay and Schmidt,[23] as against the quinonediazide constitution (VI) put forward by Wolff,[8] whereby the bridge link is circumvented. Morgan rejected the quinonediazide constitution because he could not adduce a quinonoid constitution for naphthalene*peri*diazo-oxide (cf. Anderson and Roedel above), and Battegay rejected it because naphthalene-1 : 2-diazo-oxide-4-sulphonic acid shows no oxidising power towards potassium iodide, a reaction to be expected from a quinone. The quinonediazide constitution is supported

by Anderson and Roedel [35] on the ground that the absorption spectra of the naphthalenediazo-oxides resemble those of *o*-quinones, such as the naphthaquinones, benzil, and azibenzil (Ph·CO·CN_2·Ph). Taylor and Baker [26] have, however, shown that the difficulties of both the oxygen–nitrogen bond and the quinonediazide constitutions can be resolved if the diazo-oxides are resonance hybrids as shown in (VII). Hodgson [29] has elaborated the idea for the substituted diazo-oxides, whilst Hodgson and Birtwell [31] suggested that the 4-halogenonaphthalene-1 : 2-diazo-oxides are hybrids of Taylor and Baker's form with the quinonediazide form :—



Such ideas appeal to the reason and imagination at the present time (1949), but it cannot be too strongly emphasised that they are as yet not backed by such measurements as have, for example, determined the constitution of the azides.

Since 4 : 6-dinitrobenzene-2 : 1-diazo-oxide (XI) is a detonating explosive (cf. p. 354), the thermal decomposition of this and four other nitrobenzenediazo-oxides shown below have been examined by Vaughan and Phillips,[36] using the technique for explosives in the solid phase :—



The diazo-oxides, heated *in vacuo* at temperatures between 50° and 120°, afford carbon dioxide, nitric and nitrous oxides, and nitrogen, but the amount of this latter element does not reach one mol. per mol. of diazo-oxide, possibly because some coupling occurs; the predominating reaction is scission of the diazo-nitrogen. The 4 : 1-diazo-oxides (X) and (XII) evolve gas more slowly than the 2 : 1-diazo-oxides (VIII), (IX), and (XI), and Vaughan and Phillips [36] suggest that this is because in the 2 : 1-diazo-

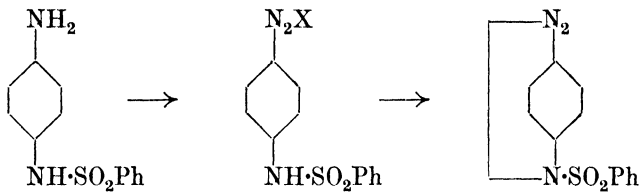
oxides the proximity of the two charges sets up an appreciable electrostatic attraction which prevents formation of the quinonoid form thus reducing the resonance energy, and with it the stability. Moreover, (IX) is less stable than (VIII), because in the latter the mesomeric effect of the nitro-group is to reduce the charge on the oxygen, and so enhance resonance, whereas in (XI) it reinforces the positive charge on the nitrogen, and so reduces resonance by increasing the amount of the " ionised " form in the hybrid.

The technical use of the diazo-oxides for diazotypes and explosives is small compared with their use for the manufacture of mordant azo dyes made by coupling diazotised *o*-hydroxyamines of the benzene and naphthalene series with suitable coupling components, especially those in which the azo link enters *ortho* to a hydroxy-group so that *oo'*-dihydroxyazo dyes are formed.

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Diazoimines.—An acidic imino-group *para* to the diazo-group causes the appearance of compounds of the same type as the diazo-oxides. They are called diazoimines, and have been the subject of extensive studies by Morgan and his school. They are derived from monoacylated *p*-diamines and are easily obtainable from aqueous solution whenever the acylating agent is sufficiently negative to confer a strong negative charge on the imino hydrogen. An arylsulphonyl-group does this most effectively, and one of the simplest *p*-diazoimines is derived from benzenesulphonyl-*p*-phenylenediamine [2,3,4]:—



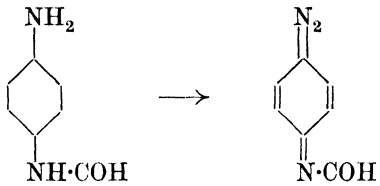
On diazotisation in aqueous acid a diazonium salt, anion denoted by X, is obtained, and many of these salts are well crystallised and of considerable stability, but the addition of alkali or of acetate at once precipitates the yellow diazoimine. Such diazoimines are also formed from benzenesulphonylbenzidine [8] or the bis- and tris-sulphonyl compounds obtained from *p*-phenylenediamine and benzene-*m*-disulphonyl chloride [4] and benzene-1 : 3 : 5-trisulphonyl chloride.[9] Diazoimines are not obtained from diazotised acyl-*m*-phenylene diamines or from benzenesulphonyl-1 : 5-naphthylenediamine, but the 1 : 8-isomeride forms a diazoimine which is probably a true ring compound.

The *p*-diazoimines resemble the diazo-oxides in their general behaviour, but are less stable and more reactive. Like the diazo-oxides, they are yellow, carry water of crystallisation, and are explosive; they possess the simple molecular weight,[4] and are often sensitive to light. They add directly to primary arylamines, which have the power to couple with diazo-compounds; *e.g.*, with α- and β-naphthylamine the aminoazo-compounds are formed apparently through a quinonoid addition product.[9]

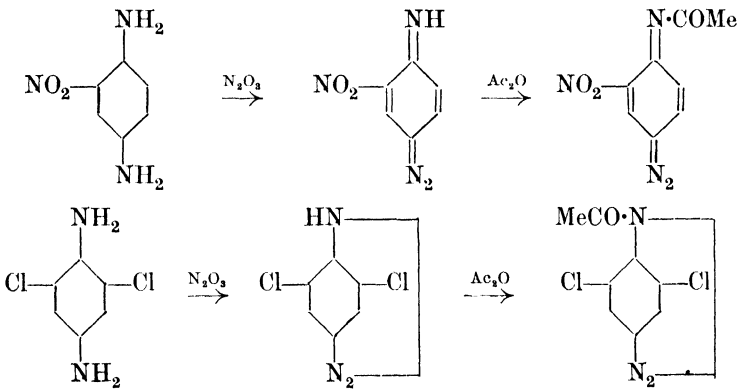
Substitution of one amino-group in *p*-phenylenediamine by a phenyl nucleus makes the imino-group sufficiently acidic to form a *p*-diazoimine, and hence addition of alkali to diazotised *p*-aminodiphenylamine forms a *p*-diazoimine or *p*-quinonediazide as a yellow explosive precipitate [11]; this substance, however, differs from the diazoimines described above in not having the power to couple and in not regenerating the diazonium salt with strong acids.

For some years attempts to prepare diazoimines from *p*-diamines acylated with carboxylic acid residues failed; for example, the addition of acetate to an acid aqueous solution of diazotised acetyl- or benzoyl-*p*-phenylene diamine gives no yellow precipitate, though eventually Dimroth, Leichtlin, and Friedemann [12] succeeded in preparing a diazoimine from the

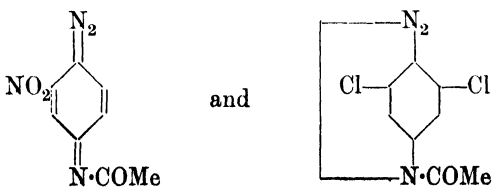
latter compound by the action of caustic soda. Morgan and Upton [11] were, however, convinced that such compounds can be brought into existence, and they eventually succeeded by acting on the base with nitrous anhydride dissolved in acetone. " Nitrous acid gases " (cf. p. 18) are liquefied, and then freed from nitrogen peroxide by the passage of nitric oxide, causing the colour to change from green to pure blue; this is then mixed with dry acetone, and to the cold solution is added, for example, formyl-*p*-phenylene diamine until the liquid becomes pale green. On adding ether to the solution a heavy yellow crystalline precipitate is thrown down, collected, and dried *in vacuo* over phosphorus pentoxide. This substance is the *p*-diazoimine :—



It couples with aryl amines and with β-naphthol, especially if moistened with pyridine. Morgan and Cleage [13] applied the same technique to di-primary phenylene diamines prevented from tetrazotising by an *ortho* substituent (cf. p. 23), and so obtained the parent unsubstituted *p*-diazoimines. These are unstable, but can be acetylated with acetic anhydride, and so stabilised :—

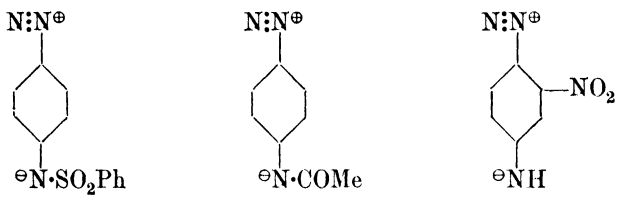


By similar treatment 3-nitro-4-aminoacetanilide and 3 : 5-dichloro-4-aminoacetanilide afford isomerides of the above diazoimines :—



Unstable internal diazoimines analogous to the above unacetylated compounds are also obtainable from the monodiazo-compounds of the diamines of the benzidine series.[5]

The *p*-diazoimines raise the same problems of constitution as do the diazo-oxides. Because Morgan was undecided between the bridge-link and the quinonoid constitution, he used the former for the colourless compounds, since their want of colour might be due to a benzenoid constitution, and the latter for the coloured, hence ostensibly quinonoid compounds, which are the majority. But the analogies between the diazo-oxides and *p*-diazoimines lead to the conclusion that the latter may well also be resonance hybrids :—



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Nitrosoacylarylamides.—With a view to throwing light on the structure of the metallic diazotates, v. Pechmann [3] benzoylated a cold aqueous alkaline solution of sodium *p*-toluene diazotate with benzoyl chloride. He obtained a product which crystallised from acetone in almost colourless needles, gave the Liebermann nitroso-reaction, and on reduction afforded benz-*p*-toluidide. He noted that his product showed a close resemblance in its reactions to nitrosoacetanilide, $Ph{\cdot}N{<}^{NO}_{COMe}$, which O. Fischer [1] made by the action of nitrous acid gases on acetanilide. v. Pechmann from his benzoylation experiments reached the conclusion that one tautomer of the diazotates must have the nitrosamine constitution, $ArN{<}^{NO}_{K}$ (cf. p. 384). Just at that time Wöhl [4] described nitrosobenzanilide prepared from sodium benzene diazotate and benzoyl chloride in 30% yield, and v. Pechmann confirmed his impression as to constitution

by acetylating sodium benzene diazotate with acetic anhydride when he obtained O. Fischer's nitrosoacetanilide.[5] Later there was a dispute between Bamberger,[10] Hantzsch,[12] and Blomstrand[15] as to whether nitrosoacylarylamides are produced both from normal and *iso*diazotates (cf. p. 133).

Although a number of nitrosoacylarylamides are readily produced by O. Fischer's method, and are apparently genuine nitroso-compounds, yet in their reactions they also behave as diazo-compounds. Because of its characteristic diazo reaction in coupling with α-naphthylamine and with α-naphthol in benzene solution, Bamberger[6, 7] pointed out that nitrosoacetanilide must be tautomeric with diazobenzene acetate :—

$$\mathrm{Ph{\cdot}N\langle^{NO}_{COMe}} \rightleftharpoons \mathrm{Ph{\cdot}N{:}N{\cdot}O{\cdot}COMe}$$

This is borne out by other reactions, including the formation of triazens and reduction with potassium sulphite to phenylhydrazinedisulphonic acid,[11] though in general nitrosoacylarylamides cannot be reduced to substituted hydrazines.[2]

The production of nitrosoacylarylamides may therefore be looked on as a special case of diazotisation, and the products as a form of diazo-compound easily isolated in the solid state. Yet they differ from the diazonium salts and the metallic diazotates in that they are readily soluble in organic solvents, being covalent compounds, and Bamberger early discovered that nitrosoacetanilide decomposes on dissolution in benzene, affording diphenyl in high yield.[11] Such reactions are due to homolysis with formation of free radicals, of which the nitrosoacylarylamides are a convenient source (cf. p. 109). Reactions of the nitrosoacylarylamides will be described in later pages under the relevant headings, like other diazo-compounds, and at this point the concern is with their preparation.

Preparation of Nitrosoacetanilide (O. Fischer,[1] Grieve, Hey [26]) :—

Acetanilide (20 g.) is dissolved in glacial acetic acid (100 c.c.), and nitrous acid gases are passed in at 5—10° until the colour is dark green. The whole is then poured into water, and the yellow solid is collected, washed, and dried on a tile. The material thus prepared should be crystalline, having m. p. 50—1° (decomp.), and it can be recrystallised from ether or light petroleum, when the melting point rises to 51—52°, but the keeping quality is inferior to the less pure material, which can be kept in a desiccator for a few days without serious loss.[26]

The reaction fails with the acetyl derivatives of many common arylamines, like *p*-nitroaniline, *o*-chloroaniline, α- and β-naphthylamine, which afford only tars by this process, and acet-*p*-anisidide, which is nitrated to 3-nitro-4-acetamidophenetol.[27]

A much improved method has been introduced by France, Heilbron, and Hey,[28] who replace the nitrous acid gases by nitrosyl chloride used either as gas or in solution in acetic acid or acetic anhydride, sufficient acetate being present to combine with the hydrochloric acid formed :—

$$\mathrm{Ar{\cdot}NHAc + NOCl + KOAc = Ar{\cdot}N(NO){\cdot}Ac + KCl + AcOH}$$

The yield and quality of the product are superior to that obtained with nitrous fumes, and nitroso-derivatives are obtained from acylarylamides which fail to react with nitrous acid gases such as the nitroacetanilides. The reaction is carried out as follows :—

A solution of acetanilide (5 g.) in a mixture of glacial acetic acid (35 c.c.) and acetic anhydride (15 c.c.) containing fused potassium acetate (5 g.) and phosphorus pentoxide (0·5 g.) is stirred at 8° while a 25% solution of nitrosyl chloride (3 g.) in acetic anhydride is slowly added. After fifteen minutes the yellow reaction solution is poured into ice-water when nitrosoacetanilide (4·7 g.) separates as a yellow, crystalline solid, m. p. 50—51° (decomp.).

N-Nitrosoacet-α-naphthalide is made by adding acet-α-naphthalide to nitrosylsulphuric, using the same technique as that employed for diazotising weakly basic amines in this medium.[29]

Nitroso-compounds have been made by O. Fischer's method from arylamines substituted by a variety of acid radicals. Among the carboxylic amides, O. Fischer [2] made nitroso-oxanilide and nitrosoformanilide, whilst unstable nitroso-compounds are obtained from phenyl- and *o*-tolyl-phthalamic acid, for example, *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NPh{\cdot}NO$ [19]; nitrosobenz-*o*-toluidide [21] is also made in this way. The arylsulphamic acids also afford stable nitroso-compounds [9, 14] such as *p*-tolylnitrososulphamic acid, *p*-$C_6H_4Me{\cdot}N(NO){\cdot}SO_3H$, and nitroso-ψ-cumidinesulphamic acid, 1 : 2 : 4 : 5-$C_6H_2Me_3{\cdot}N(NO){\cdot}SO_3H$.[24] Finally, nitroso-compounds having the same characteristics as nitrosoacetanilide are formed from phenylurea and other monoarylureas [18, 23]; *NN'*-diphenylurea forms mononitrosodiphenylurea which couples with phenols,[20] whilst nitrososemicarbazide [8] and nitrosophenylurethane [22] have been described.

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DIAZONIUM SALTS

By virtue of their capacity to function as strong bases, the diazo-compounds form salts with all strong inorganic acids, as well as a number of organic acids, especially arylsulphonic acids (cf. p. 83). They have also a marked capacity to form double salts, and since many of these find technical application, they are discussed in the chapter on stabilised diazo-compounds.

In view of the fact that the diazo-compound must appear as the salt of the acid used in the diazotisation reaction (unless some form of internal salt formation occurs), and since at least two molecules of the acid are required, the choice of this acid is usually determined by cost and convenience in handling. The acids which commonly come into use are therefore sulphuric, hydrochloric, and nitric acids, less commonly hydrobromic acid. As the sulphates and nitrates are less soluble than the halides, the former are indicated where isolation of the diazonium salt is desired.

When the nature of the acid radical is a matter of concern, the required anion may be introduced either by the above direct method or by double decomposition, which is the common practice. Examples of the first method, except for the four acids mentioned above, are few though Hantzsch and Vock [11] made diazonium fluorides by this means and Vorländer [14] the perchlorates.

The chief point to remark concerning salt formation by double decomposition is that the new salt is usually of a lesser degree of solubility in water, in which solvent the reaction is generally carried out, than the one from which it was made, and thus a means is afforded of precipitating and collecting diazonium salts in the solid state. The stability of the solid salts so obtained varies widely, and while some are stable, most chromates and perchlorates are explosively unstable. Hepburn [8] sought to turn to account the great insolubility of the diazonium tungstates for use in printing. He printed cloth with tungstates, dried, and passed the cloth through a diazo solution, when the insoluble diazonium tungstate was formed in the cloth, which, after washing, was passed through alkaline β-naphthol solution, whereupon the insoluble azo dye was formed in the printed areas.

All diazonium salts when in solution in water are highly dissociated, and therefore, as might be expected, change in the anion has little effect on the behaviour of the cation. The diazonium cyanides and sulphites, produced by double decomposition with cyanides and sulphites respectively, have only a transient existence passing at once into the diazo-

cyanides and diazosulphonates which are discussed under separate headings.

A list of anions with some notes on their salts with diazonium cations is given in the table below.

TABLE II

Salts of Diazonium Cations with Various Anions

Anion.	Amines affording diazonium cation.	Diazonium salts.	Refs.
Acetate	*p*-Aminobenzanilide	Cases of isolation few; acetates always unstable.	6, 17
Azide	*p*-Nitroaniline 4-Aminobenzophenone	By interaction of the *iso*diazohydroxide with ethyl azidoformate, $N_3 \cdot CO \cdot OEt$.	10
Carbonate	*p*-Bromoaniline *p*-Aminobenzamide	Difficult to isolate.	6, 12, 17
Chromate	General reaction	Coloured; explosive (cf. p. 354); most diazonium chromates easily isolated; some, *e.g.*, from *p*-nitroaniline, of considerable solubility.	1, 9, 22
Cobaltinitrite	General reaction		6, 21, 23
Fluoride	General reaction	Contain HF, *e.g.*, 2 : 4 : 6 : 1-$C_6H_2Br_3 \cdot N_2F,HF,2H_2O$.	11
Hydroferricyanide	General reaction		3, 9
Iodide	Aniline *p*-Chloroaniline Di-iodoaniline	Most diazonium iodides unstable, decomposing into nitrogen and aryl iodide.	5
Molybdate	General reaction	Usually very sparingly soluble.	17
Nitrite	*p*-Bromoaniline *p*-Aminobenzanilide		6, 12
	1-Nitro-2-naphthylamine	Formed by interchange (cf. p. 125).	
Perchlorate	General reaction		14, 15,
	p-Phenylenediamine	Sparingly soluble and very explosive.	18
Phosphomolybdate Phosphotungstate	*p*-Aminoalkylbenzamide	Probably general reaction.	17
Picrate	Aniline Aminomethylindole Aminophenylindole	Probably isolable in many cases besides those cited; likely to be very explosive.	2, 13, 20
Sulphinate	*o*-Nitroaniline	Only case of isolation; all other sulphinates pass at once to diazosulphones.	19
Thioacetate	General reaction		16
Thiocyanate	Aniline, *p*-chloroaniline	Explosive.	7
Thiosulphate	Benzidine, dianisidine, other diaminodiphenyls		4
Tungstate	General reaction	Very sparingly soluble.	8, 9

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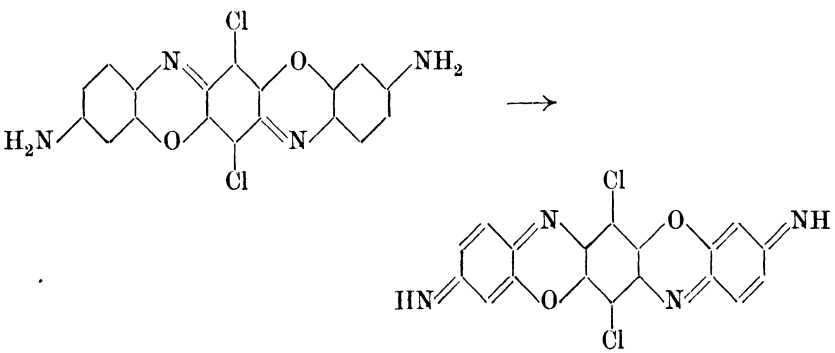
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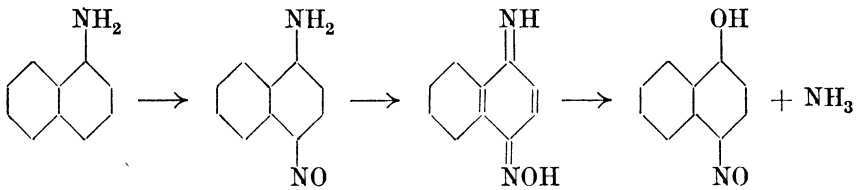
For an account of double salts with complex anions cf. p. 80.

FAILURE OF THE DIAZOTISATION REACTION

With the means at their disposal the early workers failed to diazotise a number of amines, chiefly those containing several negative substituents, such as picramide and pentabromoaniline, but few have since proved entirely resistant when all the resources of the methods now known have been brought to bear. Schmidt and Schall [4] failed to diazotise 6-amino-diphenic acid (6-amino-2 : 2′-dicarboxydiphenyl), as did also Benda [7] with 3 : 5-dinitro-4-aminobenzene-1-arsonic acid, whilst Albert and Ritchie [14] failed with 1-aminoacridine, which affords a non-coupling precipitate by the direct method. Failure to produce a diazo-compound may be due to oxidation of the amine by the nitrous acid or to formation of a nitroso-compound or both these reactions. Stein [1] noticed the oxidising effect of nitrous acid as *p* : *p*′-diaminodiphenylmethane sulphone, which gives a brilliant blue colour with nitrous acid (cf. p. 350), whilst oxidation products of uncertain constitution are produced from di-aminomethoxycoumarin,[3] 9-aminoanthracene,[6] and 3 : 3′-diamino-4 : 4′-dihydroxy-1-arsenobenzene {[: As·$C_6H_3(NH_2)$·OH-3 : 4]$_2$ Salvarsan}.[11] *p*-Aminotriphendioxazines [10] are oxidised to the quinone-imine :—



The formation of nitroso-compounds is interesting in that it is observed with amines which can be easily diazotised or tetrazotised under other conditions. Thus 4 : 6-diamino*iso*phthalaldehyde [13] can be diazotised in nitrosylsulphuric acid, but by the direct method it affords the 5-nitroso derivative. 2-Aminoresorcinal [5] only affords a nitroso-compound, but if one equivalent of nitrite is added all at once to one of *m*-phenylenediamine dissolved in two equivalents of hydrochloric acid, yields of nitroso-*m*-phenylene diamine as high as 20% may result.[2] On the other hand, strongly basic amines which are easily diazotised by the direct method may afford nitroso-compounds when treated with nitrosylsulphuric acid.[8, 9] Blangy [12] found that if α-naphthylamine is dissolved in nitrosylsulphuric acid it is diazotised if the solution is carefully diluted at once, but if reaction is allowed to proceed the product is 4-nitroso-1-naphthylamine, tautomeric with 1 : 4-naphthaquinonimine oxime, and giving 1 : 4-nitroso-naphthol and ammonia on warming with dilute acid :—



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THEORIES OF THE DIAZOTISATION REACTION AND ITS VELOCITY

Resonance involving the amino-group and the aromatic nucleus in primary arylamines reduces the basicity of the nitrogen atom as compared with that of the primary saturated aliphatic amines, and it is for this reason that the arylamines are convertible by nitrous acid into isolable diazonium salts, whereas in the aliphatic series the diazonium group, unable to resonate, has but a transitory existence, since it is immediately replaced, usually by hydroxyl.

The manifold reactivity of the diazo-compounds so invited study of their chemical transformations that many years elapsed after their discovery before any inquiry was made as to the mechanism by which the diazotisation reaction occurs. Bamberger [1] ventured the opinion that diazotisation is analogous to the rearrangement of the arylnitroamines to nitroarylamines, diazo-compounds arising by rearrangement of unstable primary arylnitrosamines, which are the first product of the action of nitrous acid on arylamines :—

$$Ar{\cdot}NH_2 \xrightarrow{N_2O_3} Ar{\cdot}NH{\cdot}NO \longrightarrow Ar{\cdot}N{:}N{\cdot}OH$$

However, a survey of the methods of diazotisation brings out clearly the fact that the *sine que non* for the production of a diazonium salt is that the amine must be present as a salt before attack by nitrous acid commences. Hantzsch and Schümann [2] based their view, which is still that accepted by many chemists, on this fact, their general equation being :—

$$(Ar{\cdot}NH_3)X + HNO_2 = (Ar{\cdot}N_2)X + 2H_2O$$

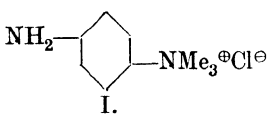
The implications of this view are that the nitrous acid acts in its undissociated form with the cation of the ammonium salt. A criterion by which the idea can be judged is the speed of diazotisation of different amines, though the technique for measuring so fast a reaction is by no means easy. The method adopted by Hantzsch and Schümann consisted in diazotisation by the direct method, and in order to slow down the reaction sufficiently they worked with solutions at N/1000. They measured the consumption of nitrous acid as time went on by zinc iodide-starch (Tromsdorff's method), though Schümann [3] later showed that the conductivity of the solution also gives a measure of the rate, provided certain assumptions are made. With one molecule of free acid and at 0° the velocity constants found were : Diazo-compound from : aniline, 0·036; *p*-toluidine, 0·038; *m*-xylidine, 0·041; *p*-bromoaniline, 0·045. *p*-Nitroaniline, being less basic, gave lower values. The figures satisfy the equation for a reaction of the second order, and all subsequent measurements have confirmed that diazotisation is a second-order reaction. It can hence be concluded that all arylammonium cations probably react with nitrous acid at speeds of the same high order, provided the base is so strong that salt formation is complete with acid at the concentration of the experiment. Naturally, rise in temperature increases the speed of the reaction.

Another technique the use of which has in one form or another displaced the method of Hantzsch and Schümann is the spectrophotometric method of Tassily.[4, 5, 6] Here again N/1000 solutions must be used, and the extent of diazotisation is measured by the depth of colour produced on coupling an aliquot portion of the diazo solution with a naphthol sulphonic acid in presence of excess of alkali, which stops the diazotisation reaction.

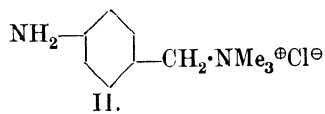
Tassily observed that the speed of diazotisation of sulphanilic acid increases with the concentration.

Böeseken, Brandsma, and Schoutissen [7, 12] examined the velocity of diazotisation by the photometric method, and showed that with amines of the same order of basicity diazotisation is accelerated by substituents in the sequence *ortho* > *para* > *meta*, the last having but little effect. Substituents which alter the basicity, however, introduce two opposed effects. Thus negative substituents cause acceleration of the velocity, but at the same time reduce the basicity, and hence for a given acid concentration there is a smaller concentration of the ammonium salt with amines of lower basicity, and hence a lower velocity of diazotisation, since the Dutch school agree with Hantzsch and Schümann that it is the ammonium salt which is diazotised.

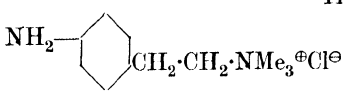
To test the dual proposition that in the absence of excess mineral acid amines diazotise at different velocities, the order being identical with the order of basicity, and that the rate is not appreciably altered in presence of more acid than that necessary to form the ammonium salt, Reilly and Drumm [11] measured the velocity of diazotisation of a series of three amines in which the basicity was progressively reduced by the influence of a quaternary ammonium group acting at the *para* position to the primary amino-group:



I.



II.



III.

Using the colorimetric technique, they found that the amine (III), in which the amino-group is most strongly basic, because most completely shielded from the quaternary ammonium group, diazotises faster than either (I) or (II) with one equivalent of acid, but that all react at the same velocity with excess of acid. The stability of the diazonium salts produced is in the reverse order.

Ueno and Suzuki [10] examined a series of no fewer than forty-seven amines, and established or confirmed the following points concerning the diazotisation reaction :—

1. The velocity of diazotisation increases as the concentration of hydrochloric acid rises from 0·05*N* to 4*N*.
2. The velocity is three to four times greater at 10° than at 0°.
3. Substituents increase velocity in the ascending order $Cl < CO_2H < SO_3H < NO_2$.
4. Substituents in the *ortho* position have the greatest effect on the velocity, whilst those at *para* and *meta* have less. Alkyl and alkoxy groups have no effect.

5. The velocity of diazotisation is much greater with hydrobromic acid than with hydrochloric acid, whilst with nitric acid, sulphuric acid, and naphthalene-1 : 5-disulphonic acid the velocity is less.

To the above may be added Schoutissen's [14] findings on the effect of acidity of the velocity of diazotisation of *p*-toluidine, *o*-, *m*-, and *p*-chloroaniline and anthranilic acid :—

1. The velocity is not inversely proportional to the excess of hydrochloric acid, and therefore reaction is not between the free amine and nitrous acid.
2. The reaction takes place with the salt of the amine.
3. Experimental and calculated velocities do not agree, and mostly the influence is less than that accounted for by decreasing hydrolysis of the amine salt.
4. Excess of hydrochloric acid increases the velocity for all amines by (*a*) decreasing hydrolysis and (*b*) a specific action (cf. 5 above).

E. Rostovtzeva [13] measured the velocity of diazotisation of a number of aromatic amines relative to benzidine, thus obtaining a series of characteristic ratios with the aid of which the content of either constituent of a known binary mixture can be determined from the measurement of its characteristic ratio. K. Rostovtzeva,[15] having determined the velocity of diazotisation of *o*- and *p*-toluidine and *o*-, *m*-, and *p*-nitroaniline, used the results for the determination of binary mixtures.

Both Earl and his co-workers and Kenner have attempted to formulate a general theory for the interaction of nitrous acid with primary, secondary, and tertiary aromatic amines and primary and secondary aliphatic amines. From this viewpoint diazotisation is only a part of a larger problem. Earl and Hills [17] showed that the course of the initial interaction of aniline with nitrous acid is the same as for methylaniline and nitrous acid, and Earl [18] then prepared aniline nitrite in the dry state, and found that the dry solid kept at — 6° to — 8° under nitrogen in one hour changes in part into diazoaminobenzene and benzenediazonium nitrite. Earl and Laurence [21] found that other arylamine nitrites behave in the same way. The interaction of primary aromatic amines with nitrous acid in a methanol solution of hydrochloric acid can be followed by the dilatometer or conductiometrically. The volume–time curves are not very satisfactory, but the conductivity–time curves all show an initial period of steadily falling conductivity followed by a rapid rise until the evolution of nitrogen commences.[10] Reaction can also be followed by changes in pH.[20] Finally, Earl and Hills [22, 24] concluded that the primary reaction is between free amine and undissociated nitrous acid acting as a nitroso-compound :—

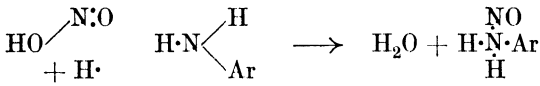
$$HO{\cdot}N{:}O + ArNH_2 = (HO)_2N{\cdot}NHAr$$

Schmid [16] also reached the conclusion that it is chiefly only the undis-

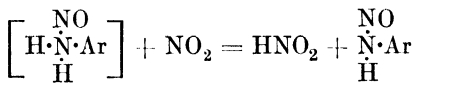
sociated aniline which reacts with nitrous acid, though he considered the measurable reaction in hydrochloric acid at greater than 0·4N to be :—

$$PhNH_3Cl + HNO_2 = PhN_2^+ + Cl^- + 2H_2O$$

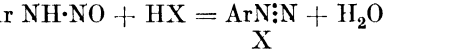
Kenner [23] points out that the chemistry of nitrous acid is still only imperfectly understood, in spite of the work of Abel,[8] and that there is evidence to show that it is primarily nucleophilic, and hence must react with a proton before its nitroso-group can combine with nucleophilic amines :—



Completion of this reaction requires elimination of a proton from the nitrosammonium ion, and this is the function of the anion of weakly acid nitrous acid :—



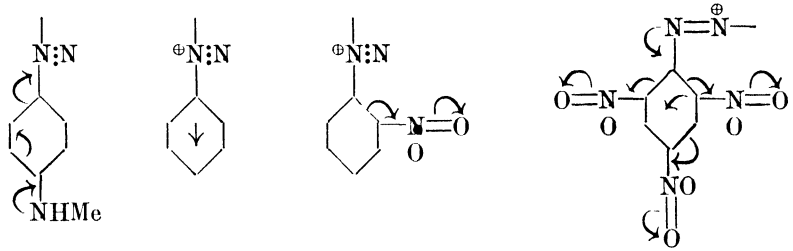
The nitrosamine in presence of an acid gives the diazonium salt and water :—



Thus the basic principle of Hantzsch and Schümann is opposed by these three last writers, who regard the function of the acid in the diazotisation reaction not as necessary to form an ammonium salt, but to provide a proportion of hydrolytically dissociated base in a state accessible to HNO_2. This tallies with the experimental observation that weak bases can often be diazotised if present in suspension in an aqueous acid in a sufficiently finely divided form. On the above view the small amount of base in solution is largely dissociated, and therefore quickly diazotised, and so the suspended base is drawn into solution and is itself diazotised, with rapid completion of the reaction.

The question arises as to what part the aromatic nucleus plays in the diazotisation reaction, for it cannot be without influence, else there is no reason why the reaction should be unknown in the aliphatic series. The cause of the existence of the aromatic diazo-compounds is the unsaturation of the aromatic nucleus, since the negative field arising from the unshared electrons stabilises the positive charge on the pentavalent nitrogen atom of the diazonium salts, thus permitting it to form a cation of greater or less stability. The widely varying properties of the diazo-compounds arise from the drift imparted by substituents to these unshared electrons, and the equilibrium between diazonium and diazo-electromer is due to this movement of charges. Negative groups in the *ortho* and/or *para* positions intensify the electron drift away from the nitrogen atom,

and so increase the stability of the diazonium salt up to a point, after which the inductive effect may become so strong that the positive pole is transferred to the nitrogen atom farthest from the aromatic nucleus, and the diazo-electromer, ArN:N·X, becomes stable, as is shown by the capacity of trinitrodiazobenzene to couple in strongly acid solution (cf. p. 196). Positive substituents, by balancing or reversing the inductive effect, lower the stability, and the following diagrams represent these intramolecular forces in terms of the electron theory of valency :—



No doubt if unsaturated aliphatic amines could be made in which the carbon chain could exert an inductive effect on the amino-group such amines would afford diazo-compounds, but such amines are extremely unstable, and it has so far proved impossible to bring them to the test of reaction with nitrous acid.

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DIAZO-COMPOUNDS FROM SOURCES OTHER THAN THE ACTION OF NITROUS ACID ON AMINES

From time to time reactions have been discovered which afford diazo-compounds by means entirely different from any variants of the reaction between an amine and nitrous acid. Such reactions can conveniently be arranged in three groups :—

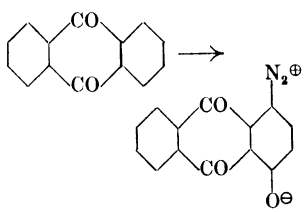
1. Oxidation reactions.
2. Reduction reactions.
3. Scission reactions by which part of a more complex molecule appears as a diazo-compound.

The gist of the several groups can be most readily apprehended by a tabular arrangement (Tables III, IV, and V), and the criterion of oxidation or reduction is the fate of the initial aromatic nucleus which is converted into a diazo-compound.

The reaction shown in Table IV by which excess of nitrous acid converts

TABLE III

Oxidation Reactions Leading to Diazo-Compounds

Aromatic compound.	Oxidising agent.	Reaction.	Refs.
Arylhydrazines	Mercuric oxide	$PhNH{\cdot}NH_2, H_2SO_4 + O_2 = PhN_2{\cdot}HSO_4 + 2H_2O$	1
	Mercuric acetate		2
	Bromine	$PhNH{\cdot}NH_2 + 2Br_2 \longrightarrow PhNBr{\cdot}NBr_2 \longrightarrow PhN_2{\cdot}Br + p\text{-}C_6H_4Br{\cdot}N_2Br$	3, 4, 8
	Nitrous acid	$PhNH{\cdot}NH_2, HCl \longrightarrow PhN_2{\cdot}Cl$	5
	Ag salts in exposed photographic emulsion		9
Nitrosophenyl-hydrazine	Nitrogen trioxide	$PhN(NO){\cdot}NH_2 \longrightarrow PhN_2{\cdot}NO_3$	6
Anthraquinone	Nitrous acid with mercury catalyst		7

1. E. Fischer, *Ann.*, 1877, **190**, 99.
2. Bamberger, *Ber.*, 1899, **32**, 1809.
3. L. Michaelis, *ibid.*, 1893, **26**, 2190.
4. Chattaway, *J.C.S.*, 1908, **93**, 852–8.
5. Altschul, *J. pr. Chem.*, 1896, [ii], **54**, 496.
6. Rügheimer, *Ber.*, 1900, **33**, 1718.
7. Bayer, B.P. 27,373/04; D.R.P. 161,954 (Fr., **8**, 252).
8. Vaubel, *J. pr. Chem.*, 1894, [ii], **49**, 341; 1897, [ii], **55**, 220.
9. DuPont, U.S.P. 2,339,213.

TABLE IV

Reduction or Condensation Reactions Leading to Diazo-Compounds

Aromatic compound.	Reducing agent.	Reaction.	Refs.
Nitrosophenol	Nitrous acid	$OH{\cdot}C_6H_4{\cdot}NO + 3HNO_2 = OH{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_3 + HNO_3 + H_2O$	1
p-Nitrosodiphenylamine	,, ,,	$PhNH{\cdot}C_6H_4{\cdot}NO + 3HNO_2 = PhNH{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_3 + HNO_3 + H_2O$	2, 3
p-Nitrosodimethyl aniline	,, ,,	$Me_2N{\cdot}C_6H_4{\cdot}NO + 3HNO_2 = Me_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_3 + HNO_3 + H_2O$	7
Nitrosobenzene	Hydroxylamine	$PhNO + NH_2OH = PhN_2{\cdot}OH + H_2O$	4
Nitrosobenzene	Nitrous acid	Course of reaction in question	5
Thionylphenylhydrazine	Acetyl chloride	$PhN{:}N{\cdot}S{\cdot}OH + MeCOCl = PhN_2Cl + S + AcOH$	6

1. Jäger, *Ber.*, 1875, **8**, 895.
2. Ikuta, *Ann.*, 1888, **243**, 283.
3. Hantzsch, *Ber.*, 1902, **35**, 893.
4. Bamberger, *ibid.*, 1895, **28**, 1218. See also p. 131.
5. *idem*, *ibid.*, 1918, **51**, 634.
6. A. Michaelis, Ruhl, *Ann.*, 1892, **270**, 117.
7. Hinman, Hollmann, U.S.P. 2,178,585.

TABLE V

Scission Reactions Leading to Diazo-Compounds

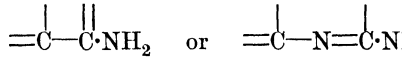
Aromatic compound.	Reagent.	Reaction.	Refs.
Diazoamino-compounds	Bromine	$PhN{:}N{\cdot}NHPh + 2Br_2 \longrightarrow PhN_2Br + NH_2{\cdot}C_6H_2Br_3$	1
Mercury-diphenyl, -ditolyl, -dinaphthyl	Nitrogen trioxide	$HgAr_2 + 2N_2O_3 \longrightarrow ArN_2{\cdot}NO_3 + HgArNO_3$	2, 3, 9
Nitrosophenylglycine	Alcoholic HCl	$PhN(NO){\cdot}CH_2{\cdot}CO_2H \longrightarrow$ *p*-diazophenylhydroxylamine	4
Azo-compounds	Lead peroxide	$Ph{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + 3H_2SO_4 + 2PbO2 = PhN_2{\cdot}SO_4H + C_{10}H_6O_2 + 2PbSO_4 + 3H_2O$	5
	Nitric acid	$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OMe + 3HNO_3 = NO_2{\cdot}C_6H_4N_2{\cdot}NO_3 + (NO_2)_2C_6H_3{\cdot}OMe + 2H_2O$	6, 8
	Chromium trioxide	$p\text{-}NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH + CrO_3 \longrightarrow p\text{-}NH_2{\cdot}C_6H_4N_2{\cdot}CrO_4H$	7

1. Griess, *Phil. Trans.*, 1864, **154**, 668.
2. Bamberger, *Ber.*, 1897, **30**, 506.
3. J. Kunz, *ibid.*, 1898, **31**, 1528.
4. O. Fischer, *ibid.*, 1899, **32**, 247.
5. Lauth, *Bull. Soc. chim.*, 1891, [iii], **6**, 94.
6. O. Schmidt, *Ber.*, 1905, **38**, 3201.
7. Meldola, Eynon, *J.C.S.*, 1905, **87**, 1–5.
8. Rowe, Levin, *J.S.D. & C.*, 1924, **40**, 219.
9. Makarova, Nesmejanov, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 771–9.

a nitroso-compound into a diazonium nitrate is of interest, because it may be that the diazo-compounds which appear when wool or casein is treated for some hours with excess of cold dilute nitrous acid arise in this way—for example, from tyrosine (cf. p. 355). It has also been patented as a method of manufacturing the *p*-dialkylaminobenzenediazonium salts which are used for diazotype emulsions.

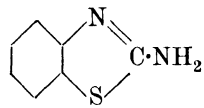
HETEROCYCLIC DIAZO-COMPOUNDS

The amino-group is diazotisable when attached to an unsaturated heterocyclic ring which reduces the basicity of the nitrogen by resonance in the same way as does the aromatic ring, and hence a number of non-aromatic diazo-compounds are known. Morgan and Burgess [30] pointed out that such diazotisable amines contain the group $\geqslant C{\cdot}NH_2$ and one other centre of unsaturation, usually another double bond, giving structures such as :—



The amines vary in the ease with which they may be diazotised, and the diazonium salts vary greatly in stability. Thus 3-aminopyridine is easily diazotised by the direct method,[47] whilst 4-aminopyridine requires the method of Witt [32] or other methods using strong acids,[47] as does 5-aminoacridine,[54] which may be regarded 2 : 3 : 5 : 6-dibenzpyridine. Compounds containing acid groups, such as 5-aminouracil-4-carboxylic acid,[3] respond to the inverted method.

Diazotisation of 2-Aminobenzthiazole.[52]



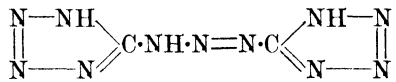
2-Aminobenzthiazole (150) is dissolved in formic acid (250), and the solution is added to a cooled mixture of 96% sulphuric acid (1100) and water (500); the sulphate of the base is precipitated. Then there is added slowly with stirring at −5 to −10° a solution of sodium nitrite (69) dissolved in water (500 parts). The coupling to form an azo dye is carried out as soon as diazotisation is complete. 6-Nitro-2-aminobenzthiazole is diazotised in the same way,[53] but 2-aminobenzthiazole-6-carboxylic acid [43] is diazotised in nitrosylsulphuric acid.

There are some peculiarities to be noted among the heterocyclic diazo-compounds. Some pass easily, even in dilute acid solution, into unreactive *iso*diazotates; among these are 4-methyl-2-diazotriazole [7] and 3-diazoindazole.[9, 10] Replacement of the diazo-group by halogen may be extremely facile, and the product of diazotisation in concentrated hydrochloric acid consists entirely or in part of the compound in which chlorine has replaced the diazo-group; examples of this are the production of 2-chloro-4- [31] and -6-picoline [29] from 2-amino-4- and -6-picoline, and 3-chloropyridine from 3-aminopyridine.[38] Heating with dilute sulphuric acid usually replaces the heterocyclic diazo nitrogen by hydroxyl, though

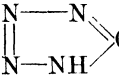
Hunter [34] failed to convert 2-diazobenzthiazole into 2-hydroxybenzthiazole, and the diazo-group in 3 : 5-dimethyl-4-diazo*iso*-oxazole [30] is not replaceable by hydroxyl, ethoxy, or the sulphuric acid radical. Diazotisation of 5-aminotetrazole with excess of nitrite in presence of copper sulphate gives 5-nitrotetrazole,[45] the diazo-group being replaced by a nitro-group. The diamines of the pyridine series have not been tetrazotised; 2 : 6-diaminopyridine [28] with nitrous acid affords a nitroso-derivative, and nitrous acid converts 3 : 4-diaminopyridine [46] or 2-chloro-3-amino-4-butylaminopyridine into 3 : 4-pyridinotriazoles.[49]

The decomposition of the 4-diazo-pyrazoles and -pyrazolones [33] by heat in aqueous solution follows the unimolecular law, but the rate is greater for 5-diazo-1 : 2 : 4-triazole,[36] showing that two reactions are in progress.

The aliphatic compound aminoguanidine, $NH_2{\cdot}C(:NH){\cdot}NH{\cdot}NH_2$, when treated with nitrous acid affords salts which can couple to form azo-compounds.[55] This is because tetrazolediazonium salts are formed by ring-closure, the mode of ring-closure and the products varying with conditions. Nitrous acid in acetic acid solution produces the ditetrazolyltriazen [44, 56];

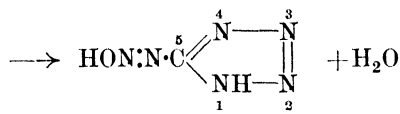


Reiley, Teegan, and Carey [56] have also shown that aminoguanidine and nitrous acid interact in two other ways: (*a*) to form an azide, $NH_2{\cdot}C(:NH){\cdot}N_3$, which isomerises to 5-amino-1 : 2 : 3 : 4-tetrazole,



which then diazotises, or (*b*) in neutral solution there is formed 1-guanyl-4-nitrosoaminoguanyl*iso*tetrazene, which with alkali regenerates aminoguanidine and forms 1 : 2 : 3 : 4-tetrazolediazohydroxide :—

$$NH_2{\cdot}C(:NH){\cdot}NH{\cdot}NH{\cdot}N{=}N{\cdot}C(:NH){\cdot}NH{\cdot}N{:}NOH \longrightarrow$$
$$NH_2{\cdot}C(:NH){\cdot}NH{\cdot}NH_2 + HON{:}N{\cdot}C(:NH){\cdot}NH{\cdot}N{:}NOH$$



2-Diazobenzthiazole and its substituted derivatives [40, 52, 53] have been patented as components for azo dyes for cellulose acetate, and those of 3-diazoindole [42] for ice colours. Azo dyes having therapeutic properties are made by coupling diazotised aminopyridines with mono- or diaminopyridine [39] or with *m*-phenylenediamine or *m*-aminophenol.[51] Diazotised aminotriazoles and -tetrazoles [41] couple with suitable components to form azo dyes which in turn form metallic complexes.

TABLE VI

Diazotisable Heterocyclic Amino-Compounds

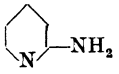
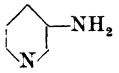
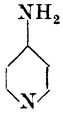
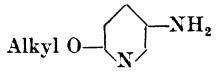
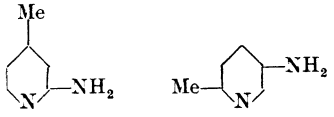
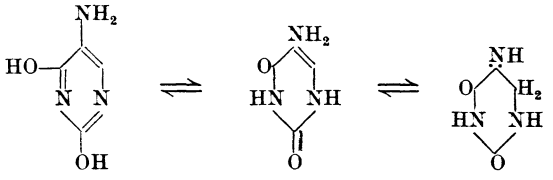
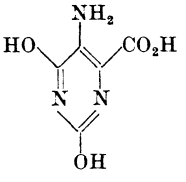
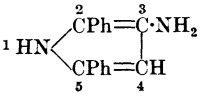
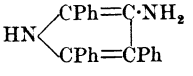
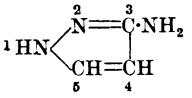
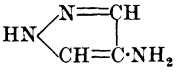
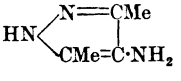
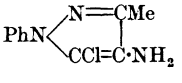
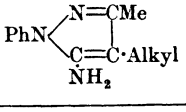
Series.	Amino-compound.	Constitution.	Ref.
Pyridine	2-Aminopyridine		26, 31, 47
	3-Aminopyridine		8, 38, 47
	4-Aminopyridine		32, 38, 47
	3-Amino-6-alkoxypyridine (Alkyl = Me, Et, Bu)		39, 51
	2 : 4-, 2 : 6-Aminopicoline		31, 29
Pyrimidine	5-Amino-2 : 4-dihydroxypyrimidine (5-Aminouracil)		3
	5-Aminouracil-4-carboxylic acid	 and tautomers	5
Pyrrole	3-Amino-2 : 5-diphenylpyrrole		14
	3-Amino-2 : 4 : 5-triphenylpyrrole		14
Pyrazole	3-Aminopyrazole		12
	4-Aminopyrazole		12
	4-Amino-3 : 5-dimethylpyrazole		12
	5-Chloro-4-amino-1-phenyl-3-methylpyrazole		25
	5-Amino-1-phenyl-3-methyl-4-alkylpyrazoles (Alkyl = Me, Et, Pr^{a}, CH_2Ph)		22

TABLE VI—*continued.*

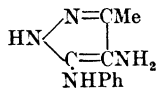
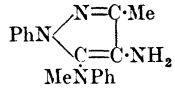
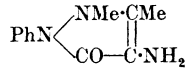
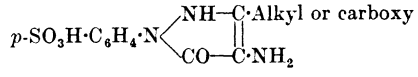
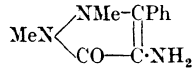
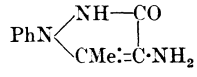
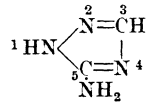
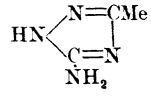
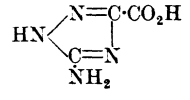
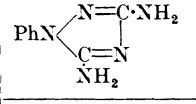
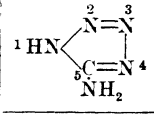
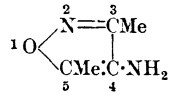
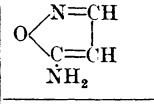
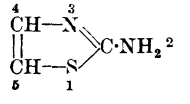
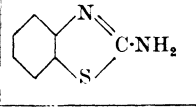
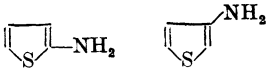
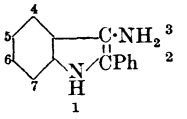
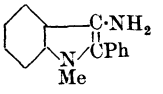
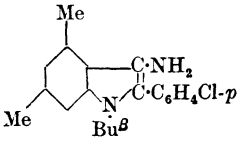
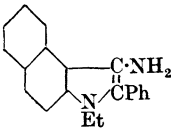
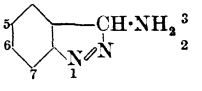
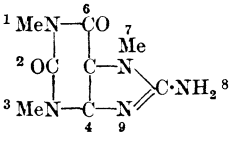
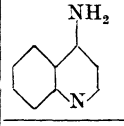
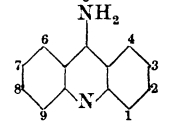
Series.	Amino-compound.	Constitution.	Ref.
Pyrazole—*continued*	4-Amino-5-anilino-3-methylpyrazole		24
	4-Amino-5-methylanilino-1-phenyl-3-methylpyrazole		19
	4-Amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone (Aminoantipyrine)		6, 17, 18, 20
	4-Amino-1-*p*-sulphophenyl-3-alkyl- or carboxy-5-pyrazolone		57
	4-Amino-3-phenyl-1 : 2-dimethyl-5-pyrazolone		16
	4-Amino-1-phenyl-5-methyl-3-pyrazolone		15
Triazole	5-Amino-1 : 2 : 4-triazole		7, 36
	5-Amino-3-methyl-1 : 2 : 4-triazole		7, 36
	5-Amino-3-carboxy-1 : 2 : 4-triazole		41
	3 : 5-Diamino-1-phenyl-1 : 2 : 4-triazole (Phenylguanazole)		41
Tetrazole	5-Amino-1 : 2 : 3 : 4-tetrazole		4, 56
*iso*Oxazole	4-Amino-3 : 5-dimethyl*iso*oxazole		30
	5-Amino*iso*oxazole		37, 50
Thiazole	2-Aminothiazole		1, 2, 23
	2-Aminobenzthiazole		34, 52, 53

TABLE VI—*continued.*

Series.	Amino-compound.	Constitution.	Ref.
Thiophen	2- and 3-Aminothiophen		35, 58
Indole	3-Amino-2-phenylindole		13, 48
	3-Amino-2-phenyl-1-methylindole		42
	3-Amino-2-*p*-chlorophenyl-4 : 6-dimethyl-1-*iso*-butylindole		42
	3-Amino-2-phenyl-1-ethyl-4 : 5-benzindole		42
Indazole	3-Aminoindazole		9, 10
Purine	1 : 3 : 7-Trimethyl-2 : 6-diketo-8-iminohexahydropurine (8-Aminocaffeine)		11
Quinoline	4-Aminoquinoline		47
Acridine	5-Aminoacridine		54

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CHAPTER II

THE STABILITY OF DIAZO-COMPOUNDS IN THE SOLID STATE AND IN SOLUTION

STABILITY OF DIAZO-COMPOUNDS—STABILISED DIAZO-COMPOUNDS—VARIATION OF STABILITY WITH pH—RELATION BETWEEN pH AND CONSTITUTION OF DIAZO-COMPOUNDS—CONSTITUTIONS OF COMMERCIAL ICE COLOUR BASES.

THE STABILITY OF DIAZO-COMPOUNDS

Diazo-Salts in the Solid State. All diazo-salts which have been isolated in the solid state should be treated with the greatest care, even when damp, and still more so if dry or if they have been in storage for any length of time. Precautions with a new solid diazo-salt should include limiting the mass of any specimen to a few grammes, handling it on open saucers and storing it in thin-walled specimen tubes so that there is the minimum of glass to fly in an explosion, while the operator should wear splinter-proof goggles. Precautions can only be relaxed when prolonged experience has shown an individual to be quite safe. References to damage caused by explosions are to be found in the literature onwards from the first paper published by Griess,[1] who wrote of 4 : 6-dinitrobenzene-2 : 1-diazo-oxide : " Dieser Körper erträgt nicht die Hitze des Wasserbades sondern zersetzt sich durch dieselbe unter heftige Explosion."*

The anion has a considerable effect in determining the explosibility of a given diazo-salt. Usually the chloride and sulphate are less dangerous than the nitrate, while the introduction of nitro-groups into the nucleus further increases explosiveness. The sparingly soluble and apparently stable diazobenzene-*p*-sulphonic acid obtained from sulphanilic acid is notorious in respect of its fickleness, Wichelhaus [9] and Cain both having left warning of its treachery, and Bamberger [5a] has recorded a violent explosion due to *p*-nitrobenzenediazonium nitrate. But while some diazo-compounds can actually be used as explosives (cf. p. 354), research has also revealed means by which solid diazo-compounds can be safely introduced into commerce when they are known generically as " stabilised diazo-compounds ", and an account of these forms the subject of the next section (cf. p. 69).

Diazo-Salts in Solution. The want of a solvent in which reaction can proceed prevents smooth and continuous decomposition of diazo-salts in the solid state, hence when the molecule is excited to the rupturing

* This substance cannot endure the heat of the water-bath but is decomposed by it with a violent explosion.

point explosion ensues. When in solution decomposition can proceed steadily at all temperatures until the process has reached completion. Much study has been given to this process when taking place in aqueous solution, in order to obtain knowledge as to the nature of the process itself, of the effects of substituents, and to compare the stability of various diazo-compounds with one another.

A considerable number of workers have taken part in the researches which have brought the knowledge of the subject to its present level, and although there is some disagreement between them on certain points, the main body of knowledge is firmly established. Though earlier work had been carried out by Oddo,[6, 7] and by Hirsch,[2] the foundations of exact quantitative measurements were laid by Hausser and Muller,[3, 4, 5] Hantzsch,[8, 21] Euler,[10] and Cain and Nicoll.[11, 12] These showed, mostly by measurement of the rate of nitrogen evolution, that in acid solution the decomposition of a diazo-compound which is in complete solution follows the ordinary law for a unimolecular reaction, namely :—

$$K = \frac{1}{t} \log \frac{A}{A - x}$$

The products of the decomposition do not interfere with the reaction except in the naphthalene series, where the naphthols which are formed remove the diazo-compound by coupling when they have reached a certain concentration. The tetrazo-compounds of the diphenyl series do not strictly obey the unimolecular law.

Cain and Nicoll [12] investigated the relation between K, the velocity constant, and the temperature, finding the relation to follow the Arrhenius expression for an irreversible reaction :—

$$K_{t_1} = K_{t_0} e^{A \frac{T_1 - T_0}{T_1 T_0}}$$

where A is a constant and T_1 and T_0 are the absolute temperatures corresponding to K_{t_1} and K_{t_0}. Euler checked experimentally the calculated values of Cain and Nicoll, finding good agreement. The work which has been done by Yamamoto and the Japanese school has further confirmed the above finding.[28, 35, 39, 40, 41]

Moelwyn-Hughes and Johnson [48] studied the decomposition of benzenediazonium chloride in water as an example of a unimolecular reaction in which the relation between the velocity constant and the temperature is given by the equation

$$\frac{d \ln K}{dt} = \frac{E_A}{RT^2}$$

where E_A is the apparent energy of activation. But $E_A = E + JT$, where J is a constant, and hence substituting and integrating

$$\ln K = C + \frac{J}{R} \ln \mathrm{T} - \frac{E}{RT}$$

These workers prepared pure benzene diazonium chloride by the method of Knoevenagel, and made solutions of known concentration in water, the velocity of decomposition being determined manometrically with precautions against supersaturation of the water by the evolved nitrogen. Now, the diazonium salts being highly ionised in solution, break down according to the unimolecular law at any given temperature, irrespective of the anion, so long as it be that of a strong mineral acid, such as hydrochloric, hydrobromic, sulphuric, or nitric acids.[13, 15, 21] The main equation for the decomposition is :—

$$ArN_2^{\oplus}X^{\ominus} + H_2O = ArOH + H^{\oplus}X^{\ominus} + N_2$$

Moelwyn-Hughes and Johnson showed that when X = Cl no other reaction occurs over the range of concentration used by them (0·053—0·011 g.-mol. per l.), and from their measurements they determined $J = -35{\cdot}76$ cal. per g.-mol. per degree, $J/R = -18$ (where $R = 1{\cdot}9869$ cal. per g.-mol. per degree) and $E = 38{,}200$ cal. and hence their final expression is :

$$\ln K = 157{\cdot}067 - \frac{38{,}200}{RT} - 18 \ln T$$

Then the Arrhenius equation becomes :—

$$\ln K = 35{\cdot}6457 - \frac{27025}{RT}$$

Their measurements thus give $E_A = 27{,}025$ cal./g.-mol. as against 27,030 cal./g.-mol. found by Cain and Nicoll.[12] These workers therefore conclude that the results show that it is the ion $PhN_2^{\oplus}$ which decomposes and that there is no evidence for or against the view that free radicals are also involved in the reaction. Further, most of the activation energy appears to be drawn from vibrational quanta.

Crossley, Kienle, and Benbrook [47] carried out a similar investigation, covering not only benzenediazonium chloride, but twenty-four of its mono-substituted derivatives. Using the Arrhenius equation, they found $E = 27{,}300$ cal./g.-mol. for benzenediazonium chloride, and for other diazonium salts found it to vary from 22,800 cal./g.-mol. for 3-diazodiphenyl to 33,200 cal./g.-mol. for *m*-nitrodiazobenzene. They also showed that the reaction velocity is the same in deuterium oxide as in water. There is an induction period in the decomposition of *o*-methoxybenzenediazonium chloride.[54]

The velocity of decomposition is hardly affected by the amount of free mineral acid present unless high concentrations are reached. Cain [14] found that the velocity falls when much sulphuric acid is present. Moelwyn-Hughes and Johnson found a 15% increase in 5·1*N*-hydrochloric acid, which Crossley, Kienle, and Benbrook confirmed, saying that the velocity increases up to 10*N* and then falls. It is immaterial whether the

solution is agitated or not, though if not agitated the nitrogen may not escape smoothly due to supersaturation of the water by the gas.[17, 18, 19, 20]

Blumberger [29] has pointed out that the decomposition which produces phenol is not the only one possible, since there may also occur the reactions

$$ArN_2{\cdot}Cl \longrightarrow ArCl + N_2$$

$$ArN_2^{\oplus} + HCl = ArCl + N_2 + H^+$$

No acid is produced in these reactions, and hence Euler's failure in the attempt to use the acid produced in the decomposition as a measure of the total reaction. Further, a solution of a diazonium sulphate may contain ions of $[ArN_2{\cdot}SO_4]^{\ominus}$, which may well decompose more slowly than the ion $ArN_2^{\oplus}$. Blumberger found support for this view, in that by adding chlorides to weakly acid solutions of benzenediazonium chloride he was able to increase the yield of chlorobenzene. Crossley, Kienle, and Benbrook [47] found that the yield of phenol rises from 24·3% at 2·36 mols. of water to 95·2% at 1268 mols. of water per mol. of benzenediazonium chloride, though both Hantzsch and Cain have shown that the velocity of decomposition is not affected by concentration of the diazonium salt. Hantzsch thought Schwalbe, who held the opposite view, to be in error, but Snow [33] has brought forward evidence to show that in concentrated solutions the rate of decomposition does fall somewhat.

Substituents in the aryl nucleus have a marked effect on the stability of diazo-compounds, so that there is an enormous difference between the most stable and the least stable compounds known. It is, however, impossible to predict what stability any given diazo-compound will possess beyond the general rule that negative substituents increase stability. Agreement has also been lacking even as to the experimentally determined order in which the various diazo-compounds fall, but below is given a comprehensive list published by Snow,[33] who measured the rate of decomposition of the diazonium chlorides at 20°. In the list theamines are arranged in descending order of the stability of their diazonium chlorides :

1. *p*-Chloroaniline.
2. *m*-Nitroaniline.
3. *m*-4-Nitroxylidine.
4. *o*-Nitroaniline.
5. *o*-Anisidine.
6. *p*-Nitroaniline.
7. *p*-Bromoaniline.
8. *o*-Phenetidine.
9. *p*-Iodoaniline.
10. 5-Aminosalicylic acid.
11. *p*-Toluidine.
12. Aminoazobenzene.
13. *p*-Aminophenol.
14. *p*-Phenylene diamine (diazotised).
15. Picramic acid.
16. Sulphanilic acid.
17. *p*-Aminobenzoic acid.
18. α-Naphthylamine.
19. *p*-Anisidine.
20. β-Naphthylamine.
21. *m*-4-Xylidine.
22. Anthranilic acid.
23. Aminoazotoluene.
24. *m*-Aminobenzoic acid.
25. *o*-4-Xylidine.
26. *o*-3-Xylidine.
27. Aniline.
28. *o*-Toluidine.
29. *m*-Toluidine.
30. *m*-Anisidine.
31. *p*-Xylidine.
32. *p*-Phenylenediamine (tetrazotised).

While variation of the anion has but little effect on the stability of

solutions of diazonium salts, other substances can be added which have a considerable effect. Certain metallic salts which form double salts with diazonium salts, and also arylsulphonic acids, have the effect of slowing up decomposition, and these two groups, being of technical importance, are treated under the heading of stabilised diazo-compounds (cf. p. 69). Neutral metallic salts can in some cases cause slowing down of decomposition, while in other cases the effect is nil. Schwalbe [15] found the rate of decomposition of *p*-nitrodiazobenzene to be halved by the addition of salt at the rate of 90 g. per litre, and Hantzsch and Thompson [21] found a 40% decrease in the velocity of decomposition of the same diazo-compound by increasing salt from 6 to 12 g. per litre; this stabilising effect has been patented.[9a] Viktorov [31] has stated that for salts having the same anion as the *p*-nitrodiazobenzene, decomposition is speediest for the most basic cation, and Sieber [26] and Lesur [46] both say that the presence of tungstates or boric acid lowers the velocity of decomposition. Knecht and Platt [23] found evidence that the traces of nitrate with which all technical sodium nitrite is contaminated has a deleterious effect on diazo-compounds, and they added small quantities of reducing agents, such as metabisulphite, to diazo solutions in order to remove nitrate, and Viktorov [32] has confirmed that metabisulphite and bisulphite, but not hydrosulphite, retard decomposition during the first few hours. Maleic acid retards decomposition of diazo-compounds in printing pastes [53] while sulphamic acid and its salts stabilise solutions of 4-chloro-2-nitrodiazobenzene.[52]

That excess of nitrous acid is harmful to the stability of diazo solutions was discovered by both Schwalbe and Hantzsch. The latter showed that the decomposition is at first accelerated, but returns to the normal rate when the nitrous acid has been used up. When ferrous ions are present—as, for instance, in technical diazotisation, where iron may come in contact with the acid diazo solution—excess nitrous acid has a stabilising effect, since it oxidises the ferrous to ferric ions, and whereas the former cause rapid decomposition, the latter are harmless. The following table shows how great is this effect with *o*-chlorodiazobenzene [27]:

Original content of base in solution, 0·925 g. per litre, and figures are gms. per litre remaining after the time given.

	1 Hr.	Loss, %.	2 Hr.	Loss, %.	3 Hr.	Loss, %.
Without HNO_2, Fe^{II} present	0·508	45	0·214	77	0·00	100
With HNO_2, Fe^{III} present.	0·853	8	0·807	13	0·71	23

Colloidal metals bring about rapid destruction of diazo-compounds in solution. Euler found that 0·0002 g. per litre of colloidal platinum raises the velocity of decomposition six-fold. Copper has special activity in

bringing about the decomposition and condensation of diazo-compounds (cf. p. 277); the action of cupric salts and cupric sulphide in accelerating the decomposition of diazobenzene has been studied by Blumberger,[29] colloidal organic substances, provided they do not react with nitrous acid or diazo-compounds, have no effect, though dispersing agents have been patented as stabilisers.[38] In experiments with benzenediazonium chloride Pray [24] added gelatin, dextrin, starch, agar, and egg-albumin, and found no change in either the velocity of decomposition or the rate of evolution of nitrogen, but Oddo and Indovina [37] said that a suspension of alizarine accelerates decomposition. Pray [25] also determined the velocity of decomposition in a number of aliphatic alcohols and acids, the following values given being the unimolecular constant $\times$ 0·4343 $\times$ 10^4: water 25·0, methanol and ethanol both 53·5, *n*-propanol 52·0, *iso*propanol 69·0, *n*-butanol 50, *iso*butanol 54, pentanol 46·3, formic acid 18·6, acetic acid 18·7, propionic acid 18·9, and butyric acid 23·0. In mixtures of water and methanol the velocity is almost exactly proportional to the methanol content. This work was continued by Waring and Abrams,[49] who used the isomeric pentanols as solvents and also the last four acids given above. The alcohols and the acids give two parallel lines for the plot of log PZ *v* E, one molecule of alcohol disappearing for each molecule of benzenediazonium chloride decomposed. Waring and Abrams concluded that the decomposition is a radical reaction because (*a*) it is difficult to explain the production of aldehyde (cf. p. 268) on an ionic basis, and (*b*) the activation energy is about 10,000 cal./mol. too high for an ionic reaction.

The preceding remarks apply to solutions of diazo-compounds either acid at the start of the decomposition or becoming acid as the decomposition proceeds. The measurements were nearly all made before the technique of using buffer salts had been introduced and the determination of pH with the glass electrode was unknown. Both Cain [14] and Hantzsch found that adding the salt of an organic acid to the diazo solution did not alter the velocity of decomposition until all acidity to Congo had disappeared, but on adding excess of sodium acetate changes occur. Thus diazobenzene acetate retains the same rate of decomposition as diazobenzene chloride, but *p*-nitrodiazobenzene chloride on mixing with acetate shows a ten-fold increase in the velocity constant. If bicarbonate is used instead of acetate a rapid initial decomposition eventually gives place to a state where the unimolecular reaction again sets in.[28] The following figures for the amount of decomposition against acidity are taken from the tables in the paper by Marriott [44] on the stabilising effect of arylsulphonic acids (cf. p. 83), and show clearly how important is the matter of accurate control of acidity if comparable results are to be obtained.

One point emerging from the following table to which reference will be made again later is that whereas some diazo-compounds typified by diazotised 4-chloro-*o*-toluidine, show but little change in rate of decomposition

TABLE VII

Relation of Acidity to Decomposition of Diazo-Compounds

Diazo-compound from 5-chloro-*o*-toluidine.			Diazo-compound from 4-chloro-*o*-toluidine.			Diazo-compound from *p*-nitro-aniline.			Diazo-compound from *m*-nitro-*p*-toluidine.		
pH.	Percentage decomposition.		pH.	Percentage decomposition.		pH.	Percentage decomposition.		pH.	Percentage decomposition.	
	127 hr.	240 hr.		21 hr.	43 hr.		30 hr.	47 hr.		18 hr.	21 hr.
7·5	96	—	8·3	62	—	6·5	64	—	5·8	74	—
6·5	—	85	7·2	62	—	5·6	—	80·5	5·1	—	34
5·1	—	40	6·0	—	64	3·0	—	4·0	3·5	—	0·0
3·6	13	—	2·0	—	44	—	—	—	—	—	—
2·6	—	5	—	—	—	—	—	—	—	—	—

with pH, others, typified by *p*-nitrodiazobenzene and diazotised *m*-nitro-*p*-toluidine, show great changes in stability for small changes in pH.

Some investigations have been carried out on the fully alkaline side of the neutral point. What is being measured here is the stability of metallic diazotates, and, as will be shown later, there are involved not single chemical individuals, as is the case with diazonium salts, but whole families of compounds which change from one form to another at great speed. Moreover, the diazotates couple with the phenol formed by decomposition so that a large part of the reaction-product consists of azo-compounds. Resinous substances are also formed. Hodgson and Marsden [51] allowed stirred aqueous solutions of diazobenzene buffered at pH 10·5, 8·8, 6·7, 5·3, 5·2, and 4·2 to decompose at room temperature, and separated the phenol, and mono-, bis-, and tris-benzeneazophenol produced. They found that coupling increases relative to the rate of decomposition as pH increases, and that the formation of trisbenzeneazophenol is a maximum at pH 8·8. Mono- and bis-arylazophenols are also formed when the solution is kept neutral by calcium carbonate throughout the decomposition.[50] Haggerty and Hadler [34] said that the velocity of decomposition increases in alkaline solution, thus bearing out Blumberger,[30] who showed by plotting alkalinity against decomposition rate that there is a maximum velocity of decomposition for diazobenzene at pH 12·7, and suggested that at greater concentrations of alkali the more stable *iso*-diazotate ions are in the majority. Naphthalene-α-diazonium chloride behaves in the same way, for Yamamoto [41] found that treatment with acetate increases the velocity of decomposition 3·5 times, sodium carbonate 800 times, and caustic soda still further. Jolles and Camiglieri [36] examined the normal diazotates derived from aniline, *o*-, *m*-, and *p*-toluidine, *p*-anisidine, *o*- and *p*-phenetidine, and α-naphthylamine, and concluded that for diazotates the rules for the effects of substituents are the reverse

of those which apply for diazonium salts, and that alkoxy-groups in the *o*- and *p*-positions increase the velocity of decomposition of the diazotates. Jolles [38a] found that there appear small quantities of the hydrocarbon originally substituted by the primary amino-group, such as benzene, toluene, and naphthalene, along with the diazo-resins which are the main product of the spontaneous decomposition of diazo-compounds in alkaline solution.

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STABILISED DIAZO-COMPOUNDS

In 1880 Thomas and Robert Holliday were granted patents for dyeing cotton by impregnating the fibre with β-naphthol followed by treatment with a diazo-compound, whereby a water-insoluble azo pigment was formed in the fibre. This was not a fundamentally new method in the art of dyeing, for it was known to colour cloth and yarn by precipitating into the fibre metallic oxides by a two-bath process, and similar methods had been used for mordanting. Although this process utilising the coupling power of diazo-compounds with phenols and amines to dye cotton in fast and brilliant shades is elegant in its simplicity, it nevertheless only came but gradually into general use. For many years after 1880 only two amines were available for commercial use, *p*-nitroaniline and β-naphthylamine, the former giving on a β-naphthol ground the shade known as Para Red, the latter a bluer red known as Vacanceine Red. They competed with alizarine in the Turkey-Red trade. The supply of amines was uncertain, the price high, and the quality often poor, particularly of *p*-nitroaniline, which was usually contaminated with varying quantities of the *ortho*-isomer. Moreover, the best conditions for coupling were not known, while doubtless diazotisation, carried out as it was in the dyehouse in rough-and-ready fashion, was often far from satisfactory. It was from the ice used in the latter operation that the colours became known in the trade as Ice Colours. The basic idea of the process being so attractive, attention was paid to it on the Continent, and Koechlin first showed that sodium acetate could be used to obtain consistent results in coupling, while the addition of Turkey-Red oil to the β-naphthol padding-bath was a revolutionary improvement. With these improvements the method was extended by the employment of diazotised α-naphthylamine for clarets, of tetrazotised benzidine for puce, and of tetrazotised dianisidine for navy blues. It was not, however, until 1894 that Friedländer, in Volume IV of his *Fortschritte*, devoted a section to patents on the art, and in the introduction to that section he voiced what was a commonly held opinion: that the discovery of a means of stabilising diazo-compounds in the solid state was necessary to ensure the survival of this class of dyes on any large scale. What the dyer needed was a powder which by mere solution in water would provide him with the desired diazo-bath. In 1898 Fried-

länder noted how further spread of the Ice Colours was hanging fire for want of more success in the attack on this problem, for by this time the other requirement—that of pure bases such as *p*-nitroaniline of first-class quality—had been overcome. The calico-printers in particular wanted stabilised diazo-compounds, because they wished to expand the art of printing thickened diazo-compounds on prepared cloth in multi-colour machines.

A three-fold problem was set to the chemists—namely, (i) to find means of separating the very soluble diazo-compounds from water without causing decomposition in the process; (ii) to obtain the diazo-compound in a solid form in which it could be kept in safety; (iii) to ensure that the solid would dissolve again in water to a clear solution of useful concentration. The term " stabilised diazo-compound " has therefore come to designate a diazo-compound so treated or combined that it can be preserved in the solid state for a period measurable at least by weeks at the ordinary temperature; in which the explosive properties have been annulled, and which upon solution in water will afford a solution in which the original diazo-compound displays its coupling power immediately or when liberated by suitable treatment.

Fifty years of research have provided the dyer to-day with such substances as those of which the last generation dreamed, and which eliminate from the dye-house and print-works the necessity for carrying out the operation of diazotisation, and put at the colour user's command not only a large range, but one that comprises diazo-compounds which he could not possibly prepare himself. In addition, they are at a standard of strength which is constant and reliable.

The driving force behind all this activity was reinforced when it was discovered that the arylamides of 2 : 3-hydroxynaphthoic acid, and some other aromatic *o*-hydroxycarboxylic acids in which coupling is also *ortho* to the hydroxy-group, afford with suitable diazo-compounds Ice Colours which approach the vat dyes in fastness and, among the reds, surpass them in brilliancy. Thus the two series have become for some purposes complementary to one another, and of great importance in the fast-colour trade.

In England the stabilised diazo-compounds are usually known in the trade as Fast Colour Salts, while the corresponding amines, even when actually handled as hydrochlorides, are known as Fast Colour Bases. A table is appended to this chapter in which are set such constitutions of the Fast Colour Bases as have been made public. Without exception the amines are free from substituent groups able to form salts with alkalis, and so allow soap to loosen the pigment from the fibre. Tens of thousands of diazo-compounds of this kind have been prepared, combined with *o*-hydroxycarboxyarylamides, and the dyeings tested for their fastness properties, so that the marketed components are all chosen warriors of

a host. The favourite diazo-compounds in use are derived from arylamines, which comprise chloro-, dichloro-, nitro-, and chloronitro-anilines, toluidines, and anisidines, as well as various naphthylamines, aminoanthraquinones, aminodiphenylamines, and aminoazo-compounds.

As the cost of stabilised diazo-compounds per active unit must of necessity be higher than that of the base, the equilibrium between the usage of either form by the trade varies with time and place. Where hanks and warps are to be dyed in large quantities, diazotisation of the base on the spot is often preferred, as being cheaper than the use of stabilised diazo-compounds, but for information concerning the application of the Ice Colour, treatises on the art of dyeing should be consulted.

No one method of stabilisation is applicable to all diazo-compounds, and moreover the different means employed permit of different forms of technical application, and the calico-printers, rather than the dyers, have turned to best account in their art all those variations in the forms in which the stabilised diazo-compounds have been offered to the dyestuff users.

The diversity of chemical types which embrace the stabilised diazo-compounds may be conveniently classified in two groups :—

Group 1. Compounds stable in neutral or acid solution and showing the reactions of diazo-ions immediately on solution in water.

The subdivisions of this group are :—

Section i. Diazo-compounds which are stable as diazonium sulphates or chlorides.
ii. Diazo-compounds stabilised as complex salts.
iii. Diazo-compounds stabilised as salts of arylsulphonic acids.
iv. Sundry forms of mixture of amine with nitrite, acid, and coupling component.

Group 2. Compounds stable in neutral or alkaline solution and requiring an acid treatment in order to regenerate the diazo-compound.

The subdivisions of this group are :—

Section i. Metallic salts of the acid isomeric forms of the diazo-compounds, the *iso*diazotates or nitrosamines. Cf. p. 128.
ii. Diazoamino- and diazoimino-compounds. Cf. p. 157.
iii. Diazosulphonates, $Ar{\cdot}N{:}N{\cdot}SO_3Na$. Cf. p. 147.

The members of Group 1 are sometimes referred to as " Active " stabilised diazo-compounds, while those of Group 2 are called " Passive ". The active group (with the Section iv) consists entirely of diazonium salts, and forms a compact whole which has really been removed *en bloc* from Chapter I.

In the passive group are substances obtained from diazonium salts by the action of various reagents, and they will be found in their appropriate place in the scheme of the reactions of the diazo-compounds, thus bringing

out the points at which the pure chemistry of the diazo-compounds impinges on their industrial application.

Stabilised diazo-compounds are usually standardised, so that when fresh they contain 20% of available diazo-compound. At first sight this may appear somewhat weak, but it will be found that when stabilisers of relatively high molecular weight are used, such as the naphthalene-polysulphonic acids, the available proportion of diazo-compounds of low molecular weight is not much greater even in a chemically pure state, so that the manufacturer often has but little margin for adjustment to standard.

SECTION I. DIAZO-COMPOUNDS STABILISED AS DIAZONIUM SULPHATES AND CHLORIDES

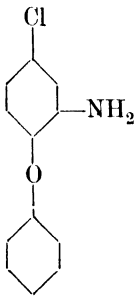
Of the diazo-compounds first in use as Ice Colour components *p*-nitrodiazobenzene was of outstanding stability, and, as was earlier remarked, stability is further enhanced by increase in acidity. The problem of marketing this diazo-compound in solid form was therefore first solved by evaporating an acid solution to small bulk under vacuum at a temperature not over 45°, and then binding the remaining water as crystal water by adding anhydrous salts such as sodium sulphate or aluminium sulphate. The resulting solid mass was ground, standardised, and passed into commerce as Azophor Red (M.L.B.).[1] Tetrazotised dianisidine is amenable to the same treatment.

In another means to the same end the operation of evaporating the water was avoided by diazotising the *p*-nitroaniline in concentrated sulphuric acid by passing in nitrous acid gases, and then solidifying with calcined sodium sulphate.[3] Thus the dyers were furnished with Nitrazol C (Cassella). It was further claimed that large quantities of mineral salts increase the stability of admixed diazonium salts [4] and that oxalic acid is particularly beneficial for tetrazotised diaminoazo-compounds.[2] The era of Para Red dyeing reached its peak during the first decade of the twentieth century, when enormous quantities of *p*-nitrodiazobenzene stabilised as above were made and sold by various makers, and as late as 1913 the process was still further modified by effecting diazotisation of the *p*-nitroaniline in sulphuric acid by nitrosylsulphuric acid, partly removing the acid by magnesia, and then solidifying the whole with calcined sodium sulphate.[5] When the dry preparations of the above type had been dissolved in water by the dyer, the excess mineral acid had to be removed by addition of a reagent such as sodium acetate, before the bath was ready to receive the padded yarn or cloth. *p*-Nitrodiazobenzene is no longer stabilised by the above methods, and since 1920 its usage has greatly declined, its place being taken by diazo-compounds which give shades faster to light, kier-boiling, and chlorine.

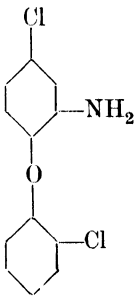
For many years *p*-nitrodiazobenzene and tetrazodianisyl enjoyed the

distinction of being the only diazo-compounds in commerce requiring no stabiliser other than free mineral acid, but now considerable additions to this small class have appeared. Easily isolated stable diazonium salts are naturally attractive to the makers, because the cost of stabilisers is saved and the solubility of diazonium salts in water is good.

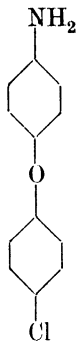
Both the 2- and 4-aminophenol aryl ethers and their substitution products have long been valued for the production of fine red and pink shades with the 2 : 3-hydroxynaphthoic arylamides. They are obtained generally by condensation of the chloronitrobenzenes with phenols and cresols, followed by reduction. Four typical ethers of this series are :



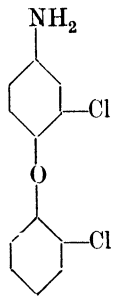
(Ref. 8.)



(Ref. 15.)



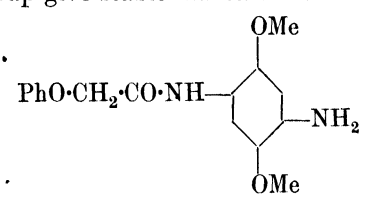
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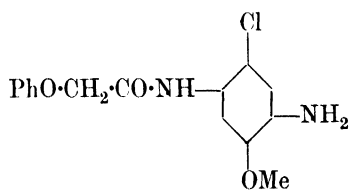


(Ref. 18.)

The diazonium salts derived from these bases can be salted from an acid solution and are stable when dry and mixed with standardising diluents.[8, 13, 14,15, 18] Further, alkali salts of sulphuric acid monoalkyl esters increase the stability of diazonium salts of diaryl ethers.[23]

p-Phenylenediamine and some of its substituted derivatives form stable diazo-derivatives. *p*-Phenylenediamine itself can be tetrazotised in nitrosylsulphuric acid and the solid tetrazonium sulphate, after isolation by pouring the solution on ice and cooling to — 15°, or diluting with methanol, ethanol, or acetone at the same temperature, is collected, mixed with an inorganic sulphate, and dried.[17] 2 : 6-Dichloro-*p*-phenylenediamine is diazotised only in the 4-amino-group and the diazonium salts are stable affording brown Ice Colours.[12] 2 : 5-Disubstituted *p*-phenylenediamines in which the 4-amino-group is acylated by the phenoxyacetyl [4] group give stable diazonium chlorides which are salted from solution :—[16]

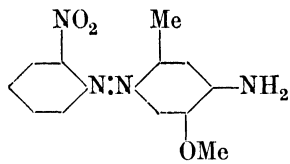




Diazonium salts of the *p*-aminodiphenylamines are easily isolated, and it is claimed that they can be preserved against the injurious effects

of alkalis if freed from oxidation products and excess nitrous acid and mixed with buffer salts,[7] or they can be dried with magnesium sulphate.[23]

Aminoazobenzene is the parent member of a third group of amino-compounds yielding stable diazonium salts which can be precipitated by excess sulphuric acid. An ether-group *ortho* to the amino-group particularly enhances stability in the diazo-derivatives of bases such as :—[6]



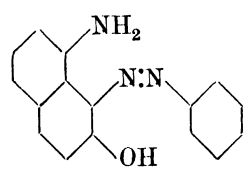
The diazo-compounds of the above bases are useful for Ice Colours of deep shade, such as blacks.

Both *o*- and *m*-aminoazotoluene yield diazo-compounds of the same order of stability as the above, and indeed it has been claimed that such salts are more stable than the previously known double compounds with zinc and cadmium chlorides.[11] As an example of the method of preparation :—

o-Aminoazotoluene (225) is added with stirring to water (4500), then 32% hydrochloric acid (345) is added, and after cooling to 10° there is run in 20% sodium nitrite solution (360). When diazotisation is complete the solution is filtered and 78% sulphuric acid (250) is added dropwise, thus precipitating part of the acid diazonium sulphate, the rest being thrown out with anhydrous sodium sulphate (500 parts). The mixture is cooled to 5°, stirred for an hour, the acid diazonium sulphate is collected and freed from mother-liquor by pressing. The press-cake is diluted with its own weight of anhydrous sodium sulphate and dried at 40—50° with repeated turning. The product thus obtained is a reddish-brown powder.

After storage for thirty days at 40° a 20% mixture loses only 10% of its strength.

The aminoazo-compounds made by coupling diazo-compounds in alkaline medium with 1 : 7-aminonaphthol afford stable diazonium chlorides.[24] A typical base of this kind is :—



Lastly, the wheel has come full circle, and it has been shown that many substituted benzenediazonium sulphates, which in earlier years might have been suspected of being dangerously unstable, can be isolated by diazotising the amines in sulphuric acid of about 85% concentration

with nitrosylsulphuric acid, and then precipitating at temperatures well below 0° with organic liquids miscible with the acid, such as the lower aliphatic alcohols. The precipitated diazonium sulphate is collected, and the free sulphuric acid in the cake is determined, and there is mixed into it sufficient mild alkali to neutralise the acid and to provide a stabilising diluent. Among the amines mentioned as being suitable for this process are the nitroanilines, the mono-, di-, and poly-halogenoanilines, certain chloronitroanilines, and nitro- and halogenoaminophenol ethers.[21] A similar result is obtained by diazotising in non-hydroxylic solvents such as acetone or ethyl acetate [9] or the acid sulphate of an amine, together with a dehydrating agent such as aluminium sulphate, is suspended in a liquid not miscible with water, such as toluene, chlorobenzene, or tetrachloroethane, and diazotised with an alkyl nitrite, nitrosyl chloride, or nitrous gases; the water produced in the diazotisation is taken up by the dehydrating agent and removal of the liquid vehicle leaves a dry stable diazonium sulphate.[19]

m-Nitrobenzenediazonium sulphate separates on cooling a solution of *m*-nitroaniline diazotised in nitrosylsulphuric acid and after collecting on an acid-proof filter, is obtained as a dry, stable, powder by mixing with enough mild alkali to neutralise adhering acid,[20] while the diazo-derivatives of *o*-aminocarboxylic acids, such as anthranilic acid and 5-acetamido-2-aminobenzoic acid, can be salted from solution and dried *in vacuo* at 40—50°.[10]

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1	M.L.B.	21,227/94	557,228	85,387	**4**, 673	242,575	—
2	Kinzelberger	—	—	93,109	**4**, 686	—	—
3	Cassella	15,353/98	—	97,933	**5**, 482	268,261	—
4	*Idem*	—	—	C11,066	**7**, 359	323,981	—
5	*Idem*	23,945/13	—	281,098	**12**, 310	473,864	—
6	I.G.	305,498	—	—	—	—	—
7	I.G.	—	—	515,205	**17**, 1057	—	—
8	S.C.I.	363,950	1,875,243	545,852	**18**, 1073	717,194	150,001
9	S.C.I.	—	—	575,832	**19**, 1812	727,293	152,611
10	S.C.I.	—	1,993,433	—	—	778,834	171,038
11	I.G.	399,753	1,975,409	586,354	**20**, 1225	755,816	169,690
12	I.G.	403,013	2,067,132 2,118,986	586,355	**20**, 1222	755,889	170,764
13	I.G.	—	—	605,577	**21**, 968	—	—
14	I.G.	—	2,018,095	606,942	**21**, 969	—	—
15	I.G.	—	—	607,536	**21**, 971	771,798	—
16	S.C.I.	434,158	2,032,110	607,870	**21**, 1419	778,602	174,081
17	I.G.	440,424	—	611,463	**21**, 967	775,038	—
18	I.G.	440,964	2,027,066	609,476	**21**, 975	775,463	—
19	I.G.	—	—	611,398	**21**, 977	777,126	177,940
20	I.G.	—	—	622,306	**22**, 864	775,963	—
21	I.G.	441,085	2,106,539	629,478	**23**, 878	776,009	177,263
22	I.G.	—	—	638,264	**23**, 876	—	—
23	I.G.	475,942	2,129,136	654,448	—	819,012	199,458
24	Du Pont	531,625	2,193,998	—	—	—	—
25	May Chem. Corp.	—	2,266,229	—	—	—	—

SECTION II. COMPLEX SALTS OF THE DIAZO-COMPOUNDS AND THEIR USE AS STABILISED DIAZO-COMPOUNDS

Diazonium salts form double salts with a number of metallic salts, and these co-ordination compounds provide a means of isolation from aqueous solution, since their solubility is less than that of the parent diazonium salt, ranging from complete insolubility to a degree of easy solubility which nevertheless permits the double salt to be salted from solution. Polyvalent metals may form two or more series of double salts corresponding with the various co-ordination numbers of the element.

For descriptive purposes the double salts are here divided into two groups :—

A. Double salts with simple anions.

B. Double salts with complex anions.

Representatives of both classes have been patented for use as stabilised diazo-compounds, while they are also intermediates for a number of replacement reactions, especially replacement by halogen, and by metals to form organo-metallic compounds.

A. Double Salts with Simple Anions. Griess, appreciating the basic nature of the diazo-compounds, prepared the double salts of benzenediazonium chloride with auric chloride, $PhN_2Cl,AuCl_3$, and platinous chloride, $PhN_2Cl,PtCl_2$,[1] but some years elapsed before it was realised how general is the tendency of diazonium halides to form double salts with metallic halides. As a result twenty-four years elapsed before the double salt of benzenediazonium chloride and platinic chloride, $(PhN_2Cl)_2PtCl_4$, was described.[6] So strong is this tendency to co-ordinate that Hantzsch prepared dry double salts of benzenediazonium chloride with hydrochloric acid, *e.g.*, such salts as $(PhN_2Cl)_3,HCl$.[11] For a long time he held the acid to be structurally combined in the molecule of the diazo-compound, but eventually he altered his view.[24] A double hydrofluoride has also been prepared from tribromobenzenediazonium fluoride, $C_6H_2Br_3{\cdot}N_2F,HF,2H_2O$.[12]

Griess [2] also recorded the preparation of the first double salt of benzenediazonium chloride and a base metal chloride—namely, the one formed from stannic chloride—and he found it to have the composition $(PhN_2Cl)_2SnCl_4$. Double salts with mercuric chloride are well known; Hantzsch [7] obtained one having the composition $PhN_2Cl,HgCl_2,H_2O$ and another p-$C_6H_4Cl{\cdot}N_2Cl,2HgCl_2,2H_2O$,[9] whilst Nesmejanov [23] has prepared a number having the general composition $ArN_2Cl,HgCl_2$. Because of their usefulness in the preparation of organo-metallic compounds, the Russian chemists [27] have made a close study of double halides derived from diazotised aniline, the chloro- and nitroanilines, the toluidines, o-phenetidine, p-bromo- and p-iodoaniline and p-aminophenol with zinc, thallium, stannic, plumbic, bismuth, auric, platinic, and ferric chlorides.

Thallic chloride forms two series of salts, $ArN_2Cl,TlCl_3$ and $(ArN_2Cl)_2,TlCl_3$.[26] From the *p*-dialkylaminobenzenediazonium chlorides Schmidt and Maier [25] have prepared double salts with mercurous, ferric, zinc, and cadmium chlorides. Hodgson and Sibbald [31] give $ArN_2Cl,FeCl_3$ as the general composition of the ferric chloride double salts. Hantzsch and Davidson [10] prepared a series of double halides from diazophenol, including such compounds as $p\text{-}OH\cdot C_6H_4\cdot N_2I,HgI_2$, which on treatment with alcohol gives the more stable $p\text{-}OH\cdot C_6H_4\cdot N_2I,HgI_2,\overset{\ominus}{O}\cdot C_6H_4\cdot\overset{\oplus}{N}_2$, where the complex is associated with one molecule of the diazo-oxide. Analogous cadmium salts also exist, $p\text{-}OH\cdot C_6H_4\cdot N_2I,CdI_2,\overset{\ominus}{O}\cdot C_6H_4\cdot\overset{\oplus}{N}_2$ and $p\text{-}OH\cdot C_6H_4\cdot N_2Cl,2CdCl_2,\overset{\ominus}{O}\cdot C_6H_4\cdot\overset{\oplus}{N}_2,H_2O$.

The chlorides of the arsenic group of metalloids all form double salts with diazonium chlorides. Földi [16] showed that *p*-toluenediazonium chloride affords four kinds of double salts with arsenic trichloride:

(i) $C_6H_4Me\cdot N_2Cl,AsCl_3$, (ii) $C_6H_4Me\cdot N_2Cl,2AsCl_3$,
(iii) $C_6H_4Me\cdot N_2Cl,AsCl_2\cdot OH$,

and (iv) $C_6H_4Me\cdot N_2Cl,AsCl_3,AsCl_2\cdot OH$. The first two are unstable and sensitive to water, being obtained only from solutions saturated with hydrochloric acid; (iv) easily loses hydrochloric acid and passes into $C_6H_4Me\cdot N_2\cdot As_2Cl_5O$, and if its alcoholic solution is treated with ether, (iii) is produced. Földi also made the salt $C_6H_4Me\cdot N_2\cdot AsBr_3\cdot OH$. Antimony trichloride affords May's double salt, $PhN_2Cl,SbCl_3$,[13] and analogous salts; it also combines with benzene-*p*-tetrazonium chloride.[21] Two series of double salts with bismuth chloride have been prepared, $ArN_2Cl,BiCl_3$[20, 22], and a salt $(p\text{-}C_6H_4Me\cdot N_2Cl)_3BiCl_3$.[29] The members of the first series may contain one to three molecules of crystal water,[14] and Supniewsky [19] said that they are explosive.

When a diazonium chloride is added to a hydrochloric acid solution of lead tetrachloride a yellow crystalline precipitate is formed [17, 18] Chattaway and his co-workers ascribe to it the constitution :—

$(ArN_2)_2\begin{bmatrix}Cl & & Cl\\ Cl & Pb & Cl\\ Cl & & Cl\end{bmatrix}$ analogous to the chloroplatinates: $(ArN_2)_2\begin{bmatrix}Cl & & Cl\\ Cl & Pt & Cl\\ Cl & & Cl\end{bmatrix}$

Addition of benzenediazonium chloride to a solution of iodine trichloride in concentrated hydrochloric acid brings about precipitation of the tetrachloride as yellow prisms, PhN_2Cl,ICl_3 or $ArN_2\begin{bmatrix}Cl & Cl\\ Cl & I\\ & Cl\end{bmatrix}$

A number of double thiocyanates, some of them strongly coloured and unstable, have been described by Korczynski and his co-workers [15]; among them are salts such as $(m\text{-}NO_2\cdot C_6H_4\cdot N_2\cdot SCN)_2,Co(SCN)_2$ (green), the uranyl and nickel salts being yellow, with brown tungsten and yellowish-orange molybdenum salts from *p*-nitrodiazobenzene, while β-diazo-

naphthalene gives $(C_{10}H_7{\cdot}N_2{\cdot}SCN)_2,Fe(SCN)_2$, $(C_{10}H_7{\cdot}N_2{\cdot}SCN)_3,Fe(SCN)_3$ (both black) and $(C_{10}H_7{\cdot}N_2{\cdot}SCN)_2,Zn(SCN)_2$ (pale yellow).

Because of the possibility that they may be intermediates in the Sandmeyer reaction, the copper double salts have aroused interest, but very few have been isolated. Lellmann and Remy [3] prepared a reddish-yellow, crystalline double salt from β-diazonaphthalene and cuprous bromide, $C_{10}H_7{\cdot}N_2Br,Cu_2Br_2$, though Hantzsch [8] said the colour must be due to the conversion of the diazonium group into a *syn*-diazo double salt.

When chemists in Europe attempted to apply Holliday's process to the printing of cloth prepared with β-naphthol, they came on many difficulties, one of which was due to decomposition of the thickened diazo solution, whereby a froth of nitrogen formed on the rollers and ruined the prints. Feer experimented with metallic salts in the hope of finding one which by stabilising the diazo-compound would eliminate the trouble. He found that zinc chloride yields a sparingly soluble double salt just as well as stannic chloride, and also that a diazosulphocyanide can be made that will keep for weeks.[4] He must have made comparative tests in practice, for later he said that the double diazo-salts of tin, mercury, and zinc are more stable than the sulphocyanides, but are too insoluble for technical use, with the exception of the zinc chloride double salts, which behave as desired, though the metal affects the print.[5] Further improvement in the stability of such pastes is claimed to result from the addition of aliphatic [95] or aromatic [96] carboxylic acids, *e.g.*, maleic, crotonic, or benzoic acids, or aliphatic sulphonic acids containing less than four carbon atoms,[97] *e.g.*, ethane-αβ-disulphonic acid. Other stabilisers which prevent frothing are unsaturated acids,[98] such as 2-methyl-2-propene-1-sulphonic acid, unsaturated esters,[99] such as diallysulphosuccinate

$$[CH_2{:}CH{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CH(SO_3H){\cdot}CO_2{\cdot}CH_2{\cdot}CH{:}CH_2],$$

or organic bases containing unsaturated radicals,[100] such as tetra-allylammonium bromide, $(CH_2{:}CH{\cdot}CH_2)_4NBr$; sulphonic acids of heterocyclic compounds [101] (quinaldine, pyridine, pyrazoles, etc.) are also effective.

Zinc chloride has remained the most-used reagent for stabilising diazo-compounds, because it combines in most cases sufficient solubility in use with isolation in good yield in the process of manufacture. When the question of stabilising a new diazo-compound arises, zinc chloride is the first reagent tried, and recourse is had to other stabilisers only when this one fails. In those cases where the double salt formation occurs it is only necessary to add zinc chloride solution to the diazonium chloride solution, when the double salt frequently commences to separate in crystalline form, the yield being increased by adding sodium chloride :—

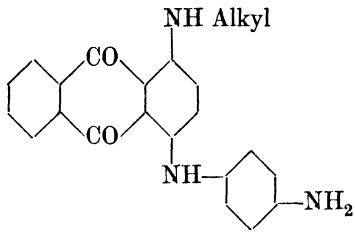
Dianisidine (510 g.) is dissolved in 10% hydrochloric acid (4100 g.) and tetrazotised with 40% sodium nitrite solution (870 g.) at 15—20°. After filtering, zinc chloride (375 g.) is added, and then salt (1000 g.), by which means the separation of the double salt is completed. The crystalline tetrazo-compound is collected, pressed, and dried, either by mixing with partly dehydrated aluminium sulphate or sodium naphthalene-

tetrasulphonate, and dried carefully at 40—50°. The dried substance is mixed with standardising agents and dyeing assistants, such as chromium and copper salts.[82]

The double salt has the constitution :—

$$\left.\begin{matrix} C_6H_3(OMe)\cdot N_2\cdot Cl \\ C_6H_3(OMe)\cdot N_2\cdot Cl \end{matrix}\right| ZnCl_2$$

The diazo- and tetrazo-derivatives of the aminoazo- and diaminoazobenzenes are readily stabilised in this way, and were the first to be the subject of a patent,[80] while the class is of some importance because certain of its members yield deep shades down to black with 2 : 3-hydroxynaphthoic arylamides.[84, 85] In the anthraquinone series zinc chloride has been applied to isolate the diazo-compound derived from 1-alkyl- or -dialkylamino-4-*p*-aminoanilinoanthraquinone,[86] which affords green shades with acetoacetarylamides :—



As has already been noted in the chapter on diazotisation, the aminodiphenylamines can be diazotised in zinc chloride solution, and so be isolated directly as the zinc chloride double salt. Variamine Blue Salt is a compound of this type.

No information has been published as to the extent to which double salts exist in solution, but it is certain that some measure of dissociation occurs so that a proportion of the diazo ions are left unprotected and will decompose if the solution is not handled carefully. Drying of the crystal pastes obtained in manufacture is therefore a matter of difficulty, as decomposition may occur in the adhering film of liquid, and unwanted insoluble substances appear when the dry powder is redissolved. Drying may therefore be performed advantageously with anhydrous salts which not only dry, but can also serve as buffers in the dye-bath. Another way of drying which gives very clean products is to wash the water out of the paste with acetone in which the double salts are insoluble.[91]

Diligent search has been made to find an equivalent of zinc chloride or to extend its use in difficult cases. For instance, it has been proposed to precipitate *p*-nitrodiazobenzene by adding first stannic chloride (less than 0·5 mol.), followed by zinc carbonate (up to 1·0 mol.),[81] or to precipitate zinc chloride or zinc chloride–stannic chloride double salts with halides of magnesium, strontium, or calcium.[88] Zinc salts of benzene- and naphthalene-sulphonic acids have also been used.[94] Cadmium salts have been patented, and in the case of diazotised *p*-aminoazobenzene it is stated that the cadmium chloride double salt is definitely superior in stability to

the zinc chloride double salt.[83] A number of double chlorides of cobaltous chloride have been described,[90, 92] for instance, *m*-chlorobenzenediazonium chloride and cobaltous chloride form a green double salt precipitated by magnesium chloride, whilst diazotised aminodiphenyl ethers have been stabilised with manganese salts.[89]

B. Double Salts with Complex Anions. Bart discovered that fluoboric acid, HBF_4 (also commonly known as borofluoric acid), when added to an aqueous solution of a diazonium chloride produces a plentiful precipitate of the sparingly soluble crystalline fluoborate. Benzenediazonium fluoborate can be obtained by diazotising aniline in fluoboric acid, and it is the double salt of benzenediazonium fluoride and boron trifluoride.[110] Funk and Binder [52] obtained the same substance by adding fluoboric acid to benzene diazohydroxide, and they considered it to be a general reaction of the alkali salts of fluoboric acid to attach themselves both to diazonium salts and to hydrazines. Wilke-Dörfurt and Balz [51, 53] have also made these substances, and describe benzenediazonium fluoborate as colourless, doubly refracting needles, sparingly soluble in water, practically insoluble in alcohol and ether. Analysis indicates the constitution $PhN_2{\cdot}F,BF_3$ or PhN_2BF_4. Diazotisation can also be carried out by treating arylamine fluoborates in alcohol with amyl nitrite.[118] Benzene-*m*- and -*p*-tetrazonium fluoborates have been prepared both by precipitation from the tetrazonium chloride [54] and by carrying out the tetrazotisation in fluoboric acid,[119] which latter method is said to give better yields; naphthalene-1 : 8-tetrazonium fluoborate has also been prepared.[58] The sparing solubility of the fluoborates has been a bar to their general use as stabilised diazo-compounds, though some have been proposed for this use.[111] 5-Nitro-2-diazotoluene [113] and 3 : 5-dinitrodiazobenzene [57] can both be stabilised as the fluoborate, whilst many fluoborates have been made as the starting point for the synthesis of aryl mercury compounds.[59] The solubility of the fluoborates can be improved by adding neutral ammonium salts or neutral salts of metals of the first or third groups in the periodic table [115]; stability in solution is improved by increasing the acidity.[114] Solid preparations which on dissolution in water give a concentrated diazo solution comprise a diazonium fluoborate mixed with a dyeing assistant such as alum and a salt of a metal of the first group of the periodic table such as potassium chloride.[120]

The fluoborates form by far the largest group of diazonium salts with complex anions which has been investigated and Nitrazol CF extra (I.G.) is *p*-nitrobenzenediazonium fluoborate,[32] but there have also been described anthraquinonediazonium cobaltinitrites,[50] whilst phosphotungstic,[121] phosphomolybdic and silicotungstic [121] acids form double salts with diazonium,[60] and tetrazonium-compounds.[61] Diazonium fluosulphonates [112] are obtained by adding fluosulphonic acid to solutions of diazonium salts, whilst complex metallic fluoric acids, such as $H[TiF_6]$,

$H_2[ZnF_4]$, and $H_3[AlF_6]$, form diazonium salts which are stable and soluble in water.[115] Diazonium salts can also be precipitated from aqueous solution as complex cyanides derived from salts such as potassium cobalticyanide, $K_3Co(CN)_6$, sodium nitroprusside, $Na_2Fe(CN)_5{\cdot}NO,2H_2O$, or potassium chromocyanide, $K_3Cr(CN)_6$ [116]; these salts can be safely dried at temperatures up to 50°.

Lange and Müller [55] have described benzenediazonium phosphorus hexafluoride and Schwechten [56] made a complex salt from 2 : 2′-tetrazodiphenyl and potassium hexathiocyanochromiate.

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80	M.L.B.	1,645/96	—	89,437	**4**, 675	—	—
81	*Idem*	—	—	94,495	**4**, 676	—	—
82	B.A.S.F. (I.G.)	238,676	1,572,715	454,894	**15**, 569	600,311	117,356 118,606–20
83	Kalle	294,248	—	491,318	**16**, 1064	657,852	138,596
84	I.G.	305,498	1,846,150	569,205	**18**, 1066	644,563	130,424
		—	1,846,151	—	—	—	132,188– 132,215
			1,889,298	—	—	—	134,091–2 134,940 137,095–7 137,099– 138,101
85	Sandoz	365,759	1,962,111	573,180	**18**, 1064	708,822	151,677 155,331–3
86	I.C.I.	376,307	2,052,386	—	—	734,899	—
87	S.C.I.	—	—	—	—	—	171,038
88	Nat. Aniline Co.	—	1,999,723	—	—	—	—
89	S.C.I.	476,143	2,131,992	670,099	—	818,683	—
90	I.G.	513,846*	—	—	—	—	—
91	Du Pont	519,574	2,171,976	—	—	—	—
92	I.G.	—	2,175,807	—	—	849,724	209,641
93	Du Pont	—	2,193,998	—	—	—	—
94	Pharma	—	2,237,885	—	—	—	—
95	Du Pont	—	2,319,265	—	—	—	—
96	*Idem*	—	2,356,618	—	—	—	—
97	Gen. Aniline & Film Corp.	—	2,381,145	—	—	—	—
98	Amer. Cyanamid	587,928	2,378,305	—	—	—	—
99	*Idem*	587,929	2,378,276	—	—	—	—
100	*Idem*	587,930	2,378,646	—	—	—	—
101	Gen. Aniline & Film Corp.	—	2,402,106	—	—	—	—

* p. 9, l. 71.

Double Salts with Complex Anions

		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.	Sw.P.	Russ.P.
110	Bart	—	—	281,055	**12**, 311	—	—	—
111	I.G.	292,100	—	478,031	**16**, 900	655,706	—	—
112	I.G.	303,527	1,847,513	I. 33,150	**18**, 1060	—	140,098 142,648	—
113	I.G.	316,691	—	—	—	—	136,915	—
114	I.G.	317,355	—	495,631	**16**, 1062	657,041	139,482	—
115	I.G.	332,227	1,825,729	—	—	—	—	—
116	I.G.	—	—	532,402	**18**, 1059	—	—	—
117	I.G.	332,630	1,799,068	557,658	**19**, 1810	672,466	143,361	—
118	Philip's Gloelamp.	—	—	—	—	743,659	—	—
119	I.G.	397,034	—	I. 43,838	—	751,306	165,828	—
120	Gen. Aniline Works	—	1,862,241	I. 34,039	—	672,466	145,295–9	—
121	Kozlov	—	—	—	—	—	—	51,868 *

* *C.A.*, 1939, **33**, 9324.

SECTION III. DIAZOARYLSULPHONATES: THEIR REACTIONS AND THEIR USE AS STABILISED DIAZO-COMPOUNDS. DIAZOARYLSULPHINATES AND DIAZOSULPHONES

Diazoarylsulphonates. Becker [30] first discovered that on addition of naphthalene-α- or -β-sulphonic acid to a solution of tetrazodiphenyl a precipitate is formed which can be collected, dried, and stored without change. When redissolved in water, in which it is sparingly soluble, evidence of tetrazodiphenyl is at once shown by the familiar coupling reaction with β-naphthol. Becker proceeded to widen the scope of his invention by using crude naphthalenesulphonic acids,[31] and also applied the reaction to *p*-nitrodiazobenzene.[33] Feer also found that nitrobenzenesulphonic acid [32] precipitates diazo-compounds in the same way as naphthalenesulphonic acids, and in a British patent,[36] to which are appended only two examples, he claimed the manufacture of salts of diazo-compounds with sulphonic, carboxysulphonic, and polysulphonic acids of the benzene, naphthalene, and anthracene series and likewise with methyl and phenyl monosulphuric esters. He appears, therefore, to have recognised the generality of the reaction. The Fabrique de Thann et de Mulhouse acquired both Becker's and Feer's patents, and manufactured *p*-nitrodiazobenzene stabilised with naphthalene mono- and -disulphonic acids, particularly naphthalene-1 : 5-disulphonic acid, and with nitrobenzenesulphonic acid.[34, 35]

Schroeter,[1] while experimenting on the coupling of various diazo-compounds with acetylated arylaminesulphonic acids, found that in a few cases he could obtain a true azo-compound, but that with 1-acetamidonaphthalene-4- and -5-sulphonic acids he obtained unstable substances which could be crystallised from warm water, but evolved their nitrogen quantitatively on boiling their solutions. He was uncertain whether they were diazonium salts or diazoimino-compounds, and on the basis of his analysis assigned to them the alternative constitutions :—

$$NO_2{\cdot}C_6H_4\underset{\underset{N}{\vdots}}{N}{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}COMe \text{ or } NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}N(COMe){\cdot}C_{10}H_6{\cdot}SO_3H$$

The latter form is improbable. Schroeter did not detect the coupling power of the aqueous solution. At this time the Berlin Aniline Company [39] patented the stabilisation of diazo-compounds by combination with *p*-toluenesulphonyl-sulphanilic and -metanilic acids (*p*- or *m*-$SO_3H{\cdot}C_6H_4{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$-*p*) describing them in the patent as diazoimino-compounds, though the reactions given clearly indicate membership of the class of diazoarylsulphonates. Further evidence that the above might indeed all be examples of a general reaction of arylsulphonic acids with diazo-compounds was supplied by the firm of

Bayer,[37, 38] who early took patents for combining tetrazodiphenyl with β-naphtholtrisulphonic acid and 2-naphthol-1-sulphonic acid ("oxy Tobias acid") in which cases coupling is prevented by the sulphonic acid group in the 1-position of the naphthalene ring. In 1913 Witt [3] published a paper in which he briefly discussed the position in this field and described a product he had recently patented [41] formed from one molecule of *p*-nitrodiazobenzene and two molecules of naphthalene-β-sulphonic acid. He assigned to it the constitution :—

$$p\text{-}NO_2\cdot C_6H_4\cdot N{:}N\cdot SO_3\cdot C_{10}H_7, NaSO_3\cdot C_{10}H_7, H_2O$$

No analytical figures are quoted. The substance was marketed as Paranil A.

The basis of preparation of diazoarylsulphonates is a double decomposition :—

$$ArN_2\cdot X + Ar'\cdot SO_3H \rightleftharpoons ArN_2\cdot O\cdot SO_2\cdot Ar' + HX$$

If the diazoarylsulphonate is sparingly soluble or can be salted out, then the equilibrium moves to the right, and the solid diazo salt can be collected, but the strength of the diazo-compounds as bases and of the arylsulphonic acids as acids varies so much that each pair of compounds requires separate study to find the best conditions for isolation. A typical preparation is carried out as follows :—

4-Chloro-*o*-toluidine (2 : 4 : 1-$NH_2\cdot C_6H_3Cl\cdot Me$) is diazotised in dilute hydrochloric acid with sodium nitrite. Into this solution is brought at a temperature of less than 20° somewhat more than the calculated quantity (1. g.-mol.) of the sodium salt of acetylsulphanilic acid (mol. wt. 237). After a short time the separation of yellow crystals commences, and these are collected and dried at less than 50°. The dry diazonium salt of acetylsulphanilic acid is of good solubility in water, and in the solid state, either alone or mixed with diluents, is of high stability, being of low inflammability and neither explosive nor sensitive to friction.[60]

The arylsulphonates of most diazo-compounds are white, yellow, or brown solids charring on heating and without definite melting point. They deflagrate but are rarely explosive. They are often sensitive to light, and may darken quickly on exposure. They can usually be crystallised, and when pure their aqueous solutions are neutral, provided no acid groups are present as in the acid salts of polysulphonic acids. Although they are referred to in the literature both as salts and esters, they are in fact true ionisable salts of a strong acid with a strong base, and for this reason Schroeter's first representation of them as diazonium salts with the linkage through oxygen must be correct. Witt mentions a very soluble, explosive substance prepared by him from one molecule of *p*-nitrodiazobenzene and one molecule of naphthalene-β-sulphonic acid, though he does not disclose either the method of preparation or the analysis. This substance may have been a salt with the nitrogen linked to sulphur.

The stability of the diazoarylsulphonates in the solid state is doubtless due primarily to their being non-ionised and secondarily to their high molecular weight. As soon as dissolved in water they form the highly ionised system :—

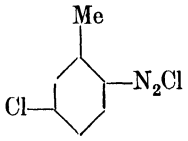
$$ArN_2 \cdot O \cdot SO_2 \cdot Ar' + H_2O \rightleftharpoons ArN_2 \cdot OH + Ar \cdot SO_3H$$

In dilute solution equilibrium travels far to the right and the diazo ions (which are themselves a system of equilibrium between diazonium and diazo-hydroxides and their ions, cf. p. 101) revert to the same order of stability which they show with any other acid radical at the same pH. It is therefore plain that addition of another arylsulphonic acid, particularly a polysulphonic acid, to a diazoarylsulphonate solution, or to a solution of any other diazonium salt, will tend to improve the keeping qualities, driving the equilibrium back to the left, and will reduce the number of fragile diazo ions by combining them with arylsulphonic ions. This is the principle underlying the stabilisation of diazo solutions by means of naphthalenetrisulphonic acid which comes into commerce for this purpose under the names of Azo Guard (I.C.I.) or Paradurol (I.G.). The principle was early appreciated, for a patent was taken by Bayer [40] in 1912 for stabilising solutions of nitrodiazo-compounds by adding small quantities of arylsulphonic acids. Viktoreff [17] has also stated that the addition of arylpolysulphonic acids increases the stability of diazo solutions, but he has published no figures.

Marriott [20] has published the results of a quantitative study of this matter using for his experiments the carefully purified sodium salts of anisol-*p*-sulphonic acid and naphthalene-1 : 5-disulphonic acid. The diazo solution under investigation was brought to the required pH by the addition of alkali, buffered at that value and brought to N/40 strength, and then the solid stabiliser was added in varying molecular proportions to aliquot portions of solution. The amount of decomposition after various times was determined by titrating the remaining diazo-compound. The experiments were made with the diazo derivatives of 4- and 5-chloro-*o*-toluidine, *p*-nitroaniline, *m*-nitro-*p*-toluidine, and *m*-toluidine. The results for the first three compounds are reproduced *in extenso* in Tables VIII, IX, X, and several points are brought out clearly.

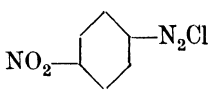
It is immediately apparent from the figures that a statement as to the stabilising effect of any particular substance on diazo-compounds is without meaning unless accompanied by a statement of the pH and temperature at which the stabilising effect is exerted, as change in acid concentration and temperature can easily overwhelm the effect due to even a high concentration of stabiliser. Further, it will be noted that the aryl radical to which the sulphonic acid group is attached is not without effect, and that naphthalene-1 : 5-disulphonic acid is more effective than anisol-*p*-sulphonic acid. The stabilising effect is only just apparent in the case

TABLE VIII

M/40 *Solution of* 5-*Chlorotoluene*-2-*diazonium Chloride*, 

	p_H 5·2. 16—17°.			p_H 6·5. 16—17°.					p_H 7·5. 16—17°.			
	Initial p_H.	Percentage decomposed after 240 hrs.	Final p_H.	Initial p_H.	Percentage decomposed after 16 hrs.	66 hrs.	240 hrs.	Final p_H.	Percentage decomposed after 7 hrs.	48 hrs.	127 hrs.	Final p_H.
No buffer	5·10	4·9	2·65	6·4	—	—	5·5	2·9	1·0	8·4	12·7	3·6
Buffer : no stabiliser	5·17	39·9	5·04	6·55	14·1	45·4	85·0	6·16	12·6	61·5	96·2	7·00
1 mol. anisolsulphonate	5·10	39·2	5·06	6·5	14·1	42·7	81·0	6·18	11·6	56·3	88·2	7·00
2 mols. ,,	5·00	37·4	5·05	6·5	12·1	38·8	77·2	6·17	11·6	54·8	86·0	6·97
3 mols. ,,	5·15	38·0	4·95	6·5	10·7	34·0	74·5	6·16	11·6	49·0	81·6	7·00
1 mol. 1 : 5-*N*-Disulphonate	5·10	40·2	4·95	6·55	11·3	34·9	75·7	6·20	10·0	49·0	83·6	7·00
2 mols. ,,	5·10	38·0	4·95	6·55	9·9	32·0	72·0	6·18	8·4	43·2	76·8	7·02
3 mols. ,,	5·05	35·3	4·90	6·5	4·5	20·8	56·5	6·16	7·4	31·6	63·8	7·02

TABLE IX

M/40 *Solution of* p-*Nitrobenzenediazonium Chloride*, 

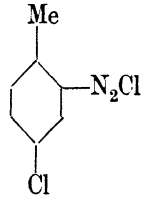
	Initial p_H 5·5. 19—20°.					Initial p_H 6·5. 19—20°.					
	Percentage decomposed after			p_H values.		Percentage decomposed after			p_H values.		
	6 hrs.	22 hrs.	47 hrs.	0·5 hrs.	106 hrs.	4·5 hrs.	12 hrs.	30 hrs.	0 hrs.	12 hrs.	32 hrs.
No buffer	1·6	3·80	4·3	3·2	3·0	—	—	—	—	—	—
Buffer : no stabiliser	11·9	38·1	80·5	5·62	5·20	12·0	31·5	64·1	6·5	6·38	6·15
1 mol. anisolsulphonate	16·8	42·2	74·1	5·62	5·20	15·2	40·8	71·2	6·5	6·38	6·05
2 mols. ,,	19·5	47·6	78·4	5·60	5·20	19·6	48·4	78·3	6·5	6·38	6·04
3 mols. ,,	30·8	54·5	86·0	5·6	5·20	28·3	52·1	87·5	6·5	6·32	6·15
1 mol. 1 : 5-*N*-disulphonate	8·6	24·3	45·4	5·57	5·25	8·2	24·2	42·1	6·5	6·32	6·15
2 mols. ,,	7·0	17·8	34·6	5·57	5·25	6·5	21·2	35·9	6·5	6·32	6·15
3 mols. ,,	6·5	16·8	28·6	5·55	5·25	4·9	19·6	30·5	6·45	6·31	6·15

of the very unstable *m*-diazotoluene at pH 5·5 and 16·0—17·0°, decomposition having reached no less than 48% in two hours with five molecular proportions of naphthalene-1 : 5-disulphonic acid.

Addition of an arylsulphonic acid also improves the solubility of sparingly soluble diazosulphonates by taking the diazo ions into solution partnered by ions of the more soluble sulphonic acid, and this solubilising

TABLE X

M/40 *Solution of* 4-*Chlorotoluene*-2-*diazonium Chloride,*



	Initial p_H 8·3. 15°.							Initial p_H 7·25. 15°.						Initial p_H 6·0. 15—16°.						
	Percentage decomposed after				p_H values.			Percentage decomposed after			p_H values.			Percentage decomposed after				p_H values.		
	3·20 hrs.	6·70 hrs.	10·20 hrs.	21·20 hrs.	0·0 hrs.	10·3 hrs.	21·6 hrs.	3·2 hrs.	7·1 hrs.	23·3 hrs.	0·25 hrs.	7·25 hrs.	23·4 hrs.	8·75 hrs.	19·0 hrs.	27·5 hrs.	43·0 hrs.	0·16 hrs.	19·5 hrs.	43·0 hrs.
No buffer	—	—	—	—	—	—	—	—	—	—	—	—	—	13·8	24·7	35·7	43·7	7·7	2·70	2·00
Buffer : no stabiliser	19·6	33·3	44·3	62·1	8·32	7·65	7·32	16·6	29·9	62·1	7·25	6·9	6·64	12·6	32·2	49·4	63·8	6·6	5·53	5·32
1 mol. anisolsulphonate	19·6	33·3	44·9	60·9	8·32	7·65	7·32	15·5	29·9	63·2	7·25	6·9	6·62	12·1	31·6	47·7	63·8	6·6	5·53	5·37
2 mols. „	19·6	33·9	44·9	58·7	8·32	7·65	7·32	16·7	30·4	62·1	7·25	6·9	6·61	14·3	31·6	47·2	62·6	6·0	5·54	5·37
1 mol. 1 : 5-*N*-disulphonate	17·2	31·6	39·7	57·5	8·32	7·65	7·34	13·2	28·2	59·2	7·25	6·9	6·62	12·1	28·8	46·6	60·9	6·0	5·54	5·37
2 mols. „	15·5	28·7	38·0	55·2	8·30	7·68	7·36	12·6	27·0	56·3	7·25	6·93	6·60	12·1	28·2	43·1	57·5	6·0	5·54	5·36
5 mols. „	13·2	23·6	29·9	47·7	8·30	7·70	7·37	10·3	21·3	50·0	7·25	6·96	6·60	9·2	23·6	38·5	50·6	6·0	5·54	5·40

action is to be seen not only with diazoarylsulphonates but also when the diazo-compound is present as a sparingly soluble metallic double salt.[48]

The dyer expects the stabilised diazo-compound to dissolve to a clear solution in water, and in the process of manufacture of such compounds special care is necessary at the drying stage, because the diazo-compound contained in the film of mother-liquor on the crystals tends to decompose unless suitable drying methods are adopted. In addition to the dessicating salts, such as the sulphates of sodium and magnesium, which have been used from the early days of manufacture, aluminium sulphate and alum only partly dehydrated (to prevent formation of basic salts) have been introduced into the technique, and they also possess the advantage of buffering the dye-bath against alkali brought in with the naphthol on the yarn.[45] Removal of water by distillation at low temperature with water-immiscible liquids,[59] by improved methods of salting,[52] or by washing with acetone [65] are methods which have been patented.

The diazoarylsulphonates are of importance, because a number of the more valuable diazo-compounds fail to give suitable double salts with metallic salts, and so must needs be stabilised in this way. The art of manufacture consists in choosing for any given diazo-compound that arylsulphonic acid which will allow the salt to be isolated in good yield, while at the same time being sufficiently soluble, either with or without the addition of another sulphonic acid, to satisfy the needs of the dyer. As one way of overcoming the difficulty of steering between the extremes of poor solubility and poor yield, it has been proposed to evaporate to dryness under vacuum at low temperatures the solution of the diazo-compound mixed with naphthalenetri- and -tetrasulphonic acids.[50] Beside the sulphonic acids of aromatic hydrocarbons, their substituted derivatives incapable of coupling with diazo-compounds also form salts, as shown in the example of acetylsulphanilic acid quoted above, and considerable activity has been displayed in trying various sulphonic acids of the benzene and naphthalene series so weighted by substituents that the desired degree of solubility may be attained. Among acids of the benzene series which have been patented are the chlorobenzenemono-, di-, and poly-sulphonic acids, as well as the acylamidobenzenesulphonic acids.[46, 55, 60, 18] Sulphobenzoic and chlorosulphobenzoic acids [51] have also been patented as specially suitable for stabilising 4-chloro- and 4-nitro-2-diazotoluene. Other acids which have been patented or described are the diphenylsulphonic acids,[53] phenolsulphonic acids,[54] chlorophenol and anisolsulphonic acids, benzene-*m*-disulphonic acid,[57] and 5-sulphosalicylic acid.[21] Benzenesulphonic acid has also been specifically patented for stabilising diazotised aminobenzonitrile,[64] nitrodiazo-compounds,[62] and aminodiaryl ethers,[61] which can also be stabilised

with naphthalenedi- and trisulphonic acids and *m*-nitrobenzenesulphonic acid.[43]

The naphthalenedisulphonic acids have been much used on account of their cheapness and accessibility, and both neutral and acid salts are known, and have been patented both for use [45] and manufacture. In certain cases the acid salts are said to be strikingly different from the neutral. Thus 3-nitro-4-diazotoluene and naphthalene-1 : 5-disulphonic acid yield a greenish crystalline salt of the structure

$$NO_4{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}O{\cdot}SO_2{\cdot}C_{10}H_6{\cdot}SO_3H,$$

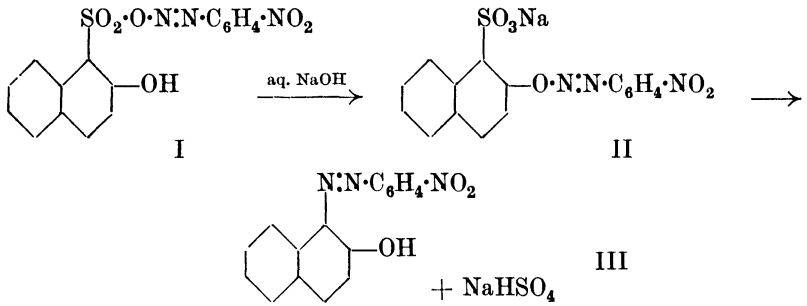
whereas the colour of the neutral salt is white or buff.[47] The mono-salts of a disulphonic acid may have the advantage of better solubility than the neutral salt, which may tend to precipitate from the solution, a condition which can be corrected by the addition of more sulphonic acid.

The salts as brought into commerce are standardised at 20% of active diazo-component. As the molecular weight of the arylsulphonic acid is nearly always greater, and often much greater, than that of the diazo-compound, the amount of the latter available even in the pure diazoarylsulphonates usually lies between 30% and 40%, which does not leave much margin for the addition of drying salts and buffers to bring the concentration down to the standard value.

There is one series of diazoarylsulphonates some members of which undergo an interesting succession of reactions if their solution is allowed to become alkaline. Mention has been made that 2-naphthol-1-sulphonic acid forms the diazosulphonate, coupling being prevented by the sulphonic acid group which occupies the only coupling position. But it has further long been known that under appropriate conditions the 1-sulphonic acid group can be ejected by the diazo-group with formation of the corresponding azo-derivative of β-naphthol (cf. p. 221). Unsulphonated diazo-compounds yield salts with 2-naphthol-1-sulphonic acid which have poor solubility in water, but which Grant Hepburn found to be readily soluble in mild alkalis without decomposition. Provided not more than one equivalent of alkali has been used, reacidification of the solution causes precipitation of the expected azo-compound, an acid alkali sulphate being eliminated. This formed the basis of a convenient means of printing calico,[42] for the alkaline solution containing the diazo-2-naphthol-1-sulphonate is quite stable, and can be thickened and printed on calico. Exposure of the dried prints to air for a few hours or passage of the cloth through a weakly acid bath brings about development of the insoluble dye in the fibre. In later years attempts were made to extend the process to cover the diazosulphonates of the 2 : 3-hydroxynaphthoic arylamide-1-sulphonic acids, but so far there has been no commercial development.[56]

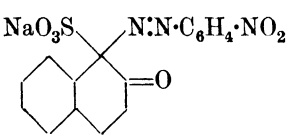
Grant Hepburn also observed the very curious fact that if more than one equivalent of caustic alkali is added to the diazoarylsulphonate

solution derived from *p*-nitrodiazobenzene and 2-naphthol-1-sulphonic acid a yellow compound is produced from which no insoluble azo-dye results on acidification. This transformation cannot be due to decomposition, for no nitrogen appears. The soluble substance intermediate between the diazoarylsulphonate and the azo-compound whose properties Grant Hepburn utilised had been investigated some years earlier by Bucherer,[2] who explained its formation as due to the migration of the *p*-nitrobenzenediazo-radical from the sulphonic group to the oxygen atom of the naphthol, thus :—



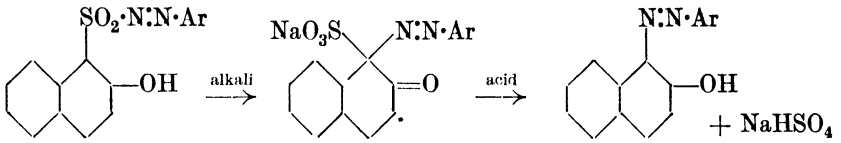
Wahl and Lantz also concurred in this opinion.[4] But this view hardly explains the profound changes brought about if the single molecular proportion of caustic alkali is exceeded, and the course of these complex reactions has been elucidated by Rowe and his co-workers in a series of papers published since 1926.

The soluble product to which Bucherer assigned the constitution (II) above must be produced by intramolecular rearrangement of the diazoarylsulphonate, because the latter does not decompose, no nitrogen being evolved, nor are diazo-ions to be found in the solution. Moreover, a free sulphonic acid group has probably resulted from the rearrangement to confer the observed solubility, and accordingly Rowe assigned to the product the hemi-quinonoid constitution [5] :—



Bucherer and his co-workers have adhered to explanations of the chemistry of these substances based on the existence of the O-azo-compounds as an essential intermediate step.[8, 13] Rowe and Peters [9] pointed out that such substances are in fact known, being stable if the β-naphthol is substituted in the 1-position by halogen, and that when acted on by alkali they either decompose or give Para Red with ejection of the substituent (cf. p. 135). But as the derivative of *p*-nitrodiazobenzene with

2-naphthol-1-sulphonic acid behaves in an entirely different way, the hemi-quinonoid constitution is the alternative which fits the facts. All aryldiazo-2-naphthol-1-sulphonates afford the hemi-quinonoid compounds, and all of these can undergo acid hydrolysis to give the corresponding azo-derivative of β-naphthol :—



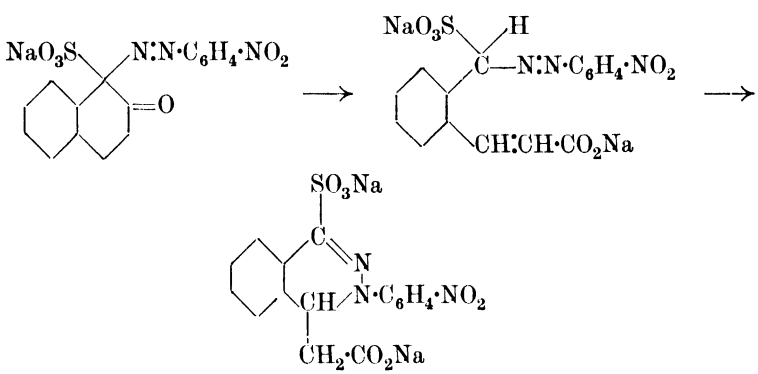
The transformation to the hemi-quinonoid compounds by caustic alkali, first observed by Grant Hepburn, is, however, peculiar (with some few exceptions) to that class in which the aryldiazo-group contains a nitro-group or groups, and takes place with diazo-compounds derived from the following amines :

o-, *m*-, and *p*-nitroaniline, 2 : 4-dinitroaniline, 4-chloro-2-nitroaniline, 4-nitroaniline-2-sulphonic acid, 2 : 6-dibromo-4-nitroaniline, 3-nitro-4-toluidine, *p*-aminoazobenzene.

The reactions fails with the diazo-compounds derived from :

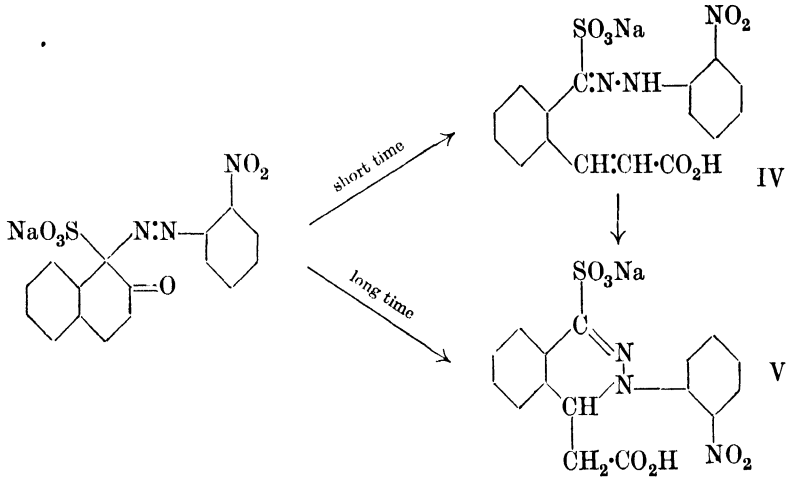
Aniline, toluidines, tribromoaniline, sulphanilic acid, dichloroaniline, *p*-aminoacetanilide, anthranilic acid, and α- and β-naphthylamine.

On adding caustic soda to a solution of the hemi-quinonoid salt which contains the *p*-nitrodiazoaryl residue, an intense crimson colour appears, soon fading to yellow, and the first product of reaction which can be isolated is disodium 4′-nitrophenyl-3 : 4-dihydrophthalazine-1-sulphonate-4-acetate. The naphthalene ring has been opened and closed again to a new heterocyclic ring thus [10] :—



The existence of the open-chain intermediate compound remained unproved until the investigation was extended to the case where the nitro-group is *ortho* to the azo-link. If cold caustic soda is allowed to act for a minute on the hemi-quinonoid substance acidification gives sodium

benzaldehyde-2′-nitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid (IV), while if reaction is allowed to continue for two days the 3 : 4-dihydrophthalazine (V) is the product [19] :—



The subsequent reactions of the phthalazines which have been worked out by Rowe and his school are complicated, but as at this stage the identity of the diazo-compounds has been entirely lost, the subject passes from the purview of this book.

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		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.	Sw.P.
30	P. Becker	—	—	81,039	4, 678	—	—
31	*Idem*	—	—	86,367	4, 679	—	—
32	Feer	—	—	88,949	4, 682	—	—
33	Becker	—	—	89,998	4, 681	—	—
34	Thann, Mulhouse	—	—	92,237	4, 679	—	—
35	*Idem*	—	—	94,280	4, 680	—	—
36	Feer	18,429/94	—	—	—	—	—
37	Bayer	8,995/95	—	92,169	4, 684	251,403	—
38	*Idem*	11,757/95	—	93,305	4, 685	251,403	—
39	Agfa	—	—	229,247	10, 786	—	—
40	Bayer	2,037/12	—	—	—	—	—
41	O. N. Witt	11,290/13	1,093,567	264,268	11, 370	458,493	—
42	Hepburn	116,360	—	—	—	—	—
43	S.C.I.	238,704	1,629,906	544,057	18, 1071	585,861	108,486 108,851–3 127,430–7
44	I.G.	246,181	1,717,453	499,294	16, 1651	614,921	121,789
45	I.G.	246,870	1,607,462	448,728	15, 577	609,746	121,311
46	I.G.	265,985	1,677,558 1,677,640	484,905	16, 1063	628,973	126,405
47	I.G.	269,212	1,744,903	499,294	16, 1651	614,921	123,638–76
48	I.G.	273,352	1,758,912	553,787	18, 1067	610,261	121,312 123,627–37
49	I.G.	275,245	1,744,149	555,406	18, 1069	33,946/ 610,261	131,082
50	S.C.I.	280,945	1,867,937	—	—	—	125,868
51	V. Chem. Met. Prod. in Aussig	—	—	559,421	19, 1815	—	—
52	S.C.I.	349,339	1,846,113	572,269	18, 1062	697,425	145,444 147,665–78
53	Du Pont	—	1,863,154	—	—	—	—
54	S.C.I.	—	1,867,937	—	—	—	—
55	S.C.I.	364,490	—	572,268	18, 1061	717,193	151,673 154,698– 154,700
56	I.C.I.	385,307	2,014,428	—	—	738,795	—
57	S.C.I.	—	—	—	—	—	160,083
58	S.C.I.	—	—	575,024	20, 1221	741,050	157,338
59	S.C.I.	393,830	1,989,541	645,934	22, 870	744,157	156,741
60	I.G.	414,768	2,022,923	593,260	20, 1227	750,619	166,218 168,350 168,924
61	S.C.I.	461,051	2,084,934	647,667	—	805,402	185,574– 185,581 186,736
62	S.C.I.	471,443	2,083,311	655,047	—	47,549/ 805,402	183,452 —
63	I.C.I.	—	2,116,131	—	—	—	—
64	I.G.	512,798	—	—	—	848,073	209,639
65	Du Pont	519,574	2,171,976	—	—	—	—
66	Du Pont	—	2,357,226	—	—	—	—

Diazoarylsulphinates and Diazosulphones. The close relationship of the arylsulphinic acids to the arylsulphonic acids might lead to the expectation that they would form similar salts with diazo-compounds. That they do so is almost certainly true, but only one case is on record in which the diazonium sulphinate has been isolated, as in general the

diazonium sulphinate rearranges at once and a diazosulphone is the substance isolated :—

$$\mathrm{Ar\overset{\cdot\cdot}{N}\cdot X + Ar'\cdot SO_2H \longrightarrow \left[Ar\cdot\overset{\cdot\cdot}{N}\cdot SO_2\cdot Ar'\right] \longrightarrow Ar\cdot N{:}N\cdot SO_2Ar'}$$

Koenigs,[1] who discovered the diazosulphones, assigned the above constitution to them, and demonstrated that they are sulphones, and not the expected sulphinates, both because of their stability and because the same substance is produced when benzenesulphonylchloride acts on phenylhydrazine as when diphenyldiazosulphone is reduced :—

$$\mathrm{Ph\cdot N_2X + Ph\cdot SO_2H \longrightarrow Ph\cdot N{:}N\cdot SO_2Ph \xrightarrow{H_2}}$$
$$\mathrm{PhNH\cdot NH\cdot SO_2\cdot Ph \longleftarrow PhNH\cdot NH_2 + PhSO_2Cl}$$

The same reaction occurs with ethanesulphinic acid.

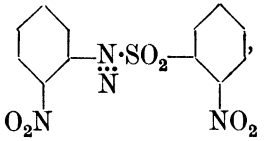
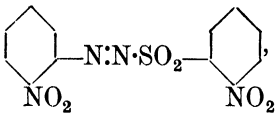
p : *p'*-Dinitrodiphenyl sulphone,

$$\mathrm{NO_2\cdot C_6H_4\cdot N_2\cdot SO_2\cdot C_6H_4\cdot NO_2},$$

has been made by the action of dry sulphur dioxide on *p*-nitrodiazobenzene hydroxide dissolved in absolute alcohol.[9]

v. Pechmann [2] made a number of diazosulphones in the hope of finding evidence among them for Hantzsch's stereochemical theory of the constitution of the diazo-compounds. v. Pechmann found that formation does not occur in the presence of caustic soda, but does in mineral acid or in alkali carbonate, while with bromine in cold chloroform the diazosulphone is split and the diazoperbromide is formed. Hantzsch and Singer [3] extended v. Pechmann's work, but came to the same conclusion—namely, that no stereoisomers exist in this series, while they confirmed the sulphone constitution by showing that the diazosulphone does not couple with phenols. Later Hantzsch found that some, particularly those containing positive substituents, will couple if alkali is present. Hantzsch and Glogauer [4] attempted to bring normal and *iso*diazotates into reaction with sulphinic acids, but found that it is only from diazonium salts that the sulphones are formed, the sulphones being decomposed by alkali into *iso*diazotate and sulphinate. When normal or *iso*diazocyanides are brought into reaction with sulphinic acids they may give a diazosulphone, as in the case of diazo-*pseudo*-cumene, but the normal diazocyanides often give an addition product which splits off the sulphinic acid, leaving the *iso*diazocyanide.[6] There are some incongruities in this series of papers which probably arose because it was not recognised that in solution an equilibrium exists between the diazonium sulphinate and the diazosulphone, while the sluggishness of reaction in aqueous solution is due to the sparing solubility of the diazosulphone, so that the active mass is small.

The diazonium sulphinates were first prepared by Claasz,[10] who discovered that the condition which prevents rearrangement to the diazosulphone is the presence of a negative group so placed as to increase the

acidity of the sulphinic acid group. Thus *o*-nitrodiazobenzene and *o*-nitrobenzenesulphinic acid yield *o* : *o'*-dinitrobenzenediazonium sulphinate,  , yellow, decomp. 100°. It can be rearranged to the diazosulphone,  , decomp. 145°. According to Claasz, the diazonium sulphinates are differentiated from the stable and inert diazosulphones in being explosive, in losing nitrogen in boiling water to give *o* : *o'*-dinitrodiphenyl sulphone, in coupling instantly with β-naphthol in alcohol solution, while their specific conductivity in alcohol is that to be expected of a diazonium salt.

Diazoarylthiosulphonates are also known, and an extensive series was investigated by Troeger and Ewers,[7] who gave them the constitution Ar·N:N·SO_2·S·Ar', where Ar' is phenyl, *o*-tolyl, and α- and β-naphthyl.

Dybowski and Hantzsch [8] also examined these substances for evidence of stereoisomerism and found none. The product they obtained from benzenethiosulphonic acid and β-diazonaphthalene consisted of some orange crystals dissolving to a clear solution in water and coupling at once with β-naphthol. They therefore considered it to be a diazonium salt. When it is dissolved in water, sulphur is rapidly eliminated with formation of the diazosulphone.

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SECTION IV. MIXTURES SERVING THE PURPOSE OF STABILISED DIAZO-COMPOUNDS

Since a solution containing a primary aromatic amine, nitrite, and an acid comprises all the components necessary for the formation of a diazo-compound it is not surprising that attempts have been made to manufacture stable mixtures of such components in powder form by such devices as complete desiccation or by protecting the amino-group from diazotisation until the desired moment by easily removed substituents.

On dissolving the powder in water the acid liberates nitrous acid, the amine is forthwith diazotised, and the mixture therefore behaves as an active stabilised diazo-compound.

Various ways of practising the art using the device of desiccation have been patented by the I.G.[12] Dry amine salts, such as the sulphate, oxalate, or naphthalene disulphonate, are mixed with dry acid salts and the correct quantity of sodium nitrite; the diazo-compound results on dissolution in water. Magnesium chloride, partly or completely dehydrated, can be added to the mixture to act as stabiliser in the solution. An obvious technical disadvantage of such mixtures is that a high degree of desiccation is essential to ensure good keeping qualities, and exposure to damp air is likely to produce rapid deterioration. Dry diazotised Variamine Blue has been mixed with nitrite and an acid salt, so as to give the easily-coupling nitrosodiazo-compound on dissolution in water.[16] Another way of keeping the components apart is to add them to different phases of an emulsion.[34]

Attempts to employ mixtures in the art of calico-printing go back to the earliest days of the Ice Colours. Schmid [1] soaked calico in thickened nitrite, then printed with an acid mixture of amine and coupling component, the azo-compound being developed by passage through ammonia. Alternatively, the fabric was printed with acid, amine, and coupling component and developed by passage through aqueous nitrite,[11] whilst Grässler [10] printed with amine, coupling component, and an ammonium salt which became acid on steaming, so developing the print. Or yarn grounded with nitrite and naphthol is immersed in a dilute acid solution of an arylamine.[14]

The introduction of the Rapidogen dyes gave fresh impetus to experiments such as the above, since it is a likely proposition that if a suitable technique based on mixtures could be elaborated, it would avoid the cost of converting the amine into the passive stabilised diazo-compound necessary for a Rapidogen-type dye. Attempts to make mixtures which behave as passive stabilised diazo-compounds have been based on temporarily solubilised amines which are mixed with nitrite and a coupling component. The mixture is stable under alkaline or neutral conditions, and when dissolved can be thickened and printed. On treating with acid the solubilising group is split away, the nitrous acid diazotises the amine, and coupling ensues. On this principle passive mixtures have been made of salts of arylsulphamic acids with nitrite and a naphthol; these give clear solutions in dilute alkali and after printing are developed by acid ageing.[15] The sodium methyl-ω-sulphonate, $Ar{\cdot}NH{\cdot}CH_2{\cdot}SO_3Na$, obtained by treating arylamines with sodium formaldehyde-bisulphite, can be used in the same way, as acetic acid suffices to split away the ω-sulphonate group and bring about diazotisation.[17] The arylnitroamines, $Ar{\cdot}NH{\cdot}NO_2$, which give stable salts in alkaline solution and lose the nitro-group very

easily in acid medium, have also been claimed,[18, 19, 20, 22] as have also the arylnitrosohydroxylamines, Ar·N(OH)·NO.[21] Prints made with the preceding mixtures can be developed by steam carrying acid vapours,[23] or after treating with aqueous mineral acid coupling is completed in basic vapours.[30] Further, the arylamines may be applied as Schiff's bases,[26, 27] or as aminosulphonamides NH_2·Ar·SO_2NHR, which are soluble in dilute alkali.[32]

The arylamides of 2 : 3-hydroxynaphthoic acid are used in such mixtures [24] which are improved if arylsulphonic acids are present [31] and thiodiglycol is also added as an assistant.[33] Protection of the coupling position in the arylamide from nitrous acid during the time the amine is being diazotised also appears necessary. Such protection can be afforded by using the formaldehyde condensation products of the arylamides which are split when the diazo-compound couples [25] or formaldehyde is added to the acid bath in which the print of amine, naphthol, and nitrite is developed.[28] Such mixtures can be applied to wool and viscose [29] as well as to calico.

Many difficulties are likely to crop up in meeting the stringent demands of technical usage with such mixtures—difficulties of solubility, of uneven rate of development, and difficulty in manufacture, which probably explains why this group has not reached the importance of those previously described.

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		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.	Sw.P.
10	Grässler	—	—	14,950	**1**, 547	—	—
11	Kalle	—	—	—	—	284,226	—
12	I.G.	260,682	—	426,033	**15**, 573	—	—
				430,621	**15**, 572		
				438,743	**15**, 574		
				442,075	**15**, 575		
				443,284	**15**, 574		
				447,069	**15**, 576		
13	I.G.	—	—	453,985	**15**, 568	—	—
14	Agfa	262,537	—	—	—	—	—
15	I.G.	262,987	1,857,230	433,276	**15**, 977	611,500	—
				449,013	**15**, 912		
				451,903	**15**, 979		
16	I.G.	307,890	1,880,959	542,780	**18**, 1054	671,483	143,680
			1,895,099				147,033–5
17	I.C.I.	374,497	1,947,433	—	—	—	—
18	Bader	430,167	2,042,696	642,716	**23**, 884	761,811	172,341
19	*Idem*	430,222	—	—	—	—	—
20	*Idem*	430,236	—	—	—	—	—
21	*Idem*	437,824	—	—	—	43,788/ 761,811	—
22	S.C.I.	441,178	2,041,455	641,769	—	788,349	174,349
23	I.G.	—	—	I. 51,562	—	801,094	—

REFERENCES—*continued.*

		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.	Sw.P.
24	S.C.I.	449,267	2,112,864	638,878 661,225	**23**, 895	783,655	—
25	S.C.I.	452,177	2,144,578	644,070	—	46,657/ 783,655	—
26	I.G.	—	—	641,874	**23**, 894	803,579	—
27	Kuhlmann	459,766	—	—	—	803,964	—
28	S.C.I.	468,189	—	—	—	—	—
29	S.C.I.	487,724	—	—	—	823,195	—
30	S.C.I.	—	—	663,496	—	—	—
31	S.C.I.	—	—	—	—	833,101	—
32	Sandoz	517,030	—	—	—	840,697	198,679
33	S.C.I.	525,099	—	—	—	849,849	203,928
34	Interchem. Corp.	—	2,309,982	—	—	—	—

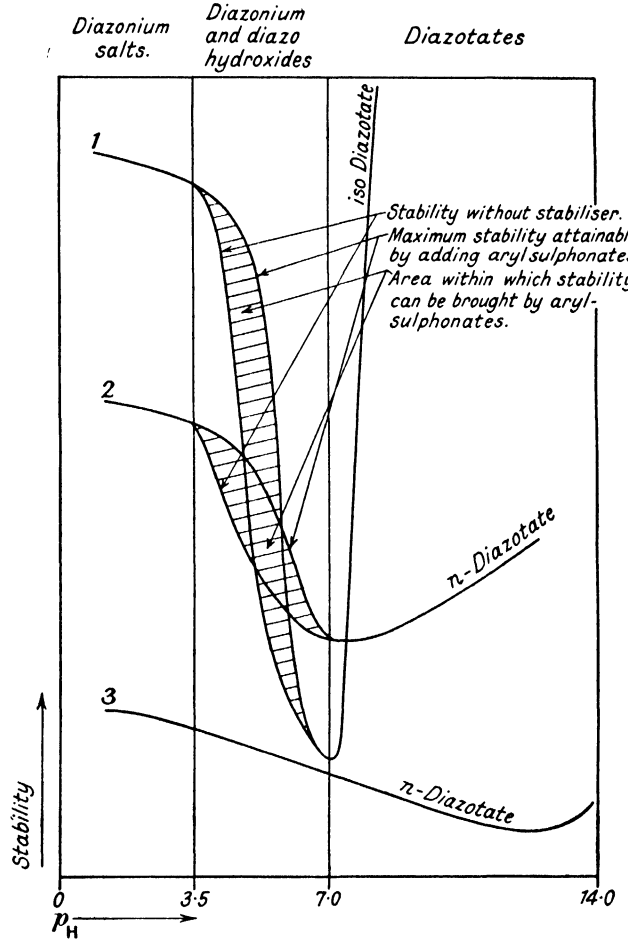
VARIATION OF STABILITY WITH pH

The foregoing discussion of the stability and stabilisation of the diazo-compounds can be summarised in a set of graphs of stability *versus* pH values. Stability may be measured by arbitrary units such as rate of evolution of nitrogen or time of half-life period of the diazo-compound at any selected temperature. If this is done the result will be a diagram having the general outlines shown on p. 99, though it must not be surprising if, when more information is available, some diazo-compounds show curves of different shapes from those now drawn, since these are necessarily speculative to some degree.

The first point to be noted concerning the above diagram is that the classical determinations of stability were made in the area pH 0—3·5. Possibly some curves cross in this area, and so account for the discrepancies in the order of stability assigned by different experimenters.

To sum up, diazo-compounds can be roughly divided into three types so far as stability is concerned. There is the negatively substituted type, in which the formation of the *iso*diazotate is so facile that the normal metallic diazotate is unknown. *p*-Nitrodiazobenzene is the representative of this type, which follows curve 1, and in which stability falls sharply to a low value as neutrality is approached, but high stability is regained once the alkaline side is reached. Secondly, there is the type of curve 2, of good stability both in acid and near the neutral point, but not greatly increasing in stability on the alkaline side, since cold alkali produces the normal metallic diazotate only; diazotised 5-chloro-*o*-toluidine is a representative of this type. Lastly, there is the type of diazobenzene itself, following curve 3, having at all times low stability, little reduced either by conversion into the salt of a weak acid or on the alkaline side, but gradually improving somewhat as the highest concentrations of alkali

are reached. The flatness of curve 3 shows why the stabilising effect of arylsulphonates is virtually undetectable in diazo-compounds of low initial stability.



THE RELATION BETWEEN pH AND CONSTITUTION OF DIAZO-COMPOUNDS

The shape of the curves of stability given above reflects the constitutional changes which take place as alkali is added to an acid solution of a diazonium salt so that there is formed in succession the diazonium hydroxide, the normal diazotate, and finally the *iso*diazotate, a stage which may require the application of heat. Conversely, by adding acid to the *iso*diazotate the series may be traversed in reverse, and at each pH value there is an equilibrium between several of the structures which the molecule of the diazo-compound can assume. The matter is introduced here because it is helpful in the subsequent discussion of the reactions of the

diazo-compounds, which are often determined by the pH at which they are carried out, and are thus linked with the stability of the diazo-compounds under reaction conditions. Questions as to the constitution of the diazo-compounds are discussed in the last chapter.

It has long been realised by inference from their reactions that a complex series of equilibria exists among the various forms of the diazo-compounds. When a pure diazonium salt composed of a diazonium cation and the anion of a strong acid is dissolved in water the solution is found to be neutral and completely ionised into two ions.[1] The chemical behaviour and stability of the diazonium ion in neutral solution is, however, different from that of the same ion in more strongly acid solution because an electromeric change occurs with production of diazo ions, the extent of the change depending on the substituents in the aryl nucleus, negative substituents assisting the rearrangement to the diazo form.[2, 5, 6] Stephenson and Waters [6] have pointed out that there is no justification for the belief that diazonium salts give rise to two isomeric cations, the diazonium cation, $Ar-N^{+}\!\equiv\!N:$ (dots represent electrons), and the diazo cation, $Ar-N=N$, since these are both canonical forms of one resonance structure, $Ar-N^{+}=N:$), but nevertheless striking reactions are known in which both forms are sharply differentiated [5] (cf. p. 196). There is also evidence [4] that for some diazonium salts there may exist the equilibrium diazonium hydroxide $\rightleftharpoons$ arylamine + nitrous acid.

Beside the above two resonance forms Mills [11] has noted that there are two others in which the aromatic nucleus is involved, viz. :—



These forms are those involved in the replacement of nuclear substituents (cf. p. 117).

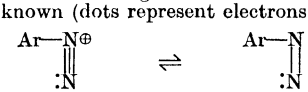
If alkali is added to the neutral diazonium salt, the diazonium hydroxide, a cation, is produced, and at once in part rearranges to the normal diazohydroxide, an anion, with which it sets up an equilibrium. When exactly one equivalent of alkali has been added the solution contains the normal diazohydroxide, both associated and dissociated, in equilibrium with the diazonium hydroxide. Cherkasskii [8, 9] has attempted to relate the reactivity of diazo-compounds with this equilibrium, high reactivity being connected with an equilibrium favouring the normal diazohydroxide. On adding further caustic alkali the more stable normal diazotate is

formed, and as this dissociates the solution contains undissociated diazotate, alkali cations, and normal diazohydroxide anions. If still more alkali is added, the proportion of undissociated normal diazohydroxide increases, and finally heat converts the normal diazotate into the *iso*diazotate, which is probably only slightly dissociated in the concentrated alkali used. The normal and *iso*diazotates are certainly not canonical forms of a common resonance structure. With the exception of the last change, all equilibria readjust themselves with great speed whenever the pH is changed, but the *iso*diazotate only returns slowly to the normal diazotate, possibly only through the diazonium salt by the action of an acid, except when irradiated.

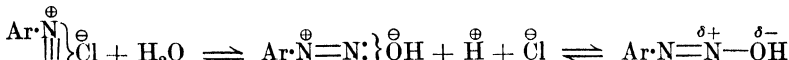
Hantzsch represented these relationships by a triangular diagram, the meaning of which is explained in the last chapter (cf. p. 390), and for the present Table XI suffices to indicate the relationship between pH and the form in which a diazo-compound exists.

TABLE XI

Relation between pH and Functional Form of Diazo-compounds

pH rising		
↓	Diazonium ions having two electromers, both extremes being known (dots represent electrons):  [Diazonium form] ⇅ [Diazo form]	Diazonium ions
	Dissociated diazonium hydroxide ⇌ (?) Undissociated	
5·5–7·0	⇅	
	Dissociated normal diazohydroxide ⇌ undissociated	*n*-Diazotate
	⇅	
	Dissociated normal diazotate ⇌ undissociated	
7·5–8·5	↓	
	Undissociated *iso*Diazotate	*iso*Diazotate
9·0		
↓	The *iso*diazotates dissociate when dissolved in water at lower pH	

The exact route by which diazonium ions become diazotate ions is not known, for example, whether undissociated diazonium hydroxide passes to dissociated or undissociated normal diazohydroxide, nor is the position of the above equilibria known. Hodgson and Marsden [10] represent the passage from diazonium chloride to diazohydroxide as :—



A further complication found by Porai-Koshits and Grachev [12] when following by electrometric titration the transition from diazonium ion to diazotate in the case of *p*-nitrodiazobenzene is that diazonium diazotates

H

can exist as transition forms. The fact that demarcation between diazonium ion and *n*-diazotate is not sharp is probably one reason why reaction products of the diazo-compounds are so often mixtures, especially when the pH of the medium is near neutrality, since several forms may be reacting at the same time, each giving a different product and/or decomposition product.

The equilibria of Table XI above occur in aqueous solution, but Hantzsch and Euler [3] suggested that the diazonium–diazo equilibrium also occurs in the solid state because they found that certain diazonium halides and thiocyanates are decolorised when strongly cooled in the solid state, the colour returning with return to a higher temperature. Hantzsch therefore suggested that the equilibrium moves in favour of the diazo form with rising temperature and that this, since it contains the azo link, is coloured.

The acquisition of further knowledge of the above equilibria is a matter of the first importance at the present stage in the development of the chemistry of the diazo-compounds. The difficulty is to devise direct means of measurement, for failing these, much theoretical argument will continue in its present weakness of moving in a circle in which the nature of the equilibria are deduced from reactions and the mechanism of the reactions is then explained in terms of the equilibria.

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TABLE XII

Constitutions of some Ice Colour Bases

Commercial name.	Constitution.	References.
Fast Black B	4 : 4′-Diaminodiphenylamine	5, 7, 12, 15, 16
G	2-Methyl-4′-*p*-aminoanilinoazobenzene	13 (p. 454), 1
LB	1-(2′-Ethoxybenzeneazo)-4-aminonaphthalene	5, 6, 7
Variamine Blue B	4-Amino-4′-methoxydiphenylamine	8, 10, 13, 14, 15
FG	4-Amino-3-methoxydiphenylamine	10, 12, 14, 15, 16
RT	4-Aminodiphenylamine	10, 14, 15
Fast Blue B	Dianisidine	6, 7, 12, 15
BB	4-Benzamido-2 : 5-diethoxyaniline	10, 12, 15, 16
R	Tolidine	6

TABLE XII—*continued.*

Commercial name.	Constitution.	References.
Fast Blue RR	4-Benzamido-2 : 5-dimethoxyaniline	10, 12, 15, 16
Blue-red O	3-Nitro-*p*-phenetidine, 3 : 4 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OEt$	12
Dark Blue R	4 : 2-$NO_2 \cdot C_6H_3(CO \cdot NMe_2) \cdot N{:}N \cdot C_6H_2(OMe)_2 \cdot NH_2$-2 : 5 : 4	13 (p. 454), 15
Bordeaux GP	3-Nitro-*p*-anisidine, 3 : 4 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OMe$	10, 12, 14, 15
BD	4-Cyano-2 : 5-dimethoxyaniline	15, 16
Ciba Bordeaux III	4-Amino-3-methoxyazobenzene	11, 12
Fast Brown V	2-Chloro-4-nitrobenzeneazo-2′-amino-5′-methyl-4′-methoxybenzene	16, cf. 11, 12, 13
Corinth B	Benzidine	6, 12, 13
LB	2-Chloro-4-benzamido-5-methoxyaniline	11, 12, 15, 16
V	2 : 4-$NO_2 \cdot C_6H_3Me \cdot N{:}N \cdot C_6H_2Me_2 \cdot NH_2$-3 : 5 : 2	13 (p. 448), 15
Garnet B	α-Naphthylamine	12
G, GB, GBC	*o*-Aminoazotoluene	1, 3, 6, 7, 15, 16
Golden Orange GR	2-Ethanesulphonyl-5-trifluoromethylaniline	14, 15, 16
Orange G, GC	*m*-Chloroaniline	3, 12, 14
GGD	3 : 5-Di-(trifluoromethyl)aniline	14, 15, 16
GR	*o*-Nitroaniline	6, 12, 14, 15, 16
LG	2-Aminodiphenylsulphone	15, 16
R	*m*-Nitroaniline	1, 12, 15
RD	2-Chloro-5-trifluoromethylaniline	14, 15
Base de Rouge Solide NK	2-Nitro-*m*-xylidine, 3 : 2 : 4 : 1-$NO_2 \cdot C_6H_2Me_2 \cdot NH_2$	13, p. 436
Fast Red AL	1-Aminoanthraquinone	7, 10, 12, 15
B	5-Nitro-*o*-anisidine, 5 : 2 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OMe$	1, 12, 14, 15
BB	*o*-Anisidine	1
FG	4-Chloro-2-aminodiphenyl ether	11, 12, 15, 16
F3G	4-Chloro-6-cyano-*m*-toluidine, 3 : 4 : 1 : 6-$NH_2 \cdot C_6H_2ClMe \cdot CN$	15, 16
FR	4 : 4′-Dichloro-2-aminodiphenyl ether	11, 12, 16
G, GL	*m*-Nitro-*p*-toluidine, 3 : 1 : 4-$NO_2 \cdot C_6H_3Me \cdot NH_2$	1, 12, 15
GG	*p*-Nitroaniline	1, 12, 14
3GL	4-Chloro-2-nitroaniline, 2 : 4 : 1-$NO_2 \cdot C_6H_3Cl \cdot NH_2$	1, 12, 14, 15
GTR	4-Ethanesulphonyl-*o*-anisidine, 2 : 1 : 4-$NH_2 \cdot C_6H_3(OMe) \cdot SO_2Et$	11, 12, 15, 16
ITR	*o*-Anisidine-4-sulphondiethylamide, 2 : 1 : 4-$NH_2 \cdot C_6H_3(OMe) \cdot SO_2 \cdot NEt_2$	10, 12, 15, 16
KB	4-Chloro-*o*-toluidine, 2 : 4 : 1-$NH_2 \cdot C_6H_3ClMe$	3, 7, 14, 15
R, RC	4-Chloro-*o*-anisidine, 2 : 4 : 1-$NH_2 \cdot C_6H_3Cl \cdot OMe$	1, 12, 14, 15
RBE	4-Amino-6-benzamido-*m*-xylene, 4 : 1 : 3 : 6-$NH_2 \cdot C_6H_2Me_2 \cdot NHBz$	6, 12
RL	5-Nitro-*o*-toluidine, 5 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$	3, 12, 14, 15
TR	5-Chloro-*o*-toluidine, 2 : 5 : 1-$NH_2 \cdot C_6H_3ClMe$	4, 14, 15
Scarlet G, GC	4-Nitro-*o*-toluidine, 4 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$	1, 6, 14, 16
GG, GGS	2 : 5-Dichloroaniline	3, 14
LG	2-Aminoanisyl-4-benzylsulphone, 2 : 1 : 4-$NH_2 \cdot C_6H_3(OMe) \cdot SO_2 \cdot CH_2Ph$	11, 12, 16
R	5-Nitro-*o*-anisidine, 4 : 2 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OMe$	1, 12
TR	6-Chloro-*o*-toluidine, 2 : 6 : 1-$NH_2 \cdot C_6H_3ClMe$	5, 12, 14
VD	4-Chloro-2-trifluoromethylaniline	14
Ciba Scarlet IV	4 : 2′-Dichloro-2-aminodiphenyl ether	11, 12
Violet I	4-Amino-5-methoxy-2-ethyl-4′-chloroazobenzene	13, p. 450
II	4-Aminobenzeneazo-1-naphthalene	13, p. 450
III	4-*p*′-Toloxyacetamido-2 : 5-dimethoxyaniline	13, p. 450
Fast Violet B	6-Benzamido-4-methoxy-*m*-toluidine, 3 : 1 : 6 : 4-$NH_2 \cdot C_6H_2Me(NHBz) \cdot OMe$	9, 15
Yellow G, GC	*o*-Chloroaniline	3, 6, 7, 14, 15

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CHAPTER III

REACTIONS OF THE DIAZO-COMPOUNDS

INTRODUCTION—CLASSIFICATION AND GENERAL DISCUSSION OF REACTION MECHANISMS. REACTIONS OF CLASS A—HALOGENATION, NITRATION, SULPHONATION—EXCHANGE OF SUBSTITUENTS BETWEEN ARYL NUCLEUS AND SOLVENT—EXCHANGE OF ANIONS WITH SUBSTITUENTS OF THE ARYL NUCLEUS.

As already mentioned, the existence of the aromatic diazo-compounds is due to the resonance of the aromatic nucleus and the diazo-group, and as resonance is modified by substituents in the aromatic nucleus, so the reactivity of the diazo-group is correspondingly modified. The effects of resonance almost invariably focus on the carbon atom to which the diazo nitrogen is attached hence the positivity of this carbon atom is affected differently by every substituent or set of substituents attached to the nucleus and so the strength of the bond by which the diazo-group is held is correspondingly varied, thus producing, for example, the variations of stability with substituents shown above in Snow's list. A crude mechanical representation is that of a system in a metastable state able to fall under gravity if disturbed, while the energy released by the fall is variable by small stages within wide limits by the movement of a weight along a screw.

From this state of affairs arises the paradox that though the formation and transformations of the diazo-compounds are among the most general of organic chemistry, yet their study unavoidably becomes one of detail because, as will be seen in the sequel, the products derived from the same reagent may alter as the long scale of diazo reactivity is traversed from one end, where the aryl nucleus carries positive substituents, to the other end, where the diazo-group comes under the influence of several negative substituents.

The great value of the diazo-compounds to the organic chemist lies in the many-sidedness of their transformations. They are themselves so unstable that were it not for their use as stepping-stones they would be even of little academic interest; they cannot even be long preserved as " nice specimens " for lecture demonstrations. But, though unstable, it is possible to control and direct the channels of their activity so that they afford a range of derivatives not surpassed by any other functional group. The interaction of reagents with the diazo-compounds follows three general reaction modes :—

(*a*) The aryl nucleus may be substituted or its substituents changed without the diazo-group being affected.

(*b*) The diazo-group may react to give derivatives in which the diazo nitrogen atoms are retained.

(*c*) The nitrogen is eliminated and another element or radical becomes attached to the same carbon atom of the aryl nucleus.

The second type of reaction would be notable if it were represented only by the azo dyes, and the third affords an indirect means of synthesis of many substances not attainable by direct substitution, *e.g.*, the β-halogenonaphthalenes and β-nitronaphthalene. In short, wherever an aryl radical can be substituted by an amino-group of known orientation there the possibility exists of making a series of derivatives of the same orientation.

The derivatives of the diazo-compounds are accordingly grouped under the scheme below in five classes, among which Class A corresponds with (*a*) above, Classes B and C with (*b*), while Class D covers both (*b*) and (*c*), forming a connecting link with Class E, which corresponds with the reaction mode (*c*).

CLASS A. Derivatives Formed by Substitution or by Changes in the Substituents of the Aryl Nucleus.

Group 1. Halogenation, nitration, sulphonation . . p. 115
2. Exchange of substituents between aryl nucleus and solvent 117
3. Exchange of diazonium anions with substituents of the aryl nucleus. 124

CLASS B. Derivatives in which the Diazo-group is Involved but Remains Functionally Intact.

Group 1. Metallic diazotates and diazoanhydrides . . . 126
2. O-Azo-compounds, the diazo ethers 139
3. Diazocyanides 142
4. Diazosulphonates 147
5. Diazoperhalides 153
6. Diazosulphides 155

CLASS C. Derivatives in which the Diazo-function Disappears, but the Diazo-nitrogen Atoms Remain in the New Molecule.

Group 1. Diazo-amino and -imino compounds or triazens . . 157
2. Oxidation products 179
3. Reduction products; the arylhydrazines . . . 183
4. Arylazides and other compounds derived from nitrogen-containing substances 187
5. S-Azo-compounds; diazo-thioethers 192
6. Azo-compounds formed by the coupling reaction. . 194

CLASS D. Ring Compounds formed from Diazo-compounds in which, (a) *the Diazo-nitrogen Atoms Remain in the Ring* (*Groups* 1—5), (b) *a Ring is Formed with Elimination of the Diazo-nitrogen Atoms* (*Groups* 6—10).

Group 1. Cinnoline . . . . . p. 241
2. Indazole 245
3. Triazole 247
4. Triazine 251
5. Thiodiazole 253
6. Phenanthrene and related compounds . . . 254
7. Fluorene and fluorenone 258
8. Diphenylene oxide and diphenylene sulphide . . 261
9. Carbazole 263
10. Other ring compounds 265

CLASS E. Derivatives formed by Replacement of the Diazo-group by :

Group 1. Hydrogen 268
2. Halogens 275
3. Nitro- and amino-groups; carbimides (*iso*cyanates); azo-compounds not formed by coupling . . . 293
4. Hydroxyl, which may be esterified and etherified . 302
5. The cyano-group, aryl radicals and other C·C links . 309
6. Sulphur-, selenium-, and tellurium-containing radicals 323
7. Arsenic-, antimony- and bismuth-containing radicals . 330
8. Metals 336

The mechanism by which the reactions of Class A come about call for no comment here, for they are the mechanism by which analogous reactions occur as the result of interplay of substituents among other types of aromatic compounds.

In the reactions of Classes B and C, with the exception of the formation of metallic diazotates, ionised or ionisable diazo-compounds are converted into compounds having covalent links.

It is the mechanism of the replacement reactions of Classes D and E, referred to by some writers as the decomposition reactions, that have aroused so much speculation, especially in the last decade, and it must be admitted that they are as yet by no means understood in many of their aspects, while for some no satisfactory hypothesis has been propounded. To avoid dissipation of the discussion a broad survey of current theory is made here, and the subsequent detailed accounts of various replacements will be used as illustrations with comments on any peculiarities. Moreover, the presentation of old facts in a new light will suggest fresh experiments to the enquiring mind.

Waters [16] has pointed out that there can be distinguished three different reaction-types by which the replacement reactions occur in solution, and these in effect represent three different ways by which the nitrogen acquires the two electrons necessary for its disengagement as the free element. The reaction-types are as follows :—

Type I. Ionic reactions of an aryl cation formed by decomposition of a diazonium cation in acid solution; possibly also the decomposition of solid diazonium salts or diazonium-metallic double salts under the influence of heat.

Type II. Non-ionic reactions of diazo salts or of *n*-diazohydroxides in non-ionising organic solvents or in aqueous solution about the neutral point.

Type III. Reactions in which replacement only occurs in presence of another substance, often a cuprous salt or copper, which may be oxidised during the reaction. Here are included the reactions generally known as the Sandmeyer, Gattermann, and Pschorr reactions.

Whether Waters' explanation of the reaction mechanisms stands the test of time or not, the division into the above three types is the beginning of a rational classification of the replacement reactions, and it will be utilised as far as possible in this volume. The three types are discussed in general below, but it must be pointed out that in practice more than one reaction-type may be in operation at the same time, each at different rates and levels of intensity, while too often authors gloss over the fact that the main product of reaction is an uncompromising tar from which but small quantities of recognisable substances can be extracted.

Replacement Reactions of Type I.—Reactions of this type are initiated by the decomposition of a dissociated diazonium cation in acid solution when the disengaging nitrogen acquires both the necessary electrons from the C·N link, thus leaving an aryl cation (dots represent electrons) :—

$$(\mathrm{Ar{:}N{:::}N{:}})^{\oplus}\,X^{\ominus} \longrightarrow \mathrm{Ar}^{\oplus} + {:}\mathrm{N{:::}N{:}} + X^{\ominus}$$

Acquisition by the nitrogen of both electrons from one link is called heterolysis.

The aryl cation may combine directly with an anion, and this simple ionic mechanism accounts for the formation of phenols :—

$$\mathrm{Ar}^{\oplus} + \mathrm{HO}^{\ominus}\mathrm{H}^{\oplus} = \mathrm{ArOH} + \mathrm{H}^{\oplus}$$

Replacement by chlorine or bromine in concentrated aqueous hydrochloric or hydrobromic acid takes place by the same mechanism :—

$$\mathrm{Ar}^{\oplus} + \mathrm{Cl}^{\ominus} = \mathrm{ArCl}$$

Waters [16] has pointed out that the latter reaction can proceed in preference to the former, since the electron affinity of chlorine (93 kg.-cals.)

is less than the energy of fission of an O—H link (100 kg.-cals.). Since no electrons are supplied from any external source, diazo-compounds do not act as oxidising agents in replacements of this type.

Replacement Reactions of Type II.—Nitrosoacylarylamides dissolved in liquid aromatic hydrocarbons or other non-ionising organic liquid decompose at room temperature with evolution of nitrogen and the production of diaryls or other compounds derived, by union of the aryl nucleus of the diazo-compound with atoms or groups of the solvent molecules. This is an easily-studied example of a reaction also shown by diazoanhydrides and diazosulphides, while in the Gomberg reaction (cf. p. 316) substances similar to those produced by the decomposition of the nitrosoacylarylamides are extracted by the water-immiscible layer with which they react. Grieve and Hey [3] marshalled evidence to show that both the course of the above reaction and the nature of the product preclude an ionic reaction of Type I, and put forward the view that free neutral radicals are formed which combine with the solvent molecules giving arylated derivatives thereof. If nitrosoacetanilide is written as its tautomer, undissociated diazobenzene acetate, then it is seen that two free radicals are produced if the nitrogen takes one electron from each link by which it is held in the molecule (dots represent electrons, and an asterisk denotes a free radical) :—

$$\mathrm{Ph{:}N{:::}N{:}CO_2Me} \longrightarrow \mathrm{Ph^* + {:}N{:::}N{:} + {*}CO_2Me}$$

This process is called homolysis, as opposed to heterolysis, by which the aryl cations of the Type I reactions are produced.

There are two main pillars for the above view, while in addition Hey and Waters [4, 20] have shown that they fit in with other known free radical reactions. The first is that the decomposition of the nitrosoacetarylamides is unimolecular and independent of the solvent, and the second is that the aryl radical resulting from this decomposition when substituting another benzenoid molecule always enters *ortho* or *para* to the existing substituents, no matter whether they are *ortho*- and *para*-directing or *meta*-directing, thus indicating that the entering aryl radical is not ionised. Further, Waters [5] showed that dry nitrosoacetanilide dissolved in dry *n*-hexane, *cyclo*hexane, diethyl ether, dioxan, acetone, ethyl acetate, acetonitrile, or acetic anhydride affords benzene among the products of decomposition, chiefly tar, while from methyl and ethyl iodides, ethyl bromide, bromoform, chloroform, and carbon tetrachloride the halogen is abstracted giving iodo-, bromo-, and chlorobenzene. These results can be accounted for by the reactions :—

$$\mathrm{Ph^* + RH = C_6H_6\ (+\ R^*)},\ \text{and}\ \mathrm{Ph^* + RHal = PhHal\ (+\ R^*)}$$

The tendency of free radicals to appropriate hydrogen from any compound with which they come in contact is one which Waters has laid down as diagnostic of free radicals, but this does not preclude the occur-

rence of the reverse reaction Ph* + RH = PhR + H*; this indeed may be the basis of the Pschorr reaction (cf. p. 254).

The nitrogen liberated in the decomposition of nitrosoacetanilide is mixed with carbon dioxide, the presence of which can be accounted for as arising from the break-up of acetate radicals :—

$$CH_3{\cdot}COO^* \longrightarrow CO_2 + CH_3^* \ (\longrightarrow CH_3{\cdot}CH_3)$$

If metals are present when nitrosoacetanilide decomposes in carbon disulphide or carbon tetrachloride they are attacked by the free acetate radicals even in presence of chalk; thus salts, usually the acetate, are formed from zinc, iron, copper, tin, lead, antimony, and mercury. The last metal shaken in carbon tetrachloride with nitrosoacetanilide affords phenylmercurichloride, PhHgCl.

Dry benzenediazonium chloride, though but sparingly soluble in organic liquids, behaves similarly to nitrosoacetanilide.[6] Thus, when suspended in acetone, hexane, carbon tetrachloride, ethyl iodide, or ethyl acetate, there are produced chlorobenzene and hydrochloric acid as the main products, though in acetone in presence of chalk the products are benzene and chloroacetone. If metals are present with acetone and chalk they are attacked; mercury affords, as above, phenylmercurichloride, while triphenylstibine dichloride, Ph_3SbCl_2, is obtained from antimony.[8] Benzenediazonium chloride can function as a source of free radicals in the same way as nitrosoacetanilide if it first rearranges to diazobenzene chloride, $\mathrm{Ph\overset{\cdot\cdot}{N}{:}N} \longrightarrow \mathrm{Ph{\cdot}N{:}N{\cdot}\overset{\cdot\cdot}{Cl}}$, a likely reaction in a non-hydroxylic solvent. The escaping nitrogen then acquires an electron from each covalent link, leaving a free phenyl radical and a neutral chlorine atom (dots represent electrons) :—

$$Ph{:}N{:::}N{:}Cl \longrightarrow Ph^* + N_2 + Cl^*$$

Further evidence for the analogy between nitrosoacetanilide and benzenediazonium chloride when decomposing in neutral organic liquids is that when stirred with *cyclo*hexene and chalk the products are *cyclo*hex-2-enyl acetate and *-cyclo*hex-2-enyl chloride, the former arising from free acetate radicals, and the latter from the neutral chlorine atoms.[13]

The general oxidising powers of the diazo-compounds are shown in the above-mentioned formation of organo-metallic compounds or metallic salts, and after similar experiments with thirty-eight metals Waters [10] concluded that, when using benzenediazonium chloride as the source of free phenyl radicals, organo-metallic compounds are only formed when covalent compounds are the result of reaction. No aryl derivatives are thus produced from gold, thallium, germanium, lead, bismuth, or magnesium, though the neutral chlorine atoms produce their chlorides, as it does with all elements of metallic character, just as it chlorinates the acetone. Aryl derivatives are formed from mercury, tin, arsenic, anti-

mony, sulphur, selenium, and tellurium. The last element is well known for its capacity to combine with free radicals, and under the above conditions diphenyltellurium dichloride is formed [9]; sulphur and selenium afford diphenyl sulphide and diphenyl selenide respectively.[9] Further evidence for the presence of free phenyl radicals is that diphenyl accompanies the organo-metallic compounds, and its amount is increased if benzene is mixed with the acetone, while if naphthalene is added α- and β-phenylnaphthalene are formed. Chlorobenzene is the only product when copper is present, most probably because once cuprous chloride has been formed it plays its usual part in replacing the diazo-group by chlorine. If the acetone is replaced by an ester or nitrile, with or without a metal, the chief product is tar from which benzene and chlorobenzene can be isolated [11]; if diethyl ether is present acetaldehyde is always found, but higher ethers are inert.

Not all covalent diazo-compounds can produce free radicals. Stephenson and Waters [12] have examined the diazocyanides, but they do not afford free radicals in non-ionising solvents, including benzene, *cyclo*hexane, carbon tetrachloride, and diethyl ether. The labile diazocyanides do not lose nitrogen, but pass into the stable diazocyanides, in which decomposition can only be induced with copper powder; the product is a tar.

The hall-marks of the Type II reaction are therefore that, owing to the random combination of free radicals, more than one product (counting tar as a product) is formed, and that the effects of irreversible oxidation are seen in the system.

The oxidising effects, especially of the *n*-diazohydroxides and the *n*-diazotates, have attracted the attention of the Italian chemists, who have collected many examples, among them the oxidation of inorganic salts such as ferrous, manganous, and cerous salts to salts of higher valency and leucoindigotin to indigotin.[1] To account for this oxidising power Jolles and Busoni [2] assign the constitution (Ar·N:NH):O to the *n*-diazohydroxides, and suppose that, the oxygen having been given up, the residual hypothetical phenyldi-imide, PhN:NH, decomposes into Ph, H, and N_2. Jolles has actually noted that the phenyl and hydrogen need not necessarily combine with each other, though benzene appears in the products of decomposition. Another step and he would have crystallised the concept of free phenyl radicals derived from diazo-compounds, which was to commence its development in England three years later.

Hey and Waters demonstrated the production of free radicals by the homolytic scission of covalent diazo-compounds in non-ionising solvents, whereas Jolles and the Italian chemists carried out their experiments in aqueous solution. There are many facts recorded in the literature which suggest that the Type II reaction occurs commonly among diazo-compounds in aqueous solutions near the neutral point. In the Gomberg reaction for the synthesis of asymmetric diaryls aqueous alkali diazotates

are shaken with a water-immiscible non-ionising liquid in which the products of reaction of free aryl radicals appear. Whether the radicals are formed in the aqueous solution and are afterwards extracted by the organic liquid, or whether diazobenzenehydroxide is extracted and then decomposes, is not yet determined. According to Waters,[7] the source of the phenyl radicals when sodium benzene *n*-diazotate decomposes in aqueous solution is the undissociated diazobenzene hydroxide with which it is in equilibrium (dots represent electrons) :—

$$PH{:}N{::}N{:}OH = Ph^{*} + N_2 + OH^{*}$$

Waters' evidence for this view is that on shaking aqueous sodium benzenediazotate with *cyclo*hexane or with carbon disulphide there is formed benzene in the former and diphenyldisulphide in the latter, both formed by the action of free phenyl radicals.

It has been suggested [19] that a number of reactions of the diazo-compounds for which no reaction mechanism has so far been advanced, and which occur in neutral or alkaline solution with formation of several compounds as a water-insoluble phase, may be in part due to free radicals arising by homolysis of undissociated diazohydroxides, and such reactions are assisted if a reducing agent is present. The symmetrical azo-compounds of the benzene series (cf. p. 296), formed by reduction of positively-substituted diazo-compounds with ammoniacal cuprous oxide, may be produced by interaction of aryl radicals with dissociated diazo cations :—

$$Ar^{*} + ArN_2^{\oplus} + e = Ar{\cdot}N_2{\cdot}Ar$$

The formation of diphenyleneazone (cf. p. 266) may also be another example of this reaction.

Diaryls and arylazodiaryls also appear in these reactions in varying proportions, and it is possible that they arise in part by free radical reactions, for once some free radicals have been formed a number of reactions may proceed. For example, the undissociated diazohydroxide itself may be attacked by free radicals :—

$$Ph^{*} + PhN_2OH = Ph{\cdot}C_6H_4{\cdot}N_2OH + H^{*}$$

Then the undissociated *p*-diphenyldiazohydroxide may in turn break up :—

$$Ph{\cdot}C_6H_4{\cdot}N_2OH = PhC_6H_4^{*} + N_2 + OH^{*}$$

The diphenyl radical under the influence of a reducing agent, especially potassium ferrocyanide (cf. p. 298) or sodium cuprothiosulphite (cf. p. 325), combines with the diazobenzene cation, giving benzeneazodiphenyl :—

$$PhC_6H_4^{*} + PhN_2^{\oplus} + e = Ph{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$$

Benzeneazodiphenyl can also be formed from the dissociated 4-diazodiphenyl cation and a phenyl radical in presence of a reducing agent :—

$$Ph^{*} + Ph{\cdot}C_6H_4N_2^{\oplus} + e = Ph{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$$

Jolles in 1931 surmised that the diazo-resins (cf. p. 307) are built up in the same way as benzeneazodiphenyl, which may be a unit of their constitution, and in view of possibilities such as the above, which by no means exhaust those which can be conceived, it is not surprising that tars so frequently result from the reactions of diazo-compounds. Moreover, the tar can function as an extractor of free radicals or their precursors from the aqueous phase, and in the tar-phase can occur reactions such as :—

$$Ph{\cdot}C_6H_4{*} + Ph{*} = Ph{\cdot}C_6H_4{\cdot}Ph \quad \text{Terphenyl}$$

$$Ph{\cdot}C_6H_4{*} + PhC_6H_4{*} = Ph{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}Ph \quad \text{Quaterphenyl}$$

These hydrocarbons are in fact isolable from the tar formed when diazobenzene is reduced with alcohol and copper powder (cf. p. 313).

The extraction effect by the products of reaction themselves is one way in which it is possible that completely random combination of radicals with any contiguous solvent or solute molecule is limited. Another possible controlling agent is the likelihood that radicals formed at the surface of an insoluble reducing agent are held there until combination with other radicals also held at the surface has taken place; such a juxtaposition with the reducing agent also facilitates the transfer of electrons from the reducing agent. The fact that in spite of the possibilities only a limited number of products can be isolated from any given reaction shows that some such mechanism exists.

Beside the homolytic scission of undissociated diazo-compounds there is yet another way in which free aryl radicals may be formed, *viz.*, from diazonium cations in the presence of a reducing agent able to supply a single electron to the CN link, so allowing the nitrogen to escape :—

$$ArN_2^{\oplus} + e = Ar{\cdot} + N_2$$

This single electron transfer is suggested by Waters as the mechanism of replacement of the diazo-group by iodine (cf. p. 290).

Considerations such as the above open a vista of new ideas and new avenues of experiment to discover more of the nature of the Type II reactions. With understanding will come control and new synthesis to justify Hey's [17] appelation of the chemistry of free radicals as the "New Organic Chemistry". It must, however, be added that there are chemists who ignore or deny the fact that diazo-compounds can undergo homolytic scission, and doubt that free radicals if formed can be responsible for any considerable proportion of the reaction products. Thus Kenner [18] ascribes reactions of the type mentioned above to oxidation and reduction, whilst Hodgson [21, 22] has affirmed his belief that free radicals are not produced by the decomposition of diazo-compounds, the main ground for his contention being that the two bonds by which the nitrogen is held are not of equal strength, hence it is impossible for simultaneous scission to occur and so free radicals cannot be formed. He has therefore adduced

ionic mechanisms [23] for all the reactions of the diazo-compounds.* These views have been challenged by Hey and Waters [24] and the exchange is likely further to stimulate interest in the reaction mechanisms of the diazo-compounds.

Replacement Reactions of Type III.—In reactions of this type, which are usually carried out in acid aqueous medium, the diazonium salt forms a complex, which may or may not be isolable, and is, indeed, often suppositious, with a metallic salt which in effect passes anions from the solution to replace the diazo-group. Held within the locus of the metallic salt, the diazo-compound is in a region of abnormally high concentration of anions, and thus replacement of the diazo-group is brought about without interference by water. The criterion of the Type III reaction is therefore that even if the anions are in low concentration in the reaction medium, yet the complex will collect them and pass them on, so that a high yield of the replacement product is obtained under conditions in which the yield would otherwise be poor. Whether oxidation effects are directly connected with Type III reactions is not yet known.

There are two schools of thought as to the nature of the mechanism which occurs within the complex. The school represented by Hodgson and his co-workers [14] regard the complex as functioning catalytically by activating the atom or group which replaces the diazo-nitrogen. Hence, as experience shows, salts other than cuprous salts can and do catalyse the replacement.

The free radical school, led by Waters,[16] also believes the reaction to be a catalysed decomposition in which a cuprous salt gives one electron to an aryl cation, so becoming a cupric salt; the resultant free radical then combines with an anion, at the same time expelling an electron which reduces the cupric salt to its original state.

Neither school therefore requires that any component of the system shall be irreversibly oxidised during reaction, and any such oxidations should be expected to result in the formation of by-products by Type II reactions.

The battle-ground of the two theories is the Sandmeyer reaction for the replacement of the diazo-group by chlorine and bromine, under which head they are discussed and compared (cf. p. 280). Replacement of the diazo-group by the nitro-, cyano-, sulphinic, and sulphonic acid groups are also Type III reactions.

One result of these theories of the Type III reactions is to focus attention on the question as to just how far the reducing agent is oxidised during reaction—a question in which chemists have so far taken but little interest.

* The papers comprising refs. 21–25 appeared after the MS. of this book was in the hands of the printer and the author regrets that this has made it impossible to include a parallel comparison of the free radical and ionic theories of reaction mechanism.

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CLASS A. DERIVATIVES FORMED BY SUBSTITUTION OR CHANGES IN SUBSTITUENTS OF THE ARYL NUCLEUS

GROUP I. HALOGENATION, NITRATION, SULPHONATION

The diazo-group is so reactive that it does not often remain unaffected by reagents which substitute the aryl nucleus. Nevertheless, in strongly acid solution it is sometimes possible to effect such substitution if the diazo-group is sufficiently stable and substitution sufficiently facile. Chief among the diazo-compounds which can be subjected to such operations are the diazo-oxides, the diazo-group being thus stabilised by anhydride formation. As early as 1881 Böhmer [1] produced 3 : 5-dibromo-4-hydroxybenzenediazonium bromide by acting on diazotised *p*-aminophenol with bromine water, but it is naphthalene-1 : 2-diazo-oxide-4-sulphonic acid ("Diazo-1 : 2 : 4-acid") which is the diazo-compound pre-eminently used for the above operations. While sulphonation [3] of this compound and of other diazo-oxides of the naphthalene series [5] has been described, it does not compare in importance with its bromination [9] and nitration [2]; the latter operation is carried out on the manufacturing scale usually on the free acid, but the zinc, iron, or copper salts may be used.[12] The nitro-compound is used to make azo chrome dyestuffs, especially by coupling with α-naphthol (cf. p. 207). "Diazo-1 : 2 : 4-acid" can also be chlorinated in sulphuric acid or in chlorosulphonic acid, both at atmospheric pressure [10] and under pressure of chlorine.[11, 22] Other

diazo-compounds of the naphthalene series can also be nitrated, including naphthalene-1 : 2-diazo-oxide-3-carboxylic acid.[7] The point of substitution of diazo-1 : 2 : 4-acid by the above reagents is the 6-position. This was proved by Ruggli [13, 14] and by Battegay [15] and their co-workers by removal of the diazo-group, reduction of the nitro-group to an amino-group which is then converted into hydroxyl, thus producing 2 : 6-dihydroxynaphthalene on removal of the sulphonic acid group; by a similar process the halogeno-derivatives produce 6-halogeno-2-naphthol. On the other hand, diazotised 2 : 1-aminonaphthol-6-, -7-, or -8-sulphonic acid is nitrated at 4, whilst if a sulphonic acid group is at 4 it is replaced by the nitro-group.[19]

Anthraquinone-α- and -β-diazonium salts can be nitrated in concentrated sulphuric acid, the nitro-group entering the ring not containing the diazo-group usually at the 5-position.[17] Anthracene-β-diazonium fluoborate can also be nitrated in the α-position.[18]

The nitration of the diazo-derivatives of amines which can be diazotised in concentrated sulphuric acid, especially α-naphthylamine and its 5- or 7-sulphonic acid, has been patented,[8] but Blangey, on examination of the described process, said that under such conditions diazotisation does not occur and nitroso-compounds, such as 4-nitroso-1-naphthylamine, are the products of interaction of the above amines with nitrosylsulphuric acid.[20] Still more recently a process has been patented [21] for diazotising aniline in concentrated sulphuric acid, stabilising it in that solution with an arylsulphonic acid, *e.g.*, anthraquinone-2 : 7-disulphonic acid, and nitrating; the product affords the same shade with ice-colour components as *p*-nitrodiazobenzene stabilised with anthraquinone-2 : 7-disulphonic acid. A variation of the method is to diazotise aniline in concentrated hydrofluoric acid and then nitrate in that medium.[21]

A hydroxy-group which is not *ortho* to a diazo-group can be acetylated in acetic anhydride without affecting the diazo-group,[6] while diazo-compounds derived from 4-aminodiphenylamine, *p*-aminophenol, or monodiazotised *p*-phenylenediamine can be condensed with aldehydes such as formaldehyde, crotonaldehyde, 2 : 4-dichlorobenzaldehyde, or phenanthraquinone sulphonic acid, without impairment of the diazo function.[16]

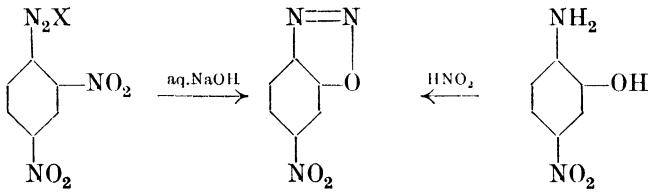
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GROUP 2. EXCHANGE OF SUBSTITUENTS BETWEEN ARYL NUCLEUS AND SOLVENT

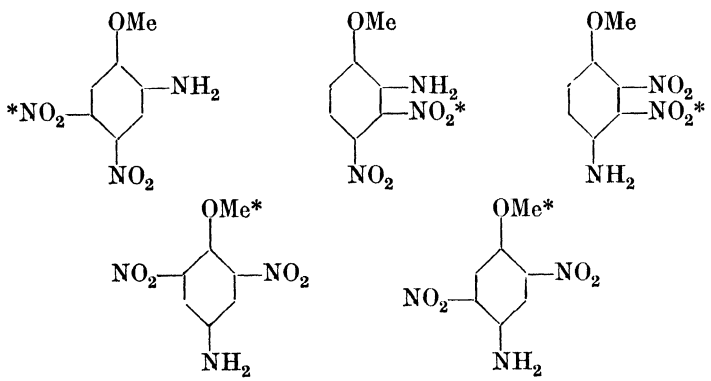
When the amino-group in an aromatic amine is converted into the diazo-group a considerable effect is exerted on other groups occupying the *ortho* or *para* positions in the same benzene ring. With the exception of the alkoxy-group, the substituents affected are the negative substituents which induce high stability in the diazo-salts as long as the anions of a strong acid are present in the solution, but when the latter are withdrawn by adding alkalis or the alkali salts of weak acids, the stability falls rapidly (see p. 98). Destruction of the diazo-group does not, however, necessarily ensue from this loss of stability, but instead one of the substituents may, by the action of the water, be exchanged for hydroxyl, with which the diazo-group immediately forms a stable internal anhydride, thus arresting further change. For example, salts of 2 : 4-dinitrodiazobenzene when treated with weak aqueous alkalis lose the *ortho*-nitro-group, and the 4-nitrobenzene-1 : 2-diazo-oxide thus formed is identical with the substance obtained by diazotising 5-nitro-2-aminophenol [45] : –



From the above the expectation naturally arises that the attempt to diazotise amines having negative groups *ortho* and *para* to the amino-group in the presence of weak acids will lead to the production of diazo-oxides instead of diazonium salts. This is precisely what occurs, and it was through the unexpected appearance of examples of the exchange of substituents that it has become recognised as a reaction to which an extensive class of diazo-compounds is susceptible.

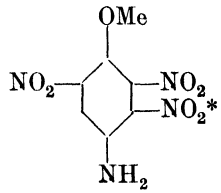
For more than a decade Meldola and his school carried on research among the polynitroanisidines as to the conditions under which substituents are exchanged. If these compounds are diazotised in sulphuric acid or nitric acid the diazo-sulphate or -nitrate results in the usual way. If diazotised in hydrochloric acid a nitro-group *ortho* to the amino-group may be exchanged for chlorine; for example, 2 : 3-dinitro-*p*-anisidine thus affords 2-chloro-3-nitro-4-methoxybenzenediazonium chloride,[8] and 1-nitro-2-naphthylamine similarly affords 1-chloro-2-diazonaphthalene.[9, 25, 26] Diazotisation of 2 : 5-dichloro-4-nitroaniline in aqueous hydrochloric acid followed by treatment with potassium iodide affords 2 : 4 : 5-trichloro-1-iodobenzene, the nitro-group *para* to the diazonium-group being replaced by chlorine.[28] That the exchange is with chlorine and not with hydroxyl is probably due to the same reason that the diazo-group can be replaced by chlorine rather than by hydroxyl in aqueous hydrochloric acid (cf. p. 276), *viz.*, that the electron affinity of chlorine (93 kg.-cals.) is less than the energy of fission of an O—H bond (110 kg.-cals.).

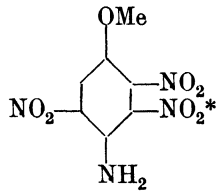
When, however, the dinitroanisidines are diazotised in glacial acetic acid either a nitro-group or a methoxy-group may be exchanged, according to the orientation of the substituents. Among the compounds the configurations of which are given below the removable groups are marked by an asterisk [6, 14] :—



In summing up these results Meldola and Hay [18] reached and confirmed the conclusion that in this series a group only becomes sufficiently mobile to be exchanged during the act of diazotisation if two conditions are fulfilled. These conditions are that the mobile group shall be *ortho* or *para* to the diazo-group, and in addition have a nitro-group in its other *ortho* position to act as " activator." Such activating groups will be found in each of the five compounds above, but are lacking in 4 : 6-dinitro-3-anisidine [1 : 3 : 4 : 6-$(NO_2)_2 \cdot C_6H_2(NH_2) \cdot OMe$], hence in the latter neither a nitro- nor a methoxy-group can be eliminated during diazotis-

ation. If conditions are such that either a nitro- or a methoxy-group can be exchanged, then it is the nitro-group which goes. This point was settled by Meldola and Reverdin,[22] who prepared the two trinitroanisidines :—





In each case above the *ortho*-nitro-group exchanges for hydroxyl on diazotisation, but it must be noted that no exchange occurs if the molecule already contains a free hydroxyl group *ortho* or *para* to the diazo-group, as the demands of stability are immediately satisfied by diazo-oxide formation, without the occurrence of exchange. Thus when 2 : 3-dinitro-4-aminophenol is diazotised in concentrated sulphuric acid the yellow diazo-oxide is precipitated immediately on dilution.[20]

There is a further point of interest in those nitroanisidines in which the nitro-group is exchangeable, in that they are self-diazotising once the diazotisation reaction has commenced. Thus Meldola and Eyre [7] started the diazotisation of 4 : 5-dinitro-*o*-anisidine with one quarter the theoretical amount of nitrous acid, but found that nevertheless the formation of the diazo-oxide continued by the utilisation of the nitrous acid generated as the nitro-group was split off the benzene ring in exchange for hydroxyl.

The rule given above to determine which group shall be exchanged is peculiar to the polynitroanisidines, where the methoxy-group, a positive group, stands either *ortho* or *para* to the amino-group. In the *meta* position it has no effect. If both the *ortho* and the *para* positions to the diazo-group are occupied by negative groups, then almost invariably the *ortho*-group will be found to be labile in some degree, and sometimes so labile that it is exchanged in acid solution. For example, 2 : 4-dinitro-1-naphthylamine on diazotisation rapidly exchanges the nitro-group at 2 for hydroxyl, giving 4-nitronaphthalene-1 : 2-diazo-oxide.[4, 24] If in diazo-compounds of the benzene series negative groups occupy both positions *ortho* to the diazo-group, then one may be exchanged, though not very easily, as is shown in the case of 2 : 6-dibromodiazobenzene below.

Whilst some groups in certain positions are exchanged even during diazotisation, especially if " activated " by other substituents, as described above, negative groups or atoms *ortho* or *para* to the diazo-group can often be exchanged by treatment of the diazonium salt with alkaline solutions. The exchange may take place so rapidly that other reactions of the diazo-group are suppressed. Thus, when Gaess and Ammelburg [7] attempted to remove the diazo-group from diazotised 1 : 6-dinitro-2-

naphthylamine by the usual method of boiling with alcohol, they found that the nitro-group at 1 is replaced by hydroxyl; the diazo-oxide is then formed, and this is not attacked by alcohol.

The arsonic acid group has sufficient negative effect to cause the exchange of the nitro-group for hydroxyl in diazotised 2-nitro-1-amino-4-arsonic acid, giving benzene-1 : 2-diazo-oxide-4-arsonic acid.[23, 57] The sulphonic acid group is exchanged for hydroxyl when compounds such as 2-naphthylamine-1 : 5 : 7-trisulphonic acid [48] or 1-naphthylamine-2 : 4-disulphonic acid [52] are diazotised and treated with aqueous sodium carbonate. The sulphonic acid group appears in the solution as sulphite, and as the solution is often used directly for the manufacture of azo dyes, this reducing agent can have deleterious results. Accordingly, an equivalent of hypochlorite [55] or hydrogen peroxide [56] is added to the sodium carbonate solution in which the exchange reaction occurs, thus oxidising the sulphite to sulphate.

Many cases of the exchange of chlorine and bromine atoms for hydroxyl are known and have been studied. Silberstein [1] early obtained 2 : 4-dibromo-1 : 2-diazophenol by heating 2 : 4 : 6-tribromobenzenediazonium nitrate in acetic acid, though aqueous alkali is a more effective reagent.[12, 16] Meldola and Streatfeild [3] diazotised 1 : 4-dibromo-2-naphthylamine sulphate in glacial acetic acid, and after diluting with water warmed the solution; no nitrogen was given off, but hydrobromic acid was found in the liquid from which the insoluble 4-bromonaphthalene-1 : 2-diazo-oxide had been collected. Orton studied the exchange of halogen atoms extensively, and as a result constructed the table of the relative rates of exchange shown below.[12]

TABLE XIII

Relative Rates of Exchange of Halogen Atoms for Hydroxyl

Diazo-compound from :	Percentage of 1 mol. of halogen set free at room temperature in 24 hours.
2 : 4-Dibromo-1-naphthylamine	97
2 : 4 : 6-Tribromo-3-nitroaniline	93
2 : 4-Dibromo-5-nitroaniline	80
1-Chloro-2-naphthylamine	76
2 : 3 : 4 : 6-Tetrabromoaniline	74
2 : 4 : 6-Tribromoaniline	64
2 : 4 : 6-Trichloroaniline	63
2 : 6-Dibromoaniline	24
2 : 4-Dichloroaniline	trace

Orton was further interested in the mechanism of the exchange reaction, and was concerned to know whether transformation proceeds directly from the diazonium ion or through a diazotate. He showed that both tribromobenzenediazonium sulphate and normal sodium tribromo-

benzenediazotate are stable, and that exchange for hydroxyl occurs at intermediate values of pH.[13] He suggested a mechanism operating through intermediate quinonoid forms between diazonium hydroxide and diazo-oxide, but Mills [27] has shown that the exchange reaction is a direct result of resonance in the molecule of the diazo-compound.

The exchange reaction for hydroxyl is of considerable technical importance, because the replacement of the substituent *ortho* to the diazo-group by hydroxyl means that *ortho*-hydroxyazo-compounds are formed on coupling, and as such compounds have the power to form very stable co-ordination compounds with metallic salts and oxides, this is an easy way to the synthesis of mordant azo-dyes. There are therefore to be found in the literature a number of references, mostly patents, for the manufacture of *ortho*-hydroxydiazo-compounds by this means, and these are grouped together in the table below according to the group exchanged.

TABLE XIV

Amines Exchanging a Substituent for Hydroxyl from their Diazo Derivatives

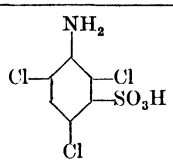
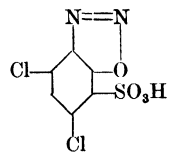
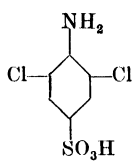
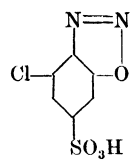
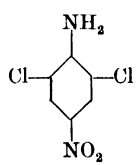
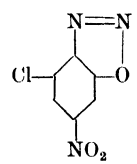
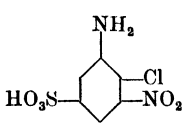
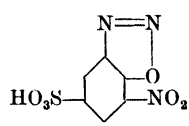
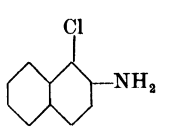
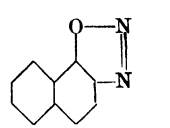
Substituent exchanged.	Amine diazotised.	Diazo-oxide.	References.
Halogen			43
			15
			21
			46
			44

TABLE XIV—*continued.*

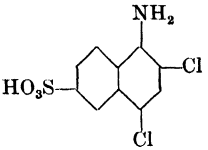
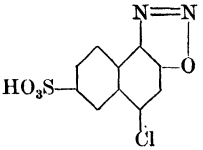
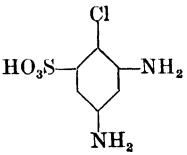
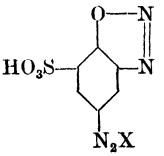
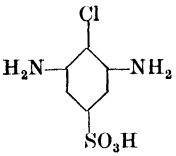
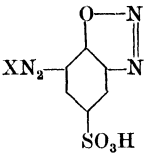
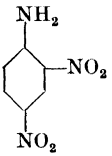
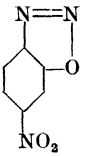
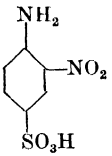
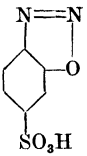
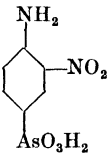
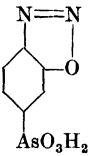
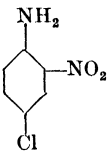
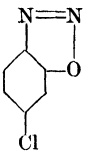
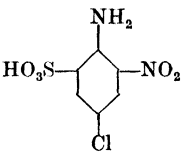
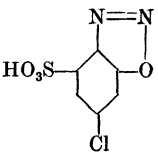
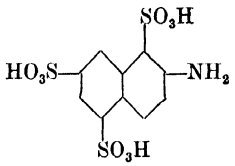
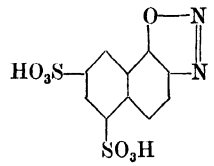
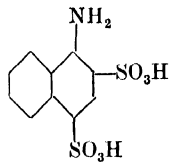
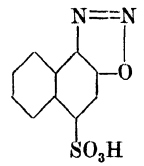
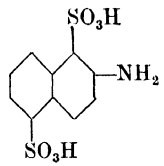
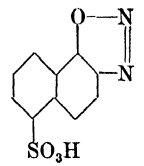
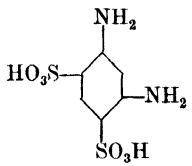
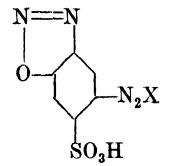
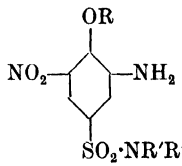
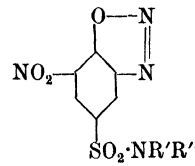
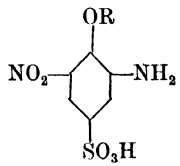
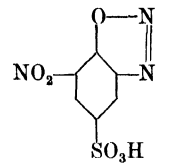
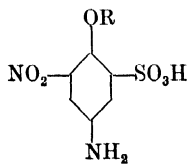
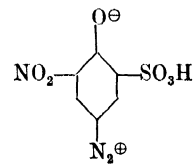
Substituent exchanged.	Amine diazotised.	Diazo-oxide.	References.
Halogen—*contd.*			50
			40
			41
Nitro-group			45
			42
			57
			58
			59

TABLE XIV—*continued.*

Substituent exchanged.	Amine diazotised.	Diazo-oxide.	References.
Sulphonic acid group			48
			52
			55
			51
Alkoxy-group (R = Alkyl)			60
			60
			60

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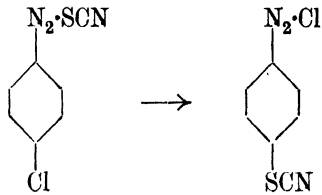
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		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.
40	B.A.S.F.	16,811/01	—	—	—	—
41	*Idem*	1,561/02	—	—	—	—
42	*Idem*	—	—	138,268	**6**, 894	315,932
43	*Idem*	—	—	139,327	**6**, 896	—
44	*Idem*	6,615/02	710,059	145,906	**7**, 400	319,868
45	*Idem*	—	—	144,640	**7**, 380	—
46	*Idem*	12,584/02	—	141,750	**7**, 99	—
47	M.L.B.	—	—	148,085	**7**, 98	—
48	M.L.B.	23,993/02	737,967	F.16,863	**7**, 405	328,137
49	B.A.S.F.	—	—	148,882	**7**, 402	—
50	*Idem*	16,995/03	—	—	—	—
51	M.L.B.	18,283/03	—	—	—	—
52	B.A.S.F.	27,372/03	—	156,440	**8**, 656	338,819
53	*Idem*	—	—	157,325	**8**, 657	—
54	M.L.B.	—	—	158,532	**8**, 139	339,004
55	B.A.S.F.	4,997/04	770,177	160,536	**8**, 657	—
56	*Idem*	—	—	162,009	**8**, 659	—
57	M.L.B.	15,438/11	—	243,648	**10**, 1245	—
58	Kuhlmann	288,572	—	—	—	643,560
59	*Idem*	295,050	—	—	—	—
60	*Idem*	Appl. 161/34	2,024,864	626,134	**22**, 868	767,953

GROUP 3. EXCHANGE OF DIAZONIUM ANIONS WITH SUBSTITUENTS OF THE ARYL NUCLEUS

A small number of diazonium salts are known in which intramolecular rearrangement occurs between the diazonium anion and an *ortho* or *para*

substituent in the benzene ring. The reaction was discovered by Hantzsch and Hirsch,[1] who found that when *p*-chlorobenzenediazonium thiocyanate is dissolved in ethanol containing a drop of aqueous hydrochloric acid the substance precipitated by adding ether is *p*-thiocyanobenzenediazonium chloride, the reactions of the thiocyano anion having completely disappeared :—



The explosive *o*-chlorobenzenediazonium thiocyanate similarly rearranges to the only slightly less explosive *o*-thiocyanobenzenediazonium chloride, but the explosive *m*-isomeride does not rearrange[3]; 3 : 5-dibromo-*p*-toluenediazonium thiocynate affords two products of rearrangement.

An analogous change takes place among the bromobenzenediazonium chlorides which afford chlorobenzenediazonium bromides[2]; here also the exchanged bromine atoms must be *ortho* or *para* to the diazo-group. Hantzsch and his co-workers never observed the reverse change, nor do diazonium double salts such as tribromobenzenediazonium cadmium iodide[3] suffer rearrangement. Reaction proceeds best if there are two or more exchangeable bromine atoms and the products differ according to the conditions; for example, 2 : 4-dibromobenzenediazonium chloride in ethanol affords 2-chloro-4-bromobenzenediazonium chloride, but in ethanol saturated with hydrochloric acid the product is 2 : 4-dichlorobenzenediazonium bromide.[2] So strong is the tendency to exchange in pentabromobenzenediazonium chloride that the salt cannot be obtained free from nuclear chlorine.[4] The reaction rate is unimolecular for 2 : 4 : 6-tribromobenzenediazonium chloride in methanol[4]; the speed of reaction is inversely proportional to the dissociating power of the solvent, hence solvents fall in the order EtOH > AcOH > MeOH > H_2O.[4]

The exchange has only been observed between chlorine anions and nuclear bromine, for the reaction does not occur with tri-iodobenzenediazonium chloride or with tribromobenzenediazonium fluoride.[5]

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CHAPTER IV

REACTIONS OF THE DIAZO-COMPOUNDS (*Continued*)

CLASS B. DERIVATIVES IN WHICH THE DIAZO-GROUP IS INVOLVED BUT REMAINS FUNCTIONALLY INTACT. METALLIC DIAZOTATES AND DIAZOANHYDRIDES— DIAZO ETHERS — DIAZOCYANIDES — DIAZOSULPHONATES — DIAZOPERHALIDES — DIAZOSULPHIDES.

CLASS B. DERIVATIVES IN WHICH THE DIAZO-GROUP IS INVOLVED BUT REMAINS FUNCTIONALLY INTACT.

GROUP 1. METALLIC DIAZOTATES AND DIAZOANHYDRIDES; THE USE OF *iso*DIAZOTATES OR NITROSAMINES AS STABILISED DIAZO-COMPOUNDS

THE free base of a diazonium salt cannot be obtained by the action of alkalis, for the diazonium hydroxide at once undergoes tautomeric change, the tautomer being an acidic substance, the diazohydroxide, which at once forms a salt, a metallic diazotate. Griess [1, 2] described the isolation of potassium benzene diazotate, obtained by acting on benzenediazonium salts with an excess of cold concentrated aqueous caustic potash, which salts out the very soluble potassium salt. From the potassium salt he obtained the less soluble salts of silver, mercury, zinc, lead, barium, and calcium by the action of aqueous solutions of their chlorides. Wohl [5] also made the silver salt. Griess's observation seems to have escaped the attention of other chemists for many years, except that Curtius,[3] having made potassium and silver benzenediazotate, concluded that the structure proposed by Griess, Ph·N:N·OK, must be wrong, though the reactions of Griess's diazotate show it at once to be a diazo-compound.

Preparation of Potassium Benzene Diazotate (Bamberger [9]):—

A 15% solution of benzenediazonium chloride (10 c.c.) is dropped with stirring into a mixture of caustic potash (150 g.) and water (60 g.) at — 5°. The temperature is then allowed to rise to 15—20°, so that all the potash dissolves, and the crystals which separate are collected. The crude salt so obtained can be converted into snow-white silky needles when the substance (1 g.) is dissolved in absolute alcohol (3. c.c.) at — 5° and precipitated with ether (24—30 c.c.). The salt is hygroscopic, and soon becomes coloured pink. The same procedure can be followed to produce the normal diazotates derived from *p*-toluidine,[9] *m*- and *p*-chloro- and *m*-bromoaniline,[9] anisidine [17] and ψ-cumidine [17]; the preparation of the normal diazotate derived from sulphanilic acid has been described.[8]

The diazotates prepared as above by the immediate action of caustic alkali on diazonium salts are unstable substances easily detected by their ability to couple with naphthols in alkaline solution. They have been

called the " normal ", or " *syn* "-diazotates, the last name connoting the theoretical views of Hantzsch. In this book the name " normal " will be used, and " *iso* " for the passive form described below, because such terminology is both in accordance with long-standing usage and likewise non-committal in respect of any particular view as to their constitution.

While treatment of aqueous solutions of diazonium salts with concentrated alkali is the only means which comes into consideration for the technical manufacture of diazotates at the present time, they can also be obtained by other reactions under alkaline conditions. A number of these are due to Bamberger, who sought to establish the constitution of the diazotates by synthesis from compounds of known structure. Thus he [7, 18] obtained normal potassium diazotate by treating nitrosoacetanilide and nitroso-β-acetnaphthalide with cold concentrated caustic potash :—

$$PhN\begin{matrix}NO\\COMe\end{matrix} + 2KOH = PhN_2{\cdot}OK + MeCO_2K + H_2O$$

He [20] also shook nitrobenzene, sodamide, and β-naphthol in light petroleum, and obtained a small quantity of benzeneazo-β-naphthol, the requisite normal sodium benzene diazotate arising by the reactions :—

$$PhNO_2 + NaNH_2 = PhN_2{\cdot}ONa + H_2O$$

Bergstrom and his co-workers [30, 33] have increased the yield of sodium benzene diazotate to 30% on the nitrobenzene in this reaction by carrying it out in liquid ammonia at — 33° ; the optimum yield is reached with six molecular proportions of sodamide to one of nitrobenzene. They suggest as a possible mechanism for the reaction, firstly :—

$$PhN\begin{matrix}O\\O\end{matrix} + NaNH_2 = PhN\begin{matrix}O\\NH_2\\ONa\end{matrix}$$

and then either :—

$$PhN\begin{matrix}O\\NH_2\\ONa\end{matrix} + NaNH_2 = PhN_2{\cdot}ONa + NaOH + NH_3$$

or

$$PhN\begin{matrix}O\\NH_2\\O^{\ominus}\ Na^{\oplus}\end{matrix} - H_2O = PhN\begin{matrix}O\\:NH\end{matrix} \text{ (cf. Angeli, Jolles, p. 394).}$$

They made it certain that this reaction produces the normal diazotate by showing that an authentic sample of the *iso*diazotate will not couple with β-naphthol under the same conditions. The reaction failed when other nitro-compounds were taken in place of nitrobenzene.

Normal sodium benzene diazotate is obtained by interaction of phenylhydroxylamine, caustic soda, and benzenesulphohydroxamic acid in alcohol, and its presence is demonstrated by coupling with β-naphthol. This reaction is due to Angeli,[22] who made a long study of the action of

aqueous alkali on substances such as benzenesulphohydroxamic acid, $Ph{\cdot}SO_2{\cdot}NHOH$, which decomposes in alkaline solution to give the free radical nitroxyl or nitrosyl, NOH, and this interacts with phenylhydroxylamine, a reaction which can be represented in one of two ways :—

$$\text{(i)}\quad PhNHOH + HNO = PhN{:}N{\cdot}OH + H_2O$$

$$\text{(ii)}\quad \begin{matrix} PhNH \\ \dot{O}H \end{matrix} + HNO = \begin{matrix} PhN{:}NH \\ \downarrow \\ O \end{matrix} + H_2O$$

Lastly the arylazocarboxylic acids and arylazoxycarboxy-amides (cf. p. 146) and -anilides, which have been investigated by Italian chemists since 1922, give *n*-diazotates when treated with alcoholic caustic alkali and couple immediately with β-naphthol if it is present.[26, 29, 31, 32] The ease with which reaction occurs depends on the substituents both in the aryl nucleus and the amide group; for example, *p*-nitrobenzeneazocarboxyamide, $p\text{-}NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, couples direct with β-naphthol, whilst benzeneazoxydiphenylcarboxyamide breaks up with methyl alcohol–caustic potash thus :—

$$\begin{matrix} PhN{:}N{\cdot}CO{\cdot}NPh_2 \\ \downarrow \\ O \end{matrix} \longrightarrow \begin{matrix} (PhN{:}N)^{\ominus}K^{\oplus} \\ \downarrow \\ O \end{matrix} + NHPh_2 + CO_2$$

A similar reaction to the above is the hydrolysis of azoxysulphones, a reaction which Farrar and Gulland [34] found to produce *n*-diazotates :—

$$\begin{matrix} Ar{\cdot}SO_2{\cdot}N{:}N{\cdot}Ar' \\ \downarrow \\ O \end{matrix} + H_2O = Ar{\cdot}SO_3H + \begin{matrix} (Ar{\cdot}N{:}N)^{\ominus} \\ \downarrow \\ O \end{matrix} + H^{\oplus}$$

Schraube and Schmidt,[40, 90] chemists on the staff of the B.A.S.F., first showed that when cold aqueous caustic alkali acts on *p*-nitrobenzenediazonium chloride a similar change to that observed by Griess with benzenediazonium salts takes place, except that the product is much more stable than a normal benzene diazotate nor does it show the typical coupling reaction. The sodium salt was isolated by them as a reddish-brown powder, and on treatment with methyl iodide afforded a substance identical with the nitrosamine of N-monomethyl-*p*-nitroaniline, made by acting on that body with nitrous acid. The series of changes was therefore supposed to be :—

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl \xrightarrow{aq.NaOH} (NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}ONa) \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NNa{\cdot}NO \xrightarrow{MeI} NO_2{\cdot}C_6H_4{\cdot}N\begin{matrix} Me \\ NO \end{matrix}\quad \text{m. p. } 100°$$

The compound in brackets above represents a normal or labile form supposedly first produced by the alkali, but which has never been isolated, as it at once isomerises to the nitrosamine.

v. Pechmann and Bamberger had both already independently realised that the diazotates are tautomeric, and the idea was current that one tautomer has the constitution of a nitrosamine. The intense exploration of the diazo field was just reaching its height, and further facts bearing on the subject were soon forthcoming. Bamberger [24] had been studying the alkaline oxidation of α- and β-diazonaphthalene, and had observed among the products derived from β-diazonaphthalene a nitrogen-containing substance unable to couple with naphthols, but able to do so after acidification. α-Diazonaphthalene afforded a similar substance after treatment with caustic alkali alone.[24] Bamberger therefore called these substances "*iso*diazo"-compounds, although recognising the possible nitrosamine structure. These stable inactive diazotates have been also called "stable" or *anti*-diazotates, the latter again being due to Hantzsch, whilst among chemists engaged in industry, who have for the most part remained loyal to the original views of Schraube and Schmidt, they are still called "nitrosamines". In this book Bamberger's name *iso*diazotates will be used.

v. Pechmann and Frobenius [41] also had Schraube and Schmidt's nitrosamine in hand, but had converted it into the silver salt. This salt, however, when treated with methyl iodide does not give the nitrosamine of N-monomethyl-*p*-nitroaniline, but the methyl ether of *p*-nitrodiazobenzene, $p\text{-}NO_2\cdot C_6H_4\cdot N{:}N\cdot OMe$, nearly colourless needles, m. p. 83°. The ether shows the reactions of a diazo-compound; it couples with phenols, forms a diazoamino-compound with aniline, and is decomposed by boiling with dilute acid. v. Pechmann and Frobenius pointed out that the difference in behaviour of the alkali metal salt and the silver salt is typical of tautomeric substances in general, and in this case the tautomers which give rise to the silver and sodium salts respectively are :—

$$p\text{-}NO_2\cdot C_6H_4\cdot N{:}N\cdot OH \rightleftharpoons p\text{-}NO_2\cdot C_6H_4\cdot NH\cdot NO$$

The chemists of the B.A.S.F. made a thorough study of the reaction by which the substances they called nitrosamines could be made, and showed it to be widespread among benzenoid amines, both monoamines and diamines.[93, 96] Where negative groups are present in the nucleus, particularly *ortho* or *para* to the diazo-group, the nitrosamine is formed easily by dilute caustic alkali in the cold; 2 : 5-dichlorodiazobenzene is converted even by aqueous sodium carbonate.[92] When negative groups are not present or where the nucleus carries alkoxy groups, then more and more drastic treatment is necessary to form the *iso*diazotate, and to attain complete conversion even 60% caustic potash solution at temperatures up to 140° may be necessary. In one patented variation of the process solid caustic alkali is added to the diazo solution, which is then heated,[101] but rapid heating to the conversion temperature is the key to a good result, however the heating is brought about. A characteristic of

the conversion under these conditions is a sudden thickening of the solution when the less soluble *iso*diazotate reaches a concentration at which it is thrown out as a solid phase.

Preparation of Potassium Benzene iso*Diazotate* (Schraube and Schmidt[40]) :—

A 15% solution of benzenediazonium chloride is run at 0° into 1·5 times its volume of 75% caustic potash. The undissolved alkali dissolves and the whole is heated in a silver vessel as quickly as possible to 140°, which for a 60—70 g. charge should take three minutes. At this temperature boiling suddenly stops and the solution thickens, heating being continued at 140° for a short time. On cooling to 100° the melt is diluted with boiling water (0·5—1·0 vol.) and on cooling further the salt crystallises in yellowish leaflets. It is collected, freed from mother-liquor by pressing, dissolved in alcohol at 40—50°, filtered, and precipitated in silvery leaflets by adding ether (2 vols.). Treated with methyl iodide it affords the nitrosamine of monomethylaniline, which itself yields methylaniline on removal of the nitroso-group.

Wojciechowski [75] has described in detail the preparation of potassium *p*-chlorobenzene *iso*diazotate by the above method; he was unable to obtain the salt entirely free from caustic alkali. Patents have been granted for the manufacture of the diaryl ether *iso*diazotates [113] and *p*-cyanobenzene *iso*diazotate.[116]

A patented process claims that the yield of *iso*diazotate is improved if the diazo solution is first made weakly alkaline, and then run in a thin stream into a sufficiency of concentrated alkali kept at or above the temperature of conversion; losses due to decomposition while heating up the bulk of the cold liquid are thus avoided.

Preparation of Potassium 5-Chloro-o-toluene iso*Diazotate* [110] :—

5-Chloro-*o*-toluidine (75 g.) is diazotised in concentrated solution, made alkaline, and then allowed to run with stirring into a solution of caustic potash (400 g.) in water (200 g.) at 115°. The potassium salt of the *iso*diazotate is obtained as small light-reddish prisms in good yield, having the constitution 1 : 3 : 4-$C_6H_3ClMe{\cdot}NK{\cdot}NO$.

Less drastic methods than the above serve to prepare aqueous solutions of the *iso*diazotates, for by pouring a solution of a diazonium salt into boiling dilute caustic alkali the coupling power is found soon to disappear and a solution of *iso*diazotate is obtained, though the yield is not good.[77] Similarly, if a cold caustic alkaline solution of a diazonium compound is set aside, a race ensues between decomposition of the *n*-diazotate and its conversion into the *iso*diazotate, and the liquid poured off from the tar when the coupling reaction has disappeared is found to contain *iso*diazotate. Jolles and Camiglieri [74] give the following figures for conversion by 1·6% caustic soda at 25° in sixty hours for the diazo-compound derived from : aniline 13%, *m*-toluidine 15%, *o*-anisidine 12%, *p*-toluidine, *p*-phenetidine, *p*-anisidine, each a trace. The caustic fusion process therefore merely accelerates an existing reaction, thus diminishing loss due to decomposition of the *n*-diazotate.

From the foregoing it is seen that the diazohydroxides form two series of isomeric metallic salts, one labile, the other stable, the labile form passing spontaneously into the stable form sometimes so rapidly that

the labile form cannot be isolated, in other compounds so slowly that heat must be used to accelerate the transformation. The question of the constitution of the two series is discussed in the last chapter of this book.

There are other methods of academic interest by which the *iso*diazotates may be formed. Potassium benzene *iso*diazotate is produced by dropping nitrosomethylaniline on fused caustic potash, the reaction being formulated by Bamberger [43] as :—

$$PhN\begin{matrix}NO\\Me\end{matrix} + KOH = PhN_2{\cdot}OK + MeOH$$

Nitroso-*o*-hydroxybenzylaniline reacts similarly, but the *iso*diazotate is formed by cold aqueous caustic alkali [55] :—

$$o\text{-}OH{\cdot}C_6H_4{\cdot}CH_2N\begin{matrix}NO\\Ph\end{matrix} + NaOH = o\text{-}OH{\cdot}C_6H_4{\cdot}CH_2OH + PhNNa{\cdot}NO$$

Phenylnitramine reduced by sodium amalgam,[43] sodium stannite,[75] or zinc and ammonium chloride [49, 65] gives the *iso*diazotate :—

$$PhNH{\cdot}NO_2 \xrightarrow[NaOH]{H_2} PhNNa{\cdot}NO + H_2O$$

When hydroxylamine is added to an alcoholic solution of nitrosobenzene and α-naphthol the green colour is at once discharged and on dilution with water benzeneazo-α-naphthol is precipitated in 70% yield.[47] Apparently the diazo-compound is formed by the reaction :—

$$PhNO + H_2NOH = PhN{:}N{\cdot}OH + H_2O$$

Bamberger said that this reaction produces the *iso*diazotate because if hydroxylamine dissolved in aqueous caustic soda is added to nitrosobenzene dissolved in alcohol and the resultant solution is extracted with ether coupling with a naphthol will not take place until after acidification.

Bamberger [53] also obtained *iso*diazotates by the oxidation of *o*-hydroxyazoxybenzene, m. p. 75·5—76°, with alkaline permanganate :—

$$Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH\text{-}o \longrightarrow (?\ PhN_2{\cdot}O{\cdot}CO_2H) \longrightarrow iso\text{-}PhN_2{\cdot}ONa$$
$$\downarrow O$$

The *iso* *o*-hydroxyazoxybenzene, m. p. 108—108·5°, is only oxidised with difficulty, but also affords a trace of *iso*diazotate.

Nitrosophenylhydroxylamine can be reduced in alkaline medium with sodium amalgam,[50] or ferrous sulphate,[70] or sodium stannite [75] giving a solution which does not couple until after acidification

$$PhN\begin{matrix}NO\\OK\end{matrix} \longrightarrow PhNK{\cdot}NO \text{ or } PhN{:}N{\cdot}OK \longrightarrow [PhN{:}NO]^-K^+$$
$$\downarrow O$$

Thiele and Stollé [61, 62] described a laboratory method for making sodium benzene *iso*diazotate based on the interaction of two molecules of alkyl nitrite with one of phenylhydrazine in the presence of sodium ethoxide. Thiele assumed that the compound $\begin{matrix}\text{PhN·NH·NO}\\ \text{NO}\end{matrix}$ is formed as an intermediate and that in one of its tautomeric forms it liberates a molecule of nitrous acid to give the *iso*diazotate.

The preparation is carried out as follows :—
Phenylhydrazine (5 c.c.) is dissolved in 4N sodium methoxide (12·5 c.c.) with ether (50 c.c.); the solution is cooled externally by ice and ethyl nitrite (8·5 c.c.) is added. Nitrous oxide is given off while the desired salt crystallises, is collected and washed with ether; it is completely white and pure. Thiele characterised it as the *iso*diazotate because this salt gives a brown precipitate with ferric chloride, a blackish-violet one with copper sulphate, and a white one with mercuric nitrate. The advantage of this preparation is that it avoids the use of large quantities of caustic alkali, which is so difficult to remove from the product. The process has not been applied to other arylhydrazines.

Diazotates cannot be obtained from diazo-compounds having an hydroxyl group *ortho* or *para* to the diazo-group or a group which can be displaced for hydroxyl under the influence of alkali as diazo-oxides are formed by such molecules. Further, a methyl-group *ortho* to the diazo-group may also prevent formation of a diazotate as ring-closure to an indazole results from the action of alkali (cf. p. 245).

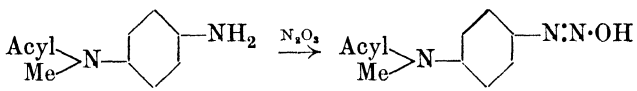
The most-used means of distinguishing the normal from the *iso*-diazotates is their reaction with β-naphthol or one of its congeners in caustic alkaline solution. The normal diazotates couple at once, and if the azo-compound is filtered off the filtrate remains clear. The *iso*-diazotates, on the other hand, do not couple at all or only slowly, and if any azo-compound which is formed is filtered off, more will slowly form in the filtrate. The greater the concentration of caustic alkali the more is coupling inhibited.[46] If the solution of naphthol and *iso*diazotate is acidified, coupling commences because the *iso*diazotate is converted into the corresponding diazonium salt, and if the acidity is then removed the coupling at once goes to completion. Again, if a drop of the solution of naphthol and *iso*diazotate is spotted on filter-paper and exposed to sunlight [76] or steamed, the azo dye is at once formed. Bucherer and v. der Recke [73] found that the reactivity of *p*-nitrobenzene *iso*diazotate increases rapidly as the alkali is neutralised with carbon dioxide, whilst Orton [60] found that in ethanol solution the same substance couples at once with β-naphthol.

Bigiavi [28] reported that normal diazotates are recognised by giving a transient purple colour with the sodium salt of nitrohydroxylamine.

Gutmann [63] showed that arsenites reduce the normal diazotates, but not the *iso*diazotates, whilst Hantzsch and Vock [58] had earlier found that *iso*diazotates are not reduced by alkaline sodium stannite which Engler [54] used to reduce normal diazotates to benzene and some phenylhydrazine.

v. Pechmann and Frobenius [4, 6] treated an alkaline solution of normal toluene *p*-diazotate with benzoyl chloride or acetic anhydride and obtained nitrosobenztoluidide and nitrosoacetoluidide. The *iso*diazotates on acylation in the above way also afford nitrosoacylarylamides. Bamberger [11] tried to show that the normal and *iso*diazotates can be distinguished by the larger yield of nitrosoacylarylamide obtained from the latter, and also that the *iso*diazotates afford a larger yield of arylhydrazine when reduced with sodium amalgam, but this was denied by Hantzsch,[16] who said that no such differences exist. Failure to use strictly defined and accurately reproducible conditions probably accounts for many of the contradictions and discrepancies to be found in the literature of the diazotates of this period.

Naturally attempts have been made to isolate the free acidic substances from which the metallic diazotates are derived. Liberation with the exact equivalent of mineral acid, of organic acids, or by carbon dioxide in inert solvents have all been tried, but the expected hydroxides, if formed initially, change at once into other substances. Morgan and Grist,[22] however, by treating *p*-aminomethylformanilide and *p*-aminomethylacetanilide dissolved in acetone with nitrogen trioxide, also dissolved in acetone, obtained formyl- and acetylmethylaminobenzene-4-diazohydroxide, substances which both decompose violently at 131—132° and couple with β-naphthol :—



Acyl = HCO and MeCO

The isolable substances derived from the normal and *iso*diazotates by the controlled action of acids are, however, different from the above and from each other. The action of not more than one equivalent of an acid on a normal diazotate does not lead to the liberation of an hydroxide, but to substances which Bamberger called diazoanhydrides and Hantzsch diazo-oxides. Griess [2] had indeed prepared diazobenzene anhydride about 1865 by acting on normal potassium diazotate with acetic acid, and he refers to the yellow explosive oil as "diese merkwurdige Verbindung", but he had no opportunity to examine the true nature or behaviour of the substance, and our knowledge of them is due chiefly to Bamberger.[9] The diazoanhydrides bear, in fact, the same relationship to the diazohydroxides that the ethers bear to the alcohols, for in place of the expected reaction :—

$$PhN{:}N{\cdot}OK + AcOH = PhN{:}N{\cdot}OH + KOAc$$

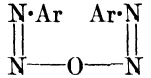
which Griess and Bamberger sought to bring about, the reaction probably takes place according to the equation :—

$$2(PhN{:}N{\cdot}OK) + 2AcOH = (PhN{:}N)_2O + 2KOAc + H_2O$$

Bamberger [24] showed that it is not necessary to isolate the normal diazotate in order to prepare the anhydride; he added one half equivalent of aqueous caustic soda to a neutral solution of *p*-chlorobenzene diazonium chloride, when the diazo anhydride was formed as a yellow, explosive precipitate, apparently by interaction of the diazonium chloride with the diazotate accompanied by rearrangement of the former :—

$$p\text{-}C_6H_4Cl\cdot N_2\cdot Cl + p\text{-}C_6H_4Cl\cdot N_2\cdot ONa \longrightarrow (p\text{-}C_6H_4Cl\cdot N_2)_2O + NaCl$$

Bamberger had some controversy with Hantzsch [10] concerning the constitution of these substances, but their properties fit well with Hantzsch's view that they are oxides, and he wrote their structural formula in accordance with his theory thus :—



The diazoanhydrides (which must not be confused with the substances generally known as diazo-oxides, cf. p. 28) are yellow, extremely explosive substances, the reactions of which are those of a normal diazotate, in that they couple with phenols, yield diazoamino-compounds with primary amines, bisdiazoamino-compounds with ammonia, and diazo ethers with alcohols. Alkalis convert them back into two molecules of the normal metallic diazotate, and mineral acids into two molecules of the diazonium salt. With cyanides and sulphites they afford the normal diazocyanides and diazosulphonates.[14] With benzene they react violently to give diaryls; for example, diazobenzene anhydride and benzene give diphenyl :—

$$(PhN{:}N)_2O + 2C_6H_6 = 2PhPh + 2H_2O + 2N_2$$

Interpreted in the light of the work of Hey (cf. p. 109) it may be postulated that the first step in the above reaction is the production of phenyl radicals, and the diazoanhydrides might prove a useful, if dangerous, source of various free aryl radicals.

When weak acids are added to aqueous solutions of *iso*diazotates the free *iso*diazohydroxides are probably formed, but soon pass into other substances of unknown constitution; if caustic alkali is added before the change is complete, then some of the *iso*diazotate is regenerated, whilst mineral acids produce the diazonium salt. Hantzsch, Schümann, and Engler [51] measured the conductivity in water of sodium *p*-nitrobenzene *iso*diazotate and potassium *p*-bromobenzene *iso*diazotate, and concluded that the salts are not hydrolytically dissociated, *i.e.*, that they are salts of strong acids. The free *iso*diazohydroxides, however, show no conductivity; this is possible if the free acid is a pseudo acid which rearranges into a neutral form immediately on liberation. Engler [54] found that the

foregoing is also true for sodium naphthalene-β-*iso*diazotate. Hantzsch and Engler thought that the inert substances into which the *iso*diazohydroxides change are the primary arylnitrosamines formed thus :—

$$\begin{matrix} \mathrm{Ar{\cdot}N} \\ \mathrm{\dot{N}{\cdot}OK} \end{matrix} \longrightarrow \begin{matrix} \mathrm{ArN} \\ \mathrm{\dot{N}{\cdot}OH} \end{matrix} \rightleftharpoons \mathrm{ArNH{\cdot}NO}$$

Where the supposed nitrosamines can be isolated other than as tar they form amorphous solids, inert to phosphorus halides, acetyl chloride in benzene, and other agents reactive towards hydroxyl. Unfortunately no alternative method of preparation of these nitrosamines, if such they be, is known so that no check with authentic specimens has been possible.

To lend further support to the above view Hantzsch and Pohl [56] diazotised certain of the polyhalogeno- and nitrohalogenoanilines which afford stable diazo-compounds, converted them into *iso*diazotates, and, acting on these with acetic acid, obtained stable yellow compounds which appeared to be the expected nitrosamines. But they were deceived, for Orton [57, 60] showed the substances to be in fact diazo-oxides that had been formed by replacement of the halogen atom or nitro-group *ortho* to the diazo-group by hydroxyl (cf. p. 117).

The potassium tribromobenzene *iso*diazotate actually exists in the strongly caustic solution used for its formation, but as soon as water is added halogen ions at once begin to appear in the solution, and the oxide is formed. Nevertheless, Hantzsch [59, 64] did not abandon his fundamental idea that the *iso*diazohydroxides actually contain a hydroxyl group even when dissolved in solvents such as benzene or chloroform, and held that the yellow substances produced by the action of carbon dioxide on such solutions is the impure primary arylnitrosamine, which he was never able to obtain analytically pure. Since the time of Hantzsch no other investigator has examined the *iso*diazohydroxides, nor does it appear an inviting field at the present time.

The technical value of the discovery made by Schraube and Schmidt was at once appreciated, for here was a method of isolating *p*-nitrodiazobenzene far superior to the ticklish process of evaporating an acid solution to dryness *in vacuo*. The B.A.S.F. put the sodium salt on the market as Nitrosamine Red. Since, when an *iso*diazotate is acidified the process of formation is reversed, and the normal reactions of the diazo-compounds again appear in the solution, the dyers had only to dissolve the stable Nitrosamine Red in acid in order to prepare developing baths for Para Red or developed cotton colours. In this direction they were not able for long to compete with the more convenient acid-stabilised diazo-compounds, which also began to come into commerce about the same time. The technical value of the nitrosamines lies in their use for calico-printing.

As has been shown above, the higher the concentration of caustic alkali the slower do the *iso*diazotates couple, and hence in strongly alkaline solution coupling is so much retarded that there is time for the mixed solutions of *iso*diazotate and naphthol to be thickened and printed on cloth. When the insoluble azo pigment is produced by coupling on or in the fibre the print is said to be developed and this is brought about by (*a*) hanging in the air overnight, (*b*) steaming in an ager, with or without a volatile organic acid, (*c*) running through weak acid, (*d*) drying on steam-heated cylinders, (*e*) exposing to strong light. In all the methods except (*e*) development is due to reduction of the alkalinity either by carbon dioxide from the air, dilution, or direct neutralisation by an acid. Exposure to daylight, which is used technically in tropical countries such as India, probably causes direct reversion of the *iso*diazotate to the normal diazotate and is quick, the pattern immediately commencing to develop as the strong light falls on the fabric. The *iso*diazotates can be printed on cloth grounded with β-naphthol, but it is usually more economical to print the mixture, and so avoid difficulties and waste in clearing the whites. The B.A.S.F. patented the main alternative technical ways of using the nitrosamines, but they did not become of technical value at the time because with the components then available the results were too erratic.[91, 99] Twenty years later the Griesheim concern found Naphtol AS ideal for preparing ready-made mixtures of *iso*diazotate and coupling component, and at once began to introduce such patented pastes and powders to the calico-printing trade.[102, 103, 104] The reliability of the prints to develop properly was also improved by adding small amounts of chromate to the paste.[105] The effect was believed to be due to lake formation, but Bucherer and Möhlau,[71] in the course of a careful study of the conditions under which *iso*diazotates are best used in printing technique, have pointed out that the azo pigments formed are not capable of lake formation, and the true action of the chromate still remains unknown.

With the growth of available components through the expansion of the Naphtol AS series, including the use of acetoacetarylamides for yellow shades,[106] and of the hydroxycarbazole carboxylamides for browns, there has been built up gradually the extensive range of the Rapid Fast colours of the I.G. Company, though dyes of this type are now being made by a number of concerns throughout the world. Patents for improvement continue to emerge. Various patents have been taken for refinements in the manufactures of powders for the market.[108, 109, 111, 112, 114, 115, 117] Bucherer has proposed to add calcium chloride to the alkaline printing paste immediately before use, or to pad the cloth with a similar substance so as to reduce rapidly the alkalinity at the time of printing, and so favour a speedy development.[107] It has been proposed to dispense wholly or in part with the caustic alkali and

replace it with a volatile oxygen-containing base, which is easily driven off by heat or steam, and so allow coupling to occur.[118]

In Table XV is shown the constitutions of a number of the most important of the Rapid Fast dyes.[66, 67, 68, 78]

TABLE XV

Composition of Rapid Fast Dyes (I.G.)

Dye.	Amine from which *iso*diazotate is derived.	Coupling component.
Blue B	Dianisidine	Naphtol AS
Bordeaux IB	5-Nitro-2-aminoanisole	AS-BOX
RH	4-Chloro-2-aminoanisole	AS-BS
Brown GGH	2 : 5-Dichloroaniline	AS-LB
IBH	4-Chloro-2-aminoanisole	AS-LB
IRH	2 : 5-Dichloroaniline	AS-BG
Golden Yellow IGH	4-Chloro-2-aminoanisole (K salt)	AS-IFG
Olive Brown IGH	*m*-Chloroaniline	AS-LB
Orange GH	*Idem*	AS-D
IGH	2-Chloro-5-trifluoromethylaniline	AS
IRH	*Idem*	AS-OL
RG	*o*-Nitroaniline	AS
RH	2 : 5-Dichloroaniline	AS-PH
Red B	5-Nitro-2-aminoanisole	AS
BB	*Idem*	AS-BS
FGH	4-Chloro-2-aminotoluene	AS-D
GG	*p*-Nitroaniline	AS
GL	3-Nitro-4-aminotoluene	AS
3GL	4-Chloro-2-nitroaniline	AS
G2H	2 : 5-Dichloroaniline	AS
GZH	2 : 4-Dichloroaniline	AS
I3GL	4-Chloro-2-nitroaniline	AS
ILB	3-Nitro-2-aminotoluene	AS-RL
IRH	5-Chloro-2-aminotoluene	AS-LT
RH	4-Chloro-2-aminoanisole	AS-OL
Scarlet ILH	2 : 5-Dichloroaniline	AS-OL
RH	4-Chloro-2-aminotoluene	AS-PH
Yellow GGH	4-Chloro-2-aminoanisole	AS-G
GH	2 : 5-Dichloroaniline	AS-G
I3GH	5-Chloro-2-aminotoluene	AS-1816

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		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.	Sw.P.
90	B.A.S.F.	20,605/93	—	78,874	**4**, 658	—	—
91	*Idem*	—	—	80,263	**4**, 668	—	—
92	*Idem*	—	531,973 } 531,975 }	81,134	**4**, 659	234,029	—
93	*Idem*	—	—	81,202	**4**, 661	—	—
94	*Idem*	—	—	81,203	**4**, 663	—	—
95	*Idem*	13,577/94	531,976	81,204	**4**, 664	—	—
96	*Idem*	—	—	81,206	**4**, 665	—	—
97	*Idem*	—	—	81,791	**4**, 669	—	—
98	*Idem*	15,305/94	—	82,446	**4**, 671	240,539	—
99	*Idem*	—	—	83,010	**4**, 671	—	—
100	*Idem*	—	—	84,389	**4**, 666	—	—
101	*Idem*	13,460/95	—	84,609	**4**, 667	234,029/4	
102	Griesheim	9,102/14	1,193,566	287,086	**12**, 364	471,123	—
103	*Idem*	6,663/15	—	291,076	**12**, 370	—	—
104	*Idem*	15,884/15	1,200,726	292,118	**13**, 472	—	—
105	*Idem*	104,108	—	298,236	**13**, 557	—	—
106	*Idem*	217,594	—	408,505	**14**, 1043	—	—
107	Bucherer	249,526	—	448,426	**15**, 579	—	—
108	I.G.	303,942	—	465,564	**16**, 893	642,079	131,799
109	I.G.	305,787	—	474,659	**16**, 1687	35,820	—
110	I.G.	307,965	1,724,062	—	—	—	—
111	I.G.	328,383	—	524,266	**18**, 1051	671,164	141,507
112	I.G.	340,534	1,915,734	540,607	**18**, 1052	689,488	147,411
113	S.C.I.	—	—	—	—	747,238	158,804
114	Kuhlmann	—	—	620,247	**22**, 867	772,061	160,644
115	Nat. Aniline	—	2,048,745	—	—	—	—
116	I.G.	481,735	2,119,891	697,804	—	825,284	—
117	Nat. Aniline	—	2,205,417	—	—	—	—
118	Gen. Aniline & Film Corp.	—	2,232,406	—	—	—	—

GROUP 2. DIAZO ETHERS

By diazo ethers are generally understood the O-ethers produced by the action of alkyl halides on metallic diazotates, under which heading they have already been mentioned (cf. p. 129). As there are two series of diazotates, the normal and the *iso*-, the two corresponding series of ethers might be expected, but such is not the case, for v. Pechmann and Frobenius showed that the nature of the product is not determined by the series to which the salt belongs, but by the metal. The silver salt of *p*-nitrodiazobenzene hydroxide affords the O-ether or diazo ether, whereas the sodium salt affords N-nitroso-*p*-nitromethylaniline, which is certainly not a diazo-compound, though v. Pechmann and Frobenius looked on it as the true *iso*diazo ether.[2] Moreover, silver benzene diazotate and silver benzene *iso*diazotate when treated with methyl iodide afford the same diazo ether [3, 6]

Bamberger's [3] method of carrying out the reaction is as follows :—

The silver benzene diazotate or *iso*diazotate (10 g.) is stirred with methyl iodide (10 g.) and ether (30 g. = 41·6 c.c.) at — 5 to — 10° for six hours in the dark. The silver iodide is then filtered off and the ether is removed *in vacuo*, leaving diazobenzene methyl ether as a yellow oil.

Diazobenzene methyl ether is an unstable oil which decomposes completely when left in an open tube for two days; it explodes on heating, couples instantly with phenols, and decomposes when left in contact with water. Bamberger and Wohl [1] both say that it can nevertheless be distilled with steam, but care must be taken not to inhale the vapour, which produces unpleasant symptoms.[8] Hantzsch says that one mode of decomposition of diazo ethers with water is scission into an arylamine and nitrous acid, and he obtained nitrous acid by sucking air over a diazo ether [15]:—

$$Ar{\cdot}N_2{\cdot}OMe + 2H_2O = ArNH_2 + MeOH + HNO_2$$

Dry hydrochloric acid converts diazobenzene methyl ether instantly into benzene diazonium chloride [15]; *p*-nitrodiazobenzene methyl ether when boiled in benzene for twelve hours gives 4-nitrodiphenyl.[9]

The methyl ether obtained from silver *p*-nitrodiazobenzene *iso*diazotate is more stable than diazobenzene methyl ether, being a yellow solid, m. p. 83°; but although obtained from an *iso*diazo salt, comparison with the original sodium *p*-nitrobenzene *iso*diazotate affords every indication that the ether belongs to the normal series. Thus it couples instantly and completely with β-naphthol both in aqueous and in benzene solution.[7] Chiefly on account of the facility with which they couple, the accepted constitution of the diazo ethers at the present time is Ar·N:N·OAlkyl.

Hantzsch [4] failed to prepare diazobenzene methyl ether from dry diazobenzene chloride and sodium methoxide in methanol; but Bamberger [12] says that the characteristic smell of a diazo ether appears when potassium *p*-chlorobenzene diazotate is shaken with aliphatic alcohols. Hantzsch and Wechsler [13] failed in attempts to find other well-crystallised ethers beside those of *p*-nitrodiazobenzene; benzyl iodide failed to give satisfactory aralkyl ethers.[13]

Despite their behaviour, concerning which there is no lack of agreement, there has been much controversy as to whether the diazo ethers are to be considered as normal or *iso*diazo-compounds, though at first sight most chemists would answer, with v. Pechmann and Frobenius, that they belong to the normal series. Hantzsch, however, considered that, notwithstanding their reactions, they must, according to his stereochemical theory, be members of the *anti*-series having the structure $\begin{matrix} Ar{\cdot}N \\ \| \\ N{\cdot}OAlkyl \end{matrix}$.[4, 5, 10] Euler [14, 16] considered the criterion of this view to be the nature of the metallic diazotates resulting from alkaline hydrolysis of the ether. He accordingly hydrolysed diazobenzene methyl ether with cold aqueous caustic soda, extracted any unchanged diazo ether with ether, and found that the resultant aqueous solution contained a compound coupling instantly and completely with β-naphthol and quite different in properties from a comparative sample of sodium benzene *iso*diazotate.

Hantzsch [15, 17, 18] disputed the interpretation of these observations, maintaining that the manifestations of the normal salts are secondary and that the primary product of hydrolysis is an *iso*diazotate. The point remains undetermined.

Beside the alkyl ethers some aryl and alkylene ethers are also known, and they are produced by the interaction of diazo-compounds with phenols or methylene-compounds so substituted that they are not able to couple. Hence they are described in the literature under the name of "O-azo-compounds", and they have played a considerable part in theories of the coupling reaction. To obtain isolable compounds a diazo-compound of good stability is necessary.

Preparation of 4-benzamidonaphthalene-1-azo-4'-nitrophenyl ether (Dimroth [19]):—*p*-Nitrophenol (0·3 g.) is dissolved in ethanol (1 c.c.) and to it is added an equivalent of sodium acetate, then ethanol is added until the sodium salt is dissolved at 0°; this solution is mixed with one of 4-benzamidonaphthalene-1-diazonium chloride (0·6 g.) dissolved in ethanol (20 c.c.). After a few minutes pieces of ice are dropped in and the ether, m. p. 115—120° (decomp.), crystallises on scratching.

The enolic form of acetyldibenzoylmethane similarly affords 4-benzamidonaphthalene-1-azo-2' : 2'-dibenzoylpropenyl ether,

$$1 : 4\text{-NHBz}\cdot C_{10}H_6\cdot N_2\cdot O\cdot CMe{:}CBz_2,$$

and ethers are also obtained from pentamethylphenol, but diazobenzene-pentamethylphenyl ether is unstable, and may explode spontaneously, and it couples instantly with α-naphthylamine hydrochloride dissolved in ethanol. Mesitol and *iso*durenol also give unstable ethers, but if the phenol is still more acidic, for example, picric acid, then sparingly soluble diazonium salts are precipitated.[19]

Measurement of electrical conductivity in acetone-water (4 : 1) distinguishes diazonium salts from O-azo-compounds, since the former are conductors and the latter are not. In Table XVI below, due to Dimroth,[19] is given a selection of values for conductivity of diazotised 4-benzamido-1-naphthylamine mixed with one equivalent of different acids and phenols. The break between acidic phenols which form salts and those forming non-ionised O-azo-compounds is apparent.

TABLE XVI

Conductivity of Phenolic Diazo-salts and O-Azo-compounds of 4-Benzamido-1-naphthylamine

Phenols and acids.	Conductivity.
Hydrochloric acid	31·37
Trichloroacetic acid	26·20
Picric acid	30·48
2 : 4-Dinitrophenol	22·00
p-Nitrophenol	2·20
Acetyldibenzoylmethane	0·26
Pentamethylphenol	0·41

According to Gebauer-Fulnegg, and Specht,[20] textiles padded with β-naphthol substituted at 1 by halogen, nitro, aryl, alkyl, or acidic groups, and then treated with diazo-compounds, are dyed with O-azo-compounds fast to washing and light.

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GROUP 3. DIAZOCYANIDES, DIAZOCARBOXYLIC ACIDS AND RELATED COMPOUNDS

When cyanides in aqueous solution act on diazo salts which are free from carboxylic or sulphonic acid groups, coloured diazocyanides are precipitated. The reaction is virtually a coupling, as the diazonium salt is converted into a derivative having in its insolubility, colour, and non-ionised state the attributes of an azo-compound :—

$$ArN_2 \cdot X + HCN = Ar \cdot N{:}N \cdot CN + HX$$

The diazocyanides are not obtained unless the reaction medium remains acid until the reaction is completed, and hence the cyanide solution is added to the acid diazonium salt solution, and not *vice versa*. Moreover, the diazocyanides exist in two forms : a labile form, which is the product obtained from the diazonium salt and the cyanide, and a stable form, into which the labile form is spontaneously converted either in solution or in the molten state. The chloro-, bromo-, and nitrobenzenediazocyanides are those which have been most studied, and they are prepared as follows by Le Fèvre and Vine [16] :—

The base, *e.g.*, *p*-chloroaniline (0·10 mol.), is dissolved in hydrochloric acid (*d*, 1·18, 45 c.c.) and water (45 c.c.) and diazotised at 5—10° with sodium nitrite (7·0 g.) dissolved in water (12 c.c.). Alcohol (50 c.c.) is added to the filtered diazo solution to prevent freezing, and after cooling to — 10° a solution of potassium cyanide (13 g.) dissolved in water (25 c.c.) is added with stirring; the final solution must be acid to litmus. The orange-coloured precipitate is collected, washed with ice-water, and

spread on a tile. The crystals are then dissolved in light petroleum with a little ether, dried with sodium sulphate, and the filtered solution is cooled with carbon dioxide, when the labile diazocyanide is obtained as small orange crystals or plates.

If the reaction between the diazo-compound and the alkali cyanide takes place in alkaline medium, the course is entirely different from that described above. A yellow oil is first formed when benzenediazonium chloride is added to potassium cyanide dissolved in excess of aqueous caustic potash; the oil redissolves to a colourless solution, from which a sparingly soluble, unstable red salt separates. This decomposes even in the cold, giving nitrogen and a smell of *iso*cyanide. The free acid is stable, and Heller and Meyer [13] have suggested for it the constitution $PhN_2{\cdot}C(:NH){\cdot}O{\cdot}N_2Ph$, benzenediazo-oxydiazobenzene carbimide. It appears to be formed by addition of the normal diazotate, formed by the action of alkali on the diazonium salt, to the labile diazocyanide; it is not formed from benzene *iso*diazotate.

Diazo-compounds and cyanides were brought into reaction as early as 1865 in the hope of replacing the diazo by the cyanido group,[1] and Griess [2,4] made some investigations with ferrocyanides in 1876, but Gabriel [3] first isolated the orange-coloured double cyanide of benzenediazocyanide and hydrocyanic acid, $PhN_2{\cdot}CN,HCN$, from a neutral reaction medium. That the diazocyanides exist in the two forms mentioned above was demonstrated by Hantzsch and Schultze,[5] who obtained the labile form of *p*-chloro- and *p*-nitrodiazobenzenecyanide by carrying out the reaction at temperatures not above — 5° under acid conditions, thus preventing the formation of Gabriel's double cyanide. Such double cyanides are decomposed by acetic acid to diazocyanide and hydrocyanic acid.[7] Above — 5° the stable form begins to appear, but conversion is best brought about by dissolving the labile form in a non-ionising solvent, *e.g.*, benzene, when conversion proceeds spontaneously following the unimolecular law, and having an activation energy of about 21·6 kg.cal. for *p*-bromobenzenediazocyanide.[16] This change is reversible, and the labile form appears when a solution of the stable diazocyanide is irradiated [10,17,18] (cf. p. 357).

Some of the leading differences between the labile and stable forms of *p*-chlorodiazobenzenecyanide are shown in the table below.

TABLE XVII

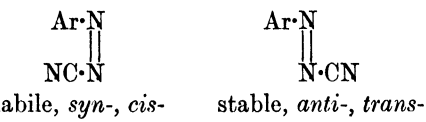
Comparison of Labile and Stable p-*Chlorodiazobenzenecyanides*

	Labile diazocyanide.	Stable diazocyanide.
Crystal form	Yellow needles	Yellow needles or brown prisms
Melting point	29°	105–6°
β-Naphthol	Couples in alcohol	Does not couple
Active copper	Affords *p*-chlorobenzonitrile	Not attacked
Metallic cyanides	Forms double cyanides	Reacts with difficulty
Alkalis	Forms addition compound	No reaction
Silver nitrate	AgCN precipitated	No reaction unless irradiated

Many diazocyanides are volatile with steam. Negative substituents, especially when *ortho* or *para* to the diazocyanide group, increase the stability of the labile form.[7]

Outside the benzene series a number of diazocyanides have been described for the reaction is one that rarely fails; α- and β-naphthalene-diazocyanides are not very stable,[7] but very well-defined labile and stable diazocyanides are obtained from 1-diazo-4-benzamidonaphthalene.[11]

Immediately on their discovery speculation at once became rife as to the nature of the labile and stable forms. Hantzsch [5] asserted that they are geometrical isomerides and called the labile form the *syn*-form and the stable form the *anti*-form having the configurations :—



labile, *syn-*, *cis-* stable, *anti-*, *trans-*

Other workers have called the two isomerides *cis-* and *trans-*, but as even yet the true nature of their isomerism is not determined beyond question, the names labile and stable will be used in this book.

All supporters of the view that the diazocyanides are geometrical isomerides have argued from analogy with the oximes with the exception of Le Fèvre and Vine, who measured dipole moments in the hope of obtaining an unequivocal proof.[15, 16] The values found by these workers are as follows :—

TABLE XVIII

Dipole Moments of Some Stable and Labile Diazocyanides

Diazobenzenecyanide derivative.	Dipole moment (D).	
	Labile.	Stable.
4-Chloro-	2·93	3·73
4-Bromo-	2·91	3·78
4-Nitro-	2·04	1·47
2-Bromo-	3·79	5·32
2 : 4 : 6-Tribromo-	3·50	4·00

Thus there can be no doubt that a change has taken place within the molecule in passing from the labile form to the stable form, but the interpretation that the isomers are geometrical is not entirely equivocal, as it involves assumptions as to the disposition of resultant forces within the molecule.

Further, the infra-red absorption spectra of labile and stable *p*-nitro-, *p*-chloro-, and *p*-bromobenzenediazocyanide and diphenyl-4 : 4′-bisdiazocyanide (which has three possible geometrical, *cis-cis*, *cis-trans*, and *trans-trans*) have been plotted by Anderson, Le Fèvre, and Savage, and those of *p*-bromo- and *s*-tribromodiazocyanide by Sheppard and Suther-

land, whilst magnetic optical rotatory power and diamagnetic susceptibility of the first four above diazocyanides have been determined by Anderson, Bedwell, and Le Fèvre [137,138,139] (p. 402). The activation energy is around 22 kg. cal./g.-mol. for the rearrangement of the labile form to the stable in solvents or in the dark.[20] The differences between the labile and stable forms are so small that structural isomerism is most unlikely, and the implications of these facts are discussed in Chapter XI (cf. p. 387).

Hantzsch [5] said that the labile diazocyanides must have the *syn*- or *cis*-form, because only thus can the elimination of nitrogen and formation of phenyl cyanide (benzonitrile) be explained and the mechanism he postulated amounted to homolytic scission with union of the two free radicals :—



The yield is not good. Hantzsch based all the replacement reactions of the diazo-compounds on this model, but enough is now known of the behaviour of free radicals to know that this mechanism is unlikely.[18]

When the labile diazocyanides are warmed with copper in non-ionising solvents—*e.g.*, benzene, carbon tetrachloride, or ether—much tar is formed with small yields of compounds such as diaryls, which indicates that under these conditions free radicals have actually been formed.[18]

The diazocyanides show all the usual addition reactions of a cyanide, *e.g.*, by adding amines, alcohols, and water. It is difficult to isolate pure compounds from reaction with the two former classes of compound because an alkaline medium is needed, and this decomposes the products, but by boiling either labile or stable diazocyanides with water or dilute acid until dissolution is complete the same diazocarbonamide is formed [6] :—

$$ArN_2{\cdot}CN + H_2O = ArN{:}N{\cdot}CONH_2$$

The aryldiazocarbonamides do not couple, and with alkali lose ammonia to form salts of the unstable aryldiazocarboxylic acids. *p*-Nitrobenzenediazocarbonamide forms a perbromide which when added to a solution of α- or β-naphthylamine in benzene or chloroform at once couples to give *p*-nitrobenzeneazo-α- or -β-naphthylamine; β-naphthol will not couple in the same solvents, but only in aqueous alcohol or aqueous alkali.[19] Bamberger and Baudisch [12] found that only labile *p*-chlorobenzenediazocyanide is attacked by hydrogen peroxide in ethereal solution in presence of magnesium carbonate, the product being *p*-chloronitrosophenylhydroxylamine $p\text{-}C_6H_4Cl{\cdot}N(NO){\cdot}OH$, with some *p*-chlorobenzenediazocarbonamide, $p\text{-}C_6H_4Cl{\cdot}N{:}N{\cdot}CONH_2$, as by-product; the latter is the main product if the magnesium carbonate is replaced by caustic soda.

Angeli [30] oxidised benzenediazocarbonamide with hydrogen peroxide to azoxybenzenecarbonamide and Pieroni,[30, 32] by acting on the respective diazocyanides with hydrochloric acid gas in moist ether, obtained *p*-bromo- and *p*-nitrobenzenediazocarbonamide, and oxidised them with hydrogen peroxide to the azoxy-compounds, which are obtained in only one form.[32] Some interest attaches to the azoxycarbonamides because when treated with aqueous alkali they afford a solution containing a normal diazotate, and have hence been suggested as a passive stabilised diazo-compound for use in Rapidogen-type dyes [34] whilst Saccardi [33] used benzenediazocarbonamide to couple with a colourless pyrrole derivative present in the skin. Two constitutions are possible for the azoxycarbonamides, $Ar{\cdot}N\overset{O}{\diagup\!\!\diagdown}N{\cdot}CONH_2$ or $Ar{\cdot}N{:}N\overset{O}{\diagup\!\!\diagdown}CO{\cdot}NH_2$. Proof that the oxygen is attached to the nitrogen atom next to the aryl nucleus is found in the fact that benzeneazoxycarbonamides cannot be brominated, the induced charges on the benzene nucleus being the same as in nitrobenzene $PhN\overset{O}{\diagup\!\!\diagdown}O$. Nor is the oxygen attached by hydroxylation of the amido-group as azobenzeneformhydroxamic acid, PhN:N·CO·NHOH, is known and is different. It is made by coupling diazobenzene acetate with the potassium salt of trinitromethane and treating the product with moist ether, when nitrogen oxides are split off [42] :—

$$PhN_2{\cdot}OAc + KO{\cdot}C(NO)(NO_2)_2 \longrightarrow PhN_2{\cdot}O{\cdot}C(NO)(NO_2)_2 \longrightarrow Ph{\cdot}N{:}N{\cdot}CO{\cdot}NHOH$$

This substance, of which substituted analogues are known,[43] does not couple with alkaline solutions of naphthols nor can it be oxidised to an azoxy-compound. When ω-dinitrotoluene is used in place of trinitromethane in the above reaction the product is benzoylazobenzene [40, 41] :—

$$PhN_2{\cdot}OAc + KO{\cdot}CPh(NO)NO_2 \longrightarrow PhN_2{\cdot}O{\cdot}CPh(NO)NO_2 \longrightarrow Ph{\cdot}N{:}N{\cdot}COPh$$

The labile and stable diazocyanides react differently towards methylmagnesium iodide and phenylmagnesium bromide; both form complexes, that from the stable isomeride being more deeply coloured. Treatment of the complexes in the usual way with 2N-sulphuric acid gives acetaldehyde and benzaldehyde from the complexes of the labile form (20% yield identified as the 2 : 4-dinitrophenylhydrazones), but none from the complexes of the stable form. Hodgson and Marsden [19] interpret this as a reaction of the labile diazocyanide reacting as an *iso*cyanide having an easily-ruptured :N·N link :—

$$Ph{\cdot}N{:}N{\cdot}\overset{\oplus}{N}{:}\overset{\ominus}{C} + MgMeI \longrightarrow Ph{\cdot}N{:}N{\cdot}N{:}CMe{\cdot}MgI \xrightarrow{H_2O} Ph{\cdot}N{:}N{\cdot}N{:}CHMe \xrightarrow{H_2O} MeCHO$$

For further comment cf. Chapter XI, p. 387.

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GROUP 4. THE DIAZOSULPHONATES; THEIR PREPARATION, REACTIONS, AND USE AS STABILISED DIAZO-COMPOUNDS

Sulphites in neutral or slightly alkaline solution act on diazo-compounds to give substances called diazosulphonates, and commonly represented by the structure $ArN_2 \cdot SO_3M$, where M is an atom of a monovalent metal or its equivalent. They thus differ from the diazo-compounds made from sulphonated arylamines in which the sulphonic acid group is attached to a carbon atom of the aromatic ring. Two forms are known, a labile form and an isomeric stable form, but the former changes easily into the latter, and the labile form can only be obtained under special conditions, hence the early workers did not know of any form beside the stable one. This reaction with sulphites is one of the most general and reliable of the diazo-compounds affording crystalline, stable, and easily isolated salts.

The diazonaphthalene-compounds are, however, an exception being converted by sulphite almost entirely into azonaphthalenes [13, 40] and it

was not until 1948 that Hodgson and Bailey isolated the stable naphthalene-α- and -β-diazosulphonates which form a small fraction of the reaction mixture. Earlier Hodgson and Marsden [24] had demonstrated the presence of the stable 4-nitronaphthalene-1-diazosulphonate in the mixture of 4 : 4′-dinitro-1 : 1′-azonaphthalene (10—20%) and 4 : 4′-dinitro-1 : 1′-dinaphthyl (*ca.* 50%) obtained from 4-nitronaphthalene-1-diazonium chloride and sulphite. The azo acid wool dye Cuba Orange (C.I. 178) is made by the action of sodium sulphite on diazotised naphthionic acid.

The diazosulphonates were early discovered, for Schmitt and Glutz [1] made the derivative of *p*-diazophenol, Griess [2] of *m*-diazobenzoic acid, whilst E. Fischer [3] used potassium benzenediazosulphonate, earlier made by Strecker and Römer,[1a] as an intermediate step in his classic work on the reduction of diazo-compounds to hydrazines. Diazosulphonates can be made from diazotates,[12,17] benzenediazosulphonates being obtained from both potassium benzene normal and *iso*-diazotate by the prolonged action of cold aqueous potassium sulphite; it is also made from nitroso-acetanilide,[16] and by the oxidation of phenylhydrazine sulphonic acid.[4] *p*-Nitrobenzenediazosulphonate is formed from *p*-nitrodiazobenzene methyl ether and alkali sulphite.[12] Hall and Gibbs [21] show that to obtain the best yields when working from a diazonium salt and sulphite the control of pH is of cardinal importance; the solution must not be acid enough to produce sulphur dioxide by decomposition of the sulphite, nor must it become alkaline, for thus deeply coloured products are formed. Only a slight excess of sulphite over the single equivalent to the diazo-compound may be used, and the solutions should be as concentrated as is convenient. The following is a typical preparation [23] :—

4-Benzamido-2 : 5-diethoxyaniline (Blue 2B base) (3 g. = 0·01 mol.) is added to boiling water (100 c.c.) and hydrochloric acid (*d* 1·18, 1·5 c.c.); when the base has dissolved, hydrochloric acid (3·0 c.c.) is added, and the whole is cooled to 15—20° giving a thick, white crystal sludge which dissolves to a green-brown diazo solution on adding sodium nitrite (0·7 g.) dissolved in water (2 c.c.). This solution is filtered, sodium acetate solution is added to remove acidity to Congo red, and it is poured into a solution of crystallised potassium sulphite (2·1 g.) in water (15 c.c.). The solution turns brown, and some brown tar separates; this is the labile diazosulphonate, for it couples with alkaline naphthols (*vide infra*). Immediately it begins to crystallise, especially if rubbed, giving pale yellow granular crystals which soon fill the mass of the liquid; after ten minutes these can be collected, pressed, and dried, giving a brownish-yellow powder.

The stable diazosulphonates as obtained above do not couple with phenols or amines even when warmed in alkaline solution with these substances. Their yellow, orange, or red colour suggest, like their stability, that the nitrogen is held in the same way as in the azo-compounds. Like some azo-compounds, they regenerate the diazonium halide when treated with chlorine.[20] The diazonium nitrate is formed when they are treated with lead or silver nitrate :—

$$PhN_2{\cdot}SO_3K + 2AgNO_3 = Ag_2SO_3 + KNO_3 + PhN_2{\cdot}NO_3$$

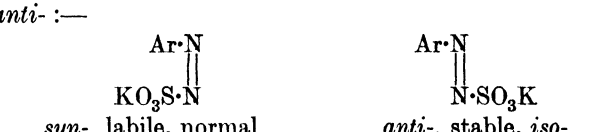
The labile form mentioned above was discovered by Hantzsch in 1894, who made labile benzenediazosulphonate by adding diazobenzene nitrate solution to an excess of alkaline potassium sulphite.[5, 6] Immediately on mixing the cold aqueous solutions very unstable, flat, orange crystals separate, and can be collected on a tile and dried. This form of the diazosulphonates is capable of coupling with phenols. Analysis is difficult on account of instability, but the composition of the crystals immediately on separation appears to be $PhN_2 \cdot SO_3K, H_2O$. Explosive decomposition may follow loss of the crystal water, which can be removed by standing over phosphorus pentoxide. Similar labile diazosulphonates can be obtained from other diazo-compounds, such as the halogenobenzene diazo salts [9]; Hantzsch and Borghaus [14] said that the nitrodiazobenzenes only form stable diazosulphonates but Hodgson and Marsden [24] mention the preparation of a labile form of *p*-nitrobenzenediazosulphonate. In aqueous solution the labile isomers quickly pass into the stable form; Hodgson [24] says the labile form is never free from the stable, and that fifteen minutes after preparation at room temperature only 33% of potassium benzenediazosulphonate remains unconverted. The stable forms are paler in colour than the labile; both forms show the same absorption spectra [18, 19] and Hodgson says that this is because the spectrum of the stable form is the only one that has been in fact observed owing to the speed with which the labile form rearranges. The sodium salt of the labile form of benzenediazosulphonate is too soluble to be salted from solution, but if a potassium salt is added, then the potassium salt of the labile form crystallises.[10]

The labile diazosulphonates are also sharply differentiated from the stable isomers, in that they react with iodine [13]:—

$$ArN_2 \cdot SO_3K + I_2 + H_2O = ArN_2 \cdot SO_4H + KI + HI$$

Hantzsch and Schmiedel therefore used titration with iodine to measure the speed of conversion of the labile into the stable form, and the influence of substituents on the change. They found that speed of conversion does not follow any definite law, and that both labile and stable forms are equally reduced to arylhydrazines.[15]

Hantzsch believed the labile and stable diazosulphonates to be, like the diazocyanides, geometrical isomerides, and he similarly called them *syn-* and *anti-*:—



syn-, labile, normal or *cis* — *anti-*, stable, *iso-* or *trans*

The above view of Hantzsch has been challenged in succession by Claus,[10] by Bamberger,[7] by Blomstrand, and by Hodgson and Marsden,[24] all of whom have made the suggestion that the difference between the

labile and stable forms is explained if they have the sulphite and sulphonate structures respectively :—

$$ArN_2{\cdot}O{\cdot}SO_2K, \text{ labile, and } ArN_2{\cdot}SO_3K, \text{ stable.}$$

Hodgson and Marsden base their argument for the sulphite–sulphonate structures on the existence and reactions of unstable complexes formed by interaction of diazo-compounds with diazosulphonates. *p*-Nitrodiazobenzene combines with stable potassium benzenediazosulphonates, giving a water-insoluble complex, stable at 0°, and coupling with alkaline β-naphthol to give *p*-nitrobenzeneazo-β-naphthol and stable diazosulphonate; to this complex is assigned the constitution :—

$$PhN_2{\cdot}SO_2{\cdot}O{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2 \text{ or } PhN_2{\cdot}\overset{\ominus}{S}O_3\}\overset{\oplus}{N}_2{\cdot}C_6H_4{\cdot}NO_2$$

The labile isomeride also affords a complex, but this couples with alkaline β-naphthol to give both benzeneazo- and *p*-nitrobenzeneazo-β-naphthol; the latter arises because the labile isomeride is never free from the stable form, so that the complex is also a mixture. The constitution of the labile complex derived from the sulphite form is therefore represented as :—

$$PhN_2{\cdot}\overset{\oplus}{O}{\cdot}\overset{\oplus}{S}{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$$
$$\overset{\ominus}{O}\quad\overset{\ominus}{O}$$

On account of their stability, ease of manufacture, and good solubility the diazosulphonates present attractions as stabilised diazo-compounds. The labile form being too unstable for technical use efforts have been made to find diazosulphonates so substituted that the stable form still has a slight reactivity sufficient to couple with alkaline naphthols or to find easy means for activating the stable form.

The diazosulphonates derived from *p*-aminodiphenylamine and its congeners are an example of the first type. These bases are much valued for the blue monoazo dyes they afford; 4-amino-4′-methoxydiphenylamine diazotised and coupled on the fibre with 2 : 3-hydroxynaphthoic arylamides is the well-known Variamine Blue of the I.G. Company. These bases cannot be converted into *iso*diazotates or triazens, because their diazo derivatives are instantly and irreversibly decomposed by alkali, the product being the explosive quinone diazide. Treatment of the diazo-compounds with neutral sulphite affords the diazosulphonates; these are of good stability under alkaline conditions, so that they can be incorporated in printing pastes with the naphthol. Coupling is then brought about by steaming. To obtain full development of the azo dye a neutral oxidising agent is often necessary, the purpose being met by an alkali chromate, whilst it is undesirable that the steam in the ager should contain acid vapours. Colours working on this principle are the Rapid-

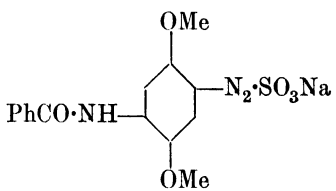
azols of the I.G. Company.[42, 48] 4 : 4′-Tetrazodiphenylamine also affords a bisdiazosulphonate, and this affords black prints by the above process.

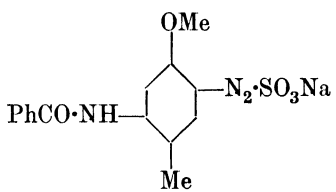
TABLE XIX

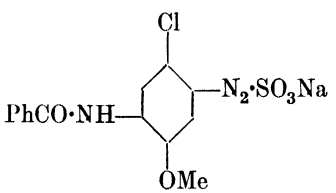
Composition of Rapidazol Dyes (I.G.) [27]

Dye.	Diazosulphonate.	Coupling component.
Rapidazol Black B	*p*-OMe·C_6H_4·NH·C_6H_4·N_2·SO_3Na-*p*	Naphthol AS-OL
Blue 1B	*Idem*	AS
Navy Blue G	*Idem*	AS-D
RR	*p*-PhNH·C_6H_4·N_2·SO_3Na	AS-D

The Fast Blue 2B type of base, *i.e.*, 2 : 5-substituted 4-benzamidoaniline, affords diazosulphonates, as described above, which also couple with naphthols on the fibre merely by neutral steaming.[44] Examples of diazosulphonates of this type are :—







The hydrazinesulphonic acids obtained by reducing the diazosulphonates of both the 4-aminodiphenylamine and Fast Blue 2B type also behave as passive stabilised diazo-compounds in textile printing.[45, 46]

The stable diazosulphonates can be activated either chemically or by light, a fact which has long been known (cf. p. 369). For chemical activation Schmidt's [20] method of regenerating a diazonium salt from the diazosulphonate has been applied, the dry salt being mixed with dry bromide-bromate and a dry acid salt such as sodium hydrogen sulphate. When this mixture is dissolved in water the acid salt liberates the bromine from the bromide-bromate, and the bromine converts the diazosulphonate into the diazonium bromide.[43, 47] Prints of a thickened solution of a diazosulphonate and a naphthol can be developed by treatment with very dilute chlorine or by hypochlorite solution.[51]

As has been remarked above, irradiation of a diazosulphonate induces the capacity to couple, and it has been proposed to develop prints by this means using either sunlight or sources of actinic light such as arc

lamps or mercury vapour lamps.[41, 49] The barrier to large-scale technical working is that all diazosulphonates are not activated at the same speed and some require too long a time to develop a full shade. The matter has been quite fully investigated by Desai, Mehta, and Thosar[23] in experiments on the use of diazosulphonates in printing. They expose solutions of diazosulphonates to Indian sunlight at noon, and note that the pH rises from 6 to 3, as the active diazo-compound is formed. Four methods are used to measure the amount of active diazo-compound: (*a*) absorption of iodine, (*b*) coupling with β-naphthol and weighing the pigment formed, (*c*) the colour-change as coupling occurs, and, (*d*) the increase in acidity. The more dilute the solution the greater the amount of active diazo-compound generated, though the process does not ever reach completion, the highest figure recorded being 76% for 4-benzamido-2 : 5-dimethoxybenzenediazosulphonate at 0·001N after 180 minutes; after this time the amount of active compound diminishes. Other diazosulphonates reach less than half this figure, and they may be divided on the above test roughly into three groups: (i) those of the Blue 2B type that develop well, (ii) a medium group typified by the chlorotoluidines, *e.g.*, 2 : 1 : 4-, 2 : 1 : 6-, and 2 : 1 : 5-$NH_2 \cdot C_6H_3ClMe$ in that order, and (iii) nitroarylamines, *e.g.*, 5 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$ and 3 : 4 : 1-$NO_2 \cdot C_6H_3(NH_2) \cdot OMe$.

A patent[52] claims that passive stabilised diazo-compounds are formed by combination of diazonium salts with sulphuric esters of tertiary amines, such as $(HO \cdot [CH_2]_2)_2N \cdot CMe_2 \cdot O \cdot SO_2H$, and that these exist in both labile and stable forms, the former deep in colour and active, the latter paler in colour and inactive. The most useful complexes are those made from diazotised diphenylamines or Fast Blue 2B bases as these can be developed after printing with naphthols either by neutral steaming or irradiation. The specification expresses no view as to the constitution of the complexes, but as they behave like diazosulphonates and no triazens are known which exist in two forms, they are mentioned here.

Sodium *p*-dimethylaminobenzenediazosulphonate, first prepared by Stollé and Gunzert,[22] has been used as a rodenticide[26] and sodium 3-chloro-4-hydroxybenzenediazosulphonate is a fungicide[26] used as 0·1% aqueous solution to treat seed oats and rye.

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		B.P.	U.S.P.	D.R.P.	Friedländer.	F.P.
40	M. Lange	—	—	78,225	*Fr.*, **4**, 1016	—
41	Haendel	309,166	—	—	—	—
42	I.G.	377,207	1,920,542	560,797	*Fr.*, **19**, 1648	735,365
43	I.C.I.	377,978	1,948,589	—	—	736,463
44	I.G.	379,279	1,970,070	560,798	*Fr.*, **19**, 1762	727,665
45	I.G.	379,280	1,968,923	563,061	*Fr.*, **19**, 1784	41,731/735,365
46	I.G.	398,846	2,018,103	578,648	*Fr.*, **20**, 1229	42,476/727,665
47	I.C.I.	414,681	—	—	—	—
48	I.G.	421,971	1,959,995	588,212	*Fr.*, **20**, 1233	43,623/735,365
49	St. Denis	—	—	—	—	760,784
50	St. Denis	440,144	—	—	—	45,829/760,784
51	St. Denis	457,718	—	—	—	795,558
52	Nat. Aniline	—	2,154,509	—	—	—
53	St. Denis	—	2,206,611	—	—	—

GROUP 5. DIAZOPERHALIDES

The diazonium halides combine by addition with two atoms of chlorine, bromine, or iodine which may be the same as or different from each other. In this way there are formed stable crystalline compounds which possess the constitution $ArN(:N)\cdot(X\,X'\,X'')$. The perbromides are the most easily obtained members of the group and were first prepared by Griess,[1] who added a solution of bromine in hydrobromic acid to an aqueous solution of benzenediazonium nitrate. The brownish-red oil which separates under these conditions crystallises on removal from the mother-liquor and removal of excess bromine by ether. Large yellow plates crystallise from ether and the perbromide is stable while kept dry, but it is decomposed by water. Hantzsch[4] pointed out the close analogy of the diazoperhalides, and the perhalides of the alkali metals, and he also

prepared nine out of the ten possible combinations of chlorine, bromine, and iodine :—

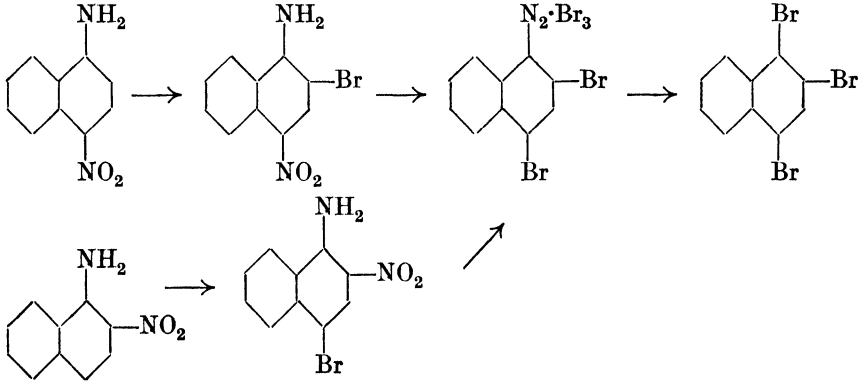
$ArN_2 \cdot I_3$	$ArN_2 \cdot Br_3$	$(ArN_2 \cdot Cl_3)$
I_2Br	Br_2Cl	$ArN_2 \cdot Cl_2Br$
I_2Cl	Br_2I	Cl_2I
	$BrClI$	

The colour of these compounds varies from almost black for the periodide to yellow for the chloroiodide.

Chattaway [7, 8] advanced the thesis that the diazo-perbromides have the constitution of N-tribromoarylhydrazines, $Ar \cdot NBr \cdot NBr_2$, because they can be obtained by the action of bromine on arylhydrazines, and are widely different from the ammonium perhalides, but the arguments advanced by Hantzsch [10] and by Forster [9] leave no room for doubt that the perhalides are true diazonium compounds. Substances of the constitution proposed by Chattaway probably cannot exist, for bromine will not add to the double bond in benzene diazocyanide to form a cyano-dibromophenylhydrazine, but ejects the cyano-group, forming first the diazonium bromide and then the perbromide if sufficient bromine is present.

The diazonium perbromides give up two atoms of bromine with ease, and will saturate ethylenic links, as in cinnamic acid.[6] They differ from the diazonium salts in that when boiled with alcohol they afford the bromohydrocarbon instead of the hydrocarbon.[2] The bromohydrocarbons are also obtained by thermal decomposition of the perbromides in solvents such as glacial acetic acid.

Consden and Kenyon [13] showed that when bromine in sufficient excess acts on 1 : 4- or 2 : 1-nitronaphthylamine both the amino- and the nitro-group are replaced by bromine through the intermediary of the diazo-perbromide. The bromine replaces the nitro group, the nitrous acid thus set free diazotises the amino group which is converted into the perbromide, which then replaces the diazo group by bromine the final product being 1 : 2 : 4-tribromonaphthalene :—



Still higher perhalides can be formed. Chattaway showed that the brown oil which separates in the preparation of the perbromide contains no fewer than nine atoms of bromine, but they can only be retained in combination if the bromine vapour is prevented from escaping.

Very stable diazonium tetrachloroiodides are formed when diazonium chlorides are poured into a strong hydrochloric acid solution of iodine trichloride; they crystallise in bright yellow prisms and are quite stable if kept dry. Chattaway [11] assigns to them the structure :—

$$ArN_2\begin{bmatrix} Cl & Cl \\ & I \\ Cl & Cl \end{bmatrix}$$

By treating an aqueous solution of a diazonium chloride with iodine trichloride, Algerino [12] obtains the diazonium dichloroiodides, $ArN_2 \cdot Cl_2I$; the three nitrobenzene diazonium dichloroiodides when treated with ammonia afford the corresponding nitrophenylazide (cf. p. 187).

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GROUP 6. DIAZOSULPHIDES

Diazo-compounds combine with hydrogen sulphide to give open-chain diazosulphides; products of different constitution are obtained according to the conditions. Thus, if hydrogen sulphide is passed into a neutral solution of *p*-nitrodiazobenzene, two molecules of the diazo-compound become attached to one atom of sulphur forming the diazosulphide $(p\text{-}NO_2 \cdot C_6H_4 \cdot N_2)_2S$.[1] This yellow compound behaves as might be expected of the sulphur analogue of Bamberger's diazo-anhydride (cf. p. 134); thus it gives an azo-compound with alkaline β-naphthol, and on boiling with benzene affords 4-nitrodiphenyl.[1] When hydrogen sulphide is passed for a longer time into a solution of *p*-nitrodiazobenzene chloride a disulphide is formed $(p\text{-}NO_2 \cdot C_6H_4 \cdot N_2)_2S_2$; this substance behaves like the monosulphide but reacts more sluggishly.[1] Some of these diazosulphides are, like their O-analogues, very unstable, and the substance formed from *p*-bromodiazobenzene and hydrogen sulphide at — 5° explodes under water at 0°.

Diazosulphides are also made by interaction of diazo-compounds with aqueous solutions of metallic sulphides and polysulphides at low temperatures; at temperatures greater than about 60° they decompose as formed, the diazo-group being replaced by sulphur (cf. p. 324). The oily diazosulphides produced by the low temperature reaction are dangerously explosive,[2, 3, 4] especially the compound formed from diazotised 4-chloro-*o*-toluidine and sodium disulphide; the oil explodes while still wet and in contact with the solution in which it is formed. A heavy beaker is shattered by the explosion of the oil formed from 0·05 mol. of the above diazo-compound.[2] A severe explosion due to just such an oily diazosulphide in aqueous suspension has also come under the notice of the author.

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CHAPTER V

REACTIONS OF THE DIAZO-COMPOUNDS (*continued*)

CLASS C. DERIVATIVES IN WHICH THE DIAZO-FUNCTION DISAPPEARS BUT THE DIAZO NITROGEN ATOMS REMAIN IN THE NEW MOLECULE. DIAZOAMINO- AND DIAZOIMINO-COMPOUNDS OR TRIAZENS—OXIDATION PRODUCTS—REDUCTION PRODUCTS—ARYLAZIDES, AND OTHER PRODUCTS OF INTERACTION WITH NITROGEN-CONTAINING BASES—S-AZO-COMPOUNDS.

CLASS C. DERIVATIVES IN WHICH THE DIAZO-FUNCTION DISAPPEARS, BUT THE DIAZO-NITROGEN ATOMS REMAIN IN THE NEW MOLECULE.

GROUP 1. THE DIAZOAMINO- AND DIAZOIMINO-COMPOUNDS OR TRIAZENS AND THEIR APPLICATIONS

Introductory.—Diazoaminobenzene, $PhN_2 \cdot NHPh$, has been known as long as diazobenzene itself, for Griess [1, 2] made it by treating an alcoholic solution of aniline with insufficient nitrous gases to produce complete diazotisation. Diazoamino-compounds always appear when the attempt is made to diazotise an arylamine with insufficient acid, provided the arylamine is not able to couple; if coupling is possible an azo-compound may appear in greater or lesser amount. As the diazotisation reaction proceeds in presence of insufficient acid the medium eventually becomes neutral when all the acid available has been combined as diazonium salt, and thereupon the latter attacks an amino hydrogen atom of the remaining undiazotised arylamine :—

$$ArN_2 \cdot X + NH_2Ar = ArN_2 \cdot NHAr + HX$$

Griess recognised both the nature of the reaction by which such diazoamino-compounds are formed and their structure to be that given above.

The core of the diazoamino-compounds, therefore, consists of a chain of three nitrogen atoms, two being united by a double link, and the simplest member of the whole family is the unknown base $HN{:}N \cdot NH_2$, triazen. Substitution of one, two, or three hydrogen atoms in triazen produces a large and varied family of derivatives, and in a completely rational nomenclature all are named as triazens. The names diazoamino and .diazoimino are therefore, strictly speaking, trivial names, but as their genesis and usage are older and more strongly entrenched in the literature than the systematic name, they will be retained here

and used interchangeably with the name triazen,* whichever is the more concise. While in many respects the two groups resemble each other, the labile hydrogen atom present in the diazoamino-compounds causes the problems associated with tautomerism to be manifested, and from the day of their discovery they have attracted the inquiries of chemists.

The subsequent discussion will be simplified if the various known permutations which arise from substitution in the triazen molecule are set out in a form available for reference. In the list below aromatic nuclei are, as usual, denoted by Ar, aliphatic, including araliphatic, by A, and rings containing a secondary nitrogen atom, and which may contain other hetero atoms, by ·NX.

1. Symmetrical and asymmetrical aromatic and mixed aromatic-aliphatic diazoamino-compounds :

$$ArN_2{\cdot}NHAr,\ ArN_2{\cdot}NHAr',\ ArN_2{\cdot}NHA.$$

2. Bisdiazoamino-compounds :

$$NH(N_2Ar)_2,\ NAr(N_2Ar')_2,\ NA(N_2Ar)_2.$$

(Note.—These compounds contain a chain of five nitrogen atoms and are named systematically as derivatives of pentaz-1 : 4-diene, HN:N·NH·N:NH.)

3. Aliphatic diazoamino-compounds : $AN_2{\cdot}NHA$.
4. Diazoimino-compounds :

$$ArN_2{\cdot}NAr'_2,\ ArN_2{\cdot}NAr{\cdot}A,\ ArN_2{\cdot}NA_2,\ ArN_2{\cdot}NX.$$

The Diazoamino- and Bisdiazoamino-compounds.

(a) *Formation.*—Diazoaminobenzene is the type-member of the symmetrical diazoamino-compounds, and the ordinary methods of preparation all depend on the controlled action of acid and nitrite on an excess of arylamine. Thus, if two molecular proportions of aniline are brought into reaction with one of sodium nitrite and one of dilute sulphuric acid, one molecule of benzene diazonium sulphate is formed, and this, by combining with the remaining molecule of aniline converts the whole into diazoaminobenzene.[14] An alternative is to use three molecular proportions of hydrochloric acid, and follow the nitrite with sufficient sodium acetate to bind all the mineral acid.[9] Such are the methods commonly used to produce symmetrical diazoamino-compounds of the type of diazoaminobenzene. Other variants of the method are known. Earl [94] points out that the essential for obtaining diazoaminobenzene of good quality is to avoid the presence of acid except that immediately used to decompose the nitrite. He thus produces a very pure form of

* This name is also spelled triazene, but in much current British usage the terminal "e" is omitted.

diazoaminobenzene by passing carbon dioxide into an aqueous emulsion of aniline with an excess of sodium nitrite and a little potassium chromate; a shaking hydrogenation apparatus serves well for this preparation. Earl also gives the following method of preparation :—

Sodium nitrite (70 g. = 1·0 mol.), glacial acetic acid (40 c.c.), and saponin (1 g.) are dissolved in water (3 l.); then aniline (120 c.c. = 1·3 mol.) is added, and the whole is stirred for two hours at room temperature, the liquid becoming filled with orange-yellow granules. The reaction mixture is then made alkaline with caustic soda, the product is collected, and dried, preferably *in vacuo* at 60—70°. The yield is 120 g. = 0·61 mol. = 93·8% on the aniline, m. p. 95—96°. One crystallisation from alcohol gives 80% of the batch as yellow crystals, m. p. 98—99°.

Diazoaminobenzene is also formed by adding solid diazobenzene salts to aniline,[33] from silver nitrite and aniline hydrochloride in non-aqueous liquids, such as benzene,[29] or by passing nitrous gases into organic solvents in which aniline hydrochloride is suspended.[38] Aniline dissolved in ether also gives diazoaminobenzene when acted on by amyl nitrite,[7] or by nitrosyl chloride.[44] The latter reagent affords symmetrical diazoamino-compounds when passed into an excess of any primary arylamine.[193]

Interaction of a diazo-compound with a primary arylamine different from that used to prepare the diazo-compound, or an alkylamine under neutral or alkaline conditions, produces an asymmetrical triazen except where coupling can occur, as with *m*-toluidine, *p*-xylidine, α- and β-naphthylamine, and *m*-diamines having at least one unsubstituted carbon atom *para* to an amino group. If coupling is prevented by suitably placed substituents, as in 4 : 6-diamino-*m*-xylene

$$[1 : 3 : 4 : 6\text{-}C_6H_2Me_2(NH_2)_2]$$

or in 1-chloro-2-naphthylamine, then diazoamino-compounds are formed, though those derived from the *m*-diamines are unstable.[58] Griess first made unsymmetrical diazoamino-compounds from diazobenzene nitrate and *p*-bromoaniline and *p*-toluidine. At the same time he discovered the important fact that whether diazobenzene acts on *p*-toluidine, or diazo-*p*-toluene on aniline, the products of both the reactions are identical.[3, 4]

When a primary aliphatic amine is presented to a diazo-compound, the tendency is for the bisdiazoamino-compound to be formed according to the equation [25] :—

$$3NH_2Alkyl + 2ArN_2{\cdot}Cl = 2NH_2Alkyl,HCl + (ArN_2)_2{\cdot}NAlkyl$$

Phenylmethyltriazen, $PhN_2{\cdot}NHMe$, can, however, be obtained by Dimroth's [63] device of interacting an aqueous alkaline solution of diazobenzene with aqueous methylamine in the presence of ether, which extracts the triazen as formed, and so prevents further reaction with the diazo-compound; the yield is 44% (on the diazobenzene), and a much smaller yield of phenylethyltriazen is similarly obtained from monoethylamine. The primary aliphatic amino-acids only form triazens slowly and

in poor yield; diazobenzene and glycine form the bisdiazoamino-compound $(PhN_2)_2N{\cdot}CH_2{\cdot}CO_2H$.[90] Nitrosoacetarylamides (cf. p. 38) with primary arylamines in non-hydroxylic solvents afford diazoamino-compounds in neutral conditions,[37] and bisdiazoamino-compounds if alkali is present [39] :—

$$2PhN(NO)Ac + NH_2Ph = (PhN_2)_2NPh + 2AcOH$$

Bisdiazoamino-compounds having an aryl nucleus attached to the central nitrogen atom are not formed in aqueous solution by direct combination of two molecules of a diazo-compound with one of a primary arylamine, but are made by combining a diazo-compound dissolved in methanol with a diaryl triazen dissolved in methanol with sodium methylate, when the bisdiazoamino-compound is at once precipitated in crystalline form; for example, diazobenzene and diazoaminotoluene thus afford diazobenzene-*p*-diazotoluenetoluidide (1-phenyl-3 : 5-di-*p*-tolyl-pentaz-1 : 4-diene), $PhN_2{\cdot}NC_6H_4Me{\cdot}N_2C_6H_4Me$, yellow needles exploding at 76°. The bisdiazoamino-compounds derived from the arylamines are less stable than those derived from the alkylamines, for they explode when struck or heated.[46]

A less direct method for preparing triazens, in which diazo-compounds are nevertheless the starting point, is Dimroth's [60] synthesis from aryl azides and a Grignard reagent :—

$$ArN_3 + Ar'Mgl \longrightarrow Ar'N(Mgl){\cdot}N{:}NAr \longrightarrow ArN_2{\cdot}NHAr' + Mgl(OH)$$

Thus phenylazide (cf. p. 187) and methylmagnesium iodide afford phenylmethyltriazen in nearly twice the yield mentioned above for the direct combination of diazobenzene with monomethylamine.[62]

The interaction of diazo-compounds with ammonia is not straightforward, for if it is sought to use ammonia instead of an amine to make less highly substituted triazens, a more complex series of reactions occurs, and the first products are not isolable. Phenyltriazen, $PhN_2{\cdot}NH_2$, which should be the first product of reaction of diazobenzene and ammonia, can only be made by reducing phenyl azide with stannous chloride in ether.[67] Diazoaminobenzene is a main part of the product obtained from diazobenzene and ammonia, and is formed because part of the diazobenzene has been converted back into aniline.[3] Griess also found that a yellow acidic substance is formed, and deposits explosive crystals if the filtrate from the diazoaminobenzene is evaporated to dryness; v. Pechmann and Frobenius [46] showed that the corresponding substance produced from diazo-*p*-toluene is the bisdiazoamide, $(C_6H_4Me{\cdot}N_2)_2NH$. They confirmed the probability of this structure by methylation, when the product was found to be identical with that obtained from two molecules of diazo-*p*-toluene and one of methylamine. They showed, too, how ammonia brings about different changes from the alkylamines, for, like other alkalis, it converts the diazo-compound into the diazotate, and then brings about its destruc-

tion by the agency of ammonium salts. Thus ammonium chloride regenerates *p*-nitroaniline from Nitrosamine Red :—

$$p\text{-}NO_2\cdot C_6H_4\cdot N(NO)Na + NH_4Cl = p\text{-}NO_2\cdot C_6H_4\cdot NH_2 + N_2 + NaCl + H_2O$$

Unconverted diazo-compound at once combines with the amine thus produced, and so the upshot of the reaction is the production of the diazoamino-compound, as Griess originally observed. The action of dry ammonia on dry benzenediazonium picrate does not produce a triazen at all but beside ammonium picrate the chief products are diphenylamine and aniline.[64]

The diazo-compounds of the anthraquinone series form triazens,[53] β-diazoanthraquinone forms a bistriazen with ethylene diamine,[51] and with ammonia a 1 : 5-di-β-anthraquinonylpentazdiene,[52] which on heating decomposes with loss of nitrogen to ββ′-dianthrimide.[54]

(b) *Reactions and Chemical Behaviour of Diazoamino-compounds.*— The diazoamino-compounds are usually yellow or orange solids, but some are colourless or brown, as are often the "technical" products. If free from carboxylic or sulphonic groups they are insoluble in water, but are soluble in organic solvents, and they are stable, as already mentioned, only under neutral or alkaline conditions; they usually explode if heated above their melting point. Nevertheless some, like phenylmethyltriazen, can be distilled with steam. Cold aqueous mineral acids split them into their components, diazo-compound and arylamine, but the ease with which this occurs depends on the substituents—for example, negative groups in the *p* : *p*′-positions makes scission slow and imperfect, whilst 1 : 3-di(2′ : 4′-dichlorophenyl)triazen is hardly affected at all by acid.[36]

Hot dilute mineral acids give a phenol, arylamine, and nitrogen :—

$$ArN_2\cdot NHAr + H_2O = ArOH + NH_2Ar + N_2$$

If the aryl radicals are different, then two phenols and two arylamines are found, except in a few special cases.[77]

Concentrated hydrogen chloride or bromide, particularly if cuprous salts are present, give the aryl chloride or bromide, arylamine, and nitrogen :—

$$ArN_2\cdot NHAr + 2HCl = ArCl + NH_2Ar,HCl + N_2$$

If reduced, a hydrazine and an arylamine result, but again if the diazoamino-compound is asymmetric two amines and two hydrazines are formed.

o- and *p*-aminodiphenyl or their homologues result from the controlled pyrogenic decomposition of diaryltriazens,[28, 34, 85] whilst Graebe and Ullmann's synthesis of carbazole from *o*-aminodiphenylamine (cf. p. 263) is based on the decomposition by heat of an internal diazoimino-compound.

Diazoaminobenzene has been said to form salts with anhydrous hydrochloric acid in non-ionising solvents [80]; it is certainly sufficiently basic to form a double salt with platinum chloride in alcohol solution.[2] On the

other hand, the imine hydrogen atom is distinctly acidic, and on replacement by metals well-defined salts are obtained.[89] The yellow sodium salt of diazoaminobenzene is produced by boiling an ethereal solution with excess of sodium [43]; when a solution of diazoaminobenzene in benzene is boiled with sodium dust (made by shaking molten sodium in hot xylene) the sodium salt is obtained as a yellow granular precipitate, and it can be obtained, also as a suspension in benzene, by distilling to dryness equivalents of diazoaminobenzene and sodium methylate in methanol, then distilling with benzene until all methanol has been carried away. The sodium salt suffers hydrolytic dissociation, but an aqueous-alcohol solution can be obtained by adding one equivalent of aqueous caustic soda to an alcohol solution of diazoaminobenzene; other diazoamino-compounds have been reported as forming sodium salts in the same way, and the imine hydrogen is replaced by boiling such solutions with alkyl halides.[58] The cupric salt, crystallisable from benzene, is made by metathesis of the sodium salt with cupric nitrate, while the lemon-yellow mercury salt, m. p. 226·5—227°, is made by stirring an aqueous suspension of diazoaminobenzene with mercury droplets in presence of air [91] :—

$$2Hg + 4PhN_2{\cdot}NHPh + O_2 = 2(PhN_2{\cdot}NPh)_2Hg + 2H_2O$$

The nickel salt is diamagnetic.[115] The colour changes in the indicator dye Clayton Yellow (C.I. 813), which is a diazoamino-compound of dehydrothiotoluidine, and is turned from yellow to orange-red by mild alkali, may be due to similar salt formation in aqueous solution.

Besides simple salts, diazoamino-compounds also form co-ordination complexes soluble in organic solvents. Thus, when an aqueous solution of sodium chloropalladinate is mixed with aqueous sodium acetate and added to diazoaminobenzene dissolved in methanol, a complex $(Ph_2N_3)_3Pd$ is precipitated; if this is dissolved in pyridine, and water is added, a bisdiazoaminobenzenepyridino complex $(Ph_2N_3)_2Pd,C_5H_5N$ is precipitated, one molecule of diazoaminobenzene being released from the original complex.[114] Mann [117] remarks that the bis-complex is almost certainly planar, and cannot recombine with the third molecule of diazoamino-compound because the latter cannot span the potential 1 : 6-position of the hexacovalent octahedron. Dwyer [114] also discovered other complexes such as the copper bisdiazoaminobenzene-bispyridine and -ethylenediamine complexes.

Some diazoamino-compounds give salts which are dimorphic; these are discussed below in connexion with the configuration of the triazens.

An important reaction of the symmetrical diaryltriazens is their rearrangement as aminoazo-compounds on gentle treatment with an acid in presence of the corresponding arylamine :—

$$ArN_2{\cdot}NHAr \longrightarrow Ar{\cdot}N{:}N{\cdot}Ar{\cdot}NH_2$$

This is the usual technical method of manufacture used for *p*-amino-

azobenzene, and much experimentation has been made to discover whether the reaction is one of intramolecular rearrangement or whether the acid causes scission into diazo-compound and amine followed by coupling. The azo link attaches itself in the *para* position to the amino group, though conditions are known in which a small amount of *ortho* coupling occurs,[72] and the reaction cannot take place if a substituent already occupies the *para* position to the amino-group. A considerable excess of arylamine improves the smoothness and completeness of the reaction; diazoaminobenzene is therefore usually converted into *p*-aminoazobenzene in a solution of aniline and aniline hydrochloride. *p*-Nitrosoaniline was early suggested tentatively as an intermediate in the reaction, but Friswell and Green,[10, 11] on closer examination of the reaction, asserted that diazobenzene is actually formed as free molecules, which then couple with the aniline to form the *p*-aminoazobenzene. If dimethylaniline is used instead of aniline as the reaction medium a considerable part of the product is *p*-dimethylaminoazobenzene, and this can only arise if diazobenzene has actually been in existence.[83] Goldschmidt and his school continued the study of the rearrangement over a long period of years, using dynamic methods and a variety of catalysts. They found the reaction velocity to be that of a unimolecular reaction,[49] that the velocity varies with different acids [50] and while at first anions were believed to be the catalytic agent responsible, they afterwards thought it not impossible that an ammonium ion, NH^3Ph', might play the part.[79] They generally used a large excess of aniline, the diazoamino-compound being dissolved at a concentration of 0·25N with the acid at 0·1N. They considered that the results showed that the reaction could not be other than one of intramolecular change proceeding through an addition product.

Japanese workers have shown that in aniline solution diazoaminobenzene forms salts; this salt formation is postulated as the step preceding scission and recoupling.[80] Rearrangement can also occur in alcoholic hydrochloric acid, though the presence of aniline increases the yield, and benzenediazoaminoazobenzene, $PhN_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}Ph$-*p*, is also found in the reaction mixture, and has been suggested as a link in the rearrangement mechanism.[84, 80] Rosenhauer [86, 88] agrees with the Japanese that scission is initiated by addition of acid to the imino-group, and at the present time the general consensus of opinion agrees with the findings of Kidd's survey [102] that rearrangement takes place through diazobenzene.

Asymmetric triazens formed by combination of β-diazonaphthalene with arylamines of the benzene series undergo rearrangement to an azo-compound by heating with the arylamine hydrochloride, and the product is always the 1-arylazo-2-naphthylamine [77] :—

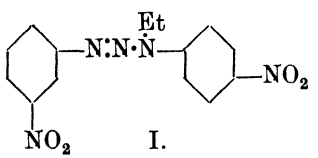
$$\beta\text{-}C_{10}H_7N_2{\cdot}NHAr + NH_2Ar,HCl \longrightarrow$$
$$[\beta\text{-}C_{10}H_7{\cdot}NH_2 + ArN_2{\cdot}Cl + NH_2Ar] \longrightarrow ArN_2{\cdot}C_{10}H_6{\cdot}NH_2 + NH_2Ar,HCl$$

The probability of the above mechanism is further supported by the fact that *p*-tolueneazo-β-naphthylamine is obtaining by heating together diazoamino-*p*-toluene, *p*-toluidine hydrochloride, and β-naphthylamine.[77]

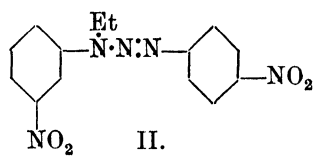
With cyanamide, dicyanodiamide, guanidine, and similar substances diazo-compounds form triazens [75] which are used as components for Rapidogen-type dyes (*vide infra*). The triazen from dicyanodiamide, $CN{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}N_2Ar$, on treatment with ether and moist hydrochloric acid,[75] or better by heating with acid in a high-boiling solvent,[215] loses the diazo-nitrogen to give an arylcyanoguanidine, $CN{\cdot}NH{\cdot}C(:NH){\cdot}NHAr$. By heating the latter with amino-compounds there is thus provided an easy route to substituted diguanides, one of which, 1-*p*-chlorophenyl-5-*iso*propyldiguanide, $p\text{-}C_6H_4Cl{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C(:NH){\cdot}NHPr^{\beta}$, is the anti-malarial drug Paludrine (I.C.I.).

(c) *Constitution of the Diazoamino-compounds.*—In respect of the constitution of the diazoamino-compounds the striking fact that in many cases only one substance, and that bearing all the marks of chemical individuality, is obtained from two dissimilar amines, no matter which is diazotised and combined with the other, early attracted the attention of chemists, and an account of the diazoamino-compounds would be incomplete without mention of the numerous researches which have been undertaken to discover how this comes about. Nor does the fact that the theory of resonance has since shown that they were unlikely to be successful in any way detract from the interest in this work which brought to light so much of the chemistry of the diazoamino-compounds.

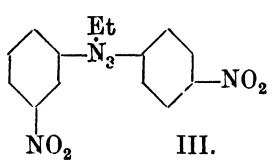
Nölting and Binder [20] found acid-splitting, reduction, acetylation, and alkylation fruitless in attempting to determine whether phenyl-*p*-tolyltriazen is $PhN_2{\cdot}NHC_6H_4Me$ or $C_6H_4MeN_2{\cdot}NHPh$. Meldola and Streatfeild were more fortunate in the choice of *m*-nitrophenyl-*p*-nitrophenyltriazen (made from *m*- and *p*-nitroaniline and their diazo-compounds) for the subject of a series of researches based on the fixation of the imine hydrogen by alkylation. They were able to isolate three isomeric ethyl derivatives :—



I.



II.

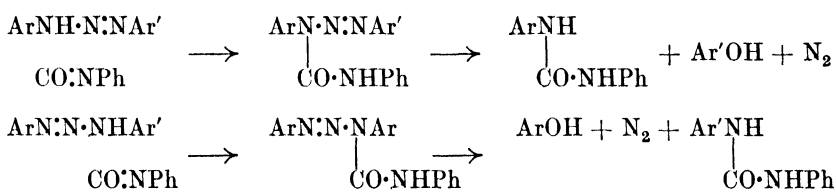


III.

(I) is obtained by coupling diazotised *m*-nitroaniline with ethyl-*p*-nitroaniline, (II) by coupling diazotised *p*-nitroaniline with ethyl-*m*-nitro-

aniline, and (III) by alkylation of the diazoamino-compound made either from *p*-nitrodiazobenzene and *m*-nitroaniline, or *vice versa*. (I) and (II) are different chemical individuals, and (III) is identical with an equimolecular mixture of (I) and (II), and hence it was concluded that the original diazoamino-compound is also an equimolecular mixture.[12, 15, 21, 24, 27] Data derived from absorption spectra by Smith and Watts [70] support this view.

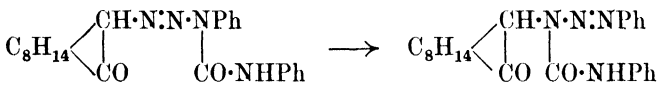
Goldschmidt and his school conducted another sustained attack on the problem, starting from the assumption that the imine hydrogen atom is not labile in non-hydroxylic solvents. In such solvents they fixed it with phenylcarbimide and hydrolysed to produce urea, phenol, and nitrogen. The scheme set out below shows how such a procedure can locate the imine hydrogen atom by the comparison of the hydrolysis products when Ar and Ar′ are two different radicals :—



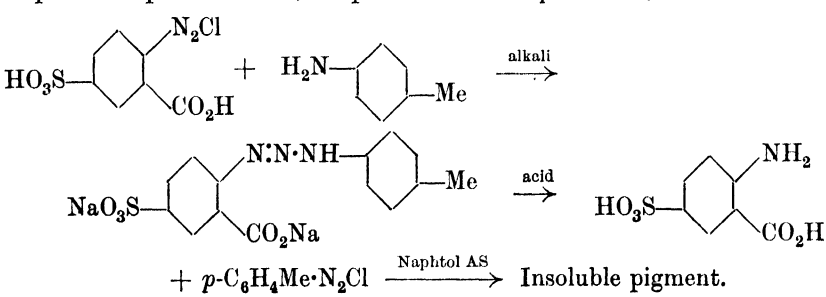
Thus the urea found after hydrolysis will have one constitution or another, according to the position in which the phenylcarbimide found the hydrogen atom to which it attached itself. Goldschmidt and Holm [22] used phenylbenzyltriazen (made from diazobenzene and monobenzylamine), $PhN_2{\cdot}NH{\cdot}CH_2Ph$, as a test case, and their hydrolysis products were phenylbenzyl urea, phenol, nitrogen, and benzyl chloride. They dismissed the latter as a by-product, and allotted to the triazen the structure given above. A number of other triazens derived from benzylamine were examined, the double-linked nitrogen being always found next to the aromatic residue; later Goldschmidt and Molinari [23] laid it down that the double link is always to be found next to the more negative radical.

Dimroth sought to settle the question for his mixed triazens, such as phenylmethyltriazen. But whereas acid scission indicated the structure $PhNH{\cdot}N_2Me$, acetylation and the reaction with phenylcarbimide just as definitely indicated the reverse, $PhN_2{\cdot}NHMe$, and he was ready to believe in the impossibility of distinguishing between either form.[62] With Eble and Gruhl he considered the still more difficult case of the bisdiazoamino-compounds, pointing out that 1 : 5-diphenyl-3-methylpentazdiene, generally supposed to be $(PhN_2)_2NMe$, might have an alternative structure, $PhN_2{\cdot}NPh{\cdot}N_2Me$, because when treated with cold hydrochloric acid it affords one molecule of diazobenzene chloride, one each of aniline hydrochloride, methyl chloride, and nitrogen. To carry the investigation further asymmetric bisdiazoamino-compounds were made for which,

beside the symmetrical structure, two other possible alternatives exist, $ArN_2{\cdot}NAr'{\cdot}N_2Me$ and $Ar'N_2{\cdot}NAr{\cdot}N_2Me$. These, when split by acid, should give different diazo-compounds if the asymmetric structures exist, but experiment shows that however the bisdiazoamino-compound is made the scission products are always the same. These results therefore caused Dimroth and his collaborators to support the symmetrical structure for the bisdiazoamino-compounds, but nevertheless inclined them to agree with Goldschmidt that phenylmethyltriazen is indeed $PhN_2{\cdot}NHMe$.[68] Nevertheless, in phenylcamphoryltriazen Forster and Garland[69] discovered a case which could reconcile Dimroth's contradictory data. They found agreement in the structure as indicated both by acid scission and by phenylcarbimide, and they produced evidence to show that this is due to wandering of the phenylcarbamic radical after attachment to the triazen molecule, a transference which they suggested had been too rapid to observe in other cases :—

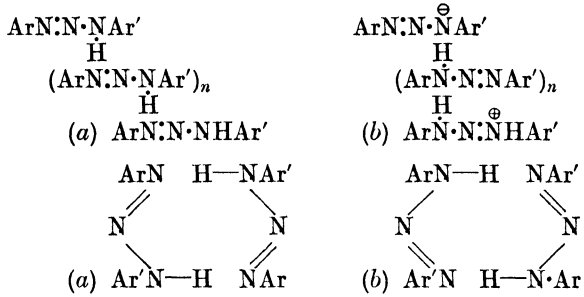


They argued that since in this triazen the doubly-linked nitrogen is attached to the alkyl radical, it probably occupies this position when lower aliphatic radicals are the substituents, and that therefore such triazens are correctly formulated as $PhHN{\cdot}N_2Alkyl$. That Goldschmidt and Molinari may have been deceived by the uncertainty of phenylcarbimide as a reagent for ascertaining structure is suggested by a patent in which use is made of the wandering of the imine hydrogen to secure a technical effect.[173] According to this invention a negatively substituted water-soluble arylamine is diazotised and combined with a less negatively substituted arylamine not having solubilising substituents. A water-soluble diazoamino-compound results, and is dissolved with a coupling-component, such as Naphtol AS, in alkaline solution, thickened, and printed. On treating the print with an acid, an insoluble pigment is produced by combination of the diazo-compound of the water-insoluble arylamine with the Naphtol. For instance, when 4-sulphoanthranilic acid is diazotised, combined with *p*-toluidine, and the diazoamino-compound is split with acid, the product is diazo-*p*-toluene, formed thus :—



A similar series of reactions is reported by Veinberg,[92] *p*-nitrodiazobenzene giving diazoamino-compounds with various aminosulphonic acids, these then rearranging to the diazosulphonic acid and *p*-nitroaniline.

Cryscopic measurements made by Hunter [99] show that asymmetrical diazoamino-compounds dissolved in benzene are associated, though to an extent as yet undetermined. Both chain and ring configurations are envisaged as possibly being formed by hydrogen-bonding thus :—

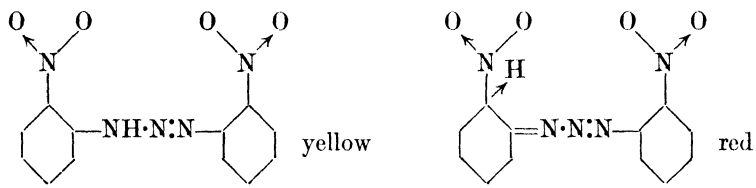


Since the physical form which is handled is a resonance hybrid of the extreme forms (*a*) and (*b*) which each dissociates to a different unimolecular form in solution an explanation is provided for the apparently anomalous results of earlier attempts to determine a supposedly fixed structure which in fact has no existence.

(d) *The Configuration of the Diazoamino-compounds.*—The possibility of geometrical isomerism exists among the triazens, as with all compounds containing an azo link, and from time to time a number of chemists have attempted to effect their resolution, but the results have never been unequivocal.[24, 57, 66, 73, 76] Le Fèvre and Vine [100] interpret their measurements of the dipole moment of diazoaminobenzene and similar triazens as showing that the angle between the two aryl nuclei, which lie in the same plane, is 140°. Nevertheless, diazoaminobenzene is said to be dimorphic and to have a labile form of m. p. 79—80°, first observed by Walther,[56] who obtained it by washing ordinary diazoaminobenzene with light petroleum; Earl and Kenner [81] have since reported this form as arising from the action of aniline on pinene nitrosochloride. Later Earl [94] suggested that Walther's form of low melting point is diazoaminobenzene mixed with benzenediazoaminoazobenzene. The latter substance is an insidious impurity in diazoaminobenzene and quickly appears whenever the latter has been in contact with anions, even at low concentration for a short time; one suspects that some chemists have had in hand diazoamino-compounds somewhat heavily contaminated with it. It can be detected by the deep orange-red colour it gives when dissolved in alcoholic caustic potash, and a criterion for the purity of diazoaminobenzene is that it should dissolve to a yellow colour in that reagent, thereby showing that it is free from benzenediazoaminoazobenzene.

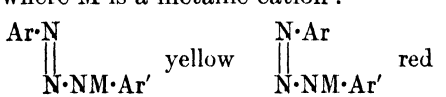
Dwyer [97] discovered that impurities of this type can be removed by adding cadmium hydroxide to a diazoamino-compound dissolved in aqueous methanol, when the diazoaminoazo-compound is precipitated as a brilliantly coloured lake.[97] Alternatively diazoaminoazo-compounds are used as reagents for cadmium ions, and are called "cadion" reagents by Dwyer [104, 106, 107] (for their use in analysis cf. p. 344).

Dwyer finds that dinitrodiazoaminobenzenes, purified as above, and having the nitro-groups *ortho* or *para* to the triazen chain, are dimorphic, having a yellow or "normal" form, obtained by crystallisation from ethanol in presence of aqueous ammonia or ammonium chloride, and a red or "*aci*-form," obtained by crystallising from ethanol or acetone containing a trace of alkali or ammonia; each form depresses the melting point of the other. On the other hand, *m* : *m*′-dinitrodiazoaminobenzene only affords a yellow form, as do also mononitrodiazoaminobenzenes.[108] Dwyer [110] considers that the yellow form is benzenoid and that the red form is quinonoid, the imine hydrogen having migrated to the nitro-group thus :—



4 : 4′-Dinitrodiazoaminobenzene also forms silver and cuprous salts which have a yellow stable form and pass into a purple *aci*-form by co-ordination with one equivalent of ammonia, pyridine, or thiourea; the *aci*-form also gives deeply coloured sodium, potassium, and barium salts, and paler cupric and mercuric salts of the benzenenoid form.

There is, however, another kind of dimorphism which is not of this type, for Mehner [59] found that 4-nitro-2- and -4-methyldiazoaminobenzene are dimorphous; Dwyer [109] confirmed the finding using purified specimens (these mononitrotriazens afford brilliant lakes with magnesium hydroxide) and says the two forms are not "normal" and *aci*-, because both forms have the same colour, do not depress each other's melting point and react at the same speed with aqueous caustic potash. Mangini [111] opposes Dwyer's thesis in its entirety, maintaining that the differences between the salts are due to geometrical isomerism, as was originally suggested by Hantzsch [42, 55] on faulty evidence (cf. p. 387), and that 3 : 3′-dinitrodiazoaminobenzene gives dimorphic salts. Mangini suggests that the light-coloured salts are *trans*-isomerides and the dark-coloured are *cis*-isomerides, thus, where M is a metallic cation :—



So the matter rests at present, though Dwyer and Earl [113] have replied that Mangini has offered no evidence that his experiments were made with triazens free from diazoaminoazo-compounds. The criteria by which such questions of configuration are judged will need refinement before a satisfactory solution is reached.

Aliphatic Diazoamino-compounds.

The purely aliphatic triazens do not fall strictly within the ambit of this book, but are mentioned here for systematic completeness. Long unknown, they were the fruit of Dimroth's sythesis of triazens from an azide and a Grignard reagent; thus dimethyltriazen, the type-member, is produced from methylazide and methylmagnesium bromide. It is exceedingly unstable even in ethereal solution below 0°, and is a liquid, m. p. — 12° and b. p. 92°, having peculiar alkaloidal smell and causing headache by inhalation of the vapour.

The Diazoimino-compounds.

Diazoimino-compounds are formed when a diazo-compound acts under alkaline conditions on a secondary amine, which may be either aromatic, aliphatic, hydroaromatic, or cyclic. Not many triaryltriazens are known, but triphenyltriazen, $PhN_2{\cdot}NPh_2$, is made by the action of diazobenzene on diphenylamine [61, 207]; the number of the other types to which reference may be found in the literature is large, dating from the time of Griess. Baeyer and Jäger [5] made the triazen from diazobenzene and dimethylamine, $PhN_2{\cdot}NMe_2$; Bernthsen and Goske [18] from monomethylaniline and monoethylaniline, $PhN_2{\cdot}NMePh$ and $PhN_2{\cdot}NEtPh$; Wallach [13] from piperidine, $PhN_2{\cdot}N{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}CH_2$; Bamberger and Wulz [31] from monomethyl-*p*-toluidine, $PhN_2{\cdot}NMe{\cdot}C_6H_4Me$-*p*, and from tetrahydroquinoline and its homologues [30]; and Henry and Dehn [118] from morpholine, $PhN_2{\cdot}N{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}O$. Compounds such as the above are colourless to pale-coloured crystalline substances, stable when heated up to about 100°. With no labile hydrogen atom remaining in the molecule, tautomeric phenomena are not possible, nor are salts formed.

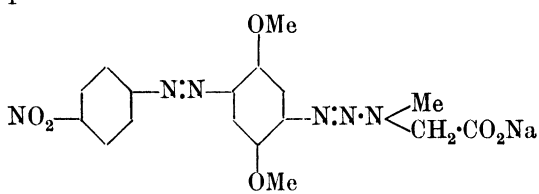
Water-soluble diazoimino-compounds, which are used in the dyestuff industry, are formed as easily as the coupling of diazo-compounds with a component which affords an azo-dye. The following example is typical of the preparation of a diazoimino-compound suitable for a printing mixture :—

. Into an aqueous solution of piperidine-3-sulphonic acid (17 g.) and sodium carbonate (20 g.) is allowed to run at 15° the diazo-solution made from 1-amino-2-methoxy-5-chlorobenzene (11·4 g.). The reaction is soon complete, and the yellow diazoimino-compound salted out with sodium chloride, collected, and dried [162] (Swiss). A triazen is similarly made from pipecolinic acid (piperidine-α-carboxylic acid).

If a diazo-compound is free to combine with either an amino- or an imino-group, as in the amidines, then the combination is with the primary amino-group.[26]

On solution in cold acid the base and the diazo-compound are regenerated, so that, as Wallach first remarked, such a solution behaves exactly as one of the diazo salt; the ease with which scission occurs varies considerably among different individuals. Like the diazoamino-compounds, rearrangement succeeds acid treatment if the molecule contains an aromatic residue in which a coupling position is available; for example, diazoimino-compounds in the tetrahydroquinoline series give azo-compounds coupled in the 6-position.[30]

Arylamines which can be coupled with diazo-compounds retain the power of coupling after conversion into a triazen. For example, *p*-nitrodiazobenzene couples in alkaline solution with the triazen from diazotised 2 : 5-dimethoxyaniline and sarcosine, thus giving the triazen of the aminoazo-compound [186] :—



Applications of the Triazens.

(a) *Dyestuffs.*—Both diazoamino- and diazoimino-compounds split off the diazo-group to form an azo-dye if warmed in solution with a phenol of sufficiently strong coupling power, such as phloroglucinol.[6, 17] The solvent can be omitted, for by melting together diazoaminobenzene and phenol, *p*-hydroxyazobenzene results, a process which was actually suggested in 1886 as a means of obtaining prints of insoluble azo-dyes on calico.[19, 152] Nevertheless, it was not until the second decade of the twentieth century that technical processes based on the use of triazens came into practice, a circumstance that may well excite the curiosity of those interested in the genesis of chemical invention.

Triazens made from diazotised Ice Colour bases and piperidine can be used as passive stabilised diazo-compounds, providing a solution of the regenerated diazo-compound when dissolved in dilute acid, and the use of such solutions for producing Ice Colours has been patented.[153, 154] Had matters remained there the triazens would have continued to be without great technical significance, but a far-reaching step was taken when the diazotised Ice Colour bases were combined with secondary amines carrying sulphonic acid to carboxyl-groups, so that the resultant triazens have solubility in water or dilute alkali. In this form they are specially suitable for calico-printing, for they can be dissolved with the

naphthol, with which no coupling occurs under alkaline conditions, and the thickened solution can be printed on calico and dried without change, nor will any change occur until the print is brought into an acid medium. In this respect they differ from the nitrosamine salts, which, given sufficient time, will couple to completion under alkaline conditions. When the print of the triazen and naphthol is acidified the diazo-compound is regenerated, and at once couples with the naphthol, which is finely divided and in intimate contact with the diazo salt. An insoluble pigment is thus formed in the fibre. The acid treatment is usually applied either by immersing the print in a hot solution of sodium sulphate acidified with acetic and formic acids,[174] or by ageing with steam carrying acetic acid vapour. On soaping off the print the imino-compound which acted as " carrier " or " stabiliser " for the diazo salt is washed out and passes away with the soap. Based on the above principle, the pioneers of this type of dyestuff, the I.G. Company, brought out a complete range of shades as their Rapidogen dyes; with the expiration of the original patents such dyes are now being manufactured by other makers.

Although this splitting and coupling on the fibre is an entirely general reaction, search has been made over a wide field to meet the demands of technical usage, for experience invariably shows that components can by no means be selected at random out of a general class, but choice must be made according to fine differences in properties only to be found by experiment. For example, two important desiderata for triazens suitable for use as components of printing mixtures are (*a*) sufficient solubility and (*b*) correct speed of scission and coupling which will ensure even development in a composite print within the time the cloth takes to pass through the ager. Further, the stabiliser should not be a substance of high molecular weight, or the bulk of triazen needed to produce a heavy shade will be unduly large, while for industrial use cost is not without consideration. It is only possible here to note the salient features of the large patent literature which these problems have brought into being; the expert has no alternative but to con over the original literature.

Among water-soluble imino-compounds which are known to have come into use are those of the general formula HN·RR′, where R and R′ are the same or different radicals one or both carrying one or more carboxylic or sulphonic acid groups; sarcosine, $HNMe{\cdot}CH_2{\cdot}CO_2H$, is the most important member of this group, which also includes dibenzylaminesulphonic acid, methylaniline-4-sulphonic acid and similar substances [157]; they are used to make triazens from bases free from strong negative substituents such as 4-chloro-2-anisidine (Fast Red RC) and the aminodiarylethers.[172] The alkyl-ω-sulphonates, $HN(Alkyl){\cdot}CH_2{\cdot}O{\cdot}SO_3Na$, formed by the action of formaldehyde-bisulphite, on primary alkylamines also belong to this group [155]; methyltaurine, $HNMe{\cdot}[CH_2]_2{\cdot}SO_3Na$, is another useful imine.[161] Among the soluble cyclic imines the sulphonic

and carboxylic acids of piperidine, especially pipecolinic acid (piperidine-α-carboxylic acid),[162] take the front place; similar acids derived from indole, tetrahydrocarbazole, and tetrahydroquinoline are also claimed, but here the increase of molecular weight begins to be a disadvantage.[169] Proline (pyrrole-α-carboxylic acid) and hydroxyproline, both commonly obtained from the hydrolysis products of proteins or glue, have been claimed,[165, 166] and a process has been worked out for recovering the triazens formed when hydrolysed glue is treated with diazo-compounds.[180] Among less useful compounds is piperazine, one imino-group of which can be used to carry a solubilising group while the other is employed for triazen formation.[168]

Imines of quite a different type are those having neither carboxy nor sulphonic acid groups, but deriving water-solubility from a number of hydroxy groups. The chief of these are the secondary sugar amines, $HN(Alkyl)\cdot CH_2\cdot[CH_2OH]_n\cdot CH_2OH$, where $n = 3$ or 4, brought into commerce by the Du Pont Company.[170] Much less soluble triazens are made from diethanolamine, while derivatives of triethanolamine have also been claimed.[179, 200] The triazens from diethanolamine are converted into more soluble polyhydroxy compounds by treatment with ethylene oxide.[208]

Stabilisers of still another type are cyanamide and cyanamide carboxylic acid [75, 176]; these have an advantage in low molecular weight, low cost, and easy scission. Also related to this group are the biguanides, guanylurea-N-sulphonic acids and N-nitroguanylureas introduced by the Calco Chemical Company [194–6]; printing pastes made from these triazens can be dried under vacuum by the manufacturer and the resultant powder only needs the addition of water by the printer to be ready for use.[198] Compounds of the type of guanyltaurine, $NH_2\cdot C(:NH)\cdot NH\cdot[CH_2]\cdot SO_3H$, introduced by the American Cyanamid Co., also belong to this family.[204]

Strongly negatively substituted diazo-compounds form with all the above groups of imines triazens which are only with difficulty split back by acid into their components, and which are therefore quite useless for Rapidogen-type dyes. Diazo-compounds of this type are stabilised with primary and secondary aromatic amines having water-solubilising groups and prevented by such substituents from coupling [158, 159, 160]; for example, 2 : 5-dichlorodiazobenzene affords a triazen with 2-ethylamino-5-sulphobenzoic acid [2 : 1 : 5-$NHEt\cdot C_6H_3(CO_2H)\cdot SO_3H$]. Other stabilisers of the same type which have been patented include aminobenzoic acids having sulphonamide substituents [182, 192] or secondary aminosulphobenzoic acids having hydroxyalkyl or *cyclo*hydroxyalkyl groups attached to the nitrogen.[201]

The most generally used method of developing Rapidogen-type dyes is by acid steam, but the process has operating disadvantages to the printer, and hence dye-makers sought means for its avoidance. One way of doing

this is to pass the dried print through cold mineral acid, and then through a bath of hot acid-binding agent [188]; another device is to pad the woollen or silk textiles with an acid substance before applying the printing paste.[187] Such operations can, however, be avoided by incorporating neutral substances in the paste which will generate acid on plain steaming, and so develop the print. For this purpose can be used either salts which generate acid by hydrolytic dissociation, *i.e.*, salts of strong acids with weak bases,[175] or substances which generate acid by hydrolysis, for example, diethyl succinate, malonamide, or sodium bromoacetate.[177, 178] An ingenious method is to use the triazens as salts of volatile organic bases instead of metallic cations; on steaming the base is removed and the triazen is split by the anion of the stabiliser.[198] Some triazens will split and couple on steaming if the alkalinity is sufficiently reduced without requiring the presence of acid. Rapidogen printing pastes containing such triazens are therefore made alkaline with a volatile oxygen-containing base, for example, β-diethylaminoethanol, $Et_2N{\cdot}[CH_2]_2{\cdot}OH$; the base volatilises on steaming and the print develops.[206] A base suitable for this process has been put on the market as Rapidogen Developer N (I.G.), for use especially with the "N" brand of Rapidogens. Salts of bases such as the acetate of β-propylaminoethanol are also used.[209]

Rapidogen-type dyes made from triazens insoluble in water are also printed from solution in organic solvents [202] and acid-generating substances, such as diethyl tartrate, can be added to such solvent mixtures to cause development [199]; the paste may also be a two-phase emulsion having the triazen dissolved in a solvent forming the discontinuous phase [211] with the coupled component in the continuous aqueous phase, or both components may be in the non-aqueous phase.[212] In spite of the cost of solvents such solutions are advantageous for certain types of fine printing with lightly etched rollers.

In Table XX is given the composition of the Rapidogen dyes and it is seen that five stabilisers suffice for the entire range.[120]

Beside the printing of cotton and regenerated cellulose triazens have patented for dyeing cellulose acetate with Ice Colours. For this purpose the diazotised Ice Colour bases are combined with secondary amines, such as diethanolamine, thus giving sparingly soluble triazens; both the triazen and the coupled component, usually an arylamide of 2 : 3-hydroxynaphthoic acid, are dispersed in a neutral dye-bath from which the fibre absorbs both. The impregnated fibre is then worked in a bath of warm, dilute acid whereupon the triazen is split and the diazo-compound combines with the coupled component giving an Ice Colour within the fibre.[185] Such triazens are claimed to afford shades so fast to soap that they withstand the degumming treatment of natural silk with which the artificial fibres are often blended. Triazens made from amidines are used similarly.[191]

Table XX

Composition of Rapidogen Dyes (I.G.)

Rapidogen dye.	Diazotised amine.	Stabiliser.	Coupling component.
Black IT	5-Nitro-2-aminoanisole	I	*
Black-brown ITR	2-Amino-4-sulphondiethylamido-anisole	II	Naphtol AS-BT
T	4-Chloro-2-aminoanisole	III	AS-BT
Blue B	4-Benzamido-2 : 5-diethoxyaniline	III + IV	AS
R	4-Benzamido-2 : 5-dimethoxy-aniline	IV	AS
Bordeaux IB	5-Nitro-2-aminoanisole	I	AS-BO
R	5-Nitro-2-aminotoluene	II	AS-D
Brown IB	4-Chloro-2-aminoanisole	III	AS-LB
IBR	*p*-Toluidine	III	AS-LB
IR	2 : 5-Dichloroaniline	II	AS-BG
IRR	5-Nitro-2-aminotoluene	II	AS-LB
Corinth IB	6-Chloro-4-benzamido-3-methoxy-aniline	I	AS-LT
Golden-yellow IFG	4-Chloro-2-aminoanisole	III	50313
Golden-orange 12G	*iso*Diazotate of 1-Trifluoromethyl-4-ethylsulphonylaniline	—	AS-D
Green B	4-Benzamido-2 : 5-diethoxyaniline	III + IV	AS-GR
Navy Blue B	Dianisidine	IV	AS
R	4-Benzamido-2 : 5-diethoxyaniline (0·6)	III + IV	AS-BO
	4-Benzamido-2 : 5-dimethoxy-aniline (0·4)	IV	
Olive brown IG	*m*-Chloraniline	V	AS-LB
Orange G	*m*-Chloroaniline	V	AS-D
12R	4-Chloro-3-aminobenzotrifluoride	I	AS-OL
R	2 : 5-Dichloroaniline	II	AS-PH
Red G	4-Chloro-2-aminotoluene	V	AS-D
GS	*Idem*	III	AS-D
12G	2-Amino-4-sulphondiethylamido-toluene	I	AS-LG
ITR	2-Amino-4-sulphondiethylamido-anisole	II	AS-ITR
R	4-Chloro-2-aminoanisole	III	AS-OL
Red-violet 2R	5-Nitro-2-amino-4-methylanisole	II	AS-BO
Scarlet 1L	2 : 5-Dichloroaniline	II	AS-OL
R	4-Chloro-2-aminotoluene	V	AS-PH
RS	*Idem*	III	AS-PH
Violet B	2-Amino-5-benzamido-4-methyl-anisole	III	AS
Yellow GS	4-Chloro-2-aminotoluene	V	AS-G
2G	4-Chloro-2-aminoanisole	III	AS-G
13G	4-Chloro-2-aminotoluene	III	AS-G
14G	5-Chloro-2-aminotoluene	III	42220

Stabilisers. I. 2-Methylamino-5-sulphobenzoic acid, 2 : 1 : 5-$NHMe{\cdot}C_6H_3(CO_2H){\cdot}SO_3H$.
II. 2-Ethylamino-5-sulphobenzoic acid.
III. Sarcosine, $NHMe{\cdot}CH_2{\cdot}CO_2H$.
IV. Methyl taurine, $NHMe{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$.
V. 2-Amino-4-sulphobenzoic acid, 2 : 1 : 4-$NH_2{\cdot}C_6H_3(CO_2H){\cdot}SO_3H$.

* Naphtol AS-SR (0·33) + β-tetralolcarboxy-2-naphthylamide (0·66).

50313 = Benzoylacetic-4-benzamido-2′ : 8′-dimethoxyanilide.
42220 = Acetoacetic-4-chloro-2′ : 5′-dimethoxyanilide.

Another application of triazens in dyestuff technology is to make a water-insoluble pigment containing an imino-group then to confer solubility by attaching the diazo derivative of an amine of high solubility in water; after application to the fibre from a neutral or alkaline bath or printing paste the diazo-compound is split off by acid leaving the pigment in the fibre.[181]

(b) *Therapeutics.*—The idea behind the use of triazens in therapeutics appears to be the same as that actuating the dyestuff technologists, viz., to solubilise a potentially active therapeutic agent in a harmless form which on scission will liberate the active drug in tissues infected by a pathogenic organism. Thus, arsanilic acid (p-$NH_2 \cdot C_6H_4 \cdot AsO_3H_2$) is diazotised and converted into triazens with bases such as dimethylamine, piperidine, and hexamethylenetetramine [78]; or arylamines containing the arsonic acid group are made into triazens with primary or secondary arylamines carrying solubilising group.[203] The latter triazens are said to split *in vivo* giving azoproteins containing arsenic. Aminosulphonamides are also converted into triazens with both types of amines used above; for example, diazotised p-aminobenzenesulphonamide is combined with 2-aminobenzoic-5-sulphonic acid or taurine.[210]

(c) *Rubber.*—The rubber industry has utilised the fact that diazoaminobenzene when heated above its melting point suddenly decomposes with evolution nitrogen, and it is therefore used as the " blowing agent " for making sponge rubber.[119] The diazoaminobenzene is milled into the rubber, in which it is soluble, before curing; the temperature reached in the curing mould causes the evolution of nitrogen, so that the vulcanised product comes out as the well-known sponge. Diazoaminobenzene can also be used to make polyvinyl chloride sponge.[216]

Diazoaminobenzene is also used as a catalyst in making artificial rubber by the copolymerisation of butadiene with acrylonitrile.[213] The polymerisation of butadiene is also brought about by a mixture of tautomeric substances, for example, a mixture of diazoaminobenzene with benzoylacetic acid.[156] 1 : 4-Dienes, including butadiene and chloroprene (2-chlorobutadiene), are also polymerised in aqueous dispersion in presence of a diazonium salt, for example, p-nitrobenzenediazonium chloride, or of triazens, for example, those derived from diazobenzene and cyanamide, or m-chlorodiazobenzene and sarcosine, and thus afford plastic polymers free from sulphur.[215] This initiation of polymerisation is due to free radicals produced by homolytic scission of the diazo-compound or the triazen.

(d) *Motor Fuel.*—Bisdiazoamino-compounds having either aryl or alkyl radicals at 3 are claimed as anti-knock agents for Diesel fuel.[205]

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150	Wolf	—	277,182	—	—	—	—
151	Wolf	—	285,335	—	—	—	—
152	B. Fischer, H. Michaelis	—	—	40,890	*Fr.* 1, 548	—	—
153	I.G.	306,844	1,880,522	525,399	*Fr.*, **18**, 1096	670,216	—
154	I.G.	308,660	1,893,991	526,879	*Fr.*, **18**, 1098	36,748	—
155	I.G.	309,610	1,879,424	502,334	*Fr.*, **17**, 1065	673,052	143,022
156	Resinotrust	314,933	—	—	—	—	144,753–4
157	I.G.	320,324	1,882,560	500,437	*Fr.*, **17**, 1058	674,638	143,023
		—	1,882,561	510,441	*Fr.*, **17**, 1060	674,195	144,756
		—	1,882,562	—	—	—	144,859
		—	—	—	—	—	148,341–3
158	I.G.	324,041	1,867,088	513,209	*Fr.*, **17**, 1062	677,579	145,151
		—	1,871,850	531,008	*Fr.*, **18**, 1055	37,246	148,962–7
		—	1,874,524	532,401	*Fr.*, **18**, 1058	37,909	149,889
		—	—	535,076	*Fr.*, **18**, 1057	—	150,173–4
		—	—	550,711	*Fr.*, **19**, 1623	—	150,784–7
		—	—	552,283	*Fr.*, **19**, 1622	—	151,141
159	I.G.	329,353	1,858,623	535,670	*Fr.*, **18**, 956	37,203	—
		—	1,882,556	—	—	—	—
160	I.G.	334,529	1,882,561	534,640	*Fr.*, **18**, 1046	690,393	—
161	I.G.	388,721	—	530,396	*Fr.*, **18**, 1049	40,315	—
162	I.G.	407,840	2,051,148	—	—	43,580	169,351
		—	—	—	—	—	171,586–9
		—	—	—	—	—	171,590–1
163	S.C.I.	—	—	G.80,257	*Fr.*, **19**, 1653	739,705	—
164	Du Pont	—	1,979,327	—	—	—	—
165	Pharma	—	1,982,681	—	—	—	—
166	Du Pont	422,195	2,008,750	—	—	758,889	—
		—	2,021,911	—	—	—	—
167	I.G.	422,488	—	—	—	—	—
168	I.C.I.	423,587	—	—	—	775,097	—
169	I.G.	427,803	—	—	—	—	—
170	Du Pont	429,618	1,968,878–9	P.68,587	*Fr.*, **22**, 876	764,755	—
171	Kuhlmann	—	—	—	—	735,698	—
172	S.C.I.	—	—	—	—	44,032	—
173	I.G.	433,878	—	I.46,720	*Fr.*, **22**, 876	769,838	175,677
174	Du Pont	435,171	2,035,518	—	—	—	—
175	I.G.	436,371	—	639,238	*Fr.*, **23**, 912	785,334	—
176	I.G.	443,222	2,054,397	614,198	*Fr.*, **22**, 872	777,401	178,541
		—	2,049,674	615,846	*Fr.*, **22**, 873	—	185,832
		—	—	624,765	*Fr.*, **22**, 874	—	177,932
177	I.G.	452,482	—	640,935	*Fr.*, **23**, 887	786,012	—
178	Du Pont	454,869	2,088,506	—	—	—	—
179	Heaton	457,763	—	—	—	811,550	—
180	I.C.I.	458,808	2,111,692	—	—	—	—
181	I.C.I.	—	2,115,149	—	—	—	—
182	Kuhlmann	459,342	2,069,461	—	—	800,876 807,893	—
183	Du Pont	463,305	—	—	—	—	—
184	Heaton	463,515	—	—	—	—	—
185	I.C.I.	464,511	2,132,456	—	—	809,615	—
186	I.G.	465,484	2,168,800	—	—	811,898	—
187	I.G.	466,846	—	639,288	*Fr.*, **23**, 908	798,425	—
188	S.C.I.	469,578	—	—	—	—	—
189	I.G.	480,169	2,124,594	—	—	824,620	202,226
		—	2,125,087	—	—	—	—
190	Du Pont	481,019	2,098,861	—	—	—	—
191	I.G.	496,678	—	—	—	—	—
192	I.G.	—	—	671,788	—	—	—

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193	Solvay Process Co.	—	2,133,037	—	—	—	—
194	Calco Chem. Co.	507,260	2,125,509	—	—	835,986	—
195	*Idem*	515,980	2,154,470	—	—	840,445	—
196	*Idem*	515,981	2,154,405	—	—	—	—
197	Du Pont	534,271	—	—	—	—	—
198	Calco Chem. Co.	535,805	—	—	—	—	—
199	Durand & Hugenin	539,912	—	—	—	—	—
200	Heaton, Howis	540,978	—	—	—	—	—
201	Kuhlmann	541,912	—	—	—	—	—
202	Interchem. Corp.	552,919	—	—	—	—	—
203	Kuhlmann	—	2,166,681	C52,257	—	—	—
204	Amer. Cyanamid	—	2,185,152	—	—	—	—
205	Socony-Vacuum Co.	—	2,188,262	—	—	—	—
206	I.G.	34,786/38	2,232,405	—	—	846,748	209,625
207	Szpilfogl	—	—	—	—	854,330	—
208	Du Pont	—	2,257,091	—	—	—	—
209	Gen. Anil. & Film Corp.	—	2,257,190	—	—	—	—
210	Winthrop Chem. Co.	—	2,308,675	—	—	—	—
211	Interchem. Corp.	—	2,309,946	—	—	—	—
212	*Idem*	—	2,310,012–3	—	—	—	—
213	F. B. Goodrich Co.	—	2,313,233	—	—	—	—
214	Du Pont	571,009	—	—	—	—	—
215	I.C.I.	576,401	2,409,832	—	—	—	—
216	Pirelli	19,027/46	—	—	—	—	—

In addition to the foregoing tabulated patents the following is a list of patents for the manufacture and use of triazens as Rapidogen-type dyes using similar components :—

Amer. Cyanamid Co., U.S.P. 2,185,154; 2,199,003; 2,200,926; 2,299,244–5; 2,314,652; 2,339,934; 2,369,307–9; 2,375,012.

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General Aniline Works, U.S.P. 2,173,324.

Interchem. Corp., U.S.P. 2,375,132.

May Chemical Corp., U.S.P. 2,267,760. F.P. 840,666.

National Aniline Co., U.S.P. 2,122,424; 2,155,942; 2,169,736–7; 2,190,841; 2,229,744.

Pharma Chemical Corp., 1,986,276; 2,105,326; 2,110,270; 2,149,703; 2,162,960.

Patents in the table above against which no patentee's name appears are equivalents of the one(s) above.

GROUP 2. OXIDATION PRODUCTS OF DIAZO-COMPOUNDS

Diazo-compounds can be oxidised in aqueous solution under carefully regulated conditions to form substances which Bamberger called " diazoic

acids ". These substances are, in fact, the aryl nitroamines, $Ar{\cdot}NH{\cdot}NO_2$, and are more suitably named as such rather than by a name which would be appropriate to the diazohydroxides. The reaction is carried out with alkaline oxidising agents, and both normal and *iso*-diazotates afford the same nitroamine. Here is provided yet another example of the way in which diazo-compounds in alkaline solution behave as if they have the nitrosamine structure — $Ar{\cdot}NH{\cdot}NO \longrightarrow Ar{\cdot}NH{\cdot}NO_2$.

Bamberger [24] prepared α-naphthylnitroamine as follows :—

α-Naphthylamine (10 g.) is melted with hot water in a dish, and hydrochloric acid, *sp. gr.* 1·18 (45 c.c.), is slowly added with stirring until a creamy mass is obtained which is cooled with ice inside and outside and diazotised with agitation with sodium nitrite (4·8 g.) dissolved in water (50 c.c.). The clear red diazo solution is filtered and run in a thin stream into a solution of potassium ferricyanide (100 g.) dissolved in water (300 c.c.) with solid caustic potash (55 g.) and chilled with an ice-salt freezing mixture. The temperature on mixing must not rise above — 4°, and after mixing the solution is set aside at 0° for fourteen hours, then filtered and poured into a dish, which is kept at room temperature in the dark for twenty-four hours, then filtered from sôme β-naphthaquinone-α-diazide. The filtrate is made acid with dilute sulphuric acid, the temperature not rising over 10°; the nitroamine crystallises from the milky emulsion and is collected, washed with ice-water, and dried on a tile. The yield of yellow crystals is 1·8—2·0 g., m. p. 123—4°.

Bamberger and Storch [1, 10] used cold, strongly alkaline potassium ferricyanide when they first demonstrated the oxidation of diazobenzene to phenylnitroamine. This reaction indicates that the normal benzene diazotate obtained by adding alkali to a benzene diazonium salt must be in equilibrium with the nitrosamine which is the body actually oxidised :—

$$PhN{:}N{\cdot}OK \text{ or } Ph\overset{O}{\overset{\uparrow}{N}}{:}NK \longrightarrow [PhNK{\cdot}NO] \longrightarrow PhNH{\cdot}NO_2$$

The yield of nitroamine is 55% [3]; later Bamberger [6, 12] obtained a better yield from previously prepared benzene *iso*diazotate. Oxidation can also be carried out with permanganate [2]; nitrosobenzene (2—3%) is also found among the oxidation products. Phenylnitroamine is also obtained by the action of cold caustic alkali on diazobenzene-perbromide [7, 11] accompanied by a little nitrosobenzene.

Hydrogen peroxide attacks only the normal diazotates of benzene and *p*-chlorobenzene; if the solution is made so strongly alkaline that the *iso*diazotates are present, then oxidation ceases. Moreover, the normal *p*-chlorobenzene diazotate affords not only *p*-chlorophenylnitroamine but also nitroso-*p*-chlorophenylhydroxylamine, $p\text{-}C_6H_4Cl{\cdot}N{<}^{NO}_{OH}$ [19]

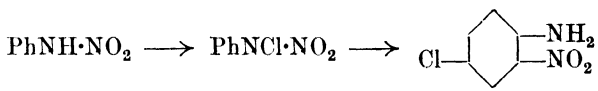
Nitrosoacetanilide is also oxidised by hydrogen peroxide to nitrosophenylhydroxylamine in 94% yield, the acetyl group being removed as acetic acid.[20] Bamberger thought that nitrosohydroxylamines are the precursors of the nitroso-compounds which appear in the oxidation of diazo-compounds by ferricyanide or permanganate because with alkaline oxidising agents they break up into nitroso-compound and alkali nitrite.

Bamberger [4] demonstrated that his diazoic acid is a nitroamine by showing the identity of the oxidation product of diazobenzene with the substance obtained by acting on aniline in ethanol solution with nitrogen pentoxide: $2NH_2Ph + N_2O_5 = 2Ph{\cdot}NH{\cdot}NO_2 + H_2O$.

Most arylnitroamines are colourless substances in which the imino-group is so acidic that they form stable salts. They are unstable, and can be preserved only in the dark and while free from acid; when exposed to light they at once begin to turn yellow as the nitro-group commences to migrate to the ring, thus forming the nitroarylamine. Phenylnitroamine affords a mixture of *o*- and *p*-nitroaniline, the former predominating.[3] The rearrangement is brought about in solution by any acid and is intramolecular, but it is not the only reaction which occurs, for Bradfield and Orton [25] reported that 2 : 4-dichloro- and 2 : 4-dibromo-phenylnitroamine always give at the same time a substance of undetermined constitution able to couple. α-Naphthylnitroamine also affords two products, giving 2-nitro-1-naphthylamine in acid medium and 1 : 2-naphthaquinone diazide (1 : 2-naphthalenediazo-oxide) in alkaline medium.[24] If rearrangement is prevented by substituents, as in 5-nitro-*m*-4-xylylnitroamine ($1 : 3 : 5 : 6\text{-}NO_2{\cdot}C_6H_2Me_2{\cdot}NH{\cdot}NO_2$), then the action of acetic-sulphuric acid produces the diazonium salt with other substances.[23]

Nitroamines are reduced back to *iso*diazotates by mild reducing agents such as zinc dust and dilute ammonium chloride.[23] When both a nuclear and a N-nitro-group are present, as, for example, in the nitroamine obtained by oxidising 4-nitro-2 : 5-dimethoxydiazobenzene, then the nuclear nitro-group is preferentially reduced by aqueous sodium sulphide, leaving the N-nitro-group untouched.[26]

The hydrogen atom of the imino-group in nitroamines can be replaced by chlorine by treatment with hypochlorite forming chloroimides in which acids cause migration of both chlorine and nitro-group to the ring [3]:—



Nevertheless, diazotates can be oxidised in weakly alkaline solution with hypochlorite to nitroamines.[16, 17, 18] Hypochlorite is the reagent chosen for technical use, and it can be used to prepare the nitroamines of the anthraquinone series,[21, 22] whilst in the benzene series it is used for diazo-compounds already having halogen substituents in the nucleus, such as 2 : 5-dichlorodiazobenzene [27]; diazo-compounds of this type give a high proportion of *iso*diazotate in weakly alkaline solution.

Like the diazo-compounds from which they are derived, the nitroamines are tautomeric, though the tautomerism is not strongly marked, and there is no doubt that it is structural. The sodium and silver salts when treated with methyl or ethyl iodide give two different ethers, just as does *p*-nitrobenzene *iso*diazotate. The ether derived from the sodium

salt has the alkyl group attached to nitrogen, and has the constitution $Ar{\cdot}NAlkyl{\cdot}NO_2$, while the ether derived from the silver salt is an O-ether, to which Bamberger [13] tentatively assigned the constitution

$$ArN{:}N\begin{matrix}\nearrow O\\ \searrow OAlkyl\end{matrix}$$

The O-ether is not well defined where the aryl radical is benzene [3] but *p*-nitrophenylnitroamine affords two well-defined ethers: the N-methyl ether, m. p. 140°, and the O-methyl ether, m. p. 109·5°.[13] The N-ethers behave like secondary nitroamines; they are hydrolysed by alkali to secondary arylamine and nitrate; sodium amalgam reduces them to the asymmetric hydrazine; on irradiation the nitro-group migrates to the ring, chiefly into the *ortho* position. The O-ethers couple on boiling with β-naphthol or on mixing with alcoholic α-naphthylamine; they are reduced by sodium amalgam to *iso*diazotate; they give off formaldehyde when heated,[23] a characteristic also of benzeneazonitronic ethers, $PhN_2{\cdot}CR{\cdot}NO{\cdot}OMe$, and some amine-oxides, $R{\cdot}NMe_2O$.

Hantzsch [8, 14, 15] attempted to derive different geometrical forms for the above ethers, and suggested that phenylnitroamine itself has the structure $\begin{matrix}Ph{\cdot}N\\ \|\ \diagup O\\ N{\cdot}HO\end{matrix}$, but the facts do not give scope to make out a strong case on these lines.

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27. S.C.I., B.P. 447,514; D.R.P. 630,967 (Fr., **23**, 883); F.P. 783,305; Sw.P. 175,350.

GROUP 3. REDUCTION PRODUCTS OF THE DIAZO-COMPOUNDS: THE ARYLHYDRAZINES

Reducing agents which do not detach the nitrogen atoms from the aryl nucleus convert diazo-compounds into arylhydrazines, $ArNH{\cdot}NH_2$, whether reduction is carried out in acid or alkaline solution. The reagent most generally applicable is sulphurous acid or alkali sulphite, and hydrazine mono- or di-sulphonic acids, in which the sulphonic acid group is attached to nitrogen, may appear as intermediate stages in the reduction. The first stage of the action of sulphite, especially in neutral solution, is the coloured diazosulphonate $ArN{:}N{\cdot}SO_3Na$ (cf. p. 147 *et seq.*), and this may, if desired, be isolated and reduced to the arylhydrazine sulphonic acid with reagents such as zinc dust and acetic acid, sulphurous acid, hydrosulphite, or stannous chloride. In the reduction of anthraquinone-α- and -β-diazonium sulphate the diazosulphonate appears as a distinct stage even when sufficient sulphite for complete reduction is taken at the outset; then on heating the yellow faintly acid solution of diazosulphonate and sulphite to 90° the solution suddenly becomes red, as reduction by sulphurous acid occurs with formation of the anthraquinonyl hydrazine disulphonic acid, $AQN(SO_3H){\cdot}NH{\cdot}SO_3H$.[22] Similar changes are seen when substituted anthraquinonediazonium salts, such as 4 : 8-dihydroxyanthraquinone-1 : 5-tetrazonium sulphate, are reduced with hot sodium bisulphite solution.[21] When, however, at least two molecular equivalents of sulphite are present, a diazonium salt of the benzene or naphthalene series is usually reduced forthwith to a hydrazine sulphonic acid, but Davies [25] has shown that substituents in the diazo-compound affect both the course of the reaction and the end-product. Thus benzenediazonium chloride and *p*-nitrobenzenediazonium chloride are differentiated as follows:—

$$PhN_2{\cdot}Cl + 2Na_2SO_3 + H_2O = PhNH{\cdot}NH{\cdot}SO_3Na + NaCl + Na_2SO_4$$

$$NO_2{\cdot}C_6H_4N_2{\cdot}Cl + 2Na_2SO_3 + H_2O = NO_2{\cdot}C_6H_4{\cdot}N_2H(SO_3Na)_2 + NaCl + NaOH$$

The first reaction has been known since 1871, when it was discovered by Strecker and Römer.[1] E. Fischer [2] showed that the hydrazinesulphonic acids of the benzene series are distinguished from the diazosulphonates in being colourless or only weakly coloured, and that they are strong reducing agents for silver and copper salts, whilst with red mercury oxide they are oxidised back to the diazosulphonate. In the anthraquinone series some hydrazine monosulphonic acids are oxidised to the diazosulphonate by air, but the disulphonic acids resist such oxidation [21]; the latter are strongly coloured substances and can be used as acid dyes for wool.[21] On boiling hydrazinesulphonic acids with dilute mineral acid the sulphonic acid groups are easily removed by hydrolysis and the arylhydrazine is freed by adding alkali.[2, 4] Reduction of a diazo-compound

to the hydrazinesulphonic acid followed by hydrolysis has become the standard industrial process for the manufacture of arylhydrazines, some of which are produced in considerable quantity.

Phenylhydrazine-*p*-sulphonic acid is made by E. Fischer's process as follows [23] :—

Sodium sulphanilate (23 kg.) is diazotised, and the solid diazo-compound (cf. p. 10) is suspended in water (200 l.), and there is added quickly a solution of sodium bisulphite made by dissolving sodium sulphite (30 kg.) in water (300 l.) and passing in sulphur dioxide until the specific gravity is 1·18. The diazo-compound dissolves with a yellow colour which soon disappears, and then hydrochloric acid (50 kg.) is added, and the solution is evaporated to crystallisation; the hydrazine is collected and recrystallised from hot water.

It has long been known that *p*-nitrodiazobenzene must be reduced to *p*-nitrophenylhydrazine with sulphite,[12] and Davies prepares that substance as follows [24] :—

Sulphur dioxide is passed into a mixture of ammonia (*sp. gr.* 0·88) (1) and ice (2 pts.) in a freezing mixture, and any free sulphur dioxide is neutralised with more ammonia; at room temperature the solution deposits ammonium sulphite and contains 0·25 g. of SO_2 per c.c.

p-Nitroaniline (10 g.), diazotised with 36% hydrochloric acid (21 c.c.), is added to the above solution (40 c.c.) mixed with ammonia (*sp. gr.* 0·88) (8 c.c.); efficient cooling is necessary, for ammonium *p*-nitrophenylhydrazine sulphonic acid separates with evolution of much heat. The salt is collected after remaining for one hour in a freezing mixture, and the yellow solid is heated for seven minutes at 70—80° with hydrochloric acid (*sp. gr.* 1·18, 20 c.c.); the blood-red solution is cooled, the precipitate is cooled in water, and the base is precipitated with sodium acetate solution. It is almost pure, and is recrystallised from ethanol in light brown leaves, m. p. 157° (decomp.); the yield is 9·0 g.

Kindlmann [29] using sodium sulphite in a similar procedure claims a 72% yield.

Some diazonium salts can be satisfactorily reduced under neutral conditions with sodium hydrosulphite [24] but when reduction is carried out under more acid conditions with bisulphite, the sulphur may combine directly with the aryl radical, the nitrogen being lost. The sulphinic acid which results then condenses with the hydrazine to form a sulphazide, $ArNH{\cdot}NH{\cdot}SO_2Ar$.[3, 8] The sulphazides are really sulphonhydrazides, and can be made by condensing arylhydrazines with sulphonyl chlorides. Grandmougin [20] obtained both sulphazide and phenylazide as by-products on reduction of benzenediazonium chloride with sodium hydrosulphite, and their formation cuts down the yield of phenylhydrazinesulphonic acid to 37%.

Diazonium salts can be reduced direct to hydrazines with stannous chloride, which is often the most convenient way of preparing hydrazines in small quantity for laboratory purposes [5] :—

$$ArN_2{\cdot}Cl + 2SnCl_2 + 4HCl = ArNH{\cdot}NH_2{,}HCl + 2SnCl_4$$

Phenylhydrazine is prepared direct from benzenediazonium chloride with this reagent as follows [5] :—

Aniline (10 g.) as a suspension of the hydrochloride in hydrochloric acid (*sp. gr.* 1·18, 200 c.c.) is diazotised with sodium nitrite (7·5 g.) dissolved in water (50 c.c.),

and to the solution is added stannous chloride (45 g.) dissolved in hydrochloric acid (*sp. gr.* 1·18, 45 c.c.), the whole being cooled in ice. Reduction is almost instantaneous, and a white crystal mass of phenylhydrazine hydrochloride is formed; the base is freed with caustic alkali, extracted with ether, and distilled.

While this method is convenient, it lacks the wide application of the method of E. Fischer, who early pointed out its limitations.[6] Among diazonium compounds which cannot be reduced to a hydrazine with stannous chloride are those of the anthraquinone series,[21, 22] *p*-nitrobenzenediazonium chloride,[10] and benzene-*o*-tetrazonium chloride, which is reduced back to *o*-phenylene diamine.[28] On the other hand, anthraquinone diazosulphonates can be reduced by stannous chloride,[22] as can *m*-nitrodiazobenzene, which affords *m*-nitrophenylhydrazine in 50% yield,[10] and *m*-oxamidodiazobenzene, which on reduction and removal of the oxalic acid residue affords *m*-aminophenylhydrazine.[7] If less than the two molecular equivalents of stannous chloride needed by the above equation is taken, no hydrazine is formed, but a mixture of compounds is obtained in which is found chiefly the azide (doubtless formed from diazo-compound and hydrazine, cf. p. 189), and the original amine with lesser quantities of phenol and parent hydrocarbon.[9]

Metallic diazotates are reduced to hydrazines by sodium amalgam in caustic alkaline solution; Bamberger [15, 16] said that normal diazotates are not reduced by sodium amalgam, but Hantzsch produced the hydrazines from normal and *iso*diazotates.[17, 18] The method is only of theoretical interest. If the medium is dilute acetic acid, sodium amalgam reduces diazobenzene back to aniline, and this, combining with unattacked diazobenzene, produces diazoaminobenzene.[14] Phenylhydrazine is also produced when benzenediazonium chloride or benzenediazosulphonate is reduced electrolytically at a mercury cathode.[27]

The action of zinc diethyl on benzenediazonium chloride in dry ether at $-15°$ is one of reduction, the principal product being αβ-diethylphenylhydrazine.[19]

There is some evidence that normal sodium benzene diazotate is reduced to phenyldi-imide, PhN:NH, a substance which has never been isolated, but the possible presence of which can be deduced from the production of β-benzoylphenylhydrazine, PhNH·NH·COPh, when diazobenzene is reduced with sodium stannite in the presence of alcohol and benzaldehyde. Angeli and Jolles [26] interpret the reaction as proceeding in two stages; in the first the normal diazotate is reduced to di-imide :—

$$\begin{array}{l} \mathrm{PhN{:}NNa + H_2 = PhN{:}NH + NaOH} \\ \quad\quad\quad\

by ascorbic acid, when an almost quantitative yield of the *l*-threonolactone of *p*-tolylhydrazido oxalate,

$$\underline{CO{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH}{\cdot}O{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_4Me\text{-}p,$$

is precipitated. Weidenhagen and Wegner [30] explain this as formed by reduction of the diazo-compound to *p*-tolyldi-imide with oxidation of the ascorbic acid to dehydroascorbic acid; the latter adds water at the keto-group, while the di-imide simultaneously removed hydrogen, and the bond at 2 : 3 is broken to give the oxalate of *l*-threonic acid,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2(CO_2H){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CO_2H;$$

this at once condenses with the *p*-tolylhydrazine and lactonises.

The arylhydrazines are strongly basic substances, usually low-melting solids when carboxy and sulphonic acid groups are absent, though some, like phenylhydrazine, are oils. Many people are sensitive to their power to cause dermatitis. They are characterised by a strong reducing action on copper and silver salts; if boiled with Fehling's solution the nitrogen is quantitatively evolved, a reaction which serves both as a means of analysis and also of generating the parent hydrocarbon of the diazo-compound.[11, 13]

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GROUP 4. REACTIONS WITH NITROGEN BASES. THE FORMATION OF ARYLAZIDES (DIAZOIMIDES, AZOIMIDES)

Diazo-compounds interact with a variety of nitrogen-containing substances able to give up hydrogen attached to nitrogen, and arylazides often appear as the predominant product; intermediate compounds containing a chain of nitrogen atoms may or may not be isolable. Phenyl azide was made by Griess [1] by interaction of diazobenzene perbromide with ammonia, and on account of this method of synthesis he called the substance diazobenzene imide, and determined the constitution as PhN_3. The compounds have for a long time passed under the name of azoimides, both in English and German writings, but as they are derivatives of hydrazoic acid, HN_3, in which the hydrogen atom has been replaced by an aryl nucleus—a fact first demonstrated by Curtius—it is better to call them by their correct systematic name rather than by a " trivial " name. The N_3 group is also known as the azido radical, and this is a convenient way of naming compounds in which it occurs more than once, *e.g.*, 4 : 4′-bisazidodiphenyl, a compound early prepared by Griess.[2] Until 1933 it was generally believed that the three nitrogen atoms are arranged in a ring, though an open-chain constitution had been suggested by some chemists; Pauling and his co-workers have now shown that they are certainly arranged in a linear form, and that the surprising stability of the aryl and alkyl azides, always one of the chief props for the ring structure, is due to high resonance energy.[46] Hence, because so much energy can be given up in the process of their formation, they appear as the chief end-products of many reactions of the diazo-compounds, and at other times in traces, being always detectable by their peculiar odour.

Phenylazide, the type member of the family of arylazides, is an oil at ordinary temperatures, and while it must be handled with care, is not so dangerous as might be feared. The oil can be distilled with steam and also under vacuum, but it explodes if boiled at atmospheric pressure; it has a peculiar penetrating odour. With increasing substitution or weight of the aryl nucleus the arylazides become solids of varying degrees of stability, usually melting with decomposition.

Although interaction of diazo-perbromides with ammonia to form arylazides is a general reaction of wide application, the diazo-compounds do not undergo the same reaction, but form bisdiazoamino-compounds with ammonia (cf. p. 160); the diazo-plumbichlorides and -iodochlorides, however, give the arylazides directly by reaction with ammonia, just as do the perbromides.[41] Substitution of a hydrogen atom in ammonia by a negative atom or group makes it possible to obtain arylazides by direct reaction with diazo-compounds. Thus a solution of chloroamine, made by adding sodium hypochlorite to cold aqueous ammonia, gives a small

yield of phenylazide when mixed with a solution of diazobenzene, possibly through a chlorodiazoamino-compound [33] :—

$$PhN_2{\cdot}OH + NH_2Cl \longrightarrow (PhN_2{\cdot}NHCl + H_2O) \longrightarrow PhN_3 + HCl$$

It is claimed that sodium N-chloro-*p*-toluene sulphonamide (" Chloramine T ") converts diazo-compounds into arylazides in good yield.[43]

Hydroxylamine reacts smoothly with diazo-compounds, and intermediate hydroxydiazoamino-compounds have been observed. At first it appeared as if the arylazide is the only end-product,[5] but it is now known that the intermediate compound can break up either to form the arylazide or to regenerate the original arylamine, according to the experimental conditions [15] :—

$$ArN_2{\cdot}Cl + NH_2OH \longrightarrow (ArN{:}N{\cdot}NHOH) \begin{cases} \longrightarrow ArNH_2 + N_2O \\ \searrow ArN_3 + H_2O \end{cases}$$

By running the diazo salt into alkaline hydroxylamine, high yields of the amine can be recovered, but if the diazo solution and hydroxylamine are mixed in weakly acid or neutral solution, and then made alkaline, the arylazide is the chief product. This latter synthesis is suitable for the preparation of the hydroxyarylazides, since the *o*- and *p*-diazobenzene oxides do not form perbromides; *m*- and *p*-hydroxyphenylazide are formed by stirring the diazo-compound with excess of hydroxylamine in sodium carbonate solution when the intermediate hydroxydiazoamino-compound slowly decomposes [29, 30] :—

$$p\text{-}\overset{\ominus}{O}{\cdot}C_6H_4{\cdot}\overset{\oplus}{N}_2 + NH_2OH \longrightarrow p\text{-}OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}NHOH \longrightarrow p\text{-}OH{\cdot}C_6H_4{\cdot}N_3 + H_2O$$

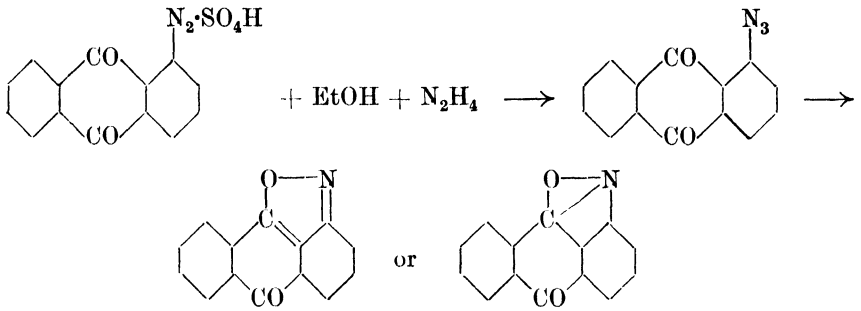
o-Hydroxyphenylazide is made by the perbromide route starting from the toluenesulphonic ester of *o*-aminophenol.[30]

Diazo-compounds attach themselves to the amino-group in N-aryl- and N-alkyl-hydroxylamines, forming stable hydroxydiazoamino-compounds of the type $ArN{:}N{\cdot}N(OH){\cdot}Ar'$. These are only decomposed by strong acids either to their generators or to nitrogen, phenols, and other decomposition products.[25, 36] On the other hand, the O-benzyl ether of hydroxylamine gives phenylazide with diazobenzene in alkaline medium :—

$$PhN_2{\cdot}OH + NH_2{\cdot}O{\cdot}CH_2Ph \longrightarrow PhN_3 + PhCH_2{\cdot}OH + H_2O$$

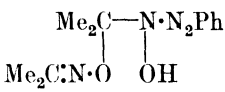
Potassium hydroxylamine mono- or di-sulphonate give good yields of the arylazide with diazo-compounds derived from negatively substituted arylamines such as *p*-nitrodiazobenzene.[28] In the anthraquinone series the hydroxydiazoamino-compounds are stable substances, and 1-(hydroxydiazoamino)anthraquinone requires treatment with acetic anhydride to remove water and form anthraquinone-1-azide.[35] The latter is an

unstable substance, and passes into anthranil,[34] which is the only product when anthraquinone-1-diazonium sulphate is treated with hydrazine in alcohol[37] :—



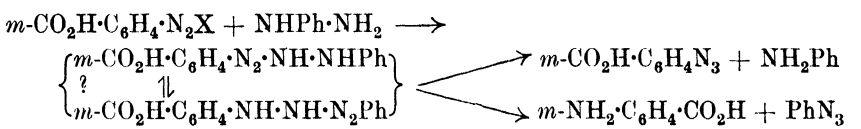
1 : 5 and 1 : 8-bisazidoanthraquinone, made by the perbromide synthesis, are stabilised when one azide group has formed the anthranil; 1 : 4-bisazidoanthraquinone slowly transforms itself into the dianthranil.[42]

Oximes condense in a similar way to hydroxylamine, except that two molecules condense with each one of the diazo-compound. Thus diazobenzene condenses with two molecules of acetone oxime to give a substance to which Bamberger[26] and Mangini[45] assigned the constitution :—



The *p*-tolyl analogue treated with sulphuric acid gives *p*-tolylazide, *p*-toluidine, and acetone oxime.

With hydrazine and the arylhydrazines the reactions of the diazo-compounds are more complicated than those above, as an intermediate compound with a chain of four nitrogen atoms is probably formed, and can tautomerise and break in two ways. Hence the interaction of phenylhydrazine with *m*-diazobenzoic acid in mineral acid solution gives phenylazide, *m*-carboxyphenylazide, aniline, and *m*-aminobenzoic acid, and the same products are obtained from diazobenzene and *m*-hydrazinobenzoic acid[3] :—



A similar result is obtained with the perbromide of diazotised sulphanilic acid and phenylhydrazine.[8] The hypothetical tautomeric intermediate shown above has never been isolated, the nearest approach being a substance formed from diazobenzene and hippurylhydrazine which is decomposed by alkali or dilute mineral acids to form chiefly phenylazide and

hippuramide, but also aniline and the decomposition products of diazo-hippuramide, *i.e.*, hydrazoic acid and hippuric acid [21] :—

$$PhN_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NHBz \begin{cases} \longrightarrow PhN_3 + NH_2{\cdot}CO{\cdot}CH_2{\cdot}NHBz \\ \longrightarrow NHBz{\cdot}CH_2{\cdot}CO_2H + HN_3 + NH_2Ph \end{cases}$$

In the simplest case of diazobenzene and hydrazine four products are obtained [21] :—

$$PhN_2Cl + N_2H_4 \longrightarrow (PhN_2{\cdot}NH{\cdot}NH_2) \begin{cases} \longrightarrow PhN_3 + NH_3 \\ \longrightarrow NH_2Ph + HN_3 \end{cases}$$

Naturally if the aryl radical is the same in the diazo-compound and the arylhydrazine, only two compounds are formed, *e.g.* [4, 5, 21] :—

$$PhN_2Cl + NHPh{\cdot}NH_2 \longrightarrow PhN_3 + NH_2Ph$$

The reaction between diazo-compounds and hydrazines explains why azides may appear as by-products in the reduction of diazo-compounds to hydrazines by stannous chloride.[10]

Benzenediazonium acetate combines at low temperature with phenylhydrazine acetate, but under these conditions it is the imino hydrogen atom which is removed, giving a fairly stable hydrazide, $PhN_2{\cdot}NPh{\cdot}NH_2$, though, as some phenylazide and aniline are also produced, the hypothetical unstable compound formed by attack of the diazobenzene on a β-hydrogen atom of the phenylhydrazine must also be formed.[23, 27] The above hydrazide on warming with *m*-phenylenediamine in alcohol gives chrysoidine, showing that diazobenzene has been regenerated.

In contrast with the arylhydrazines, the acylhydrazines give stable diazohydrazides which can be isolated and on treatment with alkali form tetrazoles by ring-closure (cf. p. 266).[32]

By substituting one of the hydrogen atoms in ammonia with an arylsulphonyl-group, the capacity to form arylazides with diazo-compounds is greatly enhanced. The main reaction of diazo-compounds with sulphonamides proceeds thus [38, 44] :—

$$ArSO_2{\cdot}NH_2 + Ar'N_2{\cdot}Cl = ArSO_2H + Ar'N_3 + HCl$$

A side-reaction which complicates the matter is the condensation of the sulphinic acid with the unused diazo-compound to form diazo-sulphone, and the reaction serves better for the synthesis of sulphinic acids than arylazides. The reaction proceeds with especial readiness with methane sulphonamide, $Me{\cdot}SO_2{\cdot}NH_2$.[40]

Diazo-compounds are converted into arylazides with special ease, and in good yield by interaction with hydrazoic acid [19] :—

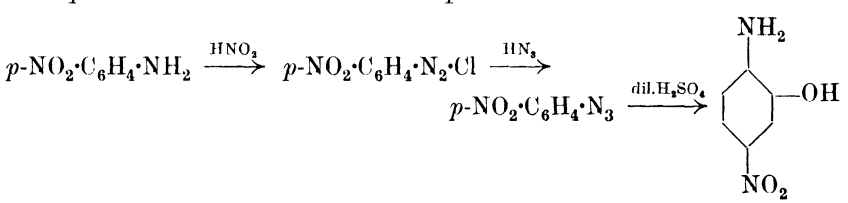
$$ArN_2{\cdot}Cl + HN_3 = ArN_3 + N_2 + HCl\ *$$

* As this reaction proceeds with loss of the diazo nitrogen atoms, it should strictly be considered under Group 3 of Section E, but it is more convenient to take it here.

This reaction has been much used, for it is more convenient than the diazo-perbromide synthesis, and it only fails when the arylazide formed is unstable in cold weakly acid solution, as is, *e.g.*, *p*-hydroxyphenylazide. This route is the only satisfactory one for the preparation of the naphthylazides, as the diazonaphthalenes give less than 5% yield of the azide with hydroxylamine or hydrazine.[31] α-Naphthylazide is prepared as follows [31]:—

α-Naphthylamine (30 g.) dissolved in acetic acid (180 c.c.) is mixed with cooling with sulphuric acid (*sp. gr.* 1·83, 80 c.c.) and diazotised with a solution of sodium nitrite (15 g.) dissolved in water (40 c.c.); after ten minutes urea (5 g.) is added to the solution, followed by sodium azide (15 g.) dissolved in water (50 c.c.). A colourless turbidity results and nitrogen is given off rapidly. After keeping at 0—3° for several hours the oil is extracted with ether and the residue is steam-distilled for four hours. The distillate is extracted with ether, and the ether solution is washed twice with aqueous hydrochloric acid (*d* 1·13), then with 20% caustic soda, and dried with calcium chloride. Removal of the ether leaves a pale oil which crystallises on keeping; weight 27 g., m. p. 12°. Attempts to distil at 2 mm. induce decomposition, and it has a persistent odour of ethoxynaphthalene.

Most arylazides are not attacked by cold concentrated hydrochloric acid, but explode in contact with concentrated sulphuric acid; [7] hot concentrated hydrochloric acid converts phenylazide into a mixture of *o*- and *p*-chloroaniline, whilst dilute sulphuric acid (approx. 50%) gives *p*-aminophenol. This reaction does not always go smoothly, and fails, *e.g.*, with *p*-bisazidobenzene, but it is often useful with the nitroarylazides.[23] For example, it is possible to prepare 5-nitro-2-aminophenol from *p*-nitroaniline *via* the diazo-compound and the azide:—



The reaction is also applicable in the naphthalene series.[31]

2 : 4-Dinitrophenylazide is split by alcoholic caustic potash into 2 : 4-dinitrophenol and potassium azide.[13]

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GROUP 5. S-AZO-COMPOUNDS OR DIAZO-THIOETHERS

Diazo-compounds do not couple with thiophenols or thionaphthols, but form thioethers which have the general constitution $ArN{:}N{\cdot}SAr'$; they are easily formed by interaction of a diazonium salt with a thiophenol in dilute caustic alkali.[1] Diazobenzene thiophenol ether is oily and unstable,[1] but diazobenzene and 2-thionaphthol combine at — 6° to form diazobenzene 2-thionaphthol ether, $PhN_2{\cdot}S{\cdot}C_{10}H_7$-β, m. p. 59·5—60·5°.[2] Polythiol-compounds, such as dithioresorcinal and 1 : 5-dithiolnaphthalene, combine twice to give bisdiazo-thioethers, $(ArN_2{\cdot}S)_2Ar'$.[4]

The diazo-thioethers are more stable than the analogous O-ethers already described under Group 2 (cf. p. 139), and are not attacked by dilute acid or alkali in the cold, but are split back to diazonium salt and thiophenol by concentrated sulphuric acid. They are destroyed by boiling water, giving nitrogen, phenols, thiophenols, and diaryl sulphides.[1] Cotton padded with an alkaline solution of 2-thionaphthol develops a beautiful pure yellow shade by treating with a solution of *p*-nitrodiazobenzene; the diazo-thioether is, however, useless as a dye, as it is not fast to hot water.[3]

Diazo-thioethers are also formed by interaction of diazo-compounds

with aliphatic compounds containing the thiol group, such as thiolacetic acid, which affords S-azo-compounds of the constitution

$$ArN_2 \cdot S \cdot CH_2 \cdot CO_2H$$ [2];

tetrazo-compounds, such as tetrazoxylene,[5] form bis-S-azo-compounds with thiolacetic acid. Thioacetic acid, Me·CO·SH, also combines with diazo-compounds.[2] The diazo ethers formed from aliphatic thiols are usually less stable than those derived from the thiophenols, whilst those derived from the xanthates are often explosive; they are of some importance, as they appear as isolable intermediate steps in the replacement of the diazo-group by sulphur-containing radicals (cf. p. 324).

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CHAPTER VI

REACTIONS OF THE DIAZO-COMPOUNDS (*continued*)

CLASS C. GROUP 6. THE FORMATION OF AZO-COMPOUNDS BY THE COUPLING REACTION. INTRODUCTORY—COUPLING OF PHENOLS AND NAPHTHOLS, AMINO-COMPOUNDS, PROTEINS, *m*-AMINO-*p*-CRESOL, AMINONAPHTHOLSULPHONIC ACIDS—PREVENTION OF MIXED COUPLINGS—COUPLING OF SUBSTANCES HAVING REACTIVE METHYLENE GROUPS, NITROPARAFFINS, PHENOL ETHERS, HYDROCARBONS—ELIMINATION OF SUBSTITUENTS—MIGRATION OF THE DIAZO-GROUP—EFFECT OF PYRIDINE—CONFIGURATION OF THE AZO-COMPOUNDS—KINETICS OF THE COUPLING REACTION—MECHANISM.

GROUP 6. FORMATION OF AZO-COMPOUNDS BY THE COUPLING REACTION

Introductory.—The diazo-compounds are oxidising agents; in the current theory of valency they are classed as cationoid reagents, *i.e.*, electron acceptors. Therefore they naturally replace a hydrogen atom attached to carbon when that atom is activated by an anionoid group, *e.g.*, hydroxyl, amino, the keto-enol complex, certain unsaturated hydrocarbon groups, and others. A covalent N·C link is formed and the diazo-compound is said to have coupled :—

$$ArN_2{\cdot}X + HR = ArN_2R + HX$$

HX may be a molecule of either acid or water. If the coupled compound contains more than one hydrogen atom of sufficient reactivity, then coupling may take place twice or more.

The products of the reaction comprise the huge family of azo-compounds. Strictly they are the C-azo-compounds, for diazo-compounds can also become attached to the nitrogen of amino-compounds, thus forming triazens (cf. Chapter V), or to oxygen, or sulphur atoms. The three latter classes of compounds are quite different from the azo-compounds proper, and the O-azo-compounds formed from highly acidic phenols are ionised salts; it is a convenient usage to denote compounds of these three classes as N-azo-, O-azo-, and S-azo-compounds.

Whatever may be the structure of the original diazo-compound, there is no doubt that the two nitrogen atoms which make the azo-link in the completed and stable azo-compound are both trivalent, a fact which is proved by reductive scission of the link to produce two molecules of amine :—

$$Ar{\cdot}N{:}N{\cdot}R \xrightarrow{2H_2} ArNH_2 + RNH_2$$

But though the azo-link is usually written as above ·N:N·, it will be shown

below that it may function as a hydrazone link, :N·NH·, in molecules which have quinonoid or keto-enol tautomeric forms.

Because the azo-compounds are strongly coloured, the presence of a diazo-compound can be detected in a solution at very low concentration, for on mixing with a solution of a colourless coupling component under correct conditions a characteristic colour at once appears. Whether the solutes in any two solutions will couple is easily determined by putting a drop of the coupling component on filter paper and adding a concentric drop of diazo solution; if coupling occurs a coloured spot at once appears. If no colour or only a weak shade appears the spot is held over an ammonia bottle, and coupling may then occur when the solution reaches the correct degree of alkalinity (*vide infra*). If the result is at all ambiguous a blank must be carried out on a spot of the diazo-compound alone, as many diazo solutions become yellow or orange on making alkaline.

The simplest monoazo-compounds are yellow to red, though by choosing appropriate diazo-compounds and coupling components monoazo dyes in shade as deep as blue and green are made. As more complex molecules are built up by diazotising azo-compounds containing amino-groups and repeating the coupling process, so an array of polyazo-compounds is marshalled in which all the colours of the visible spectrum are found as well as compound shades like black, brown, and grey. Many hundreds of these substances are used as dyestuffs for every purpose, and constitute the great class of azo dyes.

There are a number of reactions by which azo-compounds can be produced. For instance, the parent substance azobenzene, PhN:NPh, was made by Mitscherlich by distilling nitrobenzene with alcoholic potash twenty-four years before Griess discovered the diazo-compounds, but the manufacture of nearly all the azo-compounds which are used as dyestuffs depends on the coupling reaction, while the number of azo-compounds which could be made by coupling all the known diazo-compounds with all the known coupling components would run to many millions. The task in this chapter is therefore neither to discuss azo-compounds as such nor to catalogue many examples from the literature, but to consider the chemical principles of the coupling reaction so that it may be applied at need by chemists other than the few who are specialists in azo dyes.

The coupling reaction is nearly always carried out in aqueous solution, and the factor which has the dominating influence on the coupling of any particular diazo-compound with any particular second component is the pH of the solution, a factor to which the diazo-compound is especially sensitive. Early experimenters soon observed that coupling is controlled by degree of acidity; for example, Wallach [1] remarked that whereas diazobenzene and diazotoluene couple in acid solution with resorcinol, diazoxylene will not do so, but couples when alkali or alkali acetate is added. Liebermann [2] noted that the same diazo-compound will couple

with α-naphthol in more acid solution than β-naphthol, whilst Cain and Nicoll observed that diazo-compound and coupling component can exist side by side indefinitely in acid solution. Variation of pH can not only prevent coupling, but can bring about another reaction in some cases; thus diazo-compounds couple at 3 with 2-hydroxy-1 : 4-naphthaquinone in dilute acetic acid, but in warm dilute sodium carbonate nitrogen is eliminated and the aryl nucleus enters at 3. Further, couplings which will not take place in aqueous medium occur at the same pH in alcohol,[31] and methanol has been used as the coupling medium for diazo-compounds having several negative substituents with arylamines.[15] Coupling in aqueous solution can also be aided by adding naphthalene-β-sulphonic acid.[14]

Goldschmidt pointed out that it is the diazohydroxide which is active in coupling, and hence it is around the neutral point that coupling takes place most readily and most completely. In the graph of stability on page 99 the area in which coupling occurs is roughly that between pH 5·0 and 9·0 for phenols and pH 3·5 and 7·0 for arylamines. As this is the area where stability falls to a low value, the coupling reaction must always be looked on as a race between azo-compound formation and decomposition of the diazo-compound, so much so that the latter sometimes far outstrips the desired coupling. The diazodiphenylamines are a case in point, for if these are made alkaline they are irreversibly converted into quinone diazides, hence when they are to be used to develop blue dyeings on cotton padded with alkaline arylamides of 2 : 3-hydroxynaphthoic acid there are added to the bath water-soluble salts of amines unable to couple, *e.g.*, triethanolamine, or organic ammonium compounds, *e.g.*, stearylpyridinium hydroxide.[10] Phosphates are used to buffer coupling solutions of the diazo derivatives of the 4-aryloxyacetamido-2 : 5-dialkoxyanilines

$$[1 : 4 : 2 : 5\text{-}NH_2{\cdot}C_6H_2(NH{\cdot}CO{\cdot}CH_2{\cdot}OAr)(O\ Alkyl)_2],^{9}$$

and chromium salts can also be used.[13] Another type of diazo-compound which does not usually couple well above pH 7 are the diazo-oxides.

The main support for the knowledge of the existence of the diazonium-diazo equilibrium rests on coupling experiments, and an idea of the pH at which the diazonium salt begins to be converted into the diazo-compound may be gained by carrying out coupling at different degrees of acidity. When this is done it is found that as negative substituents increase in the molecule, so the diazo-compound is able to couple in increasingly acid solution, until at last coupling occurs in strong acid. Schoutissen took a series of twenty-four diazo-compounds, commencing with diazobenzene, and attempted to couple with β-naphthol in a mixture of one part of sulphuric acid (*d* 1·84) and two parts of phosphoric acid (*d* 1·7). 2 : 4 : 6-Trichlorodiazobenzene first gives indications of coupling, 2 : 4-dinitrodiazobenzene couples strongly, and the series culminates in 2 : 4 : 6-trinitrodiazobenzene. Equal with the latter is *p*-tetrazobenzene,

which couples once only, the second diazo-group not coupling until the acid has been neutralised. Not only was Schoutissen thus able to obtain asymmetric disazo-compounds, but at the same time he demonstrated that in tetrazo-compounds where both groups are attached to the same aromatic ring one diazo-group is in the diazonium form and one in the diazo-form.[7] *Ortho-* and *m*-tetrazobenzene also couple in acid solution in the same way.[11, 8]

Griess first prepared one of the simplest monoazo-compounds, *p*-hydroxyazobenzene, which he found among the products of decomposition of an aqueous solution of diazobenzene nitrate brought to neutrality with barium carbonate. He deduced correctly that diazobenzene had combined with phenol formed by decomposition of diazobenzene, and he also detected the smaller quantity of twice-coupled azo-compound, 2 : 4-bis(benzeneazo)phenol.[20] The appearance of the latter compound as the result of the attempt to couple diazobenzene with anthranil led Heller to the study of the effect of hydroxyl ions on coupling,[34] while Griess's experiments have been extended to a wider range of diazo-compounds by Hodgson and Marsden using calcium carbonate as the neutralising agent.[52]

Kekulé and Hidegh [21] in 1870 first carried out the coupling reaction as now understood by interacting diazobenzene and phenol derived from a different source and dissolved in caustic soda; they obtained *p*-hydroxyazobenzene, which they recognised as identical with Griess's product, although they had set out to obtain the O-azo-compound, $PhN_2 \cdot OPh$, a substance which still remains unknown.

Substances which will couple with diazo-compounds are included in the following classes :—

1. Phenols and naphthols.
2. Amino-compounds, including proteins.
3. Naphthol-, naphthylamine-, and aminonaphthol-sulphonic acids.
4. Substances having reactive methylene groups.

To these must be added two classes which only afford azo-compounds under exceptional conditions or with specific diazo-compounds :—

5. Phenol ethers.
6. Hydrocarbons.

The Coupling of Phenols and Naphthols.—Although phenols and naphthols can be coupled as finely-divided suspensions in water, they are usually dissolved in dilute caustic alkali, and the diazo-compound after neutralisation is added with stirring to this solution. Because most phenols and naphthols are weak acids they undergo considerable hydrolytic dissociation, and Goldschmidt showed that it is the hydrolysed phenol, and not the alkali phenate, which couples. Hence two causes

operate to stop coupling if the pH becomes too high, (*a*) the amount of dissociated phenol is diminished, (*b*) the diazo-compound may form an *iso*diazotate. It may be expected, therefore, that the limits of pH will be narrow, within which a strongly acidic phenol can be coupled with a diazo-compound like diazoxylene, which needs fully alkaline conditions for coupling, and that in general weakly acidic phenols couple best over a wide range of pH with such diazo-compounds, whilst negatively-substituted diazo-compounds are needed to form azo-compounds easily with strongly acidic phenols.

The position from which the diazo-compound first detaches a hydrogen atom when coupling with a phenol is *para* to the hydroxy-group.[23] A small amount of the *ortho*-hydroxy-azo-compound is also formed, and can be separated by distillation with steam, in which a number of these compounds, including *o*-hydroxyazobenzene itself,[27] are volatile.[40] If the *para* position is occupied, then the attack is transferred to the *ortho* position, and this transference occurs if the *para* position has already been occupied by the azo-group, hence disazo-compounds result. The tendency for this to occur is pronounced in weakly acidic phenols like thymol and carvacrol.[24] Ultimately, if the solution is made progressively and sufficiently alkaline, phenol couples three times, forming 2 : 4 : 6-trisazophenol compounds, in which all the aryl radicals may be the same or different.[28, 29, 33, 34, 35] α-Naphthol couples both at 2 and 4, and the proportions in which the two positions are attacked depends on the diazo-compound, and also on the pH, but in general strong couplers attack first at 4 and the weak couplers at 2. Separation and identification of the isomerides are easy, because those having the azo-group *para* to hydroxyl are soluble in dilute caustic alkali, while those in which it is *ortho* are insoluble or only sparingly soluble.

The capacity of phenols to couple is naturally affected by substituents; negative substituents tend to make coupling difficult, as in salicylic acid or 4-nitro-2-naphthol, whilst among fused-ring systems deactivation of the coupling position can occur, as in 5-hydroxy-6-methylhydrindene, which only couples to the extent of 30% with *p*-nitrodiazobenzene in very dilute alkali,[44, 45] and 3-hydroxypyrene, which does not couple, although 4-hydroxypyrene does so.[48] Richardson[46] made experiments in which phenol and substituted phenols (equal molecules) were coupled competitively in the same solution with *p*-nitrobenzenediazonium sulphate; an excerpt from his tabulated results is given on p. 199.

From the above it is seen that chlorine exerts a more powerful deactivating effect than bromine, whether it is *ortho* or *meta* to the coupling position, whereas iodine slightly activates the coupling position while methoxyl has, as is well known, a powerful activating influence, particularly when in the *meta* position.

Since positive substituents increase the speed with which coupling occurs, it follows that resorcinal couples more easily than phenol, *i.e.*, over a wider range of pH and with more diverse diazo-compounds, and, like phenol, it affords trisazo-compounds, the second and third azo-groups being attached at increasing pH.[30, 32] Such trisazo-compounds may be formed from three molecules of the same diazo-compound, or different diazo-compounds may be successively attached.[41] For long it was con-

TABLE XXI

Coupling of Mixtures of Phenols

Mixture of phenols.	Mol. coupling ratio.	Coupling velocity ratio.
	Phenol = 1.	Phenol = 1.
1. *o*-Chlorophenol and Phenol . .	0·63	0·51
2. *o*-Bromophenol ,, . .	0·89	0·84
3. *o*-Iodophenol ,, . .	1·09	1·13
4. *m*-Chlorophenol ,, . .	0·50	0·36
5. *m*-Bromophenol ,, . .	0·73	0·63
6. *m*-Iodophenol ,, . .	1·16	1·24
	o-Bromophenol = 1.	*o*-Bromophenol = 1.
7. *o*-Chlorophenol and *o*-Bromophenol .	0·70	0·50
8. *o*-Iodophenol ,, .	1·19	1·09
9. *o*-Cresol ,, .	4·23	6·60
10. Guaiacol ,, .	12·45	28·40

sidered that resorcinol is the only dihydric phenol which will couple, but catechol couples under the correct conditions,[25] and azo-compounds can be obtained from quinol by benzoylating one of the hydroxy-groups,[26] or converting it into the sulphuric ester.[49]

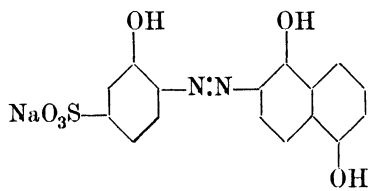
Seven of the principal mono- and poly-hydric phenols can be arranged in the following descending order of coupling power :—

Phloroglucinol, α-naphthol, resorcinol, β-naphthol, catechol, phenol, salicylic acid.

β-Naphthol is paramount in importance for the manufacture of azo dyes, while the arylamides of 2-hydroxy-3-naphthoic acid are used in large quantities for Ice Colours on cotton and insoluble pigments in substance. Coupling can occur only once, in the 1-position in the naphthalene ring, and the hydroxy-group, being *ortho* to the azo-link, is no longer able to form salts, and hence the dyes are not altered in shade by alkali or soap. The fact that β-naphthol cannot couple at 3 has been used as part of the argument for the fixity of the double links in the naphthalene nucleus.[43] α-Naphthol, if substituted in the 4-position by an acetyl group so that coupling must occur in the 2-position, gives azo-compounds which are also little affected by alkali, as does also *p*-cresol. α-Naphthol also couples at 2 in strongly alkaline medium with diazotised *o*-amino-phenol-5- or -6-sulphonic acid also substituted, *e.g.*, by halogen, at 4.[51]

Mercuration of phenols and naphthols does not prevent coupling [39] with sulphonated diazo-compounds and the azo-compounds are rendered soluble by treatment with concentrated hydrochloric acid.[50]

By analogy with α-naphthol it might be expected that 1 : 5-dihydroxynaphthalene would couple no less than four times, yet in fact it is difficult to attach more than one azo-link. O. Fischer and Bauer coupled it with diazobenzene in dilute alkali, with and without pyridine, also in aqueous alcohol in presence of acid and of sodium acetate, but each experiment gave the monobenzeneazo-compound with attachment at 4.[36] They succeeded in attaching two benzeneazo-groups at 2 and 4 in the same ring by working in concentrated aqueous alkali, but could force no more combination even in alcohol. The valuable acid chrome dyestuff, Diamond Black PV (C.I. 170), is made by coupling diazotised *o*-aminophenolsulphonic acid to 1 : 5-dihydroxynaphthalene under alkaline conditions so that coupling occurs in the 2-position, and thus the link in the azo-dyestuff molecule has two *ortho*-hydroxy-groups,[37] thus :—



Diazotised anthranilic acid, however, couples at 4.[37]

A few instances are recorded of an expected coupling reaction taking an entirely different course. For example, α-diazopyridine fails to couple with phenol, but loses nitrogen giving a mixture of α-(*o*′- and *p*′-hydroxyphenyl) pyridine,[38] and while *o*- and *p*-propenylphenol couple normally with *p*-nitrodiazobenzene in dilute alkali, yet with purified *p*-nitrobenzenediazonium sulphate in alcohol *p*-hydroxybenzaldehyde-*p*′-nitrophenylhydrazone (*p*-OH·C_6H_4·CH:N·NH·C_6H_4·NO_2-*p*′) is produced in 60% yield; *o*-propenylphenol affords the corresponding *o*-hydrazone.[42]

The Coupling of Amino-Compounds and Proteins.—Though arylamines show the same general behaviour as phenols, they are differentiated by a lower level of reactivity. They couple *para* to the amino-group, except β-naphthylamine and its congeners, which couple at the 1-position of the naphthalene ring. In aniline the 4-position is so weakly activated that few diazo-compounds can couple to form aminoazo-compounds, though 1-diazoanthraquinone is able to do so.[77] Substitution of the benzene ring by alkyl- and alkoxy-groups, provided the 4-position is left clear, facilitates attack by the diazo-compound, and aminoazo-compounds are formed easily from primary arylamines such as *p*-xylidine (1 : 2 : 5-NH_2·$C_6H_3Me_2$), cresidine (1 : 5 : 2-NH_2·C_6H_3Me·OMe), *m*-toluidine, 2 : 5-dimethoxy- and -diethoxy-aniline [1 : 2 : 5-NH_2·$C_6H_3(OEt)_2$],

and 2-chloro-5-methoxyaniline (1 : 2 : 5-$NH_2 \cdot C_6H_3Cl \cdot OMe$); the amino-azo-compounds so produced can be diazotised and coupled again and some containing the above bases are used as Ice Colour components (cf. p. 102). But these amines do not show the same capacity to form polyazo-compounds as is shown by phenol; when a free hydrogen atom is not available in the *para*-position to the amino-group the *ortho* position is rarely attacked unless strongly activated. Thus dimethyl-*p*-toluidine and *p*-chlorodimethylaniline do not couple,[72] but 4-methyl-2 : 5-dimethoxyaniline [1 : 4 : 2 : 5-$NH_2 \cdot C_6H_2Me(OMe)_2$] couples once *ortho* to the amino-group,[82] while 3-methoxy-*p*-toluidine (1 : 4 : 3-$NH_2 \cdot C_6H_3Me \cdot OMe$) couples with diazotised *o*-chloro-*p*-nitroaniline to an *o*-aminoazo-compound which can be diazotised (cf. p. 103). *o*-Aminoazo-*p*-toluene is made by rearranging diazoamino-*p*-toluene, since *p*-toluidine does not couple,[62] but *o*-aminoazobenzene cannot be made even by this method, but is made by condensation of nitrosobenzene with monobenzoyl-*o*-phenylenediamine, followed by hydrolysis [74]:—

$$PhNO + o\text{-}NH_2 \cdot C_6H_4 \cdot NHBz \longrightarrow Ph \cdot N{:}N \cdot C_6H_4 \cdot NHBz \longrightarrow Ph \cdot N{:}N \cdot C_6H_4 \cdot NH_2\text{-}o$$

As already noted, β-naphthylamine couples at 1, and so affords *o*-aminoazo-compounds, but these cannot be diazotised, but oxidise with ease to triazoles, some of which are patented as dyestuffs. α-Naphthylamine couples in both the 2- and 4-position, being more strongly activated than the amines of the benzene series; Griess refers to coupling diazobenzene with "naphthalidine".[60]

Just as resorcinol couples better than phenol, so the *m*-diamines couple more freely than the monoamines and can form disazo-compounds, first prepared by Griess by coupling diazo-compounds with chrysoidine.[61] Stable trisazo-compounds corresponding with the trisazo derivatives of resorcinol are not easy to obtain but have been reported.[89] Both monochloro- and mononitro-*m*-phenylene diamine couple well, and are used as intermediates for azo dyes. Morgan and his co-workers carried out a thorough series of researches on the coupling of *m*-diamines, and their findings may be stated in a very condensed form as follows[70]: (i) *m*-diamines having one or two substituents so placed that there is one free hydrogen atom *para* to an amino-group couple easily whether the amino-group are primary or completely alkylated, (ii) di-*p*-substituted *m*-diamines [1 : 3 : 4 : 6-$(NH_2)_2 \cdot C_6H_2 \cdot XY$] couple to form *o*-aminoazo-compounds but not easily, (iii) the substituents XY exert an influence on the course of coupling, for when both are methyl the base reacts with diazobenzene, but when both are halogen (Cl, Br, or I) only nitrodiazo-compounds will couple; when there is one methyl and one halogen (Cl or Br), diazobenzene and diazo-*p*-toluene afford only very small yields of *o*-aminoazo-compounds, (iv) progressive N-alkylation of the di-*p*-substituted diamines reduces their capacity to form azo-derivatives; the

symmetrical and asymmetrical dimethyl compounds give mixtures of triazens and azo-compounds, the trimethyl compounds give triazens, and complete alkylation suppresses reaction with diazo-compounds.

The heterocyclic 4 : 6-diaminopyrimidine couples at 5 with strongly-coupling diazonium salts.[88]

The diamines of the naphthalene series have nothing like the value of the corresponding dihydroxy-compounds as coupling components. 1 : 5- and 1 : 8-Naphthylenediamine have been used as developing agents for Primuline and direct cotton dyes diazotised on the fibre,[65 67] while dyes have been made by coupling twice with 1 : 5-naphthylene diamine, but there is no information as to where the azo-links are attached or whether the four links theoretically possible can be in fact attached.

The coupling power of primary amines may be enhanced not only by substituents in the benzene ring but also by replacement of the primary amino hydrogen atoms by aryl or alkyl groups. Both dimethylaniline and diphenylamine couple more easily than aniline; phenyl-α- and -β-naphthylamines couple once in the naphthalene ring with diazobenzene-*p*-sulphonic acid either in dilute hydrochloric acid or in acetic acid, but αβ-dinaphthylamine couples at 4 in one ring in dilute hydrochloric acid and at 2 in the other in dilute acetic acid.[60] Diphenyl-*p*-phenylene diamine, which may be looked on as a bis-diphenylamine, does not couple.[83] Karrer [75] said that aniline dialkylated with butyl and higher alkyl groups loses one of these on coupling, but Hickinbottom was not able to repeat the experiment, and found that dibutylaniline couples unchanged.[76, 85] Substitution of tertiary aromatic amines in the *ortho* position prevents coupling in the *para* position and dimethyl-*o*-toluidine is well known for its inertness to nitrous acid and to diazo-compounds,[63] though it is said to couple with 2 : 5-dichlorodiazobenzene.[71]

An easy way of securing the effect of alkylation on bases like aniline which couple with difficulty is to warm the base with an equivalent of aqueous formaldehyde-bisulphite, whereupon the base dissolves and a clear solution of the methyl-ω-sulphonate is obtained :—

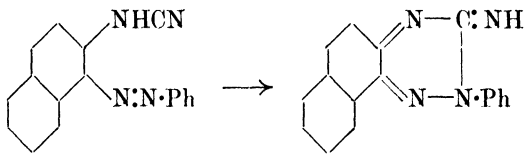
$$PhNH_2 + OH{\cdot}CH_2{\cdot}SO_3Na = PhNH{\cdot}CH_2{\cdot}SO_3Na + H_2O$$

Aniline, after conversion into the methyl-ω-sulphonate, couples readily, and as the methyl-ω-sulphonate group is easily removed by hydrolysis, this affords a means of making *p*-aminoazo-compounds. The introduction of the radicals of sulphuric or nitric acid into the amino-group to form aryl-sulphamic or -nitramic acids has the same effect (cf. p. 8). The arylcyanamides can also couple; thus diazobenzene couples with phenylcyanamide to give *p*-cyanamidoazobenzene [68, 69] :—

$$PhN_2{\cdot}Cl + NHPh{\cdot}CN = Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NHCN + HCl$$

The azo-compound formed by coupling diazobenzene with β-naphthyl-

cyanamide undergoes internal condensation to give β-naphthaphenyliminoketotriazine [73] :—



The same substance is obtained by interaction of benzeneazo-2-naphthylamine with cyanogen bromide.

Acylation of primary arylamines usually removes the power to couple just as it prevents diazotisation. Known exceptions are the azo-compounds which can be made by coupling *p*-nitrodiazobenzene with the *p*-toluenesulphonamides of α- and β-naphthylamine,[64, 78] and the internal sulphonamide, 1 : 8-naphthasultam.[79] 2-Acetamidothiophen couples at 5 with *p*-nitrobenzenediazonium chloride in acid solution.[90]

β-Anthramine can be coupled (cf. p. 225), but the amines of the anthraquinone series do not couple. Substitution of the amino-groups in benzenoid diamines by anthraquinone nuclei does not, however, prevent coupling in the benzenoid nucleus; for example, 1-amino-4-(3′-aminoanilino)anthraquinone-2-sulphonic acid couples in the 4′-position with diazotised orthanilic acid giving an olive-green dye.[84]

The position in which aminoquinolines combine with diazobenzene is shown in the table below; the products are the benzeneazo-compounds unless otherwise stated.[86]

TABLE XXII

Coupling-positions of Aminoquinolines

NH_2 at . .	2	3	4	5	6	7	8	2 : 4
Coupling at .	Triazen	4.	Fails	8 and 6	5	8	5	? 2

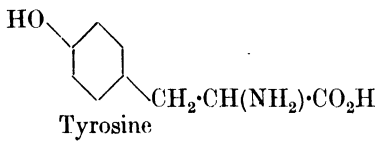
Although, as mentioned above, aniline will not generally form azo-compounds by direct coupling with diazo-compounds, the first product of reaction being diazoamino-compounds, yet aniline can be coupled with diazobenzene to form *p*-aminoazobenzene. The coupling medium is a mixture of aniline hydrochloride and aniline. To carry out the reaction sodium nitrite (1 mol.) is added to an excess of aniline (2 mols.) and aniline hydrochloride (2 mols.), whereupon an equivalent of aniline is diazotised, and at once combines with excess of aniline to form diazoaminobenzene. Such of this latter as is dissolved in the aniline and aniline hydrochloride is in equilibrium with a small amount of diazobenzene chloride formed by the action of the acid. The diazobenzene slowly couples with the aniline, and, being continually replaced from the reservoir of diazoaminobenzene, coupling goes on until the process is complete, and the reaction mass consists of *p*-aminoazobenzene hydrochloride partly dissolved in aniline. The optimum temperature is

35—40°. (For references to the controversies as to the mechanism of this reaction see Chapter V on Diazoamino-compounds.)

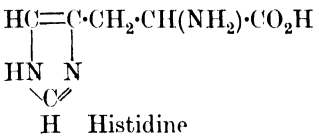
The essence of success in this coupling is, in fact, the stabilisation of the diazobenzene as its diazoamino-compound during the long period necessary for coupling, and such a coupling can be made only where a diazo-compound is to be coupled with its own amine. Thus *o*- and *m*-aminoazotoluenes are manufactured from *o*- and *m*-toluidine in the same way as *p*-aminoazobenzene. The bugbear of the process is the final separation of the *p*-aminoazo-compound from the excess base, and on the technical scale efforts are made to keep this excess as small as possible.

In a new variation of the above old-established process an aqueous paste of aniline hydrochloride is treated with nitrite solution for one hour at 0—5°, then at 20° for ten hours, 30° for four hours, and at 40° until formation of the *p*-aminazobenzene is complete.[81]

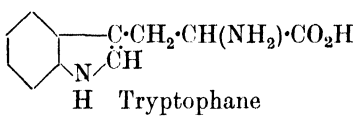
The Coupling of Proteins.—Diazo-compounds couple with protein in many of its forms, the azo links attaching themselves to the phenol ring in tyrosine to form *o*-hydroxyazo-compounds, while they form azo-compounds also with trytophane and histidine units of the protein molecule. If these compounds are removed from the protein hydrolysates the residual amino-acids form triazens, but only traces of C-azo-compounds.



Tyrosine



Histidine



Tryptophane

The capacity of proteins to couple was early discovered, and used to dye silk, which is coloured by treating with a solution of a diazo-compound in presence of acetate or alkali or with an *iso*diazotate [100]; the anthraquinone diazo-compounds can also be used.[101] The fastness of the dyeings can also be improved by coupling in presence of metallic salts,[108] and they may also be after-treated.

Proteins couple with diazotised sulphanilamides [115] or with diazotised arylamines having heavy metals attached as salts of thiols—*e.g.*, the gold salt of 4-amino-2-thiolbenzoic acid [4 : 2 : 1-$NH_2 \cdot C_6H_3(SH) \cdot CO_2H$] is diazotised and coupled with horse serum,[109] and such substances have been proposed or tried for direct use as medicaments.

Diazo-compounds couple equally well with proteins of animal origin, such as casein, fibroin, egg albumen, gelatin, and sera from the horse or fowl, and also with vegetable proteins such as zein. Although the

properties of the proteins are profoundly altered, the azo-proteins are not sharply defined substances, nor is any sharp end-point of their combination shown. Thus immunising sera lose their protective power and serological reactions in successive and discreet stages as they are combined with increasing amounts of diazo-compound, such as those from sulphanilic or *p*-aminobenzoic acid.[110] It has been shown that the total amount of diazo-compound taken up on combining diazotised arsanilic acid with casein, gelatin, or zein is greater than the amount to be expected from the tyrosine and histidine units present,[112, 113] though Pauly suggested that these are the chief points of combination[102]; the probability is great that some of the diazo-compound is combined as triazen—*e.g.*, with the proline or hydroxyproline units.

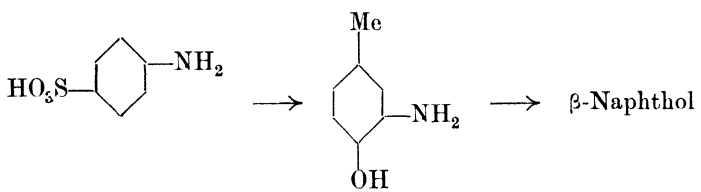
The most interesting use of the azo-proteins is that due to Landsteiner, who used them as antigens—that is to say, that when injected into animals they cause the body to produce antibodies giving immunity against the effects of the antigen.[103, 104, 105] The immune serum is detected by its power of forming a precipitate with the azo-protein or antigen which brought about its genesis, and if completely specific it forms a precipitate with no other antigen. This peak of specificity is not often attained, but so many and so varied are the known diazo-compounds that they offer great scope for varying the serological properties of the protein molecule to which they are attached. Exchange of methyl, chlorine, and amino-groups in the diazobenzene molecule does not make much difference to the immunological effect, but acid groups bring in sharper differences. Thus *o*-diazobenzoic acid coupled with albumen produces a serum which does not react with the azo-protein produced from *m*- or *p*-diazobenzoic acid, but does react with that from *o*-diazobenzoic acid itself.[106] There is some evidence that loss of specificity is due to exchange of azo-groups *in vivo*,[111] possibly by scission of triazens.

The effects of geometrical isomerism are also shown by the azo-proteins. Thus three azo-proteins are produced by diazotising *d*-, *l*-, and *meso*-aminotartranilide ($NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CHOH \cdot CHOH \cdot CO_2H$) and coupling with the same protein; antisera made against these three antigens show distinct differences. Hence, while precipitates are obtained between any one antiserum and all three antigens, yet the strongest reaction is with the homologous antigen—*i.e.*, the one that excited the production of the antiserum under test.[114] Thus the different biological effect of geometrical isomers is demonstrated by the introduction of the asymmetric molecule as an azo-compound.

The Coupling of *m*-Amino-*p*-Cresol, Naphthylamine-, Naphthol-, and Aminonaphtholsulphonic Acids.—Since the optimum pH for the coupling of a phenol and an arylamine with the same diazo-compound is likely to be different, it is readily understood that molecules which contain both a hydroxyl- and an amino-group may afford more than one azo-

compound or a mixture of azo-compounds of differing composition, according to the pH at which coupling is carried out. This is particularly the case among the naphthylamine-, naphthol-, and aminonaphthol-sulphonic acids, where azo-compounds of entirely different properties are formed according to the factor which influences coupling, and where the influence of the sulphonic acid group goes deeper than merely acting as a group directly blocking coupling in certain positions and as a solubilising agent.

There is, however, one notable compound of the benzene series which must be mentioned, *viz.*, *m*-amino-*p*-cresol (1 : 3 : 6-$NH_2 \cdot C_6H_3Me \cdot OH$). This substance only couples satisfactorily by the usual methods with diazo-compounds substituted by chlorine or nitro-groups; to bring about the coupling of other diazo-compounds, salts of thiosulphuric acid—*e.g.*, sodium thiosulphate—must be present. According to the patent,[122] stable double compounds with the diazo-compounds are formed (cf. p. 95) and release the diazo-compound slowly during the time required for the coupling. The process is used technically for the first coupling in making the chrome dye Eriochrome Verdone A (C.I. 292) :—



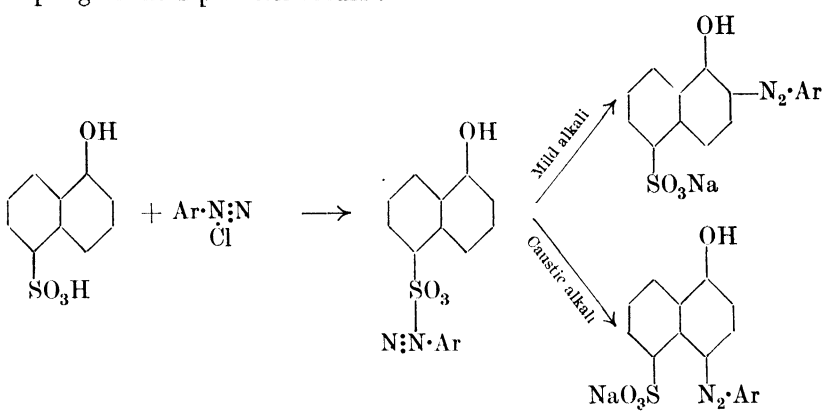
(Arrows represent successive diazotisations and couplings.)

No comment is necessary in the case of the β-naphthylamine- and β-naphthol-sulphonic acids; they couple exclusively in the 1-position with any diazo-compound.

If the amino or hydroxyl group is in the 1-position, then the diazo-compound attacks in the 4-position, unless (*a*) the 4-position is occupied, or (*b*) a sulphonic-acid group is in position 3 or 5, by which the attack is directed to the 2-position. But though this is the general rule, there are exceptions, which suggests that the diazo-compound itself causes variation of the point of excitation in the molecule with which it couples. 1-Naphthylamine-5-sulphonic acid is attacked in the 4-position by diazo-compounds with negative substituents, except diazotised sulphanilic acid, which enters exclusively *ortho*- to the amino-group; moreover, acidity in the coupling medium tends to direct attachment of the azo-link to the 2-position.[124] Similar conditions apply in the case of 1-naphthol-3-sulphonic acid, with which weak diazo-compounds couple in position 2 and strong diazo-compounds in position 4.[121] This indicates that the 2-position is less strongly activated than the 4-position, and can only be attacked by diazo-compounds reaching a higher chemical potential. As a corollary the stronger activation in the 2-position which

makes use of the diazo-compounds of lower chemical potential must be of lower frequency than that in the 4-position, otherwise all the coupling products would be *o*-hydroxyazo-compounds.[129] Illustrative of the high degree of specificity that can be displayed by the diazo-compound is the fact that diazotised 6-nitro-1-amino-2-naphthol-4-sulphonic acid attacks α-naphthol exclusively in the 2-position, thereby affording the well-known black chrome dyestuff Solochrome Black T (C. I. 203); if the nitro-group is not present at 6 some of the diazo-compound couples at 4, and the resultant dyestuff, Solochrome Black 6B (C.I. 201), is a mixture of the 2- and 4-coupled isomers.[125]

Fierz-David [128] has shown how variation in the destination of the diazo-group can happen with 1-naphthol-4-sulphonic acid, even with one and the same diazo-compound. If this acid is treated with a diazo-compound in acid solution a sparingly soluble diazonium sulphonate can be isolated, and this by careful treatment with mild alkali goes over entirely into the *ortho*-azo-dye, but if caustic soda is used, then a proportion of coupling in the 4-position occurs :—



2 : 8-Dihydroxynaphthalene-6-sulphonic acid is also anomalous in that it only couples once to form an azo-dye, then combines with a second molecule of a diazo-compound to form a diazonium salt similar to that shown above, and this salt refuses to rearrange under the action of mild or strong alkali, although two possible coupling positions are apparently still free.[128]

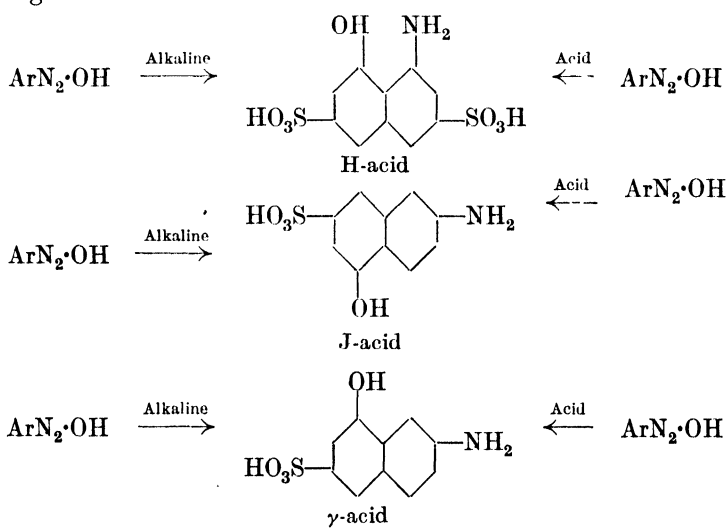
The aminonaphthols and their sulphonic acids can be divided into three classes [120] :—

1. Those which do not couple at all under any ordinary conditions—*e.g.*, 2-amino-1-naphthol-4-sulphonic acid and 1-amino-2-naphthol-3 : 6-disulphonic acid.

2. Those which form monoazo-dyes under special or peculiar conditions—*e.g.*, 1 : 2-aminonaphthol and its 6-sulphonic acid, which couple in neutral solution, and 1 : 8-aminonaphthol-4- and -5-sulphonic acid, which

with one equivalent of diazo-compound give a mixture of mono- and disazo-dyes, some aminonaphtholsulphonic acid remaining unattacked.

3. Those which couple under the usual conditions. Among these aminonaphtholsulphonic acids the point of attachment of the diazo-compound is determined entirely by the pH of the solution in which coupling takes place. In acid solutions it is the positions activated by the amino-group to which the azo-link is attached; in alkaline solution the hydroxyl group is the controlling factor. This is a matter of great technical importance, because the dyestuffs obtained by one way are entirely different in shade and fastness properties from those obtained by the other. Some aminonaphtholsulphonic acid thus couple twice, once on the amino-side and once on the hydroxy-side, as in the case of H-acid (1 : 8-aminonaphthol-3 : 6-disulphonic acid). The sulphonic acid groups cause coupling to take place in the 2- and 7-positions, so that the dyes belong to the useful *ortho*amino- and *ortho*hydroxy-azo-type; examples of the application of these couplings with H-acid are very numerous. Another important aminonaphtholsulphonic acid is J-acid (2 : 5-aminonaphthol-7-sulphonic acid), a component which confers cotton substantivity; this can be coupled twice, though not many examples are extant.[123,126,127] The first coupling is made in acid solution on the amino-side at the 1-position, and a second diazo-compound can then be attached to the monoazo-dye in alkaline solution at the 6-position.* γ-Acid (2 : 8-aminonaphthol-6-sulphonic acid), an important intermediate for acid wool dyes only couples once but that single coupling may be made in either acid or alkaline medium. The points of coupling of the three foregoing acids are shown below :—



* Diphenyl Fast Blue 2G is a dye of this type : private communication from Prof. Fierz-David.

For lists of the known aminonaphtholsulphonic acids and their coupling positions one of the numerous books on dyestuff chemistry should be consulted.

Prevention of Mixed Couplings.—For the purpose of making pure azo-compounds free from by-products which may have deleterious properties, it is desirable to be able to control the position of entry of the azo-link in molecules such as α-naphthylamine, where coupling can occur in more than one position. One way of achieving this end is to block the unwanted coupling positions with inert substituents, but it is not always easy to make the desired compounds. It is claimed that α-naphthylamine if converted into its N-sulphamic acid, α-$C_{10}H_7$·NH·SO_3H, couples exclusively in the 4-position; on removal of the sulphamic acid by hydrolysis a pure aminoazo-compound is obtained.[135] Diazotised *o*-anisidine also couples exclusively in the 4-position of α-naphthylnitramic acid, α-$C_{10}H_7$·NH·NO_3, and the resultant aminoazo-compound on treatment with nitrous acid gives the diazo derivative with elimination of the nitramic acid group.[136]

The Coupling of Substances having Reactive Methylene Groups—As might be expected, those substances of the aliphatic series which show tautomeric keto-enol constitutions are able to supply the necessary hydrogen atom to diazo-compounds, and thereby couple to form azo-compounds. V. Meyer discovered in 1877 that acetoacetic ester dissolved in aqueous alkali couples with diazobenzene,[140] while he had prepared benzeneazonitroethane in 1875 from diazobenzene and nitroethane.[190] Azo-compounds of this type are sometimes known as "mixed" azo-compounds, because an aromatic radical is joined with one of the aliphatic series by the azo-link. As with the azo-derivatives of the phenols, the number known is so great that no attempt can be made to give a list, but beside acetoacetic ester and its arylamides the following substances representing different types of aliphatic and heterocyclic substances able to couple may be mentioned: malonic ester,[145] acetylacetone,[162] glutaconic acid and ester,[158] acetone dicarboxylic acid,[148] acetone sulphonic acid,[183] ω-nitroacetophenone,[181] acetophenone-ω-sulphonic acid,[182] ligno-cellulose,[176] cyclic ketones,[160, 180] and pyrazolones, which last are of great technical importance for the manufacture of many dyes. To these must be added the nitroparaffins which make a distinct group (*vide infra*).

Much of the original interest in these azo-compounds lay in the point as to whether they are to be regarded as true azo-compounds or as hydrazones, for not only are the two forms tautomeric :—

$$\begin{array}{l} \mathrm{MeCO{\cdot}CH{\cdot}CO_2Et} \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad \mathrm{N{:}N{\cdot}Ar} \end{array} \rightleftharpoons \begin{array}{l} \mathrm{MeCO{\cdot}C{\cdot}CO_2Et} \\ \quad\quad\quad\quad \| \\ \quad\quad\quad\quad \mathrm{N{\cdot}NHAr} \end{array}$$

but, as with the hydroxyazo-compounds, the same compound is obtained

whether a diazo-compound is coupled with a keto-enol or an arylhydrazine reacts with a ketone. For example, the coupling product of diazobenzene with malonic ester (equal mols.) is identical with the phenylhydrazone of mesoxalic ester [145] : —

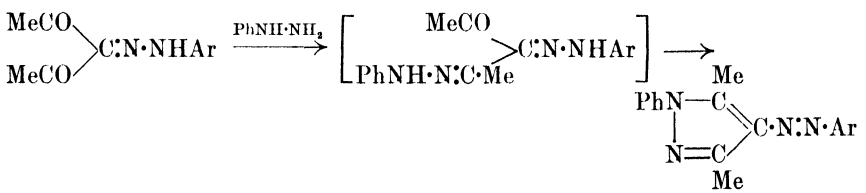
$$PhN{:}N{\cdot}CH(CO_2Et)_2 \rightleftharpoons PhNH{\cdot}N{:}C(CO_2Et)_2.$$

At the time of this and similar discoveries the matter was of considerable importance because views as to the constitution of the diazo-compounds were in a fluid state, but in passing it may be said of the controversy as to the constitution of these substances that Bülow supported the true azo-structure because he was unable to acetylate benzeneazoacetoacetic ester, nor could he bring it to react with benzoyl chloride or methyl iodide,[159] nor did he find any difference in the compound whether made from the normal or the *iso*diazotate of benzene.[157]

Japp and Klingemann,[144] on the other hand, believed benzeneazoacetone to be a hydrazone, pyruvaldehyde phenylhydrazone, because when treated with sodium ethoxide and ethylchloroacetate the resultant compound on reductive scission gives phenylglycine :—

$$\begin{array}{l} MeCO{\cdot}CH{:}N{\cdot}NHPh \\ \quad + \\ ClCH_2{\cdot}CO_2Et \end{array} \longrightarrow \begin{array}{l} MeCO{\cdot}CH{:}N{\cdot}NPh \\ \quad\quad\quad | \\ \quad\quad CH_2{\cdot}CO_2Et \end{array} \longrightarrow \begin{array}{l} MeCO{\cdot}CH_2{\cdot}NH_2 \\ PhNH{\cdot}CH_2{\cdot}CO_2H \\ \text{Phenylglycine} \end{array}$$

It was argued that had benzeneazoacetone the constitution of an azo-compound the carboethoxymethyl group could not have become attached to nitrogen, as the evidence showed it had, but to carbon. Such methods, however, are rarely decisive in attempts to settle the constitution of tautomers as is shown by the results of similar experiments with the triazens (cf. p. 164), and the view of v. Pechmann and Jenisch [148] that the hydrogen is labile tallies with present-day ideas. The change from azo-compound into hydrazone has been observed; according to Favrel [173] benzenediazonium chloride couples with chloroacetone in the presence of sodium acetate giving a reddish solid which changes rapidly into the phenylhydrazone of chloropyruvic aldehyde, $CH_2Cl{\cdot}CO{\cdot}CH{:}N{\cdot}NHPh$. By ring formation the arylhydrazones derived from diazo-compounds and acetylacetone are transformed into true azo-compounds, the 1-phenyl-3 : 5-dimethyl-4-arylazopyrrazoles, through treatment with phenylhydrazine, thus [162] :—



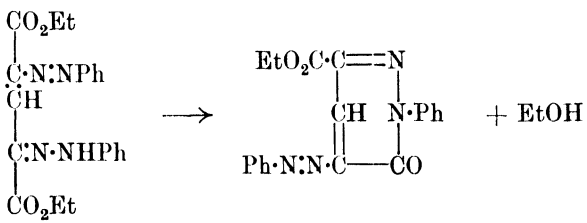
But while the attempt to settle the elusive point of the constitution of the mixed azo-compounds was for many years the mainspring of research,

it led to a thorough exploration of the chemistry of the interaction of diazo-compounds with keto-enols, and some aspects of this are worth review.

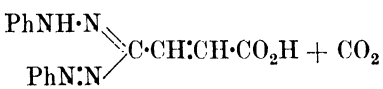
The reaction of a diazo-compound with a keto-enol carboxylic ester may be different from its reaction with the free acid. Thus, as already mentioned, acetoacetic ester and diazobenzene afford ethyl benzene-azoacetoacetate, from which the free acid is obtained by alkaline hydrolysis,[141] yet free acetoacetic acid couples with scission of carbon dioxide to give the phenylhydrazone of pyruvaldehyde [144] :—

$$MeCO{\cdot}CH_2{\cdot}CO_2H + PhN_2{\cdot}OH = MeCO{\cdot}CH{:}N{\cdot}NHPh + CO_2$$

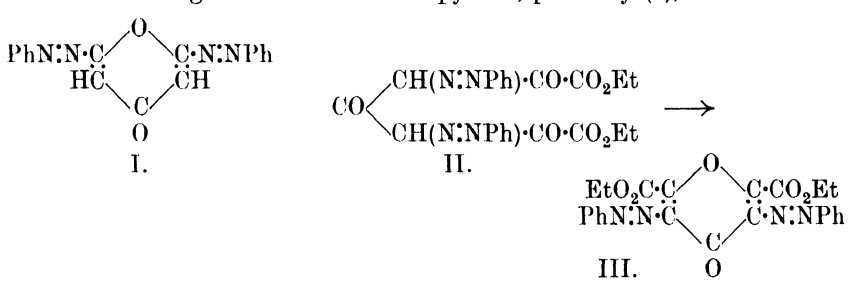
Also ethyl glutaconate, $EtO_2C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2Et$, couples with two equivalents of diazobenzene, giving the phenylhydrazone of ethyl γ-phenylazoglutaconate, which readily loses alcohol and passes over into ethyl 1-phenyl-5-benzeneazo-6-pyridazone-3-carboxylate :—



On the other hand, glutaconic acid similarly treated with two equivalents of diazobenzene affords β-(NN′-diphenylformazyl) acrylic acid and carbon dioxide :—



Chelidonic acid also loses both carboxyl groups on coupling with diazobenzene to give a bis-benzeneazopyrone, probably (I),



because it is different from the azopyrone obtained by decarboxylating the ethyl bis-benzeneazochelidonate (III) which results by removing water from ethyl bis-benzeneazoacetonedioxalate (II).[172]

Mixed azo-compounds, as the above reactions show, are also frequently formed with scission of part of the aliphatic molecule. Ethyl methyl-acetoacetate does not couple to give the methyl-substituted benzene-

azoacetoacetate, as might be expected, but acetic acid is split off, and benzeneazopropionic ester or pyruvic acid phenylhydrazone [143] is formed :—

$$PhN_2\cdot OH + MeCO\cdot CHMe\cdot CO_2Et \longrightarrow PhN{:}N\cdot CHMe\cdot CO_2Et \rightleftharpoons PhNH\cdot N{:}CMe\cdot CO_2Et + AcOH$$

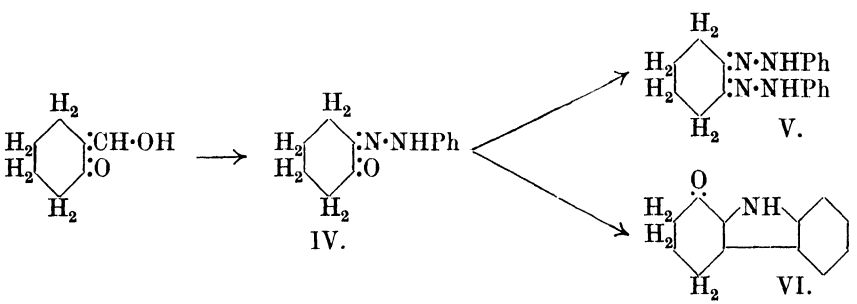
The alkali salt of the free methylacetoacetic acid, obtained by setting aside overnight a solution of the ester in caustic alkali, conforms to the behaviour of acetoacetic acid, coupling with scission of carbon dioxide to give the phenylhydrazone of diacetyl :—

$$MeCO\cdot CHMe\cdot CO_2Na + PhN_2\cdot ONa \longrightarrow MeCO\cdot CMe{:}N\cdot NHPh + Na_2CO_3$$

Carboxyl groups are often removed if attached to the carbon atom to which coupling takes place; both are lost from acetonedicarboxylic acid, which with diazobenzene affords bis-benzeneazoacetone or mesoxalic phenylhydrazone [148] :—

$$CO(CH_2\cdot CO_2H)_2 + 2PhN_2\cdot OH \longrightarrow CO(CH_2\cdot N{:}NPh)_2 \rightleftharpoons CO(CH{:}N\cdot NHPh)_2 + 2CO_2$$

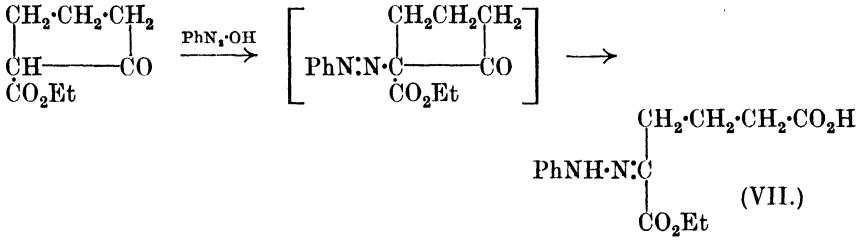
Similarly *cyclo*pentanone-2-carboxylic acid couples with removal of carbon dioxide,[160] whilst 2-hydroxymethylene*cyclo*hexanone and diazobenzene in alkaline solution form the monophenylhydrazone of *cyclo*hexan-1 : 2-dione (IV), the hydroxymethylene group being removed as formic acid [166] :—



(IV) is also obtained from *cyclo*hexanone carboxylic acid, the carboxyl group being removed,[180] whereas the ester reacts in quite a different manner (*vide infra*). In the monohydrazone (IV) the original ketonic function is not impaired, and hence with phenylhydrazine it forms an osazone (V) and undergoes Fischer's indole synthesis, producing 1-keto-1 : 2 : 3 : 4-tetrahydrocarbazole (VI).

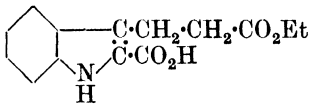
The hydrazones formed by coupling diazo-compounds with cyclic β-ketonic esters are unstable to aqueous alkali, the ring being opened to form the hydrazone of a monoester of a ketonic dicarboxylic acid; if

coupling is carried out in alkaline solution hydrazone formation and ring-opening occur simultaneously. Diazobenzene and ethyl *cyclo*pentanone carboxylate react thus in alkaline solution, giving the phenylhydrazone of ethyl hydrogen β-ketoadipate (VII) [168] :—

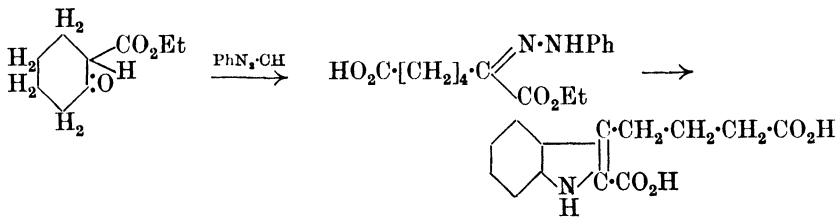


(VII.)

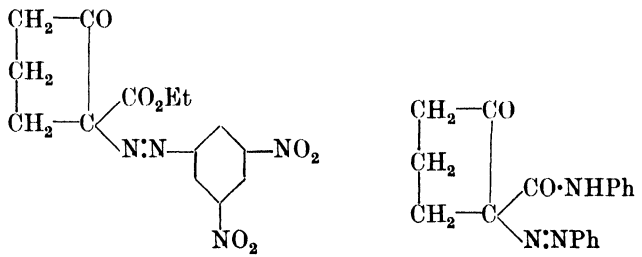
(VII) undergoes the Fischer indole synthesis, giving ethyl β-(2-carboxy-3-indolyl) propionate :—



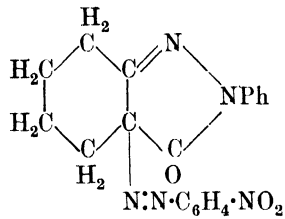
Substituted indolylpropionic acids can be made starting from various diazo-compounds,[169, 171, 178] whilst the analogous synthesis from ethyl *cyclo*hexanone-2-carboxylate leads to the phenylhydrazone of ethyl hydrogen α-ketopimelic acid, and thence to γ-(2-carboxy-3-indolyl)butyric acid [178]:—



Linstead and Wang [186] have studied the mechanism of the above coupling and ring-opening reaction, and find that it is to some extent dependant on the diazo-compound used, since 2 : 4-dinitrodiazobenzene couples with ethyl *cyclo*pentanone carboxylate to give a stable azo-compound in which the ring has not opened, whilst stable azo-compounds are also formed from other diazo-compounds when the anilide is used in place of the ester :—

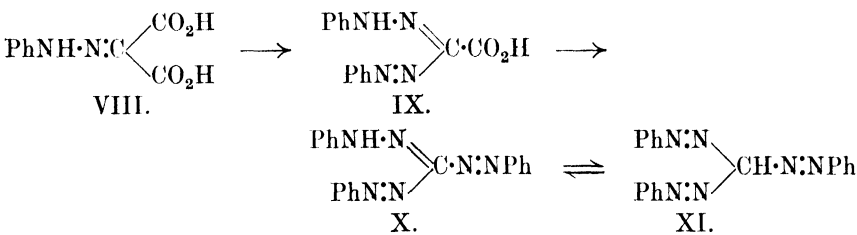


The azocarboxyanilides are also stable in the *cyclo*hexanone series. The phenylhydrazone of *cyclo*hexanone-2-carboxylic ester ring closes in the usual way to 1-phenyl-3 : 4-*cyclo*hexano-5-pyrazolone, which couples with *p*-nitrodiazobenzene to form the azo-compound :—



In this compound the *p*-nitrobenzeneazo group is only feebly attached; digestion with alcohols regenerates the pyrazolone, together with nitrogen, acetaldehyde, and nitrobenzene, the typical reaction of a diazo-compound with alcohol; with dimethylaniline the azo-group is detached in its entirety and combines to form 4-nitro-4′-dimethylaminoazobenzene.[186]

In general there is among the reactive methylene compounds nothing analogous to the tris-coupling of phenol, and if successive coupling occurs the aliphatic molecule is whittled down as each additional molecule of diazo-compound is attached. Malonic acid couples with three molecules of diazobenzene, forming first the phenylhydrazone of mesoxalic acid (VIII), then formazylcarboxylic acid (IX), and finally formazylazobenzene (X), tautomeric with tris-benzeneazomethane (XI), each coupling occurring with loss of carbon dioxide [150] :—

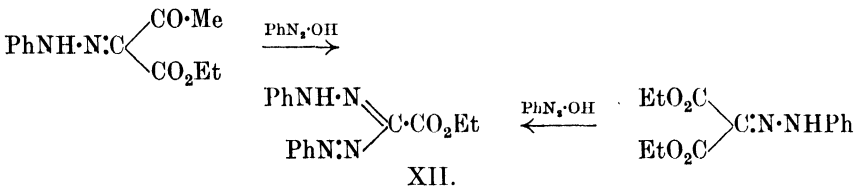


Other diazo-compounds can be used in place of diazobenzene.[163]

Many hydrazones, which may be formed either from a keto-enol and a diazo-compound or from a primary arylhydrazine and an aldehyde or ketone, are able to couple with a diazo-compound, thus producing the group $\begin{matrix}\mathrm{ArNH{\cdot}N}\\ \mathrm{ArN{:}N}\end{matrix}\!\!>\!\mathrm{C{\cdot}}$ which v. Pechmann, its discoverer, called formazyl.*

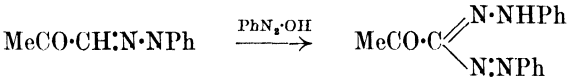
* For a strictly logical system of nomenclature for formazyl and its derivatives see Beilstein, *Handbuch*, 4th Ed., vol. 16, pp. 4–5.

Thus acetoacetic ester or malonic ester with two equivalents of diazobenzene afford ethyl formazylcarboxylate (XII) [150, 152] :—

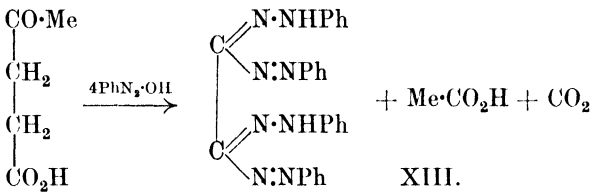


XII.

Acetoacetic acid similarly affords formazylmethyl ketone :—



at first mistaken by Bamberger for the bis-phenylhydrazone of mesoxaldehyde.[149] Diformazyl (XIII) is made from lævulinic acid and four equivalents of diazobenzene [153] :—



XIII.

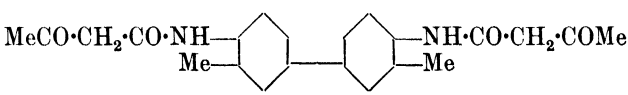
(XIII) is also made from acetonediacetic acid, and from the osazone of dihydroxytartaric acid by coupling with diazobenzene.

The formazyl-compounds are, as might be expected, tautomeric, and the same ethyl phenyl-*p*-tolylformazyl carboxylate is obtained from ethyl malonate, diazobenzene and diazo-*p*-toluene, whichever diazo-compound is coupled first.[156] Hydrazones of *as.* secondary arylhydrazines, *e.g.*, Ph·CH:N·NMePh, cannot couple with diazo-compounds, but benzaldehyde phenylhydrazone couples to form phenylformazyl $\begin{matrix}PhNH\cdot N\\ PhN:N\end{matrix}\!\!>\!C\cdot Ph$.[156]

The azo-compounds derived from the substances having reactive methylene groups resemble the *para*-coupled azo-compounds of phenol in that they form salts with dilute caustic alkalis. As the salts are soluble in water and different in colour—usually redder—from the azo-compound or hydrazone, this is a serious disadvantage when they are used as colouring matters. But the arylamides of acetoacetic ester,

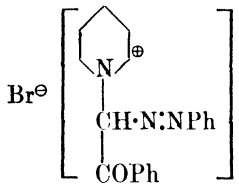
$$MeCO\cdot CH_2\cdot CO\cdot NHAr,$$

are exceptions in this respect, affording azo-compounds which are used in quantity for making yellow pigments, the best being obtained by coupling with *o*-nitrodiazo-compounds,[170, 174, 175] while bisacetoacet-*o*-tolidide,

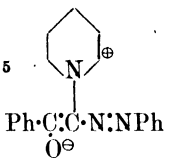


still remains the premier "Naphtol" used in the various processes employed for obtaining yellow azoic dyestuffs.

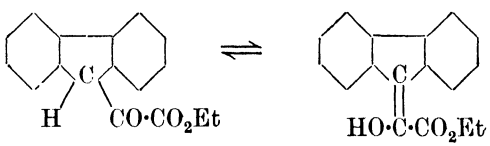
Besides the keto-enols there are other groups which contain a methylene group activated so that it couples with diazo-compounds. The quaternary compound formed from ω-bromoacetophenone and pyridine, phenacetylpyridinium bromide, couples with diazobenzene to form an azo-compound one tautomer of which is probably



giving with alkali a coloured betaine [185]

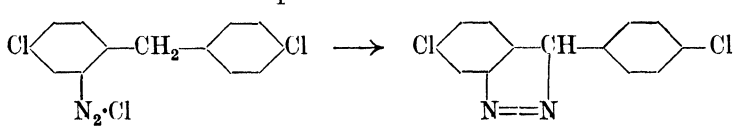


The ring methylene group in fluorene can be activated by combination with oxalic ester, forming fluorene-9-glyoxalic ester tautomeric with the enol ethyl α-hydroxy-β-diphenylene acrylate [176] :—



and this can be used to form an azo-dye image with a silver *iso*diazotate in colour photography (cf. p. 370), whereas fluorene itself does not couple.[184] According to Kuhn and Levy the enolic form alone couples, and with *p*-nitrodiazobenzene the glyoxylic ester residue is split off, and the product is fluorenone *p*-nitrophenylhydrazone.[176] By the same mechanism diazobenzene and *p*-bromodiazobenzene couple with ethyl 1 : 2 : 3 : 4-tetrahydroacridyl-1-glyoxylate in pyridine, splitting off the glyoxylic residue and giving the phenyl- and *p*-bromophenyl-hydrazone of 1-ketotetrahydroacridine.[187]

The methylene group in diphenylmethane, although not coupling with external diazo-compounds, couples with an *ortho* diazo-group in the same molecule, producing the *endo*-azo-compounds of Duval,[185] of which both mono- and dis-azo-compounds are known :—



They are typical azo-compounds, yellow or red in colour and insoluble in water.

Diazo-compounds couple, usually in weakly alkaline solution, with nitroparaffins at the same carbon atom to which the nitro-group is attached, and a number of mixed azo-compounds or hydrazones have been

described derived from diazobenzene and nitromethane,[192, 197] nitroethane,[190, 191, 193] and 2-nitropropane [191]; methazonic acid,

$$NO_2{\cdot}CH_2{\cdot}CH{:}NOH,$$

also couples with diazobenzene giving the phenylhydrazone of nitroaldoxime, $PhNH{\cdot}N{:}C(NO_2){\cdot}CH{:}NOH$.[194] Nitromethane forms more than a dozen compounds by interaction with diazobenzene.[199] The chief product formed when a solution of benzenediazonium chloride is added to nitromethane dissolved in dilute caustic soda is nitroformazyl,

$$\begin{matrix} PhNH{\cdot}N \\ PhN{:}N \end{matrix}\!\!>\!C{\cdot}NO_2,$$

with some of the single-coupled hydrazone, $PhNH{\cdot}N{:}CH{\cdot}NO_2$; the action of a third equivalent of diazobenzene is to replace the nitro-group by a phenyl radical, nitrogen being lost, thus producing phenylformazyl, $Ph{\cdot}C\begin{matrix} N{\cdot}NHPh \\ \diagup\!\!\diagdown \\ N{:}NPh \end{matrix}$.[197] But a solution of sodium benzenediazotate reacts with an alkaline solution of nitromethane with loss of nitrogen, one hydrogen atom of the methyl group being replaced by a phenyl radical, thus producing phenylnitromethane (ω-nitrotoluene) $Ph{\cdot}CH_2{\cdot}NO_2$; if more diazotate is present, diphenylnitromethane, $\begin{matrix} Ph \\ Ph \end{matrix}\!\!>\!CH{:}NO_2$, is formed, and this can couple so that benzeneazodiphenylnitromethane, $\begin{matrix} Ph \\ Ph \end{matrix}\!\!>\!C\!<\!\begin{matrix} NO_2 \\ N{:}NPh \end{matrix}$, is the end product; this compound spontaneously rearranges in boiling alcohol by migration of the nitro-group to give benzophenone nitrophenylhydrazone, $\begin{matrix} Ph \\ Ph \end{matrix}\!\!>\!C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\text{-}p$.[201]

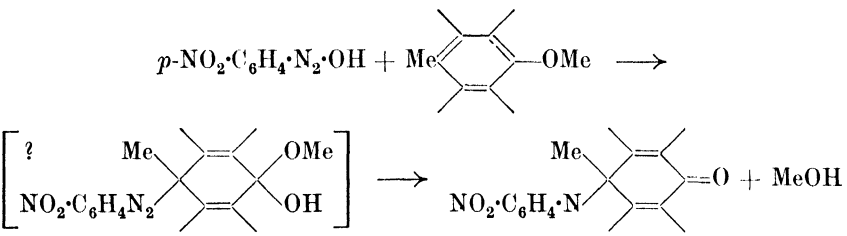
The nitroparaffins having more than one carbon atom usually couple only once, but nitroethane couples twice with 2 : 4 : 6-trichloro- or tribromo-diazobenzene giving disazo-compounds $\begin{matrix} Me \\ NO_2 \end{matrix}\!\!>\!C\!<\!\begin{matrix} N{:}N{\cdot}C_6H_2Cl_3 \\ N{:}N{\cdot}C_6H_2Cl_3 \end{matrix}$.[200] Dinitromethane couples twice giving bis-benzeneazodinitromethane, $\begin{matrix} PhN{:}N \\ PhN{:}N \end{matrix}\!\!>\!C\!<\!\begin{matrix} NO_2 \\ NO_2 \end{matrix}$.[196] The secondary nitroparaffins, such as 2-nitropropane and 2-nitrobutane, only couple once,[202] as do their amino-substituted derivatives, such as 2-nitro-1-di-*n*-butylaminobutane and N-β-nitropropylmorpholine.[203]

Like the products of interaction of diazo-compounds with keto-enols, the arylazonitroparaffins are tautomeric, and often exist chiefly as the hydrazone form, a view of which Bamberger was a strong protagonist.[198]

The Coupling of Phenol Ethers.

K. H. Meyer, on account of his views as to the mechanism of the coupling reaction, tried to couple diazo-compounds with phenol ethers. The ethers, being insoluble in aqueous media, are dissolved in glacial acetic acid, and in this medium it is found that, given sufficient time, strongly-

coupling diazo-compounds, such as *p*-nitrodiazobenzene, form azo-compounds, not indeed with monohydric phenol ethers like anisole, but with resorcinol ethers and, better still, with phloroglucinol ethers, with which latter even diazobenzene yields azo-compounds.[210] Later it was found that the still more strongly-coupling 2 : 4-dinitrodiazobenzene forms azo-compounds with anisole and phenetole.[212] One remarkable reaction of this kind is the coupling of *p*-nitrodiazobenzene with the methyl ether of 9-methylanthranol; coupling takes place at 9, although there is no replaceable hydrogen atom and the methyl ether group is simultaneously lost [212] :—



The reaction is an expression of the tendency of anthracene to react so as to pass into the stable anthraquinone structure.

The coupling of phenol ethers has also been studied by v. Auwers, chiefly from the standpoint of the effect of substituents in the ring and their effect on the point of attachment of the azo-link.[211, 213] According to him, the *para*-position to the alkoxy-group must be free, and coupling is most facile when a methyl-group occupies both meta-positions to the alkoxy-group, *i.e.*, the configuration is that of mesitylene with one methyl-group replaced by alkoxy. The notable characteristic of this coupling is, however, that it proceeds with partial or complete removal of the alkyl-group of the phenol ether, a remarkable occurrence because phenol ethers are by no means easily hydrolysed. The proportion of the alkyl-group which is removed varies with the diazo-compound, but no attempt has been made to ascertain what other factors are involved, nor is it known whether the alkoxy-group is removed and replaced by hydroxyl, or whether the alkyl-group is removed and replaced by hydrogen. Generally speaking, the yields of azo-compound are low.

Mason and Jambuserwala [214] studied the coupling of 2-methoxy-3-naphthoic acid and determined the proportion of unhydrolysed methoxyl remaining in the azo-compound they prepared. They condensed their results into the table on p. 219.

No guiding generalities can be deduced from the above list, and it is apparent that opportunities for research in this matter are by no means exhausted. A possible explanation is that the loss of the alkyl-group is connected with the extent of the polarisation of the diazo-compound at the instant of coupling (cf. p. 234).

A somewhat different example of the scission of a carbon–oxygen link on coupling is provided by the pseudourea ether hydrochloride made from β-naphthol and cyanamide hydrochloride in non-hydroxylic solvents. It has the constitution $\beta\text{-}C_{10}H_7\cdot O\cdot C(:NH)\cdot NH_2,HCl$ and is soluble in water or dilute acid and can be mixed with diazo-compounds without interaction, but coupling occurs instantly with scission of urea on making alkaline.[215]

TABLE XXIII

Scission of Methoxyl from 2-Methoxy-3-Naphthoic Acid on Coupling

Diazo-compound from :	Methoxyl groups remaining in azo-compound (proportion of one molecule).
p-Chloroaniline	nil
2 : 6-Dichloroaniline	nil
o-Nitroaniline	0·5 mol.
m- ,, ...	0·5 ,,
p- ,, ...	nil
4-Nitro-*o*-anisidine	1·0 mol., *i.e.*, 50% hydrolysis occurs
5- ,, ...	2·0 ,, ,, no ,, ,,
Sulphanilic acid	0·5 ,,
Benzidine	nil
o-Tolidine	nil

The Coupling of Hydrocarbons.

To K. H. Meyer belongs the credit of first preparing crystalline azo-compounds by the union of a diazo-salt with a hydrocarbon, though Thiele [220] and Eibner and Laue [221] had shown some years before that *cyclo*pentadiene and nitro*cyclo*pentadiene form coloured substances with diazo-compounds.[220, 221] Meyer's first attempt were failures, but on persevering he found that strongly-coupling diazo-compounds yield azo-derivatives with hydrocarbons of the butadiene series.[212, 222] Butadiene, isoprene, α-methylbutadiene, and βγ-dimethylbutadiene all couple, the last-named the most easily either in glacial acetic acid or alcohol, with *p*-nitrodiazobenzene or 2 : 4-dinitrodiazobenzene; the products are orange or red crystalline substances. The azo-compounds preserve the unsaturated butadiene radical intact as shown by their forming tetra-bromides by direct addition of bromine. Unstable hydrazo-compounds are produced from the azo-compounds by the action of reducing agents; further reduction destroys the molecule and aminobutadienes cannot be made by this means.

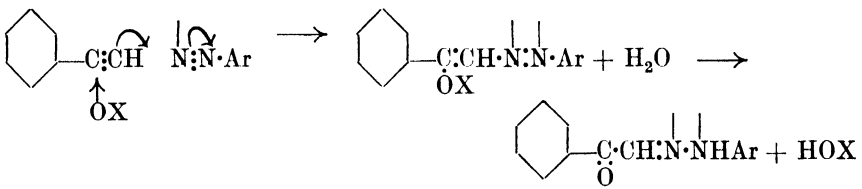
The above work has been extended and utilised by Russian chemists to determine unsaturated hydrocarbons in cracked petroleums (cf. p. 343), and butadiene can be detected by the deep yellow to red colour produced when it is passed through a solution of *p*-tetrazobenzene.[232] The Russians find that 2 : 4-dinitrodiazobenzene couples with dipropenyl, di-*iso*crotyl, βδ-dimethylbutadiene, and ααβ-trimethylethylene giving α-2 : 4-dinitrobenzeneazohexa-2 : 4-diene, α-2 : 4-dinitrobenzeneazo-αε-

dimethyl-hexa-2 : 4-diene, α-2 : 4-dinitrobenzeneazo-β-methylpenta-1 : 3-diene, and 2 : 4-dinitrobenzeneazotrimethylethylene respectively; diallyl and αα-dimethylethylene do not couple.[233] α-Phenylbutadiene couples but its dimeride does not [231]; 2 : 3-diphenylbutadiene also couples.[236] αα-Diarylethylenes couple when the aryl nuclei contain positive substituents.[228] This reaction, the mechanism of which is discussed later (cf. p. 233), is interesting because an intermediate compound can be isolated and goes over either spontaneously or by the action of acid-binding agents into the azo-compound. Tetramethyldiamindiphenylethylene ($Me_2N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2$) and dianisylethylene ($MeO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$) (4 : 4′-dimethylamino-, and 4 : 4′-dimethoxy-stilbene) are mentioned in the examples as coupling with 2-diazonaphthalene-6 : 8-disulphonic acid and *p*-nitrodiazobenzene respectively; the azo dyes are sensitive to acids and alkalis.

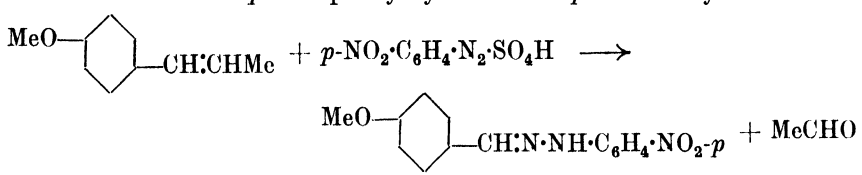
In styrene, α-phenylethylene, the induced charge on the β-carbon atom is just not sufficient to allow the formation of a sharply-defined crystalline azo-compound with 2 : 4-dinitrodiazobenzene [229, 234]; indene forms a more definite compound.[234] Phenylacetylene and *p*-methoxyphenylacetylene both couple with *p*-nitrodiazobenzene in alcohol at the same time acquiring one atom of oxygen so that the products are the *p*-nitrophenylhydrazone of phenylglyoxal and *p*-methoxyphenylglyoxal [229]:—

$$PhC{:}CH + p\text{-}NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_4H \xrightarrow{H_2O} PhCO{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2\text{-}p$$

The mechanism suggested by Ainley and Robinson is as follows:—



p-Nitrobenzenediazonium sulphate dissolved in glacial acetic acid or, better, suspended in alcohol, attacks the *n*-propenyl side-chain in anethole, *iso*apiole, *iso*safrole, and *iso*eugenol.[225, 226] The two terminal carbon atoms of the side-chain are removed as acetaldehyde, and there is formed the *p*-nitrophenylhydrazone of the corresponding aldehyde. Thus anethole affords the *p*-nitrophenylhydrazone of *p*-anisaldehyde:—



The other compounds mentioned afford the *p*-nitrophenylhydrazones of apiole, piperonal, and vanillin respectively. Quilico, the discoverer of

the reaction, suggests that the diazonium salt first adds at the double linking, and then splits off acetaldehyde, hence the mechanism is essentially similar to that of Ainley and Robinson's reaction.

The expectation that a sufficiently strongly-coupling diazo-compound would attack benzenoid hydrocarbons was realised when it was found that 2 : 4 : 6-trinitrodiazobenzene combines with mesitylene to form a crystalline azo-compound.[224] Benzene shows no sign of coupling even with this most avid of the diazo-compounds; toluene, *m*-xylene, and α-methylnaphthalene give colours, but no crystalline azo-compound. The same diazo-compound couples in sulphuric acid–glacial acetic acid with *iso*durene and pentamethylbenzene, but not with durene or bromodurene.[227] It is to be noted that only those benzenoid hydrocarbons having the mesitylene structure are able to couple; in mesitylene the three methyl groups are jointly able to cause polarisation of a hydrogen atom, whereas in durene the inductive effects of only two *ortho*-methyl groups are insufficient to polarise either of the two possible coupling positions. Attempts have been made to couple the polynuclear carcinogenetic hydrocarbons with *p*-nitrodiazobenzene in acetic acid, but only 3 : 4-benzpyrene affords a crystalline azo-compound, intensely purple in solution. Cholanthrene, 20-methylcholanthrene, 4 : 10- and 8 : 9-ace-1 : 2-benzanthracene, and 1 : 2-*cyclo*pentano- and 1 : 2-dimethyl-5 : 10-aceanthracene give deeply coloured solutions.[235]

The Elimination of Substituents in Benzenoid Rings on Coupling.

As has been mentioned above, all or part of an alkoxy-group may be split off a phenol ether in the coupling reaction, even though the azo-link does not finally become attached to the molecule in that position. So great is the energy available for the consummation of the coupling reaction (see p. 353) that substituents occupying positions to which the azo-link would normally attach itself in benzenoid rings are sometimes ejected, and the azo-compound is formed despite the blocking group. This is seen where halogen,[249, 265] methylene,[247, 248, 262] carboxyl,[245] sulphur,[246, 255] or a sulphonic acid group [260] occupy the α-position in β-naphthol or the 2 : 3-hydroxynaphthoic arylamides. Further, Smith [250] showed that whilst 1-bromo-2-naphthol-6-sulphonic acid easily couples with loss of the bromine atom no coupling occurs if the sulphonic acid group is at 8 where it exerts a steric protective influence on the bromine atom at 1. When coupling a number of diazo-compounds with α-halogeno-β-naphthols, Pollak and Gebauer-Fülnegg [261] observed that the formation of intermediate O-azo-compounds is general, but that they differ widely in their susceptibility to passage into the C-azo-compounds. Similarly Joffe [267] showed that 1-bromo-2-naphthol gives only a poor yield of *p*-nitrobenzeneazo-β-naphthol in dilute caustic soda, but if thio-

sulphate is present the yield rises to 96% of pure azo-compound; apparently the bromine is removed from the β-naphthol molecule as hypobromite, which attacks the reactants, but if it is destroyed with thiosulphate the coupling goes to completion. 1-Chloro-2-naphthol does not, however, behave in an analagous manner, but gives mostly a red O-azo-compound, even in the presence of thiosulphate.[269] Among α-naphthol derivatives 4 : 4′-dihydroxy-3 : 3′-dicarboxydinaphthyl ketone couples with loss of the two carboxy-groups,[257] whilst diazo-compounds tend to couple *para* to the hydroxy-group in *p*-hydroxybenzoic acid with removal of carbon dioxide rather than couple at the unoccupied positions *ortho* to the hydroxyl-group.[251]

In the years just before the advent of the 2 : 3-hydroxynaphthoic arylamides as grounding components for ice colours attempts were made to introduce 2-naphthol-1-sulphonates [253] and -1-carboxylates,[254] and 22′-dihydroxy-11′-dinaphthyl sulphide [256] as grounding components for use either with nitrosamines or with diazo-compounds, chiefly because they have an advantage over β-naphthol, in that they do not darken when the cloth is dried before coupling. The use of 2 : 3-hydroxynaphthoic arylamides sulphonated at 1 in conjunction with triazens and nitrosamines has also been patented.[270] β-Naphthol and the 2 : 3-hydroxynaphthoic arylamides are made soluble in dilute acid, and so applied to textiles, by attaching at 1 a dialkylaminomethyl-group which is replaced by the diazo-compound on coupling.[271] β-Naphthylamine- and alkyl-2-naphthylamine-1-sulphonates have also been patented for the purpose,[266, 268] whilst *p*′-acetamidophenyl-2-naphthylamine-1-sulphonic acid also couples with diazobenzene-*p*-sulphonic acid with loss of the 1-sulphonic acid group.[263]

The break-up of the coupled molecule can be deeper than mere scission of a blocking substituent. Thus diazo-compounds attack the alkylated aminodi- and -tri-phenylmethanes giving an aldehyde and a dialkylaminoazo-compound; the reaction with leuco Malachite Green proceeds in two stages, thus [252] :—

$$(C_6H_4{\cdot}NMe_2)_2CHPh + ArN_2{\cdot}OH \longrightarrow Ar{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2 + Me_2N{\cdot}C_6H_4{\cdot}CH(OH){\cdot}Ph + ArN_2{\cdot}OH \longrightarrow Ar{\cdot}N_2{\cdot}C_6H_4{\cdot}NMe_2 + H_2O + PhCHO$$

The hydrol is not easily isolable, but the benzaldehyde is demonstrable. *p*-Nitrodiazobenzene in alcohol suspension similarly removes the hydrocarbon side-chain from *p*-dimethylaminopropenylbenzene,

$$p\text{-}NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}Me,$$

giving 4-nitro-4′-dimethylaminoazobenzene.[264]

N-Alkyl-2-methylenedihydroquinolines [258] and N-alkyl-2-methylenetrialkylindolines [258] lose the alkyl-group attached to the cyclic nitrogen atom on coupling; according to König the products are *cis*-arylhydrazones, whereas those made from an arylhydrazine and the corresponding

aldehyde are *trans*-arylhydrazones, but on later views this is improbable (see below).

Migration of the Diazo-Group.

The attempt to couple primary aromatic amines with diazo-compounds in weakly acid solution sometimes fails to yield a single azo-compound, but instead there is obtained a mixture of two aminoazo-compounds thus :—

$$ArN_2{\cdot}X + NH_2Ar' \longrightarrow Ar{\cdot}N_2{\cdot}Ar'{\cdot}NH_2 \text{ and } Ar'{\cdot}N_2{\cdot}Ar{\cdot}NH_2$$

Instead of aminoazo-compounds suitable amines afford a mixture of triazens.

The reaction is sometimes referred to among dyestuff chemists as " diazo-exchange ", and it can be a source of annoyance when a useful compound is contaminated with one of inferior properties for the purpose in view.

A partial or complete exchange of the diazo-group between the two amines may precede the subsequent two-fold coupling, and Griess [280] first observed such an exchange on mixing diazotised sulphanilic with *p*-toluidine hydrochloride when he recovered the sulphanilic acid and found *p*-diazotoluene chloride in the solution. Similarly diazobenzene chloride can be obtained if aniline is used instead of *p*-toluidine, whilst *p*- or *m*-nitrodiazobenzene chloride will diazotise *p*-toluidine. The reverse reaction will not, however, occur,[282] nor does transfer take place in strongly acid solution, but it is not the invariable rule in diazo-exchange that diazo-compounds with negative substituents pass the diazo-group to amines with less negative substituents for a mixture of diazobenzene with *p*-bromoaniline affords a mixture of triazens among which 4 : 4′-dibromodiazoaminobenzene is present, showing that a portion of the *p*-bromoaniline has acquired diazo-nitrogen from the diazobenzene ; in the converse reaction between *p*-bromodiazobenzene and aniline no dibromodiazoaminobenzene is formed.[283]

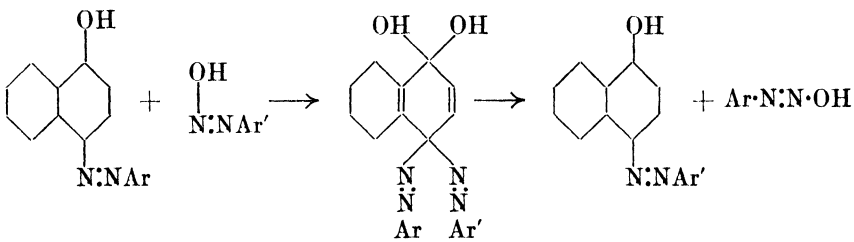
The readiest explanation of diazo-exchange is that an equilibrium exists in solution between diazo salt, amine salt, and nitrous acid and that among the nitrodiazo-compounds there is a greater degree of hydrolysis to amine and nitrous acid than among the diazo-compounds carrying more positive substituents :—

$$ArN_2{\cdot}Cl + H_2O \rightleftharpoons NH_2Ar,HCl + HNO_2$$

Hence when aniline hydrochloride is present in a weakly acid solution of *p*-nitrodiazobenzene it continually appropriates the free nitrous acid produced by the hydrolysis of the latter, until eventually the solution contains only *p*-nitroaniline and diazobenzene chloride. Such an equilibrium was surmised by Bamberger,[281] and more definite evidence was produced by Bucherer and Wolff,[284] who found that purified *p*-nitrobenzene*iso*diazotate when acidified affords a solution of *p*-nitrodiazo-

benzene in which the presence of nitrous acid can be demonstrated, the only apparent source of which is hydrolysis of the diazo-salt. The alternative suggestion that the migration proceeds through transitory formation of a triazen, ArN:N·NHAr′, where Ar′ is the more negatively substituted nucleus, is unlikely because once a triazen containing a negative substituent has been formed it is usually difficult to split back to amino- and diazo-compounds even by cold concentrated acid.

But though at first sight the inclination is to suppose that diazo-exchange precedes aberration of the coupling, yet it has been shown that azo-compounds can be attacked by diazo-compounds, and an exchange is effected with components already incorporated in the molecule; a valuable paper on this subject has been published by Filippytschew and Tschekalin.[285] They ascribe the power of one diazo-compound to eject another from an azo-compound to be due to their relative coupling activity. Thus they arrange in descending order of activity the diazo-compounds derived from *p*-nitroaniline > benzidine > dianisidine > α-naphthylamine > *m*-xylidine > aniline > 4-aminosalicylic acid. As an example of the reaction may be cited the action of tetrazotised benzidine on the azo dye made by coupling diazobenzene with acetyl H-acid. At 0·1N concentration at 0° in sodium carbonate solution exchange is complete in an hour, and an 80% yield of diazobenzene can be recovered from the solution. The authors believe the fundamental cause of this exchange to lie in keto-enol tautomerism, and as this is more pronounced in the naphthalene series than in the benzene series, so the exchange take place more easily in the dyes of the former series. They picture the reaction as proceeding by addition followed by scission of an unstable quinonoid addition product :—



The Effect of Pyridine on the Coupling Reaction.

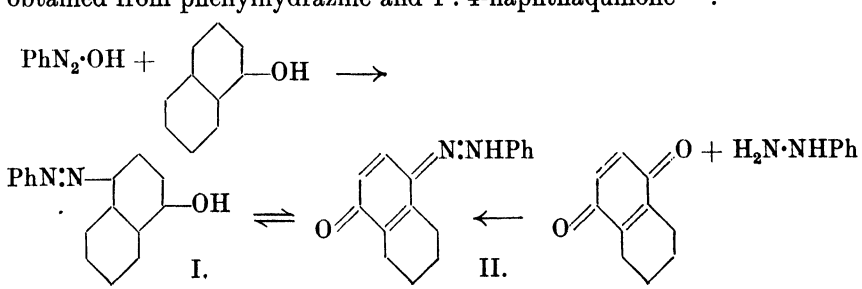
One type of azo-dyestuff, which includes some much-used direct cotton blues of good fastness, is made by coupling a diazo-compound with an amino-compound, re-diazotising the aminoazo-compound, coupling again, and so building up a chain of aromatic nuclei united by azo-links. This process cannot be continued indefinitely, and difficulties are encountered, and increase after the third repetition of the cycle, especially if " ethoxy Cleve's acid ", 2-ethoxy-1-naphthylamine-6- and/or -7-sulphonic acid is

used as third component. It is sometimes said of these long-chain azo-compounds that they lack " coupling energy ", which means to say that when they are added to the coupling component decomposition takes place much more quickly than coupling, so that only a small yield of the desired dyestuff is obtained. In these circumstances a great improvement in yield results if the coupling medium is a mixture of pyridine and water.[293]

In what manner the pyridine acts so as to bring about this exaltation of the coupling power of the diazo-compound is not known, or at least not published. No academic investigation of the matter has been published, but it hardly seems to be a mere buffering action controlling the pH. More probably there is some kind of loose combination between the diazo-compound and the pyridine which stabilises the diazo-compound during the long time necessary for coupling, in the same way that diazobenzene is conserved in the coupling with aniline to form aminoazobenzene. Hodgson and Marsden [296] suggest that in dilute acetic solution this intermediate compound is $R{\cdot}N{:}\overset{\oplus}{N}{\cdot}\overset{\oplus}{N}C_5H_5$ (with $O{\cdot}CO{\cdot}Me^{\ominus}$), where R is the remainder of the dyestuff molecule. To some degree the action of pyridine can be reproduced by a mixture of acetone and ammonia.[294]

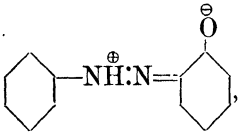
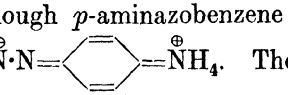
One may hazard the guess that there has been for a long period empirical knowledge of this action of pyridine, and possibly of its homologues, in the laboratories of Germany; for Heller [291] mentions the beneficial effect of quinoline in the tris-coupling of resorcinol, but says that pyridine and diethylamine did not show the same effect. Mehner [290] used pyridine in forming a triazen from diazobenzene and *m*-toluidine, Fischer and Bauer mention that they tried pyridine to improve the coupling of diazobenzene with 1 : 5-dihydroxynaphthalene,[292] whilst it is necessary to obtain a good yield of azo-compound from β-anthramine.[295]

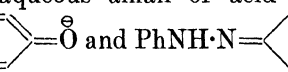
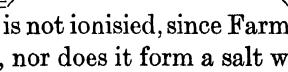
The Constitution and Configuration of the Azo-Compounds.— Like the mixed azo-compounds, the diarylazo-compounds are mesomeric, the extreme forms being azo and quinonoid respectively, and this mesomerism is shown especially by the hydroxyazo- and the aminoazo-compounds. For example, it has long been known that the product obtained by coupling diazobenzene with α-naphthol is identical with that obtained from phenylhydrazine and 1 : 4-naphthaquinone [300]:—



Another case, selected for study by K. H. Meyer and Zahn,[305] is the identity of the coupling product of diazobenzene with anthranol and the product of condensation of phenylhydrazine with 9 : 9-dibromoanthrone. Considerations of colour in solution, and the complexes formed with stannic chloride and aluminium chloride, complexes also formed by the O-benzoate, but not by the N-benzoyl derivative having the fixed hydrazone constitution, show that the free compound has probably the azo form.

Kuhn and Bär [312] made 1-benzeneazo-4-methoxynaphthalene, and the hydrazone of 1 : 4-naphthaquinone and *as*-phenylmethylhydrazine, *i.e.*, they replaced the labile hydrogen atom in each of the extreme forms I and II above and determined their absorption spectra. Comparison with the absorption spectrum of 4-benzeneazo-1-naphthol in benzene solution shows that in benzene a mixture of equal parts of the azo and hydrazo forms is present; in pyridine the azo form predominates, the quinhydrazone is the chief component in acetic acid or nitrobenzene. The equilibrium between the mesomerides therefore depends on the solvent. Similar measurements, including those for some mixed azo-compounds, have been made by Japanese workers.[314] On the other hand, Burawoy and Markowitsch [309] concluded from absorption spectra curves that *o*-hydroxyazo-compounds are always hydrazones.

The dipole moments of a number of simple monoazo-compounds have been determined by various workers [307, 315]; the values are low, and hence the configuration must be *trans* as *cis*-compounds have high dipole moments, and there cannot be present any large proportion of the hybrid ion such as  , which has been suggested for *o*-hydroxyazobenzene, though *p*-aminazobenzene probably contains some of the hybrid ion  . The dipole moments of the supposed *cis* and *trans* forms of *p* : *p*′-dihydroxyazobenzene have been measured and found to be identical,[319] thus showing that the likelihood of the differences which exist between the two modifications of the anhydrous solid [320] are due to geometrical isomerism. The evidence is further supported by the identity of the X-ray powder photographs, ebullioscopic, and polarographic measurements.[320]

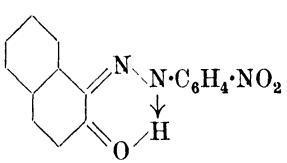
Among the *p*-hydroxyazo- and *p*-aminoazo-compounds there probably exist also in aqueous alkali or acid solution ionised forms such as  and  , though free *p*-hydroxyazobenzene is not ionisied, since Farmer and Hantzsch[302] found it to be a non-electrolyte, nor does it form a salt with ammonia in benzene solution;

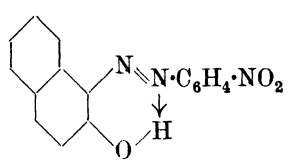
it is soluble in liquid ammonia. The inference is that the free compound has the quinone structure, and Bradley and Robinson have shown that some other azo-compounds also behave as quinones in their reaction with potassium cyanide.[310] This substance when boiled with 1-nitroso-2-naphthol, a quinonoid compound, in aqueous alcohol affords 1-amino-2-hydroxy-4-cyanonaphthalene, and the same compound is similarly produced from potassium cyanide and 1-benzeneazo-2-naphthol, thus confirming the idea that the latter has the quinonoid structure. But while potassium cyanide thus interacts with 1-benzeneazo-2-naphthol-6-sulphonic acid, and -6 : 8-disulphonic acid, *p*-sulphobenzeneazo-2-naphthol-3-carboxylic acid and its anilide and with 4-benzeneazo-1-naphthol, it does not interact with 1-benzeneazo-2-naphthylamine, *p*-aminoazobenzene, benzeneazo-*p*-cresol, or benzeneazo-*p*-hydroxydiphenyl. Again, some azo-compounds, for example 2 : 4-dinitro-4′-hydroxyazobenzene, form adducts with *cyclo*pentadiene, apparently a reaction of the quinonoid form which is especially active in this compound.[311] Other evidence for the quinhydrazone constitution of the *p*-hydroxyazo-compounds is that they condense with 2 : 4-dinitrophenylhydrazine, giving *p*-benzoquinone-bishydrazones.[306] For example, 4-nitro-4′-hydroxyazobenzene boiled in methanol with 2 : 4-dinitrophenylhydrazine gives *p*-benzoquinone-4-nitrophenylhydrazone-2 : 4-dinitrophenylhydrazone,

$$4\text{-}NO_2\cdot C_6H_4\cdot NH\cdot N{:}C_6H_4{:}N\cdot NH\cdot C_6H_3(NO_2)_2\text{-}2:4,$$

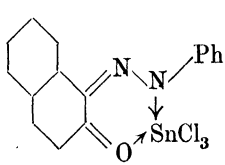
also made by the reverse process from 2 : 4-dinitro-4′-hydroxyazobenzene and *p*-nitrophenylhydrazine. *p*-Benzoquinone, unlike the naphthaquinones, does not form quinonehydrazones by reaction with arylhydrazines, excepting 2 : 4-dinitrophenylhydrazine.

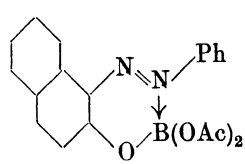
The advent of the idea of chelation saw it applied to explain the stability and insolubility in caustic alkali of the *o*-hydroxyazo-compounds, configurations for Para Red being proposed such as [308] :—



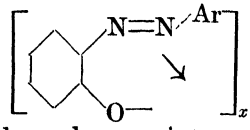
and


Mason further showed that 1-benzeneazo-2-naphthol affords a stannichloride with stannic chloride in benzene solution and a boroacetate with boroacetic anhydride, compounds which probably have such configurations as



and


The empirically discovered fact that the *o*-hydroxyazo-compounds

form metallic complexes by a process of chelation similar to the above, chiefly with chromium and copper, is the basis of their application as mordant dyes, and hence quite outside the scope of this work, but the study of such complexes leaves little doubt that they are properly represented by the configuration  M, and hence that the geometrical arrangement of the aryl groups is *trans*. Elkins and Hunter [313] point out that while this gives no positive proof that the parent azo-compound is *trans*, yet decomposition of such complexes by cold acid regenerates azo-compounds identical with the original.

From the foregoing it will be inferred that beside structural isomerism of the azo-hydrazone type the possibility of geometrical isomerism exists in all azo-compounds. Bamberger [301] said that *p*-nitrobenzeneazo-α-naphthol exists in isomeric forms, but he doubted if the isomerism is geometrical. C. V. and R. A. Gortner [303] tentatively considered that they had obtained *cis*-azobenzene by distilling hydrazobenzene from iron, but their product was probably a mixture of hydrazobenzene with azobenzene.[304] In 1937 G. S. Hartley [316, 317] detected a modification of azobenzene during photometric determinations of solubility, and separated it from the ordinary form by distribution between immiscible solvents. The new forms is produced by the action of light on ordinary azobenzene, and photometric measurement of the deepened colour due to the new form shows that an acetic acid solution exposed in shallow white trays for three to four hours to sunlight contains an equilibrium proportion of 22%, which can be extracted with light petroleum and crystallised. The differences between the known and the new forms of azobenzene are shown in the table below.

TABLE XXIV

Comparison of Properties of trans- *and* cis-*Azobenzene*

Property.	Ordinary (*trans*-) azobenzene.	Form produced by irradiation—*cis*-azobenzene.
Melting point . . .	68°	71·4° (quick heating)
Dipole moment [321] . . .	zero	3·0 D
Mol. wt. (freezing point in AcOH or C_6H_6)	182	179–190
Solubility	—	More sol. in polar solvents, *e.g.*, H_2O; less sol. in petrol

Further, the specific exaltation of the refractive index of the new form resembles that of *cis*-stilbene and *cis*-azoxybenzene,[319] but there is little difference in the absorption spectra,[324] which chiefly reflects the fact that *cis*-azobenzene, being more deeply coloured, absorbs more strongly.

The almost simultaneous discovery by A. H. Cook [318] and by Zech-

meister [320] and his co-workers that *cis*-azobenzene produced by irradiation of azobenzene in benzene or light petroleum can be removed by absorption on alumina which does not hold the *trans*-form opened the way for the examination of other azo-compounds, including hydroxy-, methoxy-, and nitro-azobenzenes, the azonaphthalenes, and bisazo-compounds.[323] Irradiation of these compounds does not invariably produce *cis*-forms, and no simple rule can yet be formulated to predict whether a *cis*-form will occur, or how stable it will be if formed. Thus, *o*-nitro-, *o* : *o'*- and *p* : *p'*-dinitroazobenzene afford no *cis*-isomeride, *p*-nitro- and *m* : *m'*-dinitroazobenzene afford *cis*-isomerides of normal stability, whilst *cis*-*m*-nitroazobenzene is very stable. *p* : *p'*-Dihydroxyazobenzene gives two different forms, both stable and preserving spectroscopic individuality even after irradiation, whilst bisbenzeneazobenzene after irradiation gives two absorption bands on alumina, the *trans*–*trans*-isomeride being washed through, whilst *cis*–*trans* remains at the top and *cis*–*cis* forms the intermediate band.

Hodgson [326] has submitted an extensive critique of the foregoing claims to the preparation of *cis*- and *trans*-azobenzene the gist of which is that certain properties of the *cis*-isomer, which are admittedly anomalous, for example, its colour, absorption spectrum, crystal form, and the large heat of conversion (12 k.cals./g.-mol.) of *cis*- into *trans*-azobenzene, can be adequately explained if the *cis*-form is in fact a double compound of azoxybenzene and hydrazobenzene.

The commercial azo dyes most probably have the *trans*-configuration because, being hydroxy- or aminoazo-compounds, the tautomeric or mesomeric forms produced in media containing hydroxyl or hydrogen ions permit free rotation, the energy of the *cis*-form is given up, and when the azo-link is again formed it is the *trans*-form which appears.[317]

Kinetics of the Coupling Reaction.—Goldschmidt [335-339] and his school first studied the kinetics of the coupling reaction, but their extensive work was carried out before accurate methods of controlling pH by means of buffers was known. Nevertheless, they discovered that the reaction is bimolecular, a finding which has not since been questioned, and they also established the important fact that in a caustic alkaline solution of phenol it is not the sodium phenate which couples, but the free phenol or phenoxide ion produced by dissociation of the sodium salt. Hence high concentration of caustic alkali prevents coupling not only because it tends to convert some diazo-compounds into their *iso*diazotates, but also because the phenol is converted into the non-ionised salt which cannot couple. Veley studied the rate of formation of Bismarck Brown in dilute aqueous solution by acting on *m*-diamines with nitrous acid and measuring the rate of formation of dyestuff by the colorimeter; here also the bimolecular law is followed.[340] Blumberger [341] obtained smooth curves for the relationship between velocity constant and concentration of caustic potash in the coupling of diazobenzene with *p*-cresol and with

salicylic acid; he detected no relation between coupling speed and decomposition of the diazobenzene which occurs parallel with the coupling.

Conant and Peterson [342] produced more concordant results than those of Goldschmidt by buffering the coupling solution so as to prevent variation in pH as the reaction proceeded. They also used the colorimetric method to measure the rate of production of the azo-compound, finding the reaction to be bimolecular over a wide range and, with the components selected, almost free from side reactions. Twenty couplings of diazo-compounds with phenols were studied, and the coupling rate was found to be a simple function of the pH, each pair being characterised by a " coupling value " defined as the pH for a given temperature and concentration of salts in the solution at which $\log k = 1$. Increase of concentration of salts in the solution tends to lower the rate of coupling slightly. Among other conclusions they formed the opinion that ultimately the rate of coupling of a diazo-compound with a hydroxy-compound is a function only of the nature of the latter. This conclusion has also been reached by Ayling, Gorvin, and Hinkel,[344] who, in a study of one of the most weakly coupling of all diazo-compounds, *p*-dimethylamino-diazobenzene chloride, remarked that while the rate of coupling, *i.e.*, the rate of disappearance of the diazo-compound, varies greatly with pH, the actual yield of azo-compound collected depends only on the coupled component.

Wistar and Bartlett [343] have extended the work of Conant and Peterson to the coupling of amino-compounds, using the colorimetric method to plot the rate *vs.* pH curves for the coupling of diazobenzene-*p*-sulphonic acid with naphthionic acid and diazobenzene with 1-naphthylamine-8-sulphonic acid. These coupling are also bimolecular. The inferences drawn from the work are dealt with below.

The Mechanism of the Coupling Reaction.—There are discernible three schools of thought on the mechanism of the coupling reaction. These postulate that the mechanism is either :—

1. Direct attack by diazonium ions on the activated hydrogen of the coupled compound.
2. Addition of diazonium or diazotate ions to the coupled compound followed by rearrangement and elimination of water.
3. A condensation of an undissociated *n*-diazohydroxide molecule with the activated hydrogen of the coupled compound.

At the outset it must be said that the work of Conant and Peterson and Wistar and Bartlett on reaction velocity *vs.* pH shows that whatever the coupling mechanism may be, the same bimolecular reaction mechanism is operative over the range pH 4·5—8·5 for naphthols and over a more acid range for amino-compounds, nor is there any reason to suppose that the same mechanism is not operative for keto-enols.

1. *Direct Attack by Diazonium Ions on the Activated Hydrogen of the*

Coupled Compound.—This school of thought has largely developed in America, led by Wistar and Bartlett [343] and Hauser and Breslow,[374] although G. M. and R. Robinson [366] showed in 1917 how the charge induced at the *p*-position in phenol allows direct substitution through the undissociated diazonium hydroxide.

Wistar and Bartlett started from the premise that in the coupling of amino-compounds the measured reaction velocity is governed by an acid-base equilibrium in one or other of the reactants :—

$$ArN_2^{\oplus} + OH^{\ominus} \rightleftharpoons ArN_2{\cdot}OH \text{ or } Ar'{\cdot}NH_2 + H \rightleftharpoons Ar'{\cdot}NH_3^{\oplus}$$

From these arise the four possibilities :—

A. The diazohydroxide couples with the ammonium ion.
B. The diazonium ion couples with the free amine.
C. The diazonium ion couples with the ammonium ion.
D. The diazohydroxide couples with the free amine.

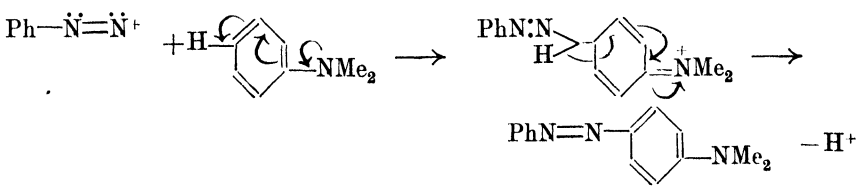
Taking known constants for diazobenzene and aniline it is possible to calculate the general shape of the velocity *vs.* pH curve for the four alternative mechanisms. The experimental curves are coincident with those for mechanisms A and B, the theoretical curves for C and D being entirely different; hence the conclusion was reached that arylaminoazo-compounds are formed by mechanism B, since the quaternary phenyl-ammonium ion is both *meta*-directing and known not to couple. This finding has been attacked by Hodgson [374] chiefly on the grounds that (*a*) the assumed rate-determining mechanism would produce a unimolecular reaction and (*b*) the relatively great concentration of buffer acids sets up the equilibrium :—

Diazonium ion + anion of buffer acid ⇌ undissociated diazo-compound, and hence that the coupling really proceeds by mechanism D.

Hauser and Breslow from experiments on the coupling of dry benzenediazonium chloride and benzenediazopiperidide with β-naphthol in dry pyridine also reached the conclusion that the diazonium ion is the active coupling agent. They represent the series of equilibria given above in terms of the resonance theory thus (dots represent electrons) :—

$$Ar{-}\overset{\oplus}{N}{\equiv}N \rightleftharpoons Ar{-}N{=}N^{+} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} Ar{-}N{=}N{-}OH \underset{H^{\oplus}}{\overset{H^{\oplus}\ OH^{\ominus}}{\rightleftharpoons}} Ar{-}N{=}N{-}OH$$

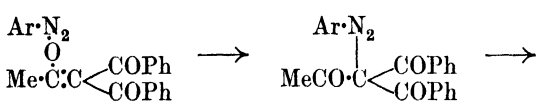
From this series they select $Ar{-}N{=}N^{+}$ as the active form and denote the mechanism of coupling with dimethylaniline as occurring thus :—



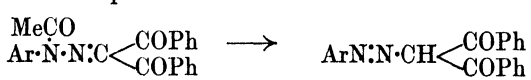
Coupling is thus represented as a displacement of a proton rather than substitution, a view also expressed by Hammett.[373] Broad generalisations as to behaviour in aqueous media cannot be drawn from experiments carried out in a medium so unique in its relationship to diazo-compounds as dry pyridine; moreover, the yield of azo-compound obtained is only 48%, showing that the conditions fall short of the best. Hodgson [375] points out the diazonium chloride may form an easily-coupling addition compound with the pyridine, or when dissolved in the dry base may rearrange into Ph·N:N·Cl, which can couple by the same mechanism as the undissociated diazohydroxide.

2. *Addition of Diazonium or Diazotate Ions to the Coupled Compound followed by Rearrangement and Elimination of Water.*—The existence of O-azo-compounds and triazens some of which can rearrange to C-azo-compounds lends support to the view that all coupling proceeds through such intermediate steps even though they are not always isolable.

Dimroth,[361] working on the action of diazo-compounds on aliphatic substances which show keto-enol tautomerism and in which the separate tautomers can be isolated, started the intermediate compound theory. He used diacetylsuccinic ester and acetyldibenzoylmethane coupled in ethanol solution with *p*-nitrodiazobenzene. He showed that the keto-form does not couple, nor can direct substitution of hydrogen occur because in the enol-form of acetyldibenzoylmethane, $MeC(OH):C(COPh)_2$, there is no hydrogen atom available at the methane carbon atom to which the azo-link eventually becomes attached. The reaction must therefore go through the O-azo-compound. Such O-azo-compounds, which are colourless, were isolated by Dimroth and Hartmann,[362] and are recognised by their instability; when dissolved they show the reaction of a diazo-compound by coupling with β-naphthol, and hence may be regarded as oxygen analogues of the triazens. When warmed with alkali the true red C-azo-compound is formed, but this is unstable, the acetyl-group migrating to nitrogen, from which it is removed by sodium ethoxide, thus :—



Colourless O-azo ether. Red C-azo-compound.



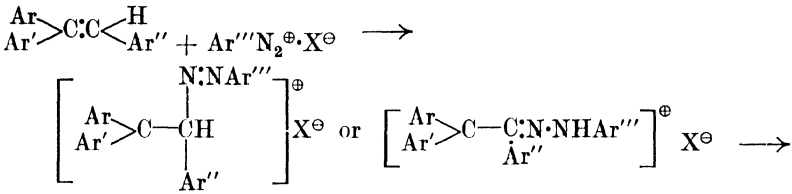
Colourless acetylhydrazone. Red C-azo-compound.

Intermediate stages can also be detected in coupling aromatic compounds, and Fierz-David [370] has published a beautiful set of micro-photographs showing the intermediate stages in the coupling of diazotised sulphanilic acid with *m*-phenylenediamine to form sulphochrysoidine. But such compounds are stable outside the optimum pH for coupling, and

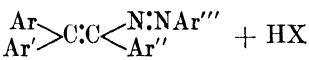
when placed in these conditions they break up, and the ordinary coupling substitution occurs, so that migration is apparent rather than real.

Karrer [75] considered the formation of intermediate oxonium or ammonium salts to be the mechanism of coupling, scission of the former accounting for the hydrolysis of phenol ethers on coupling. K. H. Meyer,[367] to evade the difficulty that Dimroth's theory could not explain the coupling of phenol ethers and hydrocarbons, postulated addition at a reactive double bond and an intermediate quinonoid addition product.

As already mentioned (p. 220), intermediate compounds occur in the coupling of the arylethylenes and the suggested mechanism is [228] :—

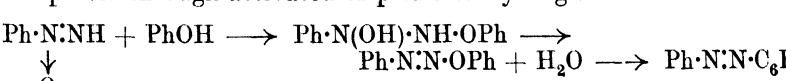


Azo- and hydrazo-tautomers of a carbenium salt



Based on this an extended and generalised theory has been propounded by Wizinger and Cyriax,[379] who, for example, coupled anthraquinone-1-diazonium chloride with αα-tetramethyldiaminodiphenylethylene in ethanol, when an addition product at once separates, and on treatment with substances removing hydrochloric acid affords αα-tetramethyl-diaminodiphenyl-β-(anthraquinone-1-azo)ethylene. Hence they say that coupling occurs in the same manner as, for example, halogenation in which an ionoid-non-ionoid carbenium salt is formed which loses acid more or less readily. Dilthey and Blankenburg [372] also regard coupling as addition of a diazonium ion to activated carbon followed by rearrangement of the salt-like compound.

Angeli [371] considered the undissociated *n*-diazohydroxide to be the active agent in coupling, the coupled compound forming an intermediate compound through activated or polarised hydrogen :—



As a general conclusion it may be said of the addition-compound theories that they have been evolved to meet exceptional examples of the coupling reaction, and that the attempts to generalise from these to all coupling reactions are not convincing.

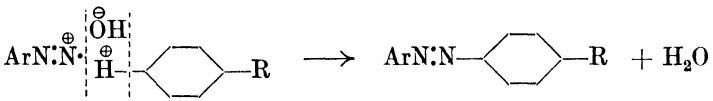
3. *Condensation of an Undissociated* n-*Diazohydroxide Molecule with the Activated Hydrogen of the Coupled Compound.*—Goldschmidt [360] first suggested that a diazotate and not a diazonium salt or ion is the active

agent in coupling, and that it is free phenol or phenoxide ion which couples and not an alkali phenate. Conant and Peterson tentatively put forward the mechanism :—

$$ArN_2{\cdot}X + OH^{\ominus} \rightleftharpoons ArN{:}N{\cdot}OH + X^{\ominus} \quad \text{Fast and reversible}$$

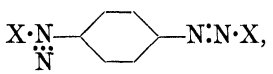
$$ArN{:}N{\cdot}OH + P \longrightarrow ArN{:}N{\cdot}P + H_2O \quad \text{Relatively slow and irreversible (P = phenol)}$$

This mechanism has been particularised by Hodgson [375-378] over a large field, and he concludes [375] that coupling is not a displacement reaction but a condensation between the polarised diazo-compound $ArN{:}\overset{\oplus}{N}{\cdot}\overset{\ominus}{X}$ and the activated state of the coupled component in which a hydrogen atom acquires an induced positive charge, as in the *para* position of phenol or a terminal hydrogen atom in butadiene. Conant and Peterson's second step can therefore be detailed as :—



R is any activating substituent, and if an azo-hydrazo hybrid is subsequently formed this state ensues as a discreet step with loss of energy after the formation of the azo-compound is complete. The same mechanism operates if the diazo-compound ejects another substituent, and is illustrated by the appearance of hypobromite in the coupling of 1-bromo-2-naphthol mentioned above; here a positively-charged bromine atom is expelled, and unites with hydroxyl to form hypobromous acid. Hodgson is explicit that it is the undissociated diazohydroxide which couples, a condition also implicit in Conant and Peterson's mechanism.

This mechanism also accounts for the fact that diazo-compounds substituted by strongly negative groups can couple in acid solution. Examples are 2 : 4 : 6-trinitrodiazobenzene and *m*- and *p*-tetrazobenzene, which Schoutissen has shown couple once in concentrated acid medium and once again at the usual pH after dilution and neutralisation. The constitution of *p*-tetrazobenzene in concentrated acid must be



i.e., it contains both the extreme resonance forms of the diazonium salt (cf. p. 100), and hence it must be the unionised " diazo salt " form on the right which couples, and that by precisely the same mechanism as the diazohydroxide, except that a molecule of acid is eliminated instead of one of water. Indeed, in the case of diazo-compounds like 2 : 4-dinitrodiazobenzene, which couple well in the region pH 3—5, it is possible that both undissociated $ArN{:}N{\cdot}X$ and $ArN{:}N{\cdot}OH$ are coupling at the same time, the proportions depending on the exact pH.

The chief difficulty with this mechanism is to understand how there can be a sufficiency of undissociated diazohydroxide at the extreme dilutions at which coupling can occur, *e.g.*, in the Griess-Ilosva test (cf. p. 349).

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CHAPTER VII

REACTIONS OF THE DIAZO-COMPOUNDS (*continued*)

CLASS D. FORMATION OF RING COMPOUNDS.

Like other derivatives of the diazo-compounds, the ring structures to which they give rise may be conveniently divided into two groups :—

A. Compounds in which the diazo nitrogen atoms are retained :—

(i) Cinnolines, (ii) Indazoles, (iii) Benztriazoles, (iv) Benztriazines, (v) Thiodiazoles (diazo sulphides).

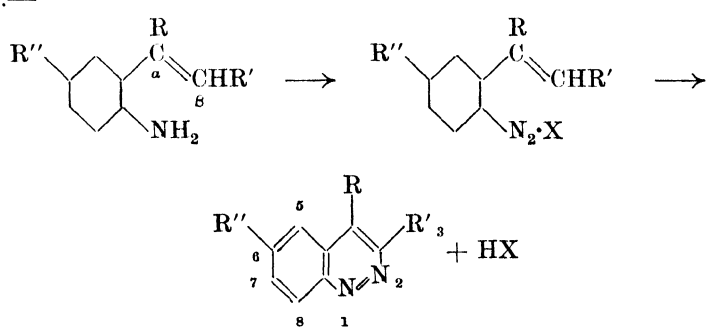
B. Compounds in which the diazo nitrogen atoms are lost :—

(i) Phenanthrene and related compounds, (ii) Fluorene and fluorenone, (iii) Dibenzfuran (diphenylene oxide) and dibenzthiophen (diphenylene sulphide), (iv) Carbazole, (v) Other ring compounds.

A. RING COMPOUNDS IN WHICH THE DIAZO NITROGEN ATOMS ARE RETAINED :—

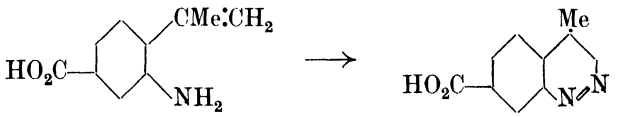
(i) **Cinnolines.**—A diazonium group attached to a benzene ring and *ortho* to an unsaturated chain can, under certain conditions, couple with the β-carbon atom of the chain to form a fused six-membered ring. The necessary underlying conditions are that the substituents of the side-chain shall induce an enhanced electron-giving power in the unsaturated β-carbon atom, and/or that the substituents in the benzene ring shall induce a displacement of electrons from the nitrogen atom of the diazo cation farthest from the benzene ring so that the covalent link between the nitrogen and carbon can be formed.

When the side-chain is ethylenic the reaction is generalised in the form :—



E. Fischer [1] showed that *o*-aminocinnamic acid (R, R″ = H, R′ = CO_2H)

on diazotisation and heating the solution replaces the diazo-group by hydroxyl, but Widman [3] converted 3-amino-4-propenylbenzoic acid (R = Me, R′, R″ = H) by diazotisation into 4-methylcinnoline-7-carboxylic acid :—

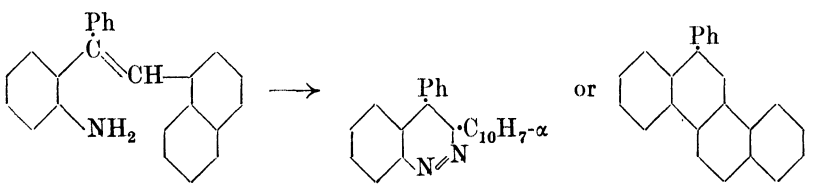


Then Stoermer and Fink [6] obtained 4-phenylcinnoline from 1-*o*-aminophenyl-1-phenylethylene (R = Ph, R′, R″ = H) in almost quantitative yield :—



Similarly, they had no difficulty in preparing 4-*p*-tolylcinnoline (R = *p*-C_6H_4Me, R′, R″ = H) and 4-phenyl-3-methylcinnoline (R = Ph, R′, R″ = Me), but they found that 2-bromo-1-*o*-aminophenyl-1-phenylethylene (R = Ph, R′ = Br, R″ = H) does not easily afford 3-bromo-4-phenylcinnoline, while to produce 4-*p*-hydroxyphenylcinnoline (R = *p*-C_6H_4OH, R′, R″ = H) diazotisation is carried out in concentrated hydrogen bromide.[7] Simpson and Stephenson [9] extended the Widman–Stoermer reaction by making a series of cinnolines having halogen at 6. For example, when nitrite solution is added to a dilute sulphuric acid solution of 1-phenyl-1-(2′-chloro-6′-aminophenyl)ethylene (R = Ph, R′ = H, R″ = Cl) at 10°, diazotisation and ring-closure occur immediately, and the cinnoline is precipitated. Summing up the experimental evidence, Simpson [10] concludes that ring-closure is prevented when R = H or CO_2H and R′ = aryl, but that if R = aryl, then cinnoline formation is so favoured that it occurs even if R′ = aryl also ; hence he was able to prepare 3 : 4-diphenyl- and 4-phenyl-3-benzylcinnoline. The initial aminotriarylethylenes can exist as *cis* and *trans* isomerides; both forms give the cinnoline.

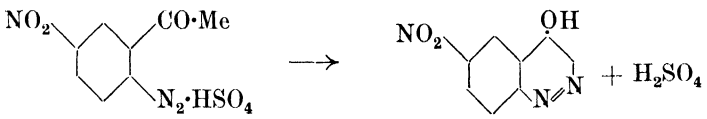
The Pschorr reaction (cf. p. 254) is always a potential competitor with cinnoline formation where R′ is aryl and, according to the conditions α-phenyl-α-*o*-aminophenyl-β-1′-naphthylethylene (I) on diazotisation gives either the cinnoline (II) or 2-phenylchrysene (III) :—



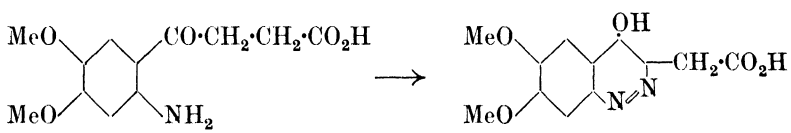
I. II. III.

4-Phenyl-3-1′-naphthylcinnoline (II) is produced by diazotising the base (I) in a mixture of hydrochloric and acetic acids and diluting the diazo solution with water. 2-Phenylchrysene is produced when the same diazo solution is poured into aqueous sodium acetate with copper powder.

4-Hydroxycinnolines are formed by diazotisation of some *o*-aminoaryl ketones. The first case observed was that provided by Borsche and Herbert,[8] who diazotised 5-nitro-2-aminoacetophenone in dilute sulphuric acid, and on keeping the solution until the diazo-reaction had disappeared found the product to be 6-nitro-4-hydroxycinnoline :—



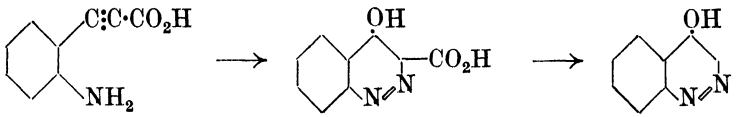
This reaction has been further examined by Leonard and Boyd [14] and by Schofield and Simpson.[12] A negative group *para* or *ortho* to the diazonium group is the condition for ring-closure to the cinnoline, and the yields are then high. When such a group is lacking, as in *o*-diazoacetophenone, the yield of cinnoline is only 10%, and phenolic products are the main result. Against this is the observation of Leonard and Boyd [14] that 4-chloroacetophenone-2-diazonium sulphate on setting aside at room temperature for twenty-eight days gives 7-chloro-4-hydroxycinnoline in 81% yield. Aryl alkyl ketones in which the alkyl group has two or more carbon atoms afford 3-substituted-4-hydroxycinnolines; for example, 5-bromo-2-aminopropiophenone affords 6-bromo-4-hydroxy-3-methylcinnoline [14] and β-(6-aminoveratroyl)propionic acid affords 4-hydroxy-6 : 7-dimethoxycinnoline-3-acetic acid :— [12]



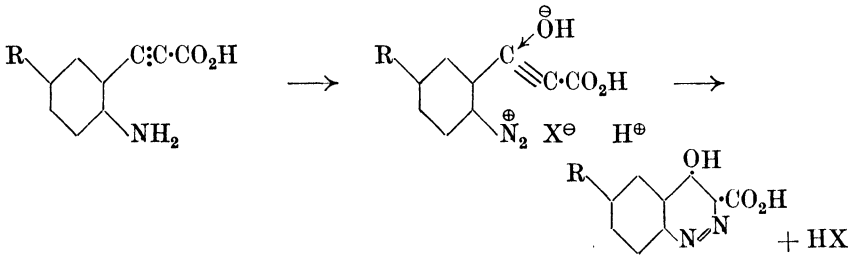
Schofield and Simpson point out that for strict analogy with the Widman–Stoermer reaction ring-closure should occur through the enolic form of the ketone, but that though this may have some effect, the chief controlling factor are the substituents, which by position and polarity increase the cationic activity of the diazonium group so that it is able to co-ordinate with the methyl group from which a proton is then expelled.

Ring-closure to an acetylenic side-chain was discovered by v. Richter,[2] who obtained 4-hydroxy-3-carboxycinnoline on boiling diazotised *o*-aminophenylpropiolic acid in aqueous solution with the object of replacing the diazo-group by hydroxyl. v. Richter claimed a quantitative

yield of 4-hydroxycinnoline-3-carboxylic acid, but Schofield and Simpson [11] obtained 62% on the *o*-nitropropiolic acid, the amine not being isolated, while Busch and Klett [4] said that formation of chlorocarbostyril is a cause of diminution of yield. The carboxy-group is easily removed by heating to 260° or by heating in benzophenone,[11] leaving 4-hydroxycinnoline :—

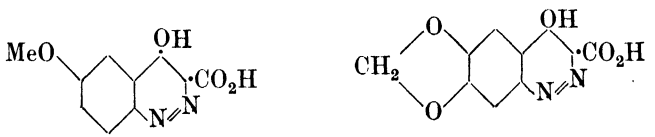


The yield is the same whether diazotisation is carried out in dilute sulphuric or hydrochloric acid.[12] It will be noted that beside ring-closure hydroxyl is also acquired at 4. Schofield and Simpson [11, 12] have discussed this reaction and, ruling out direct hydration of the acetylenic link because such hydrations usually require catalysts in a strongly acid medium, they suggest that the process is one of intramolecular co-ordination of the diazonium cation with the anionoid carbon atom followed by addition of hydroxyl ion :—



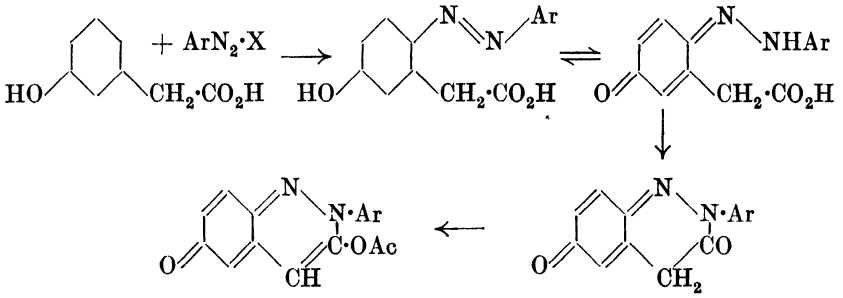
Thus in the Richter reaction the proton which is eliminated as HX comes from the solvent, whereas in the Widman–Stoermer reaction and the aminoacetophenone synthesis it is provided from the side-chain.

Schofield and Simpson [11] have made 4-hydroxycinnoline in good yield by diazotising *o*-aminophenyacetylene and further extended v. Richter's reaction to the preparation of 4-hydroxy-6-methoxycinnoline-3-carboxylic acid and 4-hydroxy-6 : 7-methylenedioxycinnoline-3-carboxylic acid :—



Kornfeld [15] discovered a quite different synthesis of the cinnoline ring in which a diazo-compound supplies the two ring nitrogen atoms. Diazo-compounds are coupled with *m*-hydroxyphenyl acetic acid and the resulting azo-compound is warmed with acetic anhydride when ring-closure occurs

by dehydration between the carboxy-group and the hydrazine form of the azo-link giving a 2-aryl-3-acetoxy-6-keto-2 : 3 : 4 : 6-tetrahydrocinnoline :—



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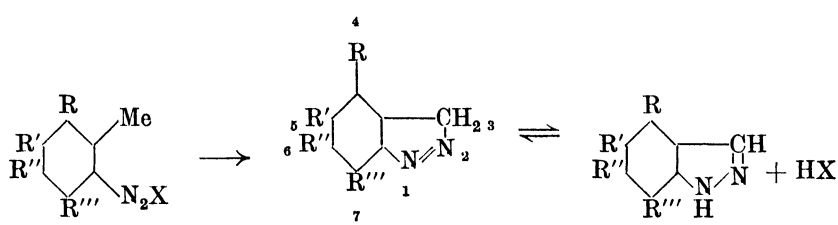
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(ii) **Indazoles.**—A diazo-group *ortho* to a methyl-group can couple internally to form the fused-ring compound 4 : 5-benzpyrazole, generally called indazole, or its derivatives :—



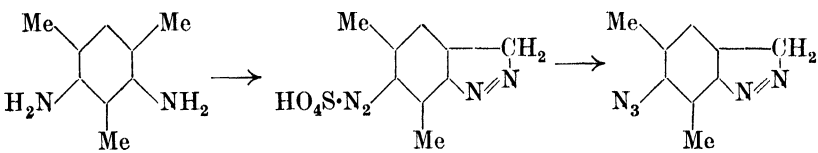
The mechanism of formation is the same as that by which cinnolines are formed by the Widman–Stoermer reaction, and the same activating forces, dependant on the substituents R, R′, R″, R‴, operate.

The indazoles had already been prepared by another synthesis before

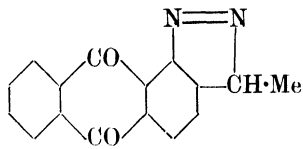
the above reaction was discovered by Witt, Nölting, and Grandmougin [1] in the attempt to convert *p*-nitro-*o*-toluidine (4 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$) into the corresponding cresol. Nölting [5] carried out a massive research on the preparation and chemistry of the indazoles, working with the nitrotoluidines, their homologues of the di- and trimethylbenzene series, and from the dinitrotoluidines. Nölting observed that indazole formation is assisted when R′ and/or R‴ = NO_2 (R, R′, R″, R‴ = H unless otherwise stated), but hindered when R′ = Me. He diazotised *p*-nitro-*o*-toluidine (4 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$), in which the nitro-group activates the methyl-group, in glacial acetic acid, and found that if the solution is set aside at room temperature the product is chiefly 6-nitro-3-(5′-nitro-2′-methylbenzeneazo)indazole, but that if it is heated 6-nitroindazole is obtained in about 80% yield. On the other hand, *m*-nitro-*o*-toluidine (5 : 1 : 2-$NO_2 \cdot C_6H_3Me \cdot NH_2$), in which the nitro-group activates the diazo-group, when similarly diazotised, affords no indazole if heated, but a good yield of 5-nitroindazole when the cold solution is set aside so that the slow process of internal coupling can proceed to completion. Hence, as Nölting remarked, the best conditions for indazole formation must be found by experiment for each diazo-compound, a point which is readily understood if the inductive effects of R, R′, R″, R‴ oppose each other.

Bamberger [4] also carried out an extensive research on indazoles, working chiefly with mesidine, which gives 5 : 7-dimethylindazole, also with *o*-toluidine, and with 1 : 3 : 4-xylidine (4 : 1 : 3-$NH_2 \cdot C_6H_3Me_2$), and his general method was to add caustic soda to the diazo solution at − 10° and keep it until the diazo reaction had disappeared. The product is a golden-yellow jelly from which, if the starting material is *o*-toluidine, dilute mineral acid extracts indazole in only 3—4% yield. Bamberger showed that the yellow residue is chiefly 3-*o*-tolueneazoindazole (9·5 g. from 25 g. of *o*-toluidine). It is formed because indazole can couple at 3 with diazo-compounds, hence as soon as some indazole has been formed in the solution it couples with some of the remaining unchanged diazo-compound. Nölting, who obtained the same yield of indazole, but who used sodium carbonate at 0° instead of caustic soda, said that azocresols are also formed with the indazole.

When Morgan and Davies [6] attempted to tetrazotise diaminomesitylene in nitrosyl sulphuric acid, one indazole ring formed at once in the cold concentrated acid, and the other diazo-group was then fixed as the azide by reaction with added sodium azide, giving 5 : 7-dimethyl-6-azidoindazole :—



In the anthraquinone series a diazo-group in the 1-position can ring-close with the α-carbon atom of alkyl-groups of two or more carbon atoms.[7] Thus 1-amino-2-ethylanthraquinone is diazotised in nitrosyl-sulphuric acid, and the diazonium sulphate is collected after diluting the solution with ice; it is then stirred with dilute aqueous sodium carbonate and brought to the boil, giving PyC-methyl-1(N) : 2-pyrazolo-anthraquinone



There is no record of a similar ring-closure of diazotised *o*-amino-ethylbenzene to 3-methylindazole; this substance, also 3-phenyl- and 3-aminoindazole, are obtained as an aberration of the reduction of diazotised *o*-aminoacetophenone, *o*-aminobenzophenone, and *o*-aminophenyl-cyanide to the respective hydrazines (cf. p. 183).

7-Nitroindazole is obtained by boiling diazotised 3-nitro-*o*-toluidine (3 : 1 : 2-NO_2·C_6H_3Me·NH_2) [8] and nitroxylidine

(1 : 3 : 5 : 6-NO_2·$C_6H_2Me_2$·NH_2)

affords 7-nitro-5-methyl indazole.[3]

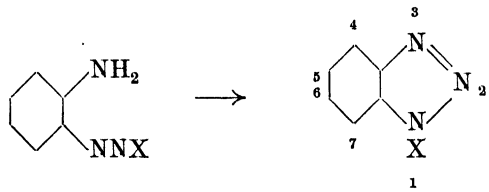
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(iii) **Triazoles.**—As already described, the primary *o*-diamines are difficult of tetrazotise (cf. p. 26) and when acted on by nitrous acid under a wide range of temperatures and acid concentrations they afford triazoles. Unless they contain water-solubilising groups, *e.g.*, carboxyl or sulphonic acid groups, they separate immediately on formation from an aqueous solution as a colourless precipitate, and are found to be both weak bases and weak acids forming hydrolytically dissociated salts with anions and cations.

The reaction was discovered as early as 1860 by Hofmann [1] working with nitro-*o*-phenylenediamine, though he did not elucidate the constitution of the triazole he had made. The reaction has since been found

to be quite general in the benzene, naphthalene, and anthraquinone [17, 20, 21] series, nor is it prevented if one of the amino-groups is secondary or monoacylated :—

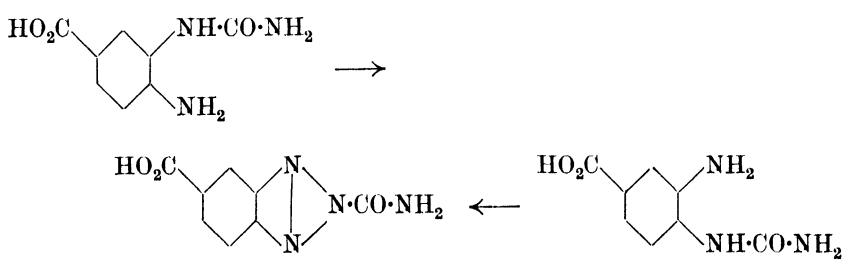


where X = aryl, aralkyl, alkyl or acyl.

The above benztriazoles are described in the literature under a variety of names, *e.g.*, azimines or diazoimines in English, azimides or azimido-compounds in German, and care must be taken not to confuse them with the arylazides, which are often called azoimides. They may be regarded as internal diazoamino- or diazoimino-compounds formed by coupling of the first diazo-group to be formed with the contiguous amine- or imino-group, but, unlike many open-chain triazens, the ring cannot be opened by acids to regenerate the diazonium salt and the amine. In this they differ from the internal diazoimino-compounds formed by certain acyl *p*-diamines on diazotisation (cf. p. 36), and from the yellow six-membered azimine formed from 1 : 8-naphthylene diamine.[3, 12, 16]

Rudolph,[6] who made the triazole from carboethoxy-*o*-phenylene-diamine, found thereby that acylation will not hinder ring-closure, and this reaction limits the usefulness in synthetic work of the monoacyl-*o*-phenylenediamines, as it is usually impossible to diazotise one amino-group, transform it, remove the acyl group, and repeat the operation, a sequence often used with acyl-*m*-and-*p*-diamines.

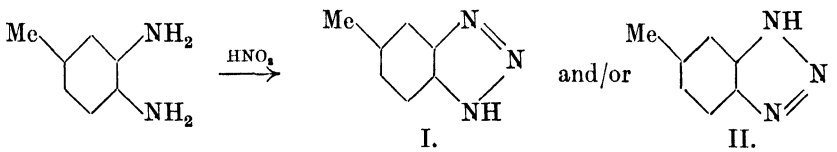
Griess,[7] who surveyed previous observations and suggested that these products of the *o*-diamines are triazoles, believed X to be attached at 2 (2 : 1 : 3-benztriazoles) because he obtained the same triazole from 4-amino-3-ureidobenzoic acid as from the 3 : 4-isomer :—



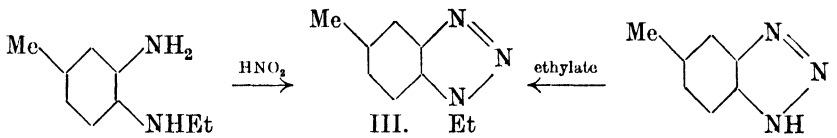
To get over the difficulty that one substance appeared where two isomers might be expected, he assigned the above constitution to the triazole; he offered no proof of his statements.

Kekulé,[5] on the other hand, taught that the substances are 1 : 2 : 3-

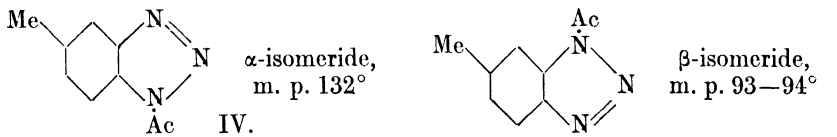
benztriazoles, and the settlement of the question induced a considerable volume of research. ' It was at once recognised that if Kekulé's constitution is correct, there must be two isomers of each triazole with a substituent at 4 or 5 or both, and the possibilities arising from 4 : 5-tolylenediamine became interesting



Nölting and Abt [10] made the triazole from 5-N-ethyl-4 : 5-tolylenediamine, and showed it to be the same substance as that obtained by ethylating (I) above :—

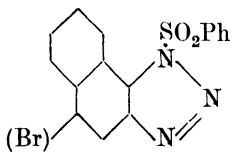
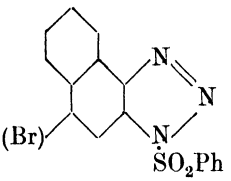


They concluded that the triazole has the constitution (III) above, and that the nitrous acid first attacks the amino-group *meta* to the methyl group, and that the diazo-compound so formed then closes the ring; they did not make the other isomeride corresponding to (III). Bössneck [9] made the 1-acetyl derivative of (I) by the action of nitrous acid on 4-amino-5-acetamidotoluene, but also did not make the other isomeride, and though Zincke and Lawson [11] made both :—

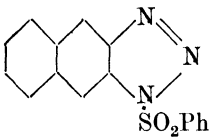
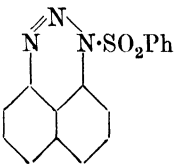


they yet supported the Griess constitution. The matter was finally clinched by Morgan and his co-workers,[20] who made both the above isomerides by unequivocal methods, and showed that hydrolysis of either gives the same triazole, a mixture of (I) and (II), which when reacetylated gives a mixture in which the α-isomeride (IV) predominates. The two triazoles can be separated, and do not change into one another in organic solvents, and have slightly different absorption spectra. Morgan and Godden [17] also showed that the expected two isomerides occur when the 4 and 5 positions in the benztriazole are occupied and also when the substituents form a ring, as in 1 : 2-naphthylenediamine. The latter, and also 4-bromo-1 : 2-naphthylenediamine, when treated with nitrous acid affords mixtures of the two isomeric naphthatriazoles, and the

isomerides are obtained separately as their benzene sulphonyl derivatives :—

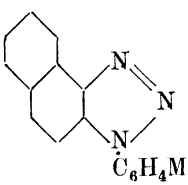
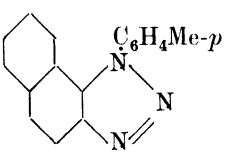
V.

VI.

2 : 3- and 1 : 8-Naphthylenediamine each give only one triazole and azimine respectively, and only one benzenesulphonyl derivative, (V) and (VI).[16]

The triazoles having an aryl nucleus at 1 are of special importance, as they are converted into carbazoles by heat, and are described later in this chapter (cf. p. 263). *o*-Aminodiphenylamine does not afford an isolable diazo-compound, as immediately it is formed the ring closes to 1-phenylbenztriazole.[15] Two isomeric 1-*p*-tolyl-1′ : 2′-naphthatriazoles should exist, but Morgan and Micklethwait were not able to prepare the isomeride (VII) [19] :—

VII.

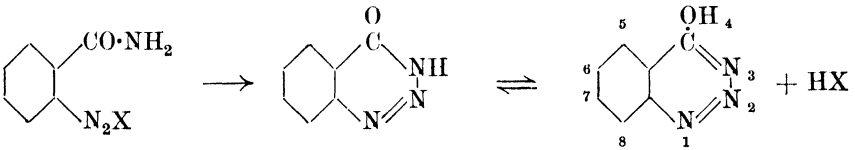
Triazoles are formed from the *o*-diaminoanthraquinones.[18, 21, 22]

REFERENCES

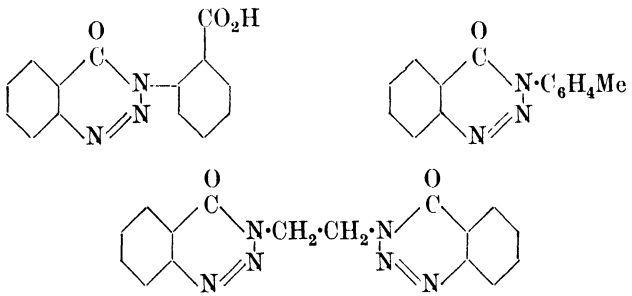
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(iv) **Benztriazines.**—Diazonium salts do not normally form triazens with carboxylamides, but diazonium salts produced by diazotising *o*-aminobenzamide at once form an internal N-azo-compound which is precipitated from the solution and is 4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, tautomeric with 4-hydroxy-1 : 2 : 3-benztriazine, also known as benzazimide [1, 2] :—



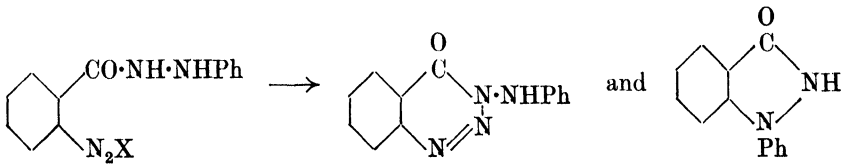
The reaction is general, and a number of 1 : 2 : 3-benztriazines substituted in either ring have been made in this way. 4-Keto-3 : 4-dihydro-1 : 2 : 3-benztriazine is obtained when diazotised ethyl anthranilate is treated with concentrated aqueous ammonia; the usual conversion of the ester to the amide occurs followed at once by ring closure.[5] N-Aryl or alkyl *o*-aminobenzamides afford 3-substituted benztriazines, such as the 3-*o*-carboxyphenyl,[13] -tolyl,[11] and $\alpha\beta$-(3′-benztriazinyl)ethane [6] derivatives :—



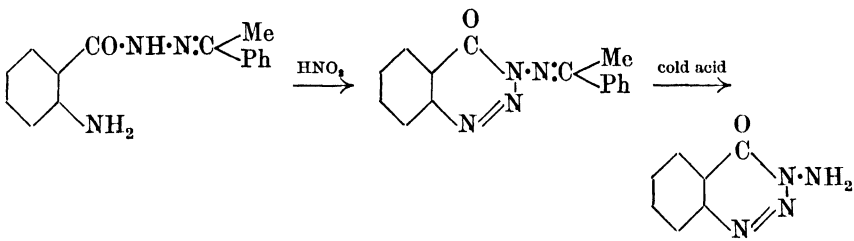
6-Nitro-4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine is made by diazotising 5-nitro-2-aminobenzamide,[7] whilst *o*-aminothiobenzamide affords 4-thioketo-1 : 2 : 3-benztriazine.[14]

o-Aminobenzhydrazide treated with two equivalents of nitrous acid gives 4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine,[17] though the 3-amino-compound is not obtained with only one equivalent of nitrous acid. But if the β-nitrogen atom of the hydrazido-group is substituted then derivatives of 3-amino-1 : 2 : 3-benztriazine are obtained. Thus diazotisation of α-(*o*′-aminobenzamido)-β-phenylhydrazine produces a mixture of 3-anilino-4-ketodihydrobenztriazine mixed with a larger proportion of

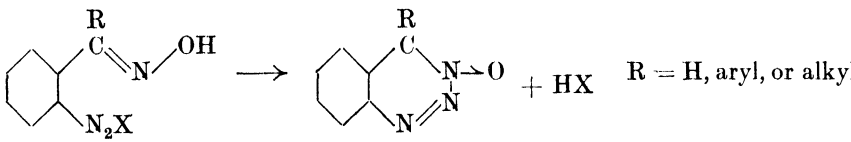
1-phenylisoindazolone, the latter formed by loss of the diazo nitrogen atoms [3, 9] :—



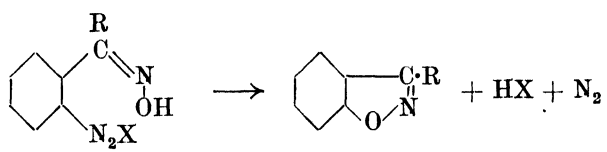
The Schiff's base from *o*-aminobenzhydrazine and acetophenone ring-closes on diazotisation to give 3-methylbenzylideneamino-4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, from which 3-amino-4-keto-3 : 4-dihydro-benztriazine is obtained by removal of acetophenone with cold acid [16] :—



Diazotisation of the oximes of *o*-aminobenzaldehyde, and its derivatives also produces benztriazines, a reaction discovered by Bamberger [8, 10] and his pupils, who called the products " indiazones " and regarded them as 3-oximes of indazole. Meisenheimer [18] and his co-workers showed that the ring closes not to carbon, as Bamberger had supposed, but to nitrogen giving a 1 : 2 : 3-benztriazine-3-oxide :—



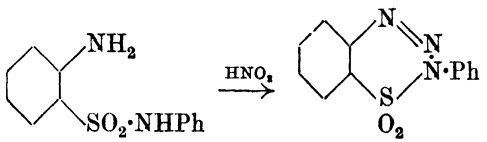
Meisenheimer used this reaction to determine the configuration of the oximes of *o*-amino-benzophenone and -acetophenone. Diazotisation of the oxime of lower melting point (the " *n*-oxime ") affords the triazine oxide, as shown above. The oxime of higher melting point (the " *h*-oxime ") gives the 3-substituted indoxazene, the link being established through oxygen with loss of the diazo nitrogen :—



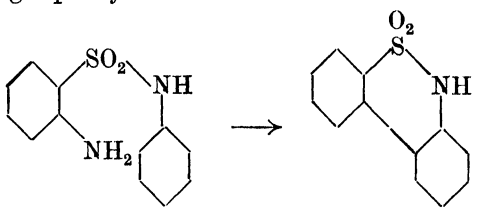
o-Aminobenzaldoxime affords a very poor yield of 1 : 2 : 3-benztriazine 3-oxide (R = H) on diazotisation, but substituted triazines are obtained

in better yield from 3 : 5-dimethyl- [8] and 3 : 6-dichloro-2-aminobenzaldoxime.[10, 18]

o-Aminosulphonamides on diazotisation ring-close to sulphontriazines.[19] *o*-Aminobenzenesulphonanilide on diazotisation in the cold affords 1-phenylbenzenesulphontriazine [15] :—



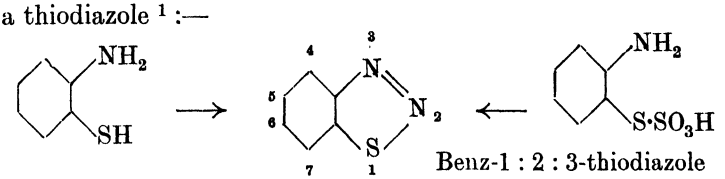
If the above diazo solution is boiled with copper, then nitrogen is eliminated giving diphenylene sultam :—



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(v). **Benzthiodiazoles (Diazo-sulphides)**.—Diazo derivatives of the *o*- and *p*-aminothiophenols are not known; the latter oxidise with extreme ease to the *p* : *p*′-diaminodiaryl disulphides, and the former instantly self-couple to give a five-membered ring fused to the benzene ring, a thiodiazole [1] :—



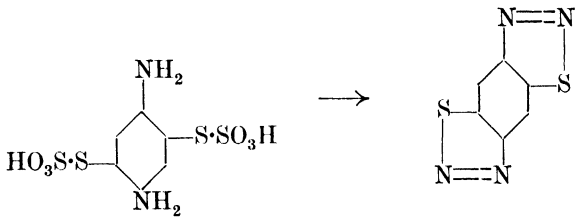
Benz-1 : 2 : 3-thiodiazole

The benzthiodiazoles are described in the older literature as diazo-

sulphides, but it is best to reserve this name for the open-chain compounds (cf. p. 155).

The above type-member of the group is an oil, b. p. 129°/10 mm.,[1] and its constitution cannot be questioned in the same way that the constitution of the analagous diazo-oxides has been so much debated; the thiodiazole ring is very stable, and no reagent has been found which will break the S·N link to reproduce the original diazo-compound or any of its derivatives. So strong is the tendency to close the ring that the *o*-aminothiosulphonic acids also form the thiodiazole with scission of the sulphonic acid group as shown above.[3]

A dithiosulphonic can be made from *p*-phenylenediamine and this on treatment in acetic acid with two equivalents of sodium nitrite at once precipitates crystalline benz-1 : 2 : 4 : 5-bisthiodiazole :—



Owing to the difficulty of preparing *o*-aminothiophenols, the number of substituted benzthiodiazoles made by the above route is small, and they have never been of other than academic importance. Jacobson [2] made 2 : 1-naphthathiodiazole by the action of nitrous acid on 2-amino-1-thionaphthol, and it has also been made by the action of phosphorus pentasulphide on the corresponding diazo-oxide, as has also the 2 : 1-isomer. 2 : 1-Naphthathiodiazole is also obtained by the action of sodium sulphide on diazotised 2-naphthylamine-1-sulphonic acid.[5]

REFERENCES

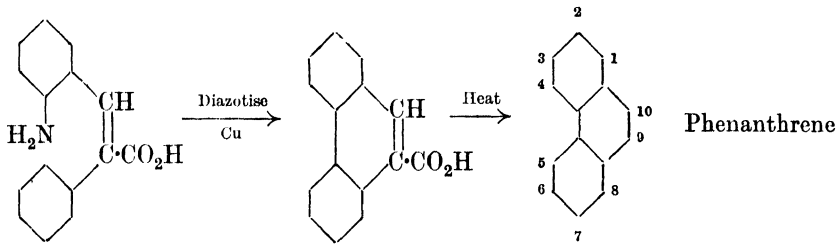
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B. RING COMPOUNDS IN WHICH THE DIAZO NITROGEN ATOMS HAVE BEEN LOST :—

(i) **Phenanthrene and other Polycarboxylic and Heterocyclic Compounds.**—The diazo-group is often easily eliminated when it is in such a position that its loss is accompanied by formation of a C·C link which completes a carbocyclic ring, so forming a more stable molecular structure. Pschorr [1] diazotised α-phenyl-*o*-aminocinnamic acid,

and on treating the diazo solution with copper powder obtained phenanthrene-9-carboxylic acid :—



Phenanthrene

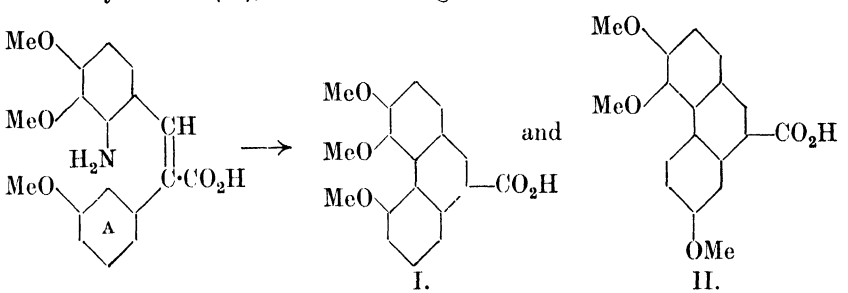
The reaction, known as Pschorr's phenanthrene synthesis, is carried out as follows :—

α-Phenyl-*o*-aminocinnamic acid (12 pts.) suspended in water (160 pts.) is diazotised by adding sulphuric acid (120 pts., *sp. gr.* 1·19), followed by sodium nitrite (4 pts.) dissolved in water (20 pts.). To the filtered diazo solution is added copper paste (14 pts.) which has been well pressed between filter-paper, and the whole is shaken until a drop no longer gives a colour with alcoholic naphthylamine; at the same time the colour of the solution changes from blue to green. The crude phenanthrene-9-carboxylic acid is collected and purified by dissolution in dilute aqueous ammonia and precipitation by dilute hydrochloric acid; it is crystallised from acetic acid. The yield is 93% of theoretical (10·37 pts.).

The carboxyl group is removed as carbon dioxide by heating to 340°, when the phenanthrene distils.

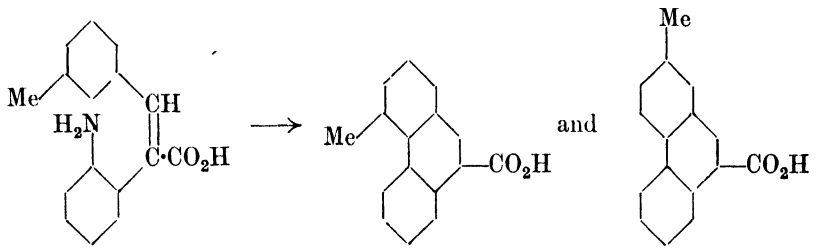
There is an alternative to the use of copper, also discovered by Pschorr. 2-Amino-3 : 4-dimethoxy-α-2′-ethoxyphenylcinnamic acid is dissolved in methanol and sulphuric acid, then diazotised with aqueous sodium nitrite, whereupon the ring-closure takes place immediately, with formation of 3 : 4-dimethoxy-8-ethoxyphenanthrene-9-carboxylic acid.

In making substituted phenanthrenes it does not matter to which ring the amino-group is attached if other substituents will be at 2 and 7 when the phenanthrene ring is formed, but two isomerides are formed if there is a substituent *meta* to the ethylenic link in the ring not carrying the diazo-group. Thus 2-amino-3 : 4-dimethoxy-α-*m*′-methoxyphenylcinnamic acid gives both 3 : 4 : 5- (I) and 3 : 4 : 7-trimethoxyphenanthrene-9-carboxylic acid (II), the former in greater amount [7] :—



This reaction shows that the ring A can rotate freely about its link with the ethylene carbon atom, and also that the methoxy-groups at

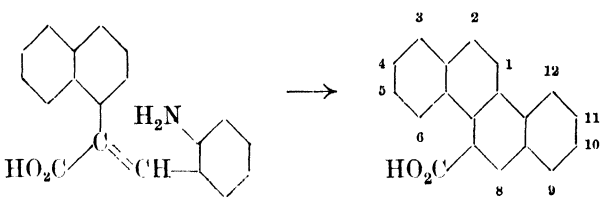
4 and 5 in the phenanthrene ring offer no steric hindrance to ring closure. The possibility of forming two isomerides can be prevented by blocking atoms, for example, 2-amino-3 : 4-dimethoxy-α-2′-bromo-5′-methoxyphenylcinnamic acid affords only 8-bromo-3 : 4 : 5-trimethoxyphenanthrene-9-carboxylic acid, which can be debrominated to (I). Other examples of the formation of two isomerides on ring-closure are known. A simple case is that of *m*-methyl-α-*o*′-aminophenylcinnamic acid,[8] which affords a mixture of 2- and 4-methylphenanthrene-9-carboxylic acid :—



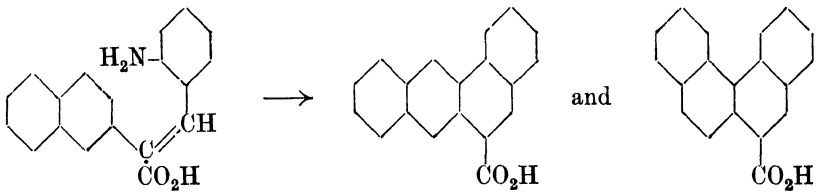
Methyl groups exert a greater steric effect than methoxy, and hence 2-amino-3-methyl-α-2′-bromo-5′-methylphenylcinnamic acid when diazotised fails to form 8-bromo-4 : 5-dimethylphenanthrene-9-carboxylic acid.[19]

Many aminophenylcinnamic acids can exist as *cis* and *trans* isomerides, and the carboxyl group performs an important function in the Pschorr reaction, in that it causes the *cis*-isomeride to be more stable than the *trans*-isomeride. Thus phenanthrene can only be made from *cis*-*o*-aminostilbene, a fact demonstrated in the same year independently by Taylor and Hobson [16] and Ruggli and Staub.[17] The latter [18] made phenanthrene from *cis*-*o*-aminostilbene by, (*a*) diazotisation and treatment with copper (61% yield), (*b*) adding amyl nitrite to *cis*-*o*-aminostilbene dissolved in alcohol (64% yield), (*c*) treating the diazo solution with sodium hypophosphite solution and a trace of copper (80% yield). Method (*b*) converts *o*-aminodibenzyl into 9 : 10-dihydrophenanthrene in about 50% yield, with *o*-hydroxydibenzyl (23%) as a by-product.[18] *cis*-*o* : *p*′-Diaminostilbene diazotised and treated with copper and alcohol gives phenanthrene in 17% yield.[20]

Besides the synthesis of the simple 4-methoxy-,[2] and 2 : 3-dimethoxyphenanthrene,[3] Pschorr's synthesis can be used to make more complex polycyclic compounds. The diazonium sulphate from α-1-naphthyl-*o*-aminocinnamic acid shaken with copper affords chrysene-7-carboxylic acid [6] :—



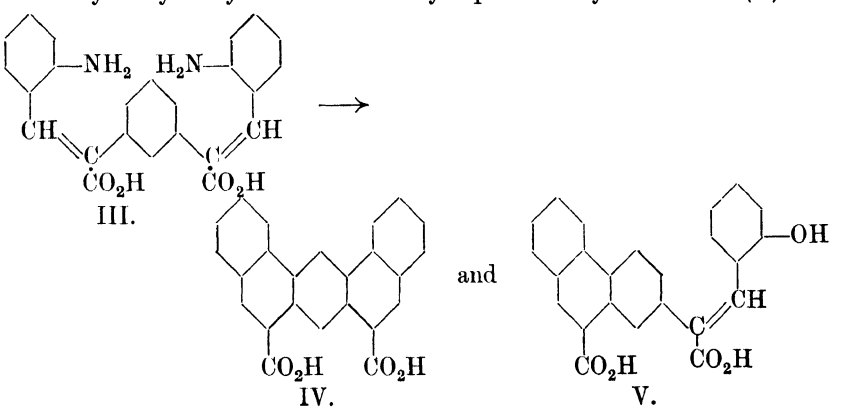
The ring-closure of the diazo derivative of the isomeric α-2-naphthyl-*o*-cinnamic acid has been thrice investigated,[6, 10] lastly by Cook [13] in his work on carcinogenetic hydrocarbons. Two compounds are formed the ring closing on either the 1 or the 3 position of the naphthalene ring :—



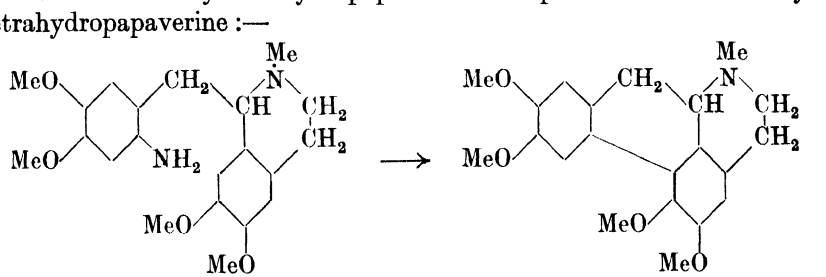
1 : 2-Benzanthracene-4-carboxylic acid. 4 : 3-Benzphenanthrene-1-carboxylic acid.

The two acids are separated by fractional crystallisation of their sodium and potassium salts.

It is also possible to close two rings simultaneously in the same molecule.[14, 15] Di-α-*o*-aminobenzylidene-*m*-phenylene diacetic acid (III) thus gives 1 : 2 : 7 : 8-dibenzanthracene-4 : 5-dicarboxylic acid (IV), but the yield is not good, as by an alternative reaction only one ring-closure occurs the other diazo-group being converted into hydroxyl with formation of α-*o*-hydroxybenzylidene-10-carboxy-2-phenanthrylacetic acid (V) :—

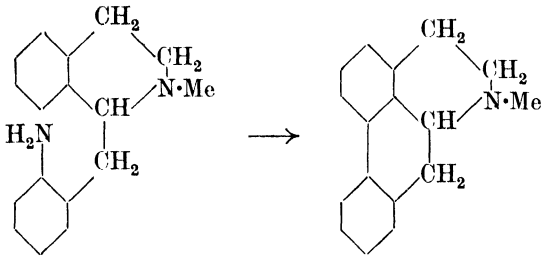


Pschorr [4] used his reaction in the synthesis of *iso*quinoline alkaloids to convert N-methyltetrahydropapaverine into phenanthreno-N-methyltetrahydropapaverine :—



This reaction has been used a number of times, one of the best examples

being the production of aporphin from 1-*o*-aminobenzyl-2-methyltetrahydroquinoline by Gadamer [12] :—



Ruggli has pointed out that the *iso*quinoline ring here performs the same function of stabilising a favourable spatial configuration as the carboxyl group performs in the cinnamic acid compounds.

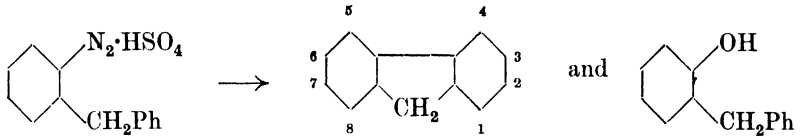
The Pschorr reaction is a Type III reaction in which the reducing agents are copper, alcohol, or hypophosphite. As yet no investigator has been sufficiently interested in the mechanism of the reaction to determine to what extent the reducing agent is oxidised. Waters suggests that the function of the reducing agent is to supply a single electron to the rupturing C·N link, and thus the diazo-nitrogen is replaced by the pole of a free radical, which then forms the bridge-link.

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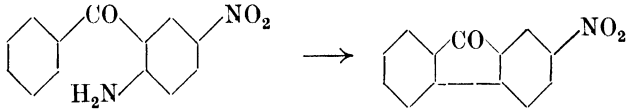
Other examples of the use of the Pschorr reaction in alkaloid synthesis are :—R. D. Haworth, W. H. Perkin, Rankin, *J.C.S.*, 1925, **127**, 2018; Robinson, Shinda, *ibid.*, **1926**, 1987; Späth, Hromatka, *Ber.*, 1928, **61**, 1334; Avenarius, Pschorr, *ibid.*, 1929, **62**, 321; Barger, Schlittler, *Helv. Chim. Acta*, 1932, **15**, 381; Schlittler, *ibid.*, 394. Other polymethoxyphenanthrenes are :—Rapson, Robinson, *J.C.S.*, **1935**, 1535; Sharp, *ibid.*, **1936**, 1234.

(ii) **Fluorene, Fluorenone, and Polycyclic Ketones.**—Fluorene and *o*-hydroxydiphenylmethane are obtained when diphenylmethane-*o*-diazonium sulphate is boiled in aqueous solution [1] :—



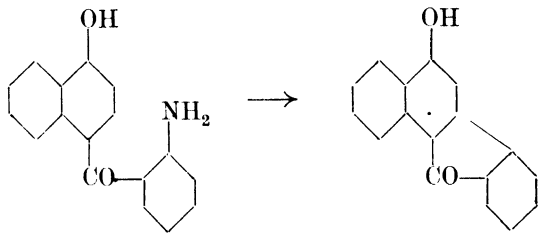
The two products are easily separated by washing with dilute aqueous caustic soda. This is the prototype of a ring-closure which can occur whenever a diazo-group is *ortho* to the methylene or ketone group in a diarylmethane or diarylketone. Thus *o*-diazobenzophenone boiled in aqueous solution gives fluorenone and *o*-hydroxybenzophenone,[3] whilst tetrazotised *o* : *o*′-diaminobenzophenone on boiling affords 1-hydroxyfluorenone and *o* : *o*′-dihydroxybenzophenone.[2]

As with Pschorr's phenanthrene synthesis, it is immaterial to which ring the diazo-group is attached so long as the other substituents are at 4 : 4′, but other substituted fluorenes and fluorenones can be obtained by unequivocal synthesis if the substituents are in the same ring with the diazo-group. For example, 3-nitro-6-aminobenzophenone affords 2-nitrofluorenone [4] :—

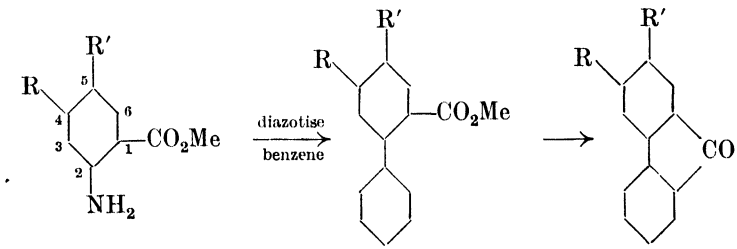


3- and 4-Bromo-,[9] 3-methyl-,[4] and 3-methoxyfluorenone [5] have been made in this way.

In the naphthalene series the production of 3-hydroxy-1 : 2-benzfluorenone by boiling the diazo-derivative 4-*o*-aminobenzoyl-1-hydroxynaphthalene has been claimed [7] :—

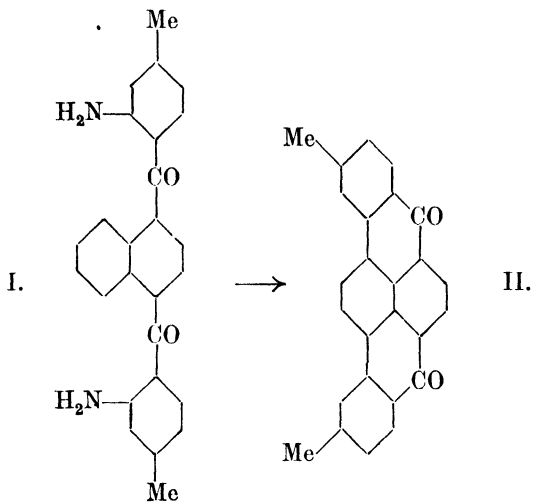


Fluorenones can also be made from substituted anthranilic esters by diazotising and combining with benzene by the Gomberg reaction (cf. p. 316) and then closing the ring through the carboxyl group [12] :—

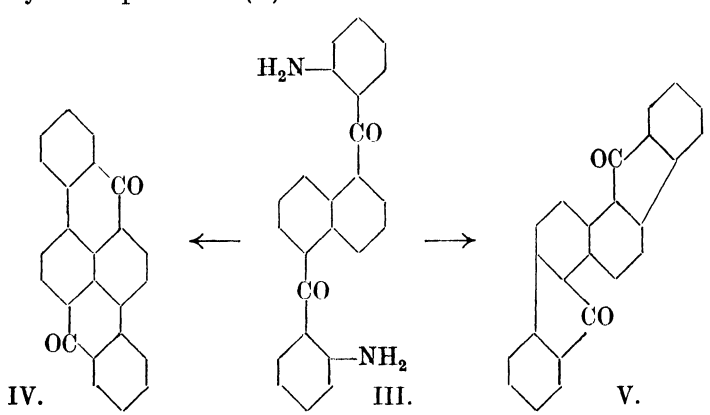


Substituents R′ may be at 4 or 5 in the anthranilic ester; 2-chloro-, 2-bromo-, 3-chloro-, 3-bromo-, and 3-nitro-fluorenone have been made by this method.

The possibility of constructing a number of complex polycyclic ketones arises with the tetrazo derivatives of 1 : 4- and 1 : 5-di-(*o*-aminoaroyl)naphthalenes.[6] The tetrazo-derivatives of 1 : 4-di-(2′-amino-5′-methylbenzoyl)naphthalene (I) on running into cold dilute hydrogen peroxide solution gives 4 : 4′-dimethyl-1 : 2 : 6 : 7-dibenzpyrene-3 : 8-quinone (II) :—



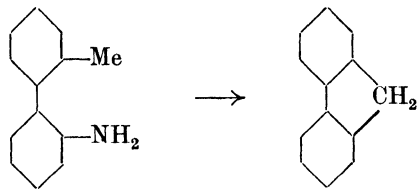
1 : 5-Di-(*o*-aminobenzoyl)naphthalene (III) similarly affords two compounds, 1 : 2 : 6 : 7-dibenzpyrene-3 : 8-quinone (IV) and 1 : 2 : 5 : 6-dibenzoylene naphthalene (V) :—



(IV) is obtained from the tetrazo-derivative of (III) by, (*a*) cold dilute hydrogen peroxide, (*b*) hot alcohol, (*c*) colourless ammoniacal cuprous oxide (reduced by hydroxylamine), and (*d*) suspending the neutral

tetrazofluoborate in water and irradiating with sunlight or a mercury vapour lamp; (V) is obtained by boiling the tetrazo solution. Boiling the tetrazo compound with lead acetate gives a mixture of (IV) and (V).

Mascarelli [8] boiled diazotised 2-amino-2′-methyldiphenyl and so produced fluorene, the ring here being closed on the methyl group with loss of nitrogen :—

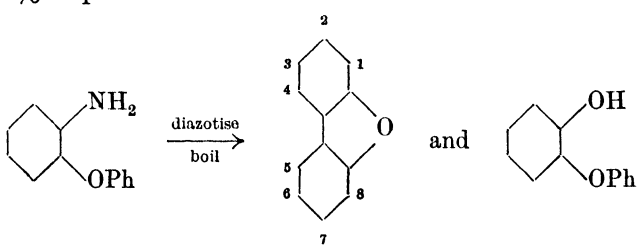


2-Amino-2′ : 4-dimethyldiphenyl treated in the same way affords an almost quantitative yield of 2-methylfluorene.[11] From experiments with a number of compounds Mascarelli [10] concludes that the reaction occurs only when substituents at 2 : 2′ and 6 : 6′ do not distort the coplanarity of the two benzene rings of the diphenyl nucleus.

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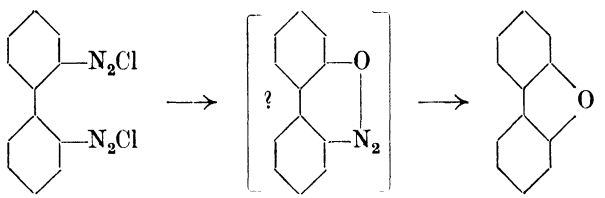
(iii) **Dibenzfuran (Diphenylene Oxide) and Dibenzthiophen (Diphenylene Sulphide).**—Dibenzfuran is formed together with *o*-hydroxydiphenyl ether when an aqueous solution of diphenyl ether *o*-diazonium sulphate is boiled or the diazo solution is dropped into boiling 50% sulphuric acid [3] :—



The resinous crude product is distilled, and the two solid products are separated with dilute caustic alkali solution. The yield of dibenzfuran

is about 30%, and though the reaction has been used to make a number of substituted dibenfurans, such as 2-nitro-, 3-chloro-, 3-chloro-7-nitro-, 3 : 6-dichloro-, 2- and 3-bromo-, 2 : 6- and 3 : 6-dibromodibenzfuran,[6] yet higher yields have not been reported. This suggests that in the diazo diphenyl ether the benzene rings lie symmetrically on each side of the oxygen atom and in the same plane, but that the ether link is distorted when the C·C link is formed. The mechanism is the Type I reaction.

This view is further supported by the fact that dibenzfuran is formed in 70% yield from a compound in which the C·C link already exists, *viz.*, 2 : 2-diaminodiphenyl. When this diamine is tetrazotised and the acid solution is boiled, dibenzfuran is produced [1, 2, 7] :—



It has been suggested that 2 : 2′-dihydroxydiphenyl is the intermediate step, but this is unlikely, for though dibenzfuran can be made from that substance, the conditions necessary to remove one molecule of water are more drastic than boiling in aqueous acid, while a substance of the constitution shown in brackets would be more likely to lose nitrogen in hot acid to form dibenzfuran. 2 : 7-Dimethyldibenzfuran is obtained when tetrazotised 2 : 2′-diamino-4 : 4′-ditolyl is run on to cold freshly-precipitated copper, but this procedure does not appear to afford a larger yield than is obtained by boiling the tetrazo solution.[4] 4 : 5-Diphenyldibenzfuran has been made in 30% yield by boiling tetrazotised 2 : 2′-diamino-6 : 6′-diphenyldiphenyl;[9] the presence of copper ions does not improve the yield.

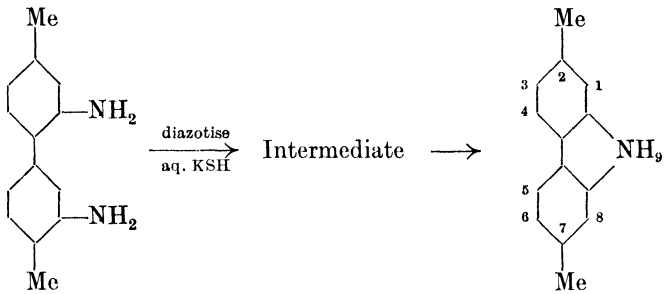
Dibenzthiophen and diphenylene disulphide have been made by Schwechten [8] from 2 : 2′-tetrazodiphenyl by adding the tetrazo solution to potassium hexathiocyanochromate; the precipitated tetrazohexathiocyanochromate is collected, dried, mixed with twice its weight of potassium chloride as diluent and heated in a long tube (cf. p. 289). Decomposition of the complex salt produces dibenzthiophen and a lesser quantity of diphenylene disulphide, both of which distil and are separated by crystallisation from methanol.

REFERENCES

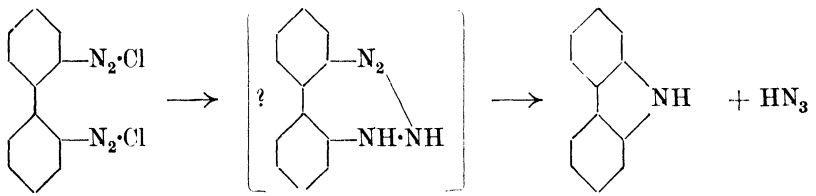
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(iv) **Carbazole.**—The action of reducing agents on 2 : 2′-tetrazodiphenyl leads to the production of considerable yields of carbazole. For example, Täuber [1] by the action of aqueous potassium hydrosulphide obtained carbazole in almost quantitative yield instead of the dibenzthiophen he had expected. Niementowski [4] used the same reagent to convert 2 : 2′-tetrazo-4 : 4′-ditolyl into 2 : 7-dimethylcarbazole, and showed the existence of a sulphur-containing intermediate of unknown constitution :—



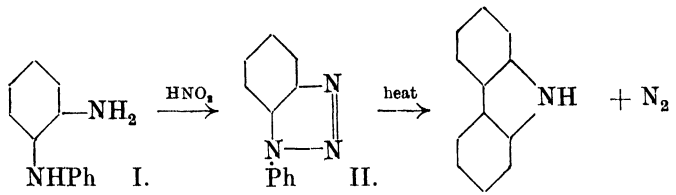
Similarly the action of cuprous chloride or cuprous bromide on 2 : 2′-tetrazodiphenyl produces only small yields of 2 : 2′-dichloro- or 2 : 2′-dibromodiphenyl; the reducing action of these reagents at 89—100° causes the formation of carbazole.[6] No explanation of the mechanism of the reaction has been given, but if it proceeds through an intermediate hydrazine, the appearance of hydrazoic acid in the liquid might be expected (cf. p. 190) :—



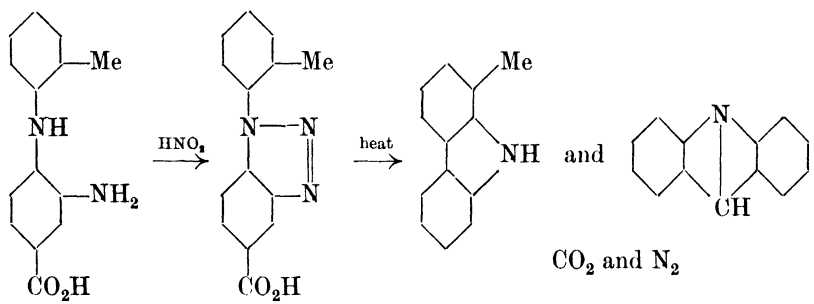
It is improbable that the reaction proceeds through 2 : 2′-dihydrazinodiphenyl, as has been suggested, because that substance is produced in equal quantity with carbazole when 2 : 2′-tetradiphenyl is reduced with stannous chloride.[1]

Graebe and Ullmann [2] tried to make carbazole by a synthesis analogous to that which they had used to make fluorenone, namely, by diazotising *o*-aminodiphenylamine (I). The expected C·C link is not, however, formed, but instead the diazo-group at once couples with the imino hydrogen atom to form the internal diazoimino-compound, 1-phenyltriazole (II), a compound already known as the product of that reaction.

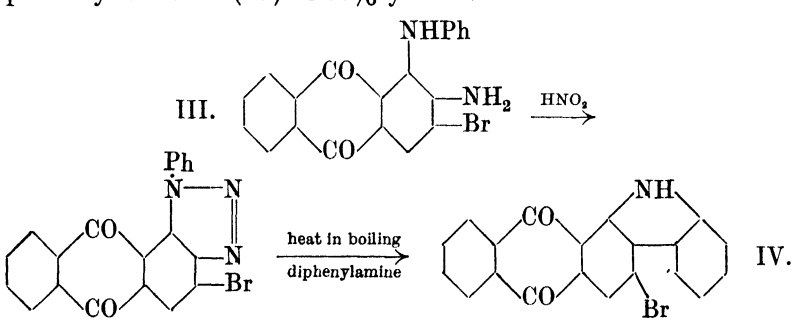
Not to be defeated, Graebe and Ullmann heated the triazole, and found that at 360° it breaks up, giving carbazole and nitrogen :—



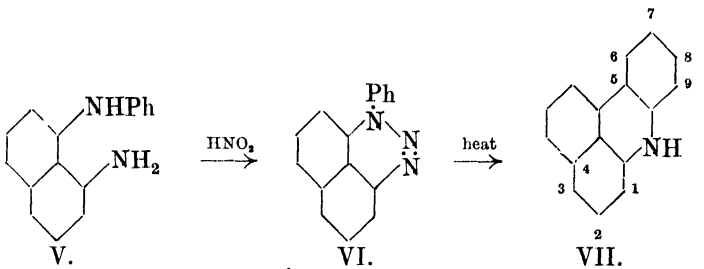
By acting with nitrous acid on substituted diphenylamines substituted carbazoles are formed.[3, 5] There is usually no difficulty in making the intermediate triazole, but its decomposition by heat is by no means uniformly satisfactory. In general the carbazole is only obtained in good yield when positive substituents are present. Thus *o*-aminodi-*p*-tolylamine can be transformed into 2 : 7-dimethylcarbazole in good yield, but the yield of 2-chlorocarbazole from 5-chloro-2-aminodiphenylamine is poor and 1-nitrocarbazole can be obtained in only 18% yield; [13] 3-benzoyl-,[10] and 3 : 6-dibenzoylcarbazole [11] are obtainable in moderate yields. Some acridine is formed when 1-*o*-tolylbenztriazole-5-carboxylic acid is decomposed into 1-methylcarbazole, nitrogen, and carbon dioxide [5] :—



Naphthacarbazoles are also made by this route which is applicable in the anthraquinone series,[8, 9] where, for example, 3-bromo-2-amino-1-anilinoanthraquinone (III) is converted through the triazole into 4-bromo-1 : 2-phthaloylcarbazole (IV) in 96% yield [7] :—

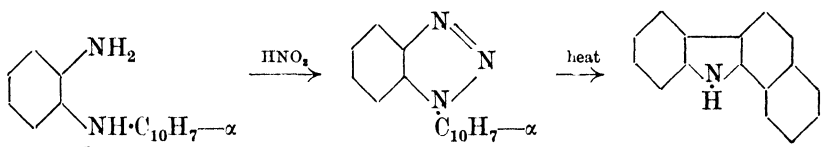


1-Amino-8-anilinonaphthalene (V) with nitrous acid forms 1-phenyl-*peri*naphthtriazole (VI), and this on heating decomposes into *meso*-[4 : 5]-benzacridan (VII) [12] :—



V. VI. VII.

The isomeric *o*-aminophenyl-α-naphthylamine (VIII) affords α-naphthylbenztriazole (IX) with nitrous acid, and on decomposition forms the C·C link with the 2-position of the naphthalene ring to give α-naphthacarbazole (X) :—



VIII. IX. X.

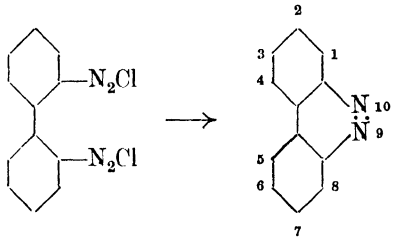
Various methods have been used to bring about the decomposition of the triazoles, including heating in an open vessel, heating with distillation of the carbazole, heating in an indifferent liquid (aniline and diphenylamine have been much used), or in a boat in a tube in a combustion furnace in a stream of inert gas, such as carbon dioxide or nitrogen.

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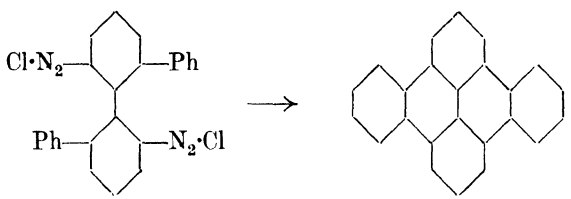
(v) Other Ring Compounds formed from Diazo-Compounds.— Beside diphenylene oxide and carbazole already mentioned other cyclic compounds are formed from 2 : 2′-tetrazodiphenyl and its homologues. When a solution of the tetrazo-compound is run into a cold acid solution

of cuprous chloride or cuprous bromide the main product is the internal azo-compound diphenyleneazone [1] :—

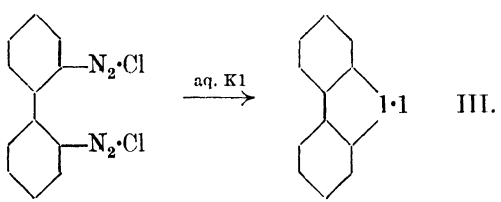


The same compound is formed in 45% yield when the tetrazodiphenyl compound is treated with alkaline sodium arsenite solution, a reagent which would be expected to produce diphenyl-2 : 2′-bisarsonic acid by the Bart reaction (cf. p. 331).[3]

2 : 2′-Tetrazo-6 : 6′-diphenyldiphenyl loses its nitrogen from a cold solution to form two C·C links to complete two 6-rings, thus forming 4 : 5 : 9 : 10-dibenzpyrene in 40% yield [2] :—

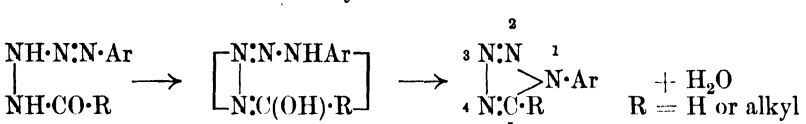


Just as the attempt to replace the two diazo-groups in 2 : 2′-tetrazodiphenyl by chlorine and bromine largely fails, so the reaction with iodides is also not normal, the chief product being a cyclic compound, diphenyleneiodonium iodide (III) [4, 5] :—



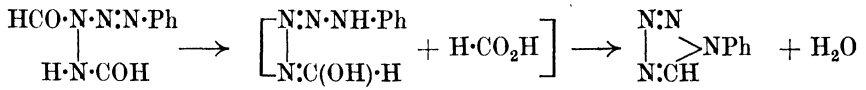
The reaction also goes smoothly with 2 : 2′-tetrazo-4 : 4′-ditolyl. On heating, the iodonium iodide rearranges to 2 : 2′-di-iododiphenyl.

1 : 2 : 3 : 4-Tetrazoles are formed by the action of caustic alkali on diazoaryl mono- and diacylhydrazides (cf. p. 183), compounds which are usually sufficiently stable to be isolated. Ring-closure is by loss of water from a tautomeric form of the hydrazide :—

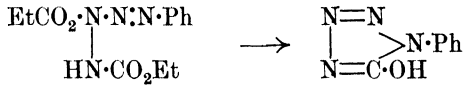


αβ-Diacylhydrazides lose by hydrolysis the acyl group attached to the same nitrogen atom as the azo-group.

The hydrazide formed by interaction of diazobenzene with αβ-diformylhydrazine is too unstable to isolate, so that if a solution of diazobenzene chloride is added to a solution of αβ-diformylhydrazine in cold dilute caustic soda 1-phenyl-1 : 2 : 3 : 4-tetrazole at once begins to separate [6] :—

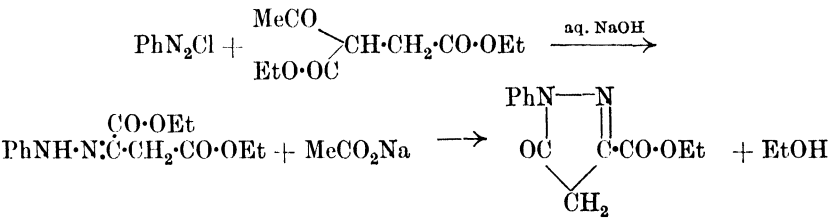


5-Hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrazole is formed similarly from diazobenzene and ethyl hydrazinedicarboxylate :—



Ring-closure may fail if the aryl radical carries negative substituents; *e.g.*, in the case above if the phenyl radical has bromine at 2 : 4 : 6.

Pyrazolones [7] are formed by ring-closure of the azo-compounds produced by coupling one equivalent of a diazo- or tetrazo-compound with compounds of the general type $CHRR'\cdot CH_2\cdot CO\cdot OR''$, where R and R′ are the same or different and are carbalkoxy, carboxyamido, cyanido, or a ketone group, and R″ is alkyl. On coupling in alkaline medium R or R′ is ejected and ring-closure ensues spontaneously in the cold by elimination of an alcohol molecule from the hydrazone tautomer of the azo-compound. Thus diazobenzene and ethyl acetosuccinate afford 1-phenyl-3-carbethoxy-5-pyrazolone by the following stages :—



If more than two equivalents of the diazo-compound is used, then ring-closure is accompanied by further coupling to give the 4-azo-derivative of the pyrazolone.[8]

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CHAPTER VIII

REACTIONS OF THE DIAZO-COMPOUNDS (*continued*)

CLASS E. DERIVATIVES FORMED BY REPLACEMENT OF THE DIAZO-GROUP—REPLACEMENT BY HYDROGEN—HALOGENS—NITROGEN-CONTAINING GROUPS—OXYGEN—CARBON-CONTAINING GROUPS—SULPHUR, SELENIUM, TELLURIUM—ARSENIC, ANTIMONY, BISMUTH, PHOSPHORUS—METALS.

CLASS E. DERIVATIVES FORMED BY THE REPLACEMENT OF THE DIAZO-GROUP

THE great usefulness of the diazo-compounds in synthesis is due to the diversity of reactions of this class in which the nitrogen is eliminated and another element or radical becomes attached to the same carbon atom of the aromatic nucleus.

GROUP 1. REPLACEMENT OF THE DIAZO-GROUP BY HYDROGEN

The diazo-group is replaced by hydrogen by a process of reduction, but this process is to be distinguished from that by which hydrazines are formed, in that to form hydrazines the diazo-compound accepts hydrogen from a powerful reducing agent, whereas when hydrogen replaces nitrogen the diazo-compound acts as an oxygen donor to a weak acceptor.

The classic reagent is ethanol, for Griess [1] discovered that benzenediazonium nitrate oxidises ethanol to acetaldehyde, being itself converted into benzene and dinitrophenol. The early investigators brought about the reaction simply by heating the alcoholic solution in which the amine had been diazotised by the method of Griess. The course of the reaction between diazo-compounds and alcohols is, however, influenced by several factors, of which the chief are, (*a*) the alcohol, (*b*) presence or absence of water, (*c*) substituents in the aryl nucleus, (*d*) the state of the diazo-compound, *i.e.*, whether the diazo-compound is brought into reaction as a diazonium salt, in which case the anion exerts an effect, or as a diazotate.

Just as the action of water on diazonium salts leads to phenols, so the action of dry alcohols leads to phenol ethers (cf. p. 306), but as the molecular weight of the alcohol used increases, the tendency is for hydrocarbons to be produced; [21, 25] addition of water to the alcohol has the same effect.[13] A large difference is sometimes found between the products obtained from methanol and ethanol, and in the Table XXV on p. 269 are shown the products obtained by Griess [9] from the three diazobenzoic acids.

TABLE XXV

Products of Interaction of the Diazobenzoic Acids with Methanol and Ethanol

Diazotised amine :	Products from :	
	Methanol.	Ethanol.
Anthranilic acid	Benzoic acid	Benzoic acid
m-Aminobenzoic acid	*m*-Methoxybenzoic acid	Benzoic acid + *m*-Ethoxybenzoic acid
p-Aminobenzoic acid	*p*-Methoxybenzoic acid	Benzoic acid + *p*-Ethoxybenzoic acid

As to the fate of the alcohol the amount of the various aldehydes produced by the reduction of benzenediazonium sulphate, has been determined quantitatively by Hodgson and Kershaw [42] :—

TABLE XXVI

Oxidation of Alcohols by Benzenediazonium Sulphate

Alcohol.	Aldehyde, mol.%.
Benzyl alcohol	19·5
Methanol	0·0
Ethanol	9·4
n-Propanol	4·7
iso-Propanol	5·0
iso-Propanol + water	3·6
n-Butanol	1·25

There are very few records of the detection of formaldehyde, and the inference is that methanol is oxidised to water and carbon dioxide or monoxide. This is not surprising, since any formaldehyde produced would react preferentially to the methanol present (*vide infra*).

It has long been known that negative substituents in the aryl nucleus, especially if *ortho* to the diazo-group, encourage the formation of hydrocarbons, and this fact has been generalised in the remark of Hodgson [53] that the greater the induced positivity on the carbon to which the diazonium-group is attached the greater the ease with which the group is replaced by hydrogen. Thus, nitrodiazonium-compounds nearly always afford the corresponding hydrocarbon, both in the benzene,[12, 20] and in the naphthalene [15] series, as do also the diazophenols,[21, 50] whilst halogens have the same effect, especially in compounds such as 2 : 4 : 6-trichloro- or -tribromo-diazobenzene,[24] which are converted into 1 : 3 : 5-trichloro- or -tribromo-benzene in high yield. Further, there are, as might be expected, many cases where the product is a mixture of phenol ether with hydrocarbon; for example, α-naphthalene diazonium sulphate in

boiling ethanol affords naphthalene (40%) and α-ethoxynaphthalene (23%), whilst the β-isomer similarly affords naphthalene (7%) and β-ethoxynaphthalene (30%).[14] α- And β-anthraquinonediazonium sulphate are decomposed by ethanol in the cold, faster on heating, to give anthraquinone, the α-isomer being reduced the quicker.[34]

When dry diazonium salts are heated with alcohols the anion is set free as acid, and this may take part in unwanted side-reactions. Hence diazonium nitrates should be avoided as the products of reaction may be nitrated. The choice between the diazonium sulphate and chloride is usually a matter of convenience in preparation. Hodgson and Foster [51] used the easily-isolated zinc chloride double salts of a number of diazonium chlorides, and found that they react with methanol and ethanol, as do the unco-ordinated diazonium chlorides.

The course of the reaction is altered so that the hydrocarbon is the sole product if diazonium salts are replaced by diazohydroxides or diazotates, as is well illustrated by the following table, due to Chamberlain.[19]

TABLE XXVII

Reaction Products of p-*Toluenediazonium Nitrate and Sulphate with Methanol*

	Diazo-nitrate.		Diazo-sulphate.	
	p-Cresol Me ether, %.	Toluene, %.	*p*-Cresol Me ether, %.	Toluene, %.
Boiling MeOH 760 mm. Hg . . .	29	trace	66	trace
„ „ 250 „ . . .	22	10	77	—
„ „ 1250 „ . . .	39	—	61	—
„ „ with sodium methoxide .	—	36	—	32
„ „ „ caustic potash . .	—	44	—	59
„ „ „ K carbonate . .	—	53	—	44
„ „ „ zinc dust . . .	—	45	—	46
„ „ „ zinc oxide . .	17	22	20	48

Other investigators have obtained results similar to the above with other diazo-compounds;[17, 18, 22] diphenyltetrazonium chloride and *m*-ditolyltetrazonium chloride with methanol give 4 : 4′-dimethoxy-diphenyl and -*m*-ditolyl respectively, but if ethanol to which sodium methoxide has been added is used, then the products are diphenyl and *m*-ditolyl.[31] Tetrazodiphenyl can be reduced step-wise.[23]

Ridge [59] has thrown some light on the mechanism by which different products are obtained from the same diazo-compound with alcohol under different conditions. When 2 : 6-dichloro-4-nitroaniline is diazotised slowly in cold concentrated sulphuric acid and alcohol is then added the product is 2 : 2′ : 6 : 6′-tetrachloro-4 : 4′-dinitrodiphenyl but if a little water is added before the alcohol then the product is 3 : 5-dichloro-1-

nitrobenzene also obtained by Hodgson and Turner's [53] method with cuprous oxide in glacial acetic acid. Ridge points out that in 2 : 6-dichloro-4-nitrobenzenediazonium sulphate the balance of the inductive and mesomeric effects of the substituents produces a critical value for the positivity of the carbon atom carrying the diazonium group. In concentrated sulphuric acid it therefore probably has the unionised form Ar·N:N·X which gives the diaryl with alcohol but if water is added it passes into the ionised form $Ar{\cdot}N{:}N^{\oplus}\}X^{\ominus}$ which gives the hydrocarbon. Further, it can be inferred that the ionised form exists in glacial acetic acid though the cuprous oxide may affect the ionisation as well as exerting a reducing effect.

The action of alcohols can be stimulated by finely-divided metals, especially in the reduction of diazo-oxides (*vide infra*); the metals do not appear to attack the diazo-compounds directly for the alcohols are oxidised just as when the metal is absent. Parsons and Bailar [45] found that copper bronze must be added to ethanol to remove the diazo-group from 4-methylazobenzene-4′-diazonium sulphate, acetaldehyde being formed, though Griess [3] decomposed diazotised aminoazobenzenesulphonic acid with ethanol alone. Hodgson and Turner [57] used copper precipitated by zinc together with alcohols to produce 1 : 6-dinitronaphthalene by replacement of the diazo-group in 1 : 6-dinitronaphthalene-2-diazonium sulphate; copper without alcohol added to the sulphuric acid–glacial acetic acid diazotisation solution affords a yield of only 10%; with copper and an alcohol the yields (in parenthesis) are: methanol (58·0%), ethanol (57·5), *iso*propanol (54·5), *n*-butanol (36·5), β-chloroethanol (36·0), *n*-propanol (35·5), *iso*-butanol (26), also methylethyl ketone (44·5), acetone (16). Similarly dry diazoniumaryl sulphonates made from a diazonium salt and naphthalene-1 : 5-disulphonic (cf. p. 85) or 2-hydroxynaphthalene-1-sulphonic acid are decomposed when suspended in ethanol or acetone with copper or zinc with production of high yields of the derivative having hydrogen in place of the diazo-group,[49] but here the appearance of an aldehyde is not usual, and Hodgson and Marsden think the reaction is an exchange of hydrogen from the sulphonic acid groups by the agency of the metal. Tobias [13] used copper and aqueous alcohol to convert diazonaphthalenesulphonic acids into naphthalenesulphonic acids, and it must be remembered that under other conditions the action of copper on diazo-compounds causes the formation of diaryls (cf. p. 311).

Because of the uncertainty of the reducing action of alcohol and the necessity of employing the diazo-compounds in the dry state, other reducing agents have been introduced. Friedländer found sodium stannite in aqueous solution to be effective,[10] and it has also been used by Eibner,[29] Bamberger and Meimberger,[16] as well as by Hantzsch and Vock (cf. p. 132). Mai [26] first employed hypophosphorous acid, also used by

Raiford and Oberst [46] (*vide infra* Table XXIX). Alexander and Burge [60] used hypophosphite to reduce *m*-nitrodiazobenzene in a mixture of water and deuterium oxide (1 : 1) and found no deuterium in the resultant nitrobenzene. They concluded that the necessary hydrogen comes from another aromatic nucleus since it is the only source not equilibrated with deuterium. Formates and formic acid also afford the hydrocarbon,[7] but alkaline ferrous sulphate gives a mixture of benzene, diphenyl, and phenylazide when oxidised by benzene diazotate.[43] Diazotised ethyl aminogallate, which is a *p*-diazo-oxide, is reduced by heating with water at 220°, or by stannous chloride.[28] Chemists seem to have overlooked that Orton and Everatt [32] pointed out that quinol is an excellent reagent for the reduction of diazo-compounds by the reaction :—

$$ArN_2{\cdot}OH + HO{\cdot}C_6H_4{\cdot}OH = ArH + O{:}C_6H_4{:}O + N_2 + H_2O$$

On adding the aqueous solution of the diazo-compound to one of quinol there is a momentary intense coloration, becoming permanent when all the diazo-compound has been added; the evolution of nitrogen commences even at 0° with considerable heat, and if the product is insoluble in water it separates. If excess of quinol is used, quinhydrone is formed and may separate. A further merit of the reagent is that the benzoquinone produced is volatile in steam, and so can be removed from water-soluble products, *e.g.*, sulphonic or carboxylic acids, leaving a clean solution for working up. A possible source of loss in the reaction is that some diazo-compound may combine with the benzoquinone to give the arylbenzoquinone (cf. p. 318). *sym*-Nitroxylene (1 : 3 : 5-$NO_2{\cdot}C_6H_3Me_2$) is made from 5-nitro-*m*-xylidine (5 : 1 : 3 : 4-$NO_2{\cdot}C_6H_2Me_2{\cdot}NH_2$) as follows using quinol as the reducing agent :—

The nitroxylidine (16·6 g. = 0·1 mol.) is dissolved in glacial acetic acid (50 c.c.), and poured into a wide-neck bottle in which has been placed ice (200 g.) followed in succession by hydrochloric acid, *sp. gr.* 1·18 (35 c.c.) and sodium nitrite (7·5 g.) dissolved in water (20 c.c.); on stoppering and shaking, a clear brownish diazo-solution is obtained, from which excess of nitrous acid is removed with sulphamic acid, and a little insoluble matter is filtered off. The solution is then mixed with one of quinol (11 g.) in water (225 c.c.) at room temperature and set aside overnight. In the morning the granular product is collected, washed with water, and steam distilled. The crude *sym*-nitroxylene dried at room temperature weighs 10·6—11·2 g., 70—74% yield, m. p. 74—75° after crystallisation from ethanol or acetic acid.

Jacobson's [35] method of diazotisation of the sulphate in ethanol followed by boiling gives yields of the same order.

Another good reducing agent introduced by Brewster and Poje [47] is formaldehyde in aqueous caustic soda, and it is most effective with diazo-compounds having positive substituents, as is shown in Table XXIX on p. 274.

For preparative purposes the replacement of the diazo-group by hydrogen is of most service in the naphthalene series, as it affords means of producing nitronaphthols, dinitronaphthalenes, and naphtholsulphonic acids not easily attainable by other routes. This often entails the

decomposition of diazo-oxides, many of which resist the action of boiling alcohol, but replace the diazo-group by hydrogen if finely-divided metal or cuprous oxide is added to the alcohol. In the preparation of 4-nitro-2-naphthol from 4-nitronaphthalene-1-diazo-2-oxide Morgan and Evens [33] obtained the results shown below.

TABLE XXVIII

Conversion of 4-Nitronaphthalene-1-diazo-2-oxide into 4-Nitro-2-naphthol

	Time of heating, hours.	Yield of nitro-naphthol, %.
Ethanol	24	45
,, plus copper . . .	12	38
,, ,, zinc	16	45
,, ,, aluminium . . .	32 *	58–64
,, ,, hypophosphorus acid .	26	53

* Ingold [36] reports that 6–8 hours is sufficient.

On the other hand, alcohol proved more effective alone than when used with zinc or aluminium in the reduction of 1-diazo-2-naphthol-4-sulphonic acid to 2-naphthol-4-sulphonic acid; [37] the same reduction can be brought about in alkaline glucose [48] in a yield claimed at greater than 90%. Alkaline sodium sulphide has been used to reduce 6-nitro-3-carboxynaphthalene-1-diazo-2-oxide to 6-nitro-2 : 3-hydroxynaphthoic acid [44] and 3-carboxynaphthalene-2-diazo-1-oxide to 1-hydroxy-3-naphthoic acid.[39]

Cuprous oxide is an active agent in the replacement of the diazo-group by hydrogen; it has been used in boiling ethanol by Ruggli and his co-workers [38] to convert 6-nitronaphthalene-1-diazo-2-oxide-4-sulphonic acid into 6-nitro-2-naphthol-4-sulphonic acid. Cuprous oxide has the further advantage that it is effective even without alcohol in a sulphuric acid–glacial acetic acid diazotisation solution. Hodgson and Birtwell [55] have prepared 1 : 3-dinitronaphthalene by the following process :—

2 : 4-Dinitro-1-naphthylamine (23·5 g.) is dissolved in sulphuric acid (90 c.c., *sp. gr.* 1·84) and treated below 10° with a solution of sodium nitrite (7·5 g.) in sulphuric acid (35 c.c., *sp. gr.* 1·84); the mixture is stirred below 20° into glacial acetic acid (375 c.c.) and stirred for thirty minutes. Then during fifteen minutes cuprous oxide (25 g.) is stirred in below 5°, the temperature is raised to 25—30°, and after fifteen minutes the evolution of nitrogen ceases. The whole is poured into water (2 l.) with ice (500 g.) and the crude 1 : 3-dinitronaphthalene is collected, washed, and pressed. It is dissolved in hot pyridine, filtered and the insoluble is washed with more pyridine (75 c.c.) then water (75 c.c.) is added to the filtrates from which on cooling there crystallises 1 : 3-dinitronaphthalene (16 g.), m. p. 146—147°.

Similarly 6-nitronaphthalene-2-diazo-1-oxide, 6-bromonaphthalene-2-diazo-1-oxide, and 4 : 5-dinitronaphthalene-1-diazo-2-oxide are decomposed, the first by adding the diazo solution to yellow cuprous oxide suspended in ethanol, and in thirty minutes gives 6-nitro-1-naphthol, the

second by boiling in ethanol with aluminium, copper, and Devarda's alloy for ten and a half hours gives 6-bromo-1-naphthol, the third by boiling in ethanol with aluminium and precipitated copper for two hours gives 4 : 5-dinitro-2-naphthol, thus illustrating the difference in method necessary for replacing the diazo-group in closely-related diazo-compounds.[56]

The alcohol used in conjunction with the cuprous oxide is not without effect, for 1 : 6-dinitro-2-naphthylamine diazotised in sulphuric acid–glacial acetic acid solution gives 1 : 6-dinitronaphthalene in the following yields (in parenthesis) with cuprous oxide and : β-chloroethanol (69·5%), methanol (60·2), *iso*propanol (59·7), ethanol (57·6), *iso*butanol (51·2), glycol (48·3), *n*-propanol (40·6), and *n*-butanol (30·0).[53] Hodgson and his co-workers [58] have found that cuprous oxide in sulphuric acid–glacial acetic acid is more effective in replacing the diazo-group by hydrogen in the naphthalene series than in the benzene series. Some of their results together with others for other reducing agents collected from the literature are cited in Table XXIX below.

TABLE XXIX

Comparison of Yields of Products by Various Reagents which Replace the Diazo-group by Hydrogen

(References are in parenthesis; only the percentage yield is entered where the product is the derivative in which the diazo-group is replaced by hydrogen; other products are named.)

	Ethanol.		Alkaline formaldehyde, %.	Sulphuric acid–glacial acetic acid, cuprous oxide, %.	Hypophosphorous acid, %.
	Diazonium salt.	Product, %.			
Aniline	Chloride	Phenetole 62 (25)	60 (40)	Diphenyl 26 (57)	60 (45)
p-Toluidine	Sulphate	40 (45)	80	23	67
p-Chloroaniline	Chloride	87 (25)	50	—	—
2 : 4-Dichloroaniline	Sulphate	45 (45)	—	—	50
2 : 5- ,,	—	—	10	39	—
sym-Tribromoaniline	Sulphate	91	—	—	94
o-Nitroaniline	,,	87 (MeOH) (20)	20	—	—
m- ,,	—	51 (MeOH) (20)	10	—	—
p- ,,	—	47 (MeOH) (20)	10	21·6	—
Benzidine	—	—	—	23	60 (26)
2 : 4-Dinitro-1-naphthylamine	—	—	—	82	—
4-Chloro-2-nitro-1-naphthylamine	—	—	—	75	—
2-Nitro-1-naphthylamine	—	—	—	70	—
4-Nitro-1-naphthylamine	—	—	—	68	—

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GROUP 2. REPLACEMENT OF THE DIAZO-GROUP BY HALOGENS

Introductory.—The replacement of the diazo-group by the halogen elements may be generalised in the form :—

$$2ArN_2{\cdot}Hal + HHal' = Ar{\cdot}Hal + Ar{\cdot}Hal' + HHal + N_2$$

Naturally if only one species of halogen ion is present, then only one halogeno-compound is formed, and the overall reaction becomes :—

$$ArN_2{\cdot}Hal \longrightarrow Ar{\cdot}Hal + N_2$$

It will be noted below that conditions are known in which the general reaction operates when two species of halogen ion are present, Ar·Hal′ being produced, and it may even predominate over Ar·Hal. The replacement can occur both in solution and in the solid state by the thermal decomposition of diazonium halides or, better, of their solid double salts.

The above generalisations conceal the fact that the reaction may be either of Type I or Type III. The uncatalysed Type I reaction can be carried out simply by heating the appropriate diazonium halide with the corresponding hydrogen halide; it is effective with all four halogens. This reaction will be called the Griess replacement reaction, for as early as 1860 Griess [1] heated diazoaminobenzoic acid with concentrated aqueous hydrogen halides and obtained halogenobenzoic acid and aminobenzoic acid, and he recognised that the acid had split the triazen molecule, and that subsequently replacement of the diazo-group by halogen had occurred. Later Griess [2] discovered that aqueous benzenediazonium sulphate reacts rapidly with cold aqueous hydrogen iodide giving iodobenzene. This latter replacement is quite general, and to convert a diazonium salt into the corresponding iodo-compound it is only necessary to add alkali iodide to the acid solution, preferably sulphuric acid, and warm gently; nitrogen is given off and the iodo-compound is formed, almost invariably in good yield. Griess also observed that as the concentration of the hydrogen halide rises, so the yield of the halogeno-derivative increases, and he pushed this principle as far as possible by isolating solid *m*-carboxybenzenediazonium sulphate and adding it to concentrated hydrogen chloride, bromide, and fluoride, and thus further inproved the yields of the corresponding *m*-halogenobenzoic acids.[6] The same point was studied by Gasiorowski and Waÿss,[7] who further increased the concentration of chlorine ions by adding calcium chloride and zinc chloride to the solution, but with only trifling increase in the yield of the chloro-derivative. Kuhn and Eichenberger [84] have patented the use of highly concentrated solutions of very soluble chlorides and bromides, such as molten calcium chloride hexahydrate, and claim the conversion of *o*-diazotoluene into *o*-chlorotoluene in yield approaching that obtained with cuprous chloride (*vide infra*). Hodgson and Sibbald [31] have tried the effect of neutral halides on the decomposition of neutral *p*-nitrobenzendiazonium chloride finding that sodium, potassium, and zinc chlorides have no effect in moderate concentration, calcium chloride gives a slight increase (from 6% to 12% yield), but with cupric chloride there is produced an 85% yield of *p*-chloronitrobenzene, a conspicuous example of a Type III reaction. General experience, however, shows that for smooth and effective replacement of

the diazo-group by the Type I reaction the halogen ions must have equivalent hydrogen cations, *i.e.*, the solution must be acid.

Two explanations of the mechanism of the Griess replacement are possible, one ionic, already mentioned as an example of the Type I reaction (cf. p. 108), while the other is a free radical mechanism mentioned under replacement by iodine (cf. p. 291). The ionic mechanism explains why, if the hydrogen halide solution is dilute, the yield of halogeno-derivative is low, a phenol being produced instead by reaction of the aryl cations with the water. It does not explain why the halogen anions must have hydrogen cations, and thus some kind of activation of the halogen anions must be invoked.

The first observation of the replacement reaction in the solid phase was also made by Griess,[2] who prepared chlorobenzene by heating diazobenzene platinichloride and diazobenzene hexachlorostannate.[6] The dry decomposition of diazonium fluoborates pioneered by Balz and Schiemann is now the standard method for the preparation of fluoroaryls, and the technique of dry decomposition of diazo salts has been improved by Schwechten so that it can now be used in laboratory to prepare fair-sized specimens (cf. p. 289).

While the treatment of diazo-compounds with concentrated aqueous acid would have sufficed for laboratory work, it is doubtful if the replacement of the diazo-group by chlorine and bromine would ever have become a general industrial operation had no better means been found, but in 1884 Sandmeyer,[4] in trying to prepare phenylacetylene from diazobenzene and copper acetylide, obtained chlorobenzene in good yield. Investigating further, he found the active agent in promoting the change to be cuprous chloride. Aniline (30 g. = 0·32 mol.) diazotised and run into cuprous chloride solution (150 c.c. of 15% solution) affords a yield of chlorobenzene (26 g. = 0·23 mol. = 72% yield on aniline) considerably better than that to be obtained by heating benzenediazonium chloride with concentrated hydrochloric acid, by which means Gasiorowski and Waÿss [7] obtained chlorobenzene in 41% yield.

The action of cuprous salts in bringing about the replacement of the diazo-group by other elements or groups by a Type III reaction, generally called the Sandmeyer reaction, is not unique, though it was for long believed to be so, but it is outstanding. Sandmeyer tried cupric and ferrous salts,[5] but found them to be without the same action as cuprous salts. Later, Körner and Contardi [19, 20, 22] showed that there are conditions under which some diazonium salts, especially those having negative substituents, can be transformed as well by cupric as by cuprous salts. This will be called the Körner–Contardi replacement reaction, and it is further discussed below (cf. p. 282). Nevertheless, for day-to-day replacement of the diazo-group by chlorine or bromine no catalyst has yet been found to challenge cuprous chloride or bromide because,

although for each reaction there is an optimum concentration and temperature, yet the cuprous salts rarely fail to deliver a good yield of the halogeno-derivative over a wide range of conditions. This property is illustrated in Table XXX below, which shows the percentage yield of *p*-chloronitrobenzene obtained at increasing dilution when *p*-nitroaniline (2·8 g.) is diazotised in hydrochloric acid (sp. gr. 1·18, 50 c.c.) and treated with cuprous chloride (4 g.), hydrated cupric chloride (6·9 g.), or hydrated ferric chloride (10·8 g.), and boiled for thirty minutes.[30]

TABLE XXX

Percentage Yields of p-*Chloronitrobenzene obtained from* p-*Nitrodiazobenzene against Dilution of Hydrochloric Acid in Presence of Cuprous and Cupric Chlorides and Ferric Chloride*

Total H_2O present, g.	Blank, %.	Cuprous chloride, %.	Cupric chloride, %.	Ferric chloride, %.
38·0	56	87·5	75	81
48·0	53	84·5	83	69
62·0	50	84·5	69	62·5
88·0	44	92·0	50	45·0
138·0	31	81·0	47	31·0
188·0	22	—	52	—

The effect shown by cuprous chloride in maintaining the yield of *p*-chloronitrobenzene with increasing dilution is characteristic of the Type III reaction of an intermediate complex. Moreover, two investigations of the rate of nitrogen evolution in the conversion of benzene- and toluenediazonium chloride into chlorobenzene and the chlorotoluenes in presence of cuprous chloride led to the conclusion that two reactions are operative side by side.[17, 18] The facts at present known therefore suggest that in the Sandmeyer reaction the chloro- and bromo-derivative produced come partly from a Type I reaction, and partly from the Type III decomposition of an intermediate complex, and that these proportions vary widely with the reaction conditions and the diazo-compound. The reaction is not catalytic in the sense that a small amount of cuprous salt will encompass the conversion of a much greater weight of diazonium salt; usually at least one half atom of copper, as cuprous halide is necessary for each molecule of diazonium halide, and some require a whole atom or a fall in yield results.

It is important to note that the diazo solution must be run into that of the cuprous halide, and not *vice versa*, for if the diazo salt is in excess the cuprous halide merely acts as a reducing agent and the product is largely a symmetrical monoazo-compound. The reason is that at the start of reaction enough cuprous salt must be added to satisfy all the diazo-compound present, otherwise catalysed and uncatalysed reactions occur side by side, the latter producing by-products. Tobias [10] noted

t stable diazo-compounds, such as those from the diazonaphthalene-
)honic acids, need but little cuprous salt, evidently because only the
ılysed reaction occurs. The extent to which the cuprous chloride is
lised has been measured by Hodgson, Birtwell, and Walker.[25]

TABLE XXXI

Oxidation of Cuprous Chloride in the Sandmeyer Reaction

Diazo-compound, 1 gm. mol.	Cupric chloride produced, gm. mol.
Diazobenzene	0·20
p-Bromodiazobenzene	0·15
p-Diazotoluene	0·17
o-Nitrodiazobenzene	0·56

The extent to which the cuprous chloride is oxidised is a measure of extent to which it has functioned as a reducing agent rather than as ıtalyst, and it would be expected that the amount of cupric chloride ned would be balanced by the formation of a corresponding amount of -compound or other by-product, but such measurements have not been published.

In Table XXXII below is shown the effect of various metallic chlorides the replacement of the diazo-group by chlorine as determined by dgson and his co-workers.[29] Unfortunately, the level of the Type I ess replacement is so high that the Type III reaction effects may be ıewhat masked, but it is to be noted that some salts actually have an ct opposing replacement by chlorine.

TABLE XXXII

Effect of Metallic Halides on the Conversion of m- *and* p-*Nitrobenzenediazonium Chloride into* m- *and* p-*Chloronitrobenzene.*

	Yield of *m*-chloronitrobenzene, %.	Yield of *p*-chloronitrobenzene, %.
ı. HCl, sp. gr. 1·16, blank (Griess reaction)	47·3	54·4
Cl_3, hydrated	54·4	60·7
$)Cl_3$	31·6	37·1
$ıCl_2$	47·3	54·4
$·Cl_3$	—	54·4
$)Cl_2$, hydrated	60·7	70·9
$)Cl_2$, hydrated, solution diluted to pink	—	10·2
lank of above	—	10·2
$ı_2Cl_2$	67·5	77·6
$ıCl_2$	67·5	77·6
$)Cl_3$	67·5	77·6
gCl_2	—	54·4
iCl_2	—	60·7
$ıCl_4$	—	60·7
$ıCl_2$	47·3	54·4

At the time of his discovery of the activity of cuprous salts, Sandmeyer suggested that their activity is due to the formation of a cuprous halide–diazonium halide complex, though he was unable to isolate any such intermediate compound. Later Lellmann and Remy [8] isolated a red crystalline cuprous bromide–naphthalene β-diazonium bromide, whilst a cuprous bromide–benzene diazonium bromide was prepared by Hantzsch.[13] These double salts are coloured, and readily decompose into cuprous salt, halogenoaryl, and nitrogen, hence Hantzsch argued that they must have a different constitution from the more easily isolated colourless diazonium double salts and may contain the azo-link. The occurrence of such salts is not, however, often visible during the progress of the reaction, though Wynne [12] saw a red intermediate compound during the conversion of *o*-toluenediazonium chloride into *o*-chlorotoluene with cuprous chloride. Evidence for the existence of complexes in solution is circumstantial. Two pieces of this evidence indicate that the halogen atom which replaces the diazo-group is derived from the cuprous salt with which the diazo salt must have been in contact. First, Hantzsch and Blagden [15] obtained *p*-chlorobromobenzene from *p*-bromobenzenediazonium bromide and cuprous chloride, and, conversely, *p*-dibromobenzene from *p*-bromobenzenediazonium chloride and cuprous bromide in methyl sulphide solution. Secondly, Hodgson and Walker,[24] having diazotised nitroarylamines, such as 2 : 4-dinitroaniline and 2 : 4-dinitro-1-naphthylamine in glacial acetic acid–sulphuric acid solution, so having in hand the diazonium sulphates, poured the solution into cuprous chloride or cuprous bromide dissolved in the corresponding hydrogen halide, and obtained the halogenonitro-compound in not less than 80% yield. Clearly the halogen atom which replaced the diazo-group came from the solution of cuprous salt, since initially the sulphate anion was attached to the diazo-group. Further, if *p*-nitrobenzenediazonium sulphate dissolved in glacial acetic acid is added to (*a*) cuprous chloride dissolved in concentrated hydrobromic acid, the weights of 4-chloro- and 4-bromo-1-nitrobenzene are in the ratio of *ca* 4 : 96, but if added to (*b*) cuprous bromide dissolved in concentrated hydrochloric acid, the ratio becomes 60 : 40; again it is the anion of the solution which predominates in the product.

There are at present two schools of thought as to the mechanism of the Sandmeyer replacement of the diazo-group by chlorine and bromine. Hodgson [25, 35] and his co-workers support and modify the classic intermediate complex idea. They picture the replacement of chlorine as proceeding by the mechanism shown in Fig. 1, thus: The diazonium cation and the complex $[Cu_2Cl_4]^{--}$ [21] form a complex which decomposes as shown by the dotted lines in the sequence (*a*) release of an electron at the carbon with separation of neutral chlorine from the complex, (*b*) evolution of nitrogen and linkage of neutral chlorine to the aryl radical, (*c*) regener-

ation of the complex anion by co-ordination of an external chlorine anion. This fundamental concept covers other replacements in which complexes are concerned. It is also to be noted that it is a catalysed reaction, in that the inorganic anion is unaltered at the completion of the reaction. Hodgson, Birtwell, and Walker point out that as the positivity of the diazonium cation increases, cupric salts and metals other than copper begin to function as halogen-carriers, until with strongly positive cations cupric salts are as effective as cuprous salts, while Hodgson and Sibbald [32] obtained good yields of chloro-derivatives by decomposing diazonium ferrichlorides in acid solution. In this conception of the reaction the initiation comes not from escaping nitrogen forcibly removing two electrons and leaving the residues to rearrange, but by donation of an electron by carbon to an anion, followed by expulsion of nitrogen. It is therefore a modified Type II reaction within the locus of the complex.

Waters has restated Hodgson's mechanism, as shown in Fig. 2 where the curved arrows represent pairs of electrons. In this modification the escaping nitrogen takes both electrons from the same link, and there ensues a Type I reaction within the locus of the complex (dots represent electrons) :—

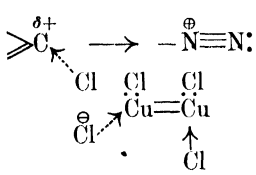


Fig. 1.

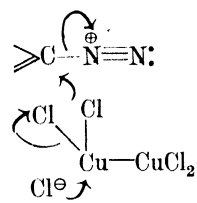


Fig. 2.

An alternative mechanism suggested by Waters [26] is that the reaction is a non-ionic decomposition of a diazonium cation brought about by a single-electron transfer from a catalyst; in other words, the Sandmeyer reaction is an oxidation–reduction process involving the production of neutral radicals from diazonium cations. Waters uses this mechanism to explain both the *almost* unique character of cuprous salts as catalysts and the course of the principal side-reactions without invoking special structural formulæ for intermediate reaction complexes. On Waters' hypothesis the cuprous cation supplies one electron to the diazonium cation according to the equation (dots represent electrons) :—

$$Cu^{\cdot +} + Ar{-}N{\equiv}N: \longrightarrow Cu^{++} + Ar^{*} + :N{\equiv}N: \qquad (A)$$

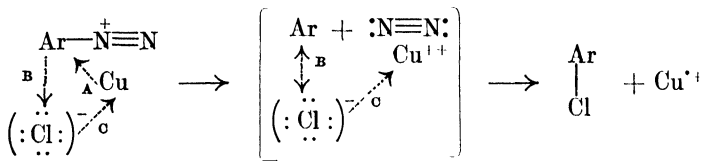
This electron transfer can occur within the complex cation of a cuprous-diazonium double salt. If halide anions are present in abundance, then the further reaction occurs :—

$$Ar^{*} + \left(:\ddot{\underset{\cdot\cdot}{Cl}}:\right)^{-} \longrightarrow Ar:\ddot{\underset{\cdot\cdot}{Cl}}: + e \qquad (B)$$

The released electron is then taken up by the cupric cation formed in (A) :—

$$e + Cu^{++} \longrightarrow Cu^{\cdot +} \qquad (C)$$

The whole cycle involving (A), (B), and (C) can be represented in one diagram thus :—



To explain why cuprous salts occupy their special place among reducing agents, Waters points out that the oxidation potential for the release of a single electron from the cuprous cation to give the cupric cation is + 0·20 volt, but that the potential for the transition elements is too high for the reaction to occur easily in acid medium :—

Mn^{++}	⟶	Mn^{+++}	oxidation potential *ca* + 1·5 volt
Ni^{++}	⟶	Ni^{+++}	very high
Co^{++}	⟶	Co^{+++}	+ 1·8 volt
Fe^{++}	⟶	Fe^{+++}	+ 0·75 volt

The stannous cation is too strong a reducing agent giving the hydrazine; As^{+++}, Sb^{+++}, and Bi^{+++} are too feeble in acid solution, while silver, lead, mercurous, and thallous halides are insoluble in water and acids. Finally, Waters asserts that the reason why nickel and cobalt are active in replacing the diazo-group by the cyano- and the thiocyano-groups is that their oxidation potential is lowered when they are converted into double cyanides.

On balance the above evidence points to the conclusion that the Sandmeyer reaction proceeds through the decomposition of a definite complex by Hodgson's mechanism not only because some of such complexes are isolable or visible during reaction, but also because so many other replacements proceed through isolable complexes with metals other than copper, and the Sandmeyer replacement by chlorine and bromine is not likely to be an exception.

Replacement of the diazo-group by chlorine or bromine can be brought about by adding Gattermann's copper [11] to the diazonium halide dissolved in the corresponding acid. The finely-divided copper is always attacked by the acid, and it is most probable that the oxidation–reduction stages are cuprous halide–copper, whereas in the Sandmeyer reaction they are cupric halide–cuprous halide. Copper hydride [23] also acts by first undergoing conversion into cuprous chloride or bromide.

The Körner–Contardi reaction occurs only with negatively substituted diazo-compounds, which easily replace the diazo-group by chlorine or

bromine, probably because they contain a large amount of the resonance form ArN:N·Cl as shown by their coupling in acid solution. One explanation is that it is the Griess reaction within the locus of an unstable double salt in solution, and thus resembles the thermal decomposition of double salts in the solid state; a further resemblance is that the solution often requires to be heated. For though cuprous salts can conceivably form labile Cu-azo-compounds by combination of the diazonium ion $ArN_2^{\oplus}$ with $[Cu_2Cl_4]^{\ominus\ominus}$, which may explain why Lellmann and Remy's salts are red, cupric chloride can only form co-ordination double salts like those of zinc chloride or stannic chloride.

The evidence as to the mechanism of the decomposition of solid diazonium salts by heat is conflicting. Schwechten [86] found that *p*-bromobenzenediazonium mercurichloride when heated with potassium bromide gave mostly *p*-dibromobenzene, *i.e.*, the replacing atom came from the diluent salt, whereas *p*-bromobenzenediazonium mercuribromide heated with potassium chloride gave *p*-dibromobenzene. This may be taken to indicate either that the nitrogen is displaced when the carbon is attacked by the nearest halogen atom which has acquired sufficient thermal energy, the view held by Hodgson for the replacement by fluorine (cf. p. 284), or that the reaction train is initiated by the escape of nitrogen when it has acquired sufficient thermal energy, and that it is replaced by the halogen atom which is nearest in space either by a Type I and Type II reaction.

Replacement of the Diazo-Group by Fluorine.—The most satisfactory reaction for the replacement of the diazo-group by fluorine is the thermal decomposition of the diazonium fluoborates (also called borofluorides) discovered by Balz and Schiemann [52]:—

$$ArN_2{\cdot}BF_4 \longrightarrow ArF + BF_3 + N_2$$

Aniline (20 g.) is diazotised in hydrochloric acid (40 c.c. *d* 1·16) with sodium nitrite (15 g.) dissolved in water (25 c.c.), and to the resultant solution of benzene diazonium chloride is added 40% fluoboric acid (60 c.c.); the precipitate of benzenediazonium fluoborate is collected, washed with a little fluoboric acid, then successively with alcohol and ether, and dried *in vacuo*. Yield 27·2 g. = 63% on aniline. The dry salt (10 g.) is placed in a distillation flask connected to a well-cooled receiver, and beyond this are two absorbers containing aqueous caustic soda to collect the boron trifluoride. On warming, the fluoborate decomposition sets in smoothly, and the product is driven over at 75—87°, giving almost pure fluorobenzene, b. p. 85°. Yield 4·8 g. = 100% on the fluoborate.

Two diazo-groups can be replaced simultaneously, as in the conversion of *m*-tetrazobenzene into *m*-difluorobenzene.[53] Hydrochloric acid (80 c.c. *d* 1·16) is added with strong stirring to a solution of sodium nitrite (15 g.) dissolved in water (50 c.c.) and ice (160 g.), and into this cold solution of nitrous acid is poured *m*-phenylenediamine hydrochloride (18 g.) dissolved in water, followed by 40% fluoboric acid (85 c.c.): the tetrazo fluoborate is collected and dried. The yield is 50—51 g. of a salt, which turns pink in the light, but is otherwise stable (decomp. 209°). When the salt (150 g.) is decomposed as described above it affords crude *m*-difluorobenzene (24·8 g.); yield on redistillation 21 g., b.p. 82—83° = 31% overall on the *m*-phenylene diamine.

This method has been used to obtain fluorobenzene,[57] fluoronitro-

benzenes,[52] fluoronaphthalenes,[54] and fluoronitronaphthalenes,[56] but it has been limited in application to products which are volatile. 2 : 4 : 6-Trichloroaniline gives 1-fluoro-2 : 4 : 6-trichlorobenzene in good yield so it is apparently not hindered by any steric effect from two ortho chlorine atoms.[55] The diazobenzoic acids[40, 42, 43] and diazobenzene-*p*-sulphonic acid,[41] which can be isolated as an internal salt, when heated with aqueous hydrofluoric acid afford the corresponding fluorobenzoic acids and *p*-fluorobenzenesulphonic acid, but the published yields are only of the order of 15—30%.

Hantzsch and Vock,[48] who first prepared diazonium fluorides, found that they do not give the arylfluorides when heated, nor have copper salts any effect in the decomposition of aqueous solutions of diazonium fluorides,[49] while a claim for a favourable effect with iron salts [50] has not been confirmed, nor is it good to act on diazonium chlorides with hydrofluoric acid, as chloro-compounds are found mixed with the fluoroaryl. The diazonium sulphates give better results, as the by-products are easily-separated phenols, the amount of which may be lessened by working in the strongest possible solution.[51]

α-Fluoronaphthalene has been made by dissolving α-naphthylamine in concentrated aqueous hydrofluoric acid in a platinum dish and adding aqueous nitrite; the amine is diazotised, and the diazonium fluoride decomposes on standing to give the α-fluoronaphthalene.[46] A further development on these lines is to dissolve aniline in anhydrous hydrofluoric acid at 5° in an iron vessel and diazotise with solid sodium nitrite; the temperature is then raised to 30—40°, when nitrogen is evolved smoothly, and passes away with the hydrofluoric acid (b. p. 19·5°), leaving sodium fluoride mixed with fluorobenzene in 87% yield.[58]

Wallach [44, 45] combined diazo-compounds in alkaline solution with piperidine, and so obtained the easily isolated and dry diazoimino-compounds, thus surmounting the difficulty of isolating the diazonium salts. The diazoimino-compounds when treated with concentrated aqueous hydrofluoric acid decompose thus :—

$$ArN_2{\cdot}NC_5H_{10} + 2HF \longrightarrow ArF + N_2 + NHC_5H_{10},HF$$

The yields from this method, where stated, are not high, and there is also the disadvantage that the product must be separated from the regenerated piperidine.

Since in aqueous solution hydrogen fluoride is not highly ionised, and moreover forms complex molecules, neither Type I nor Type III reactions can take place extensively, which accounts for the poor yields and ineffectiveness of copper salts. But in the decomposition of the dry diazonium borofluorides, $Ar\overset{\oplus}{N}_2$, $BF_4^{\ominus}$, Hodgson *et al.*[25] suggest that the same process occurs as in their mechanism for the Sandmeyer reaction (p. 280)—namely, that a polarised fluorine atom in the $BF_4^{\ominus}$ group attacks the carbon atom

attached to the diazo-group, replacing the diazo-group, thus liberating nitrogen and boron trifluoride.

Replacement of the Diazo-Group by Chlorine.—The replacement of the diazo-group by chlorine in aqueous solution in the presence of cuprous chloride is a reaction which rarely fails, and from which good yields may be expected when it is used in speculative research. To obtain the highest possible yield from any given diazo-compound the optimum temperature and concentrations must be found by trial and error;[74] generally it is best to start with the diazo solution and cuprous chloride at 0—5°, allowing the temperature to rise as reaction proceeds, and adding the diazo-compound at such speed that a brisk evolution of nitrogen takes place. It is important to add the diazo solution to the cuprous chloride, thus ensuring at all times an excess of the complex anion. If the cuprous chloride is added to the diazo solution diaryls may be formed as a by-product in considerable amount;[21] other by-products are phenols and azo-compounds. The process of adding nitrite solution to a solution of the amine and cuprous chloride was used by the early workers, and gives poor results.[75] Because he could not tetrazotise *m*-toluylene diamine [1 : 2 : 4-$C_6H_3Me(NH_2)_2$], Erdmann [73] had perforce to use this process, and by adding nitrite solution to a hot solution of the diamine and cuprous chloride in dilute hydrochloric acid he obtained 2 : 4-dichlorotoluene in 45% yield.

A convenient means of preparing the necessary cuprous chloride is as follows: Copper sulphate crystals (50 g. = 0·2 mol.) are dissolved in water (160 c.c.) with salt (29 g. = 0·5 mol.), and to the warm solution sodium sulphite crystals (29 g.) are added in portions; reduction is rapid, and finally the almost colourless solution is boiled to expel sulphur dioxide. Much of the cuprous chloride is out of solution at this stage, and can be collected if desired. Sodium sulphate crystallises if the solution is cooled to 5—15°. On adding hydrochloric acid (75 c.c., sp. gr. 1·18) the cuprous chloride dissolves, and gives a pale greenish-brown solution containing 0·1 mol. of cuprous chloride in 270—275 c.c.

In Feitler's [71] process crystallised copper sulphate (250 g.), water (500 c.c.), and salt (120 g.) are heated to solution then hydrochloric acid (1 l., *sp. gr.* 1·16) and copper turnings (130 g.) are added, and the solution boiled until decolorised; the solution is filtered and cooled in an atmosphere of carbon dioxide and made up to 2036 c.c. with hydrochloric acid, giving a 10% solution of cuprous chloride, *i.e.*, 0·5 mol. of cuprous chloride in 2036 c.c.

Angeli [72] used hypophosphites to reduce cupric salts.

Erdmann's [76] study of the preparation of *o*- and *p*-chlorotoluene shows what satisfactory results can be obtained by careful attention to reaction conditions. He noted the following optimum temperature for the decomposition of the undermentioned diazonium-cuprous chloride complexes:—

Diazobenzene-cuprous chloride	(yellow)	at about 0°
o-Diazotoluene	(red-brown)	27°
p- ,,	(yellow-brown)	30—40°
5 Diazo-2-chlorobenzaldehyde	(buff)	40—50°

If the temperature is kept below the optimum the reaction time is increased and azo-compounds appear as the by-product. Sandmeyer thought that *ortho* substituents hinder the replacement reaction, but Erdmann showed that there is no truth in this by making *o*-chlorotoluene as follows :—

To a mixture of *o*-toluidine (1 kg.) and water (1 l.) is added hydrochloric acid (1 l., *sp. gr.* 1·16), and the cooled solution is poured into a 25 l. vessel of pot or wood containing water (6 l.), and there is further added hydrochloric acid (1·5 l.) and ice (6 kg.); the amine is diazotised by stirring in slowly a solution of sodium nitrite (640 g.) in water (5 l.), and the final diazo solution is at 10° when balanced.

Crystallised cupric chloride (440 g.), hydrochloric acid (1840 c.c.), water (370 c.c.), and copper turnings (210 g.) are heated in a 4-l. flask until the solution is clear, and then cooled and poured on ice (1 kg.) in a 30-l. pot; the diazo solution is then added at once in a steady stream with stirring. A red-brown solid diazo-cuprous chloride double salt forms first, and the whole mass jellies, but as soon as the temperature rises over 27° decomposition sets in with strong nitrogen evolution, the solid disappears, and an oil floats, the temperature rising to 30—35°. The crude *o*-chlorotoluene weighs 920 g., and after two fractionations there is obtained 820 g., b. p. 156—60° = 82% yield on *o*-toluidine.

It will be noted that for each molecule of *o*-toluidine there is taken 0·63 atom of copper as cuprous chloride.

Armstrong and Wynne [74] said that naphthalene β-diazonium chloride is not readily converted into β-chloronaphthalene, but Scheid [80] carried out the preparation thus :—

β-Naphthylamine (70 g.) is dissolved in hot water (700 c.c.) with hydrochloric acid (42 c.c., *sp. gr.* 1·18), cooled to 12—15°, and more hydrochloric acid (250 c.c. *d* 1·18) is added; diazotisation is brought about with 10% sodium nitrite solution run in as a steady stream with strong stirring, but without cooling, until a positive reaction is produced on starch-iodide paper. The final temperature is 25°, and the solution is filtered from a little insoluble matter. The diazo-solution is then run into cuprous chloride (8—10 g.) dissolved in hydrochloric acid and heated on the steam bath, and the β-chloronaphthalene is distilled off with steam. Yield 85% on β-naphthylamine.

Here 0·16—0·20 atom of copper as cuprous chloride suffices to bring about the conversion of one molecule of diazo-compound.

β-Chloronaphthalene was obtained by Möhlau and Berger [77] instead of the expected β-phenylnaphthalene by acting on solid naphthalene β-diazonium chloride with aluminium chloride in benzene.

Cuprous chloride acts equally well to replace the diazo-group in compounds containing water-solubilising groups, such as the carboxyl or sulphonic acid groups, and 1 : 8-aminonaphthol-3 : 6-disulphonic acid was thus early converted into 1 : 8-chloronaphthol-3 : 6-disulphonic acid.[78] Here again the best conditions must be found by trial and error; thus if 1-diazonaphthalene-8-sulphonic acid is treated with hot cuprous chloride solution, the diazo-group is largely replaced by hydroxyl, giving naphthasultone. On the other hand, if the solid diazo-compound is added to cold cuprous chloride–hydrochloric acid and set aside for several days at room temperature until nitrogen evolution ceases, then boiled, made alkaline to precipitate copper, filtered, and salted, 1-chloronaphthalene-8-sulphonic acid is obtained in 45% yield.[87]

The labile nature of the nitro-group in 1-nitro-2-diazonaphthalene makes it possible to replace both groups by halogen in a variety of ways.[85] If diazotised in hydrochloric acid and treated with cuprous chloride, 1 : 2-dichloronaphthalene is formed or 2-chloro-1-bromonaphthalene with cuprous bromide; if diazotised in sulphuric acid and treated with copper sulphate, copper and hydrobromic acid 1 : 2-dibromonaphthalene is obtained, whilst with potassium iodide the diazonium sulphate gives 1 : 2-di-iodonaphthalene.

As has already been noted, Gattermann brought about replacement of the diazo-group by chlorine by adding copper to the solution of the diazonium chloride in hydrochloric acid, but as a reagent for the purpose it is chiefly of academic interest. The method has the disadvantage that the copper becomes entangled with chloro-compounds insoluble in water. Bertheim [83] added powdered copper slowly to *p*-diazobenzenearsonic acid until evolution of nitrogen ceased, and isolated *p*-chlorobenzenearsonic acid as the copper salt by adding copper acetate to the neutral and filtered solution; he gives no yield.

Benzenediazonium chloride affords chlorobenzene in 62% yield when it is mixed with cupric chloride and electrolysed between copper electrodes,[79] and the method has been used to convert 1-nitronaphthalene-2-diazonium chloride into 2-chloro-1-nitronaphthalene.[81]

1-Diazoanthraquinone and 1 : 5- and 1 : 8-tetrazoanthraquinone afford the corresponding chloro- or bromo-anthraquinones, both with and without the presence of cuprous salts.[82]

[Schwechten's technique [86] for the decomposition of diazonium double salts by heat is described in the next section.]

Replacement of the Diazo-Group by Bromine.—Three general methods are available for the replacement of the diazo-group by bromine. (*a*) The action of hydrobromic acid on diazonium bromides with or without metallic salts or metallic copper, (*b*) the decomposition of diazonium double salts by heat, (*c*) the action of heat on diazoperbromides.

While the diazo-group can be replaced by bromine by the action of hydrobromic acid without the use of copper salts, as in the conversion of *p*-toluidine sulphonic acid into *p*-bromotoluene sulphonic acid,[102] it is almost universal practice at the present time to use cuprous bromide in some form. In carrying out the Sandmeyer reaction it is advisable to diazotise the amine in hydrobromic acid, and so ensure the formation of the diazonium bromide; addition of a soluble bromide to a solution of another diazonium salt in the expectation of anion exchange is often unsatisfactory, and it is necessary to add the diazo-compound to the cuprous bromide and at the optimum temperature. In this respect 2 : 2′-tetrazodiphenyl is exceptional, in that to obtain 2 : 2′-dibromodiphenyl (8—10% yield), nitrite must be added to a solution of 2 : 2′-diamino-diphenyl and cuprous bromide in hydrobromic acid; [107] the chief

by-product is then carbazole. Under other conditions there is obtained a mixture of carbazole with diphenyleneazone, or the latter may be the sole isolable reaction product (cf. p. 266).

The conversion of *m*-toluidine into *m*-bromotoluene is a typical example of the Sandmeyer reaction [106] :—

m-Toluidine (50 g. = 0·468 mol.) is dissolved in hydrobromic acid (200 g., *sp. gr.* 1·49); crystals separate on cooling to 5—10°, but a clear solution is obtained on diazotising with sodium nitrite (35 g. = 0·508 mol.) dissolved in water (50 c.c.). The diazo-solution is allowed to flow into a solution of potassium bromide (150 g.), cuprous bromide (50 g. = 0·174 mol.), hydrobromic acid (30 c.c. *d* 1·49), and water (250 c.c.) kept at 100°. Nitrogen is given off, and *m*-bromotoluene floats as an oil, which is washed with caustic soda solution, then with dilute acid, and dried with solid caustic soda. Yield 47—56 g. = 0·274—0·327 mol. = 59—70%.

Ratio of amine to copper 1 mol. : 0·70 atom.

If the diazonium sulphate is used in place of the bromide the yield is not so good, and more cresol and azo-compounds are formed.

The cuprous bromide required can be made as follows :—

Crystallised copper sulphate (50 g.) and sodium bromide (52 g.) are dissolved in warm water (160 c.c.) and reduced by portion-wise addition of crystallised sodium sulphite (29 g.); cuprous bromide at once begins to separate as a heavy white precipitate, and the sulphur dioxide is driven off by boiling with stirring. If the solid is desired it can now be collected on cooling and dried *in vacuo*. Alternatively after cooling to 40—50° there is added hydrobromic acid (100 c.c. *d* 1·445), giving a pale brown solution, which must be used as soon as possible.

Oddo reduced cupric bromide with Gattermann's copper in the preparation of β-bromonaphthalene.[104]

Cumming and Muir [109] failed to convert 1-diazonaphthalene-8-sulphonic acid into 1-bromonaphthalene-8-sulphonic acid either with aqueous potassium bromide and pyridine or with cuprous bromide in sulphuric acid obtaining only naphthasultone, but were successful with diammino cuprous bromide when proceeding thus :—

Cuprous oxide (1 g.) is boiled with a solution of ammonium bromide (12 g.) in water (150 c.c.) for five minutes and filtered hot. To the cold suspension of diammino-cuprous bromide in ammonium bromide so formed is added with stirring the solid diazo-compound obtained from sodium 1-aminonaphthalene-8-sulphonic acid (10 g.). After twenty-four hours at room temperature nitrogen evolution ceases and the solution is boiled, filtered through carbon and the filtrate is salted with potassium chloride; the yield of 1-bromonaphthalene-8-sulphonic acid is small. Increase in the amount of diammino-cuprous bromide causes more rapid evolution of nitrogen, but does not increase the yield. An advantage of this cuprous salt is that a small amount suffices and that it is active in the cold to give a clean product.

A similar process gives 1-bromonaphthalene-2-sulphonic acid in 85% yield [110] and also 2-bromonaphthalene-1-sulphonic acid.[109]

Craig's [108] conversion of α-aminopyridine into α-bromopyridine is a notable example of simultaneous diazotisation and conversion without the intervention of a copper salt :—

63% Hydrobromic acid (60 c.c.) is stirred in a vessel cooled by a freezing mixture and α-aminopyridine (15 g.) is added in portions followed by bromine (24 c.c.); an

orange perbromide separates. Sodium nitrite (27·5 g.) dissolved in water (40 c.c.) is added dropwise below 0°; as the last drop is added gas is evolved and the temperature rises to 5—10°. When reaction is over caustic soda (60 g.) dissolved in water is added below 0° and the liquid is extracted with ether and the dried extract is fractionated. Yield 21·8 g. of α-bromopyridine, b.p. 91—92°/25 mm. = 87%.

Naturally the scope of application of this reaction is limited to those rare amino-compounds which resist substitution by bromine, and do not form diazoperbromides under the above conditions.

Böhmer [103] found that *p*-diazophenol sulphate gives both *p*-bromophenol and 4-bromo-4′-hydroxydiphenyl ether when heated with hydrobromic acid, apparently because the reaction of the diazo-compound with hydrobromic acid is so slow that the bromophenol also has time to react with the diazo-compound :—

$$p\text{-OH}\cdot C_6H_4\cdot N_2\cdot HSO_4 + p\text{-}C_6H_4Br\cdot OH = p\text{-}C_6H_4Br\cdot O\cdot C_6H_4\cdot OH\text{-}p + N_2 + H_2SO_4$$

The poor yields mentioned above for the conversion of 2 : 2′-diaminodiphenyl into dichloro- and dibromo-diphenyl led Schwechten [86] to reinvestigate Griess's method of decomposing double diazonium salts by heat in the presence of a diluent. He tried the easily-obtained diazonium double salts of mercuric, antimony, and stannic chlorides and bromides; he found the first to be the most satisfactory for his purpose mixed with about twice the weight of potassium chloride or bromide or ammonium chloride as diluent. Having made the dry double salt, and mixed it with the diluent a sample is heated to make sure that the decomposition is not unduly violent. If the reaction is judged to be too violent more diluent is added, and the powder is then packed into a vertical tube 1 m. long by 3 cm. in diameter so that it is half filled; the open end is connected to an air condenser. Then the tube is heated, beginning at the top of the charge, so that decomposition is started at the top and travels quietly downwards through the mass and any distillate is collected.

2 : 2′-Diaminodiphenyl (9·2 g. = 0·05 mol.) is tetrazotised in dilute sulphuric acid, and an excess of an aqueous solution of mercuric nitrate and potassium bromide is added; the precipitate of the yellow double salt is collected washed with water, then with acetone, and dried giving a yellow powder very sensitive to light, having the constitution $(C_{12}H_8N_4Br_2)(HgBr_2)_2$; the yield is 90%. The salt is mixed with double its weight of potassium bromide and heated as described above. After heating, the contents of the tube are washed with water, extracted with ether, boiled with carbon, filtered, and evaporated; the residue is crude 2 : 2′-dibromodiphenyl (13·6 g.); on crystallising from methanol there is obtained 12·5 g. of m. p. 80—81° = 80% yield.

Newman and Wise [111] say that it is best when making β-bromonaphthalene by Schwechten's process to use twice the amount of mercuric bromide necessary to form the compound $(\beta\text{-}C_{10}H_7\cdot N_2Br)_2, HgBr_2$, thus obtaining a yield of 61—65% not further increased by more mercuric bromide. They mixed the double salt with sodium bromide and effected decomposition by dropping the powder in portions into a flask heated to 90° in a glycerol bath.

The preparation of bromo-compounds by the decomposition of diazo-perbromides (cf. p. 153) is simple, and often very satisfactory. Griess [100, 101] obtained bromobenzene by mixing diazobenzene perbromide with sodium carbonate and distilling from a retort. To make β-bromo-anthraquinone [105] no diluent is necessary, and it is only necessary to heat the perbromide to 200°. Newman and Fones [112] dissolve or suspend the amine in a mixture of glacial acetic acid and 40% aqueous hydrobromic acid and pass nitrogen trioxide into the liquid until it is permanently dark; the solution is then heated when nitrogen is given off and after boiling and cooling the whole is poured into excess of 20% aqueous caustic soda and the product is isolated. Newman and Fones say that the bromo-compound is formed via the diazonium perbromide.

Replacement of the Diazo-Group by Iodine.—As has been remarked above, Griess [2] discovered how easily the diazonium-group is replaced by iodine added to the solution either as hydriodic acid or a soluble iodide, and he soon showed the applicability of his reaction by making *p*-iodonitrobenzene [120] and iodohippuric acid.[121] There are but few points of preparative technique that need be mentioned. The most important is that the amine is preferably diazotised in sulphuric acid so as to form the diazonium sulphate, which experience has shown usually gives a better yield and purer product than other salts. It is not possible to make a single-stage process by adding nitrite to a solution of amine and iodide in dilute sulphuric acid. There are in the literature many examples of the application of the reaction, which occurs in the anthraquinone series [122] with the same facility as among diazo-compounds of the benzene and naphthalene series. Occasionally the results are not satisfactory, as in the preparation of 2 : 2′-di-iododiphenyl [123] obtained in only 15% yield, whereas the 4 : 4′-isomer is obtainable in 73% yield from diphenyl-4 : 4′-tetrazonium chloride.[124] As the reaction is often of service to the organic chemist who wishes to use the easily-replaced iodine atom for synthetic work, two typical preparations are given below.

Schmidlin and Huber [125] made β-iodonaphthalene thus :—

β-Naphthylamine (100 g.), 96% sulphuric acid (71 g. = 38 c.c.), and water (4 l.) are boiled together and cooled with stirring to 0°, then diazotised by running in a solution of sodium nitrite (50 g.) dissolved in water (120 c.c.). The yellow diazo-solution is quickly filtered, and to the filtrate is added 96% sulphuric acid (36 g. = 19 c.c.) diluted with water (75 c.c.) and followed by finely-powdered potassium iodide (100 g.). The whole is set aside overnight, then heated on the steam-bath, and on cooling the β-iodonaphthalene forms a crystal layer at the bottom. Yield 120—150 g. The crude material is purified by washing with warm dilute caustic potash, then shaking with hot water; it is dried on a tile and distilled *in vacuo*, b. p. 172°/21 mm., m. p. 53—54°.

Cumming and Muir [127] made 1-iodonaphthalene-8-sulphonic acid thus :—

The sodium salt of 1-aminonaphthalene-8-sulphonic acid (10 g.) is dissolved in boiling water (200 c.c.) and precipitated with dilute sulphuric acid. After cooling to room temperature the suspension is diazotised with a slight excess of sodium nitrite, salt is added to the solution and the solid diazo-compound is collected. This is then suspended in a solution of potassium iodide (15 g.) in water (150 c.c.) with

line (1 c.c.) and set aside for two days; then, after boiling for a few minutes, thasultone is removed by filtration, and 1-iodonaphthalene-8-sulphonic acid is l from the filtrate in 70% yield.
Iodonaphthalene-1-sulphonic acid is made similarly as is also 1 : 8-iodonaphthol-phonic acid.[126]

The diazo-group is directly replaced by iodine to form iodobenzene by action of a solution of iodine in carbon disulphide on nitroso-anilide.[128]

Waters [24] has pointed out that as the oxidation potential of the iodide n is not much higher than that of the cuprous cation, it is not rising that replacement proceeds without the help copper salt. Fig. 3 shows the analogy to this hanism for replacement by chlorine (cf. p. 282). gson *et al.*[23] suggest that iodine, which is a well-wn carrier for chlorine and bromine, acts here on own behalf. In the acid solution the iodine ion is ised by the diazonium ion to a neutral atom, which bines with another to form I_2, which with an iodine ion forms the n $I_3^{\oplus}$, which interacts with the diazonium ion to form the iodo-pound; iodine is thus liberated, more I_2 is regenerated, and the tion proceeds until all the diazonium salt has been consumed.

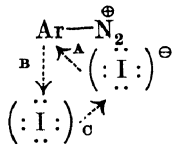


FIG. 3.

The almost explosive evolution of gas has been reported in the conver- of 2-diazodiphenyl into 2-iododiphenyl,[129] and a colleague has informed author of a similar occurrence. So far there is not enough evidence to a considered explanation, but *prima facie* the cause appears to be yed reaction due to an anti-catalyst.

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GROUP 3. REPLACEMENT OF THE DIAZO-GROUP BY THE NITRO-, AMINO-, AND CARBIMIDO-GROUPS. THE FORMATION OF AZO-COMPOUNDS BY REACTIONS OTHER THAN COUPLING.

Replacement by the Nitro-Group.—Diazonium salts are convertible into nitro-compounds by the Griess replacement, by the Sandmeyer reaction, including complexes with metals other than copper, and by the Körner–Contardi reaction.

There are a number of examples recorded of the reaction proceeding by the action of excess of nitrous acid on diazonium salts having electron-attracting substituents *ortho* and/or *para* to the diazo-group. Orton [4] added a solution of 2 : 4 : 6-tribromobenzenediazonium sulphate to a very dilute solution of potassium nitrite (20 mol. equivs.), and obtained a small yield of 2 : 4 : 6-tribromonitrobenzene, together with much 4 : 6-dibromobenzene-1 : 2-diazo oxide, while Körner and Contardi [6] left 2 : 6-dibromo-4-nitrobenzenediazonium nitrate in contact with excess of sodium nitrite and obtained 2 : 6-dibromo-1 : 4-dinitrobenzene. In similar experiments Bucherer and his co-workers [10, 11] poured a solution of *o*-, *m*-, or *p*-nitrobenzenediazonium chloride into such an excess of aqueous sodium nitrite that all mineral acid was replaced by nitrous acid; the evolution of nitrogen commences at once, and in four hours all the diazo-compound has disappeared (coupling test). The solid produced contains some nitrophenol, but pure samples of the three dinitrobenzenes were obtained by crystallisation from 80% acetic acid; no yields are given except that

β-naphthylamine (7 g.) by this process gave β-nitronaphthalene (0·4 g.), which is less than the yield obtained by Sandmeyer,[1] or by Meisenheimer and Witte.[3] Bucherer supposed that the nitro-group which becomes attached to the aromatic ring is derived from the anion of the diazonium nitrite, the whole reaction being :—

$$ArN_2{\cdot}X + NaNO_2 \longrightarrow ArN_2{\cdot}ONO + NaX \longrightarrow [Ar{\cdot}ONO] + N_2 \longrightarrow Ar{\cdot}NO_2$$

There is evidence, parallel with similar evidence for the halogen replacement, that the above is not the truth, not only on account of the improbability of the proposed rearrangement, but because Hantzsch and Blagden [2] showed that benzenediazonium nitrate, sulphate, and chloride all form complexes, different in each case, since both anion and cation combine, with potassium mercurinitrite; the complex formed from the diazonium nitrate is $(PhN_2{\cdot}NO_3)_2,Hg(NO_2)_2$. This complex decomposes in water alone into phenol and nitrophenol, but if copper is present the product is nitrobenzene, and the nitro-group must have come from the nitrito-groups in the complex. The yield is better than by the original method of Sandmeyer,[1] who converted benzenediazonium nitrate in presence of excess of nitrous acid into nitrobenzene (45% yield), using cuprous oxide as catalyst; he suggested that the reaction proceeds through a copper complex. Cuprous oxide was also used by Meisenheimer and Patzig,[5] who converted *p*-nitrodiazobenzene into *p*-dinitrobenzene (24% yield).

Hantzsch and Blagden [2] first pointed out the value of the red cupro-cupric sulphite (prepared by boiling copper carbonate or oxide with aqueous sulphur dioxide) as a catalyst for replacing the diazo- by the nitro-group. An example of its use is the following [12] :—

3-Chloro-2-toluidine (2 : 1 : 3-$NH_2{\cdot}C_6H_3Cl{\cdot}Me$) (44 g.) is dissolved in water (250 g.) and sulphuric acid (*d* 1·84, 31·5 g.) and diazotised with a solution of sodium nitrite (23·3 g.). The diazo solution is run slowly into a mixture of water (800 g.), cupro-cupric sulphite (50 g.), and sodium nitrite (150 g.); after stirring for two hours at room temperature steam is passed through the solution, and carries away 3-chloro-2-nitrotoluene (2 : 1 : 3-$NO_2{\cdot}C_6H_3Cl{\cdot}Me$), b. p. 111—112°/10 mm., in 75% yield (40 g.).

Another nitro-compound not easily accessible by means other than the diazo-reaction and made with the above catalyst is 3 : 4-dinitroanisole [3 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OMe$].[13]

Hodgson *et al.* [19] have improved this method further by adding a solid diazonium sulphate to a concentrated aqueous solution of sodium nitrite in which is suspended cupro-cupric sulphite, made by adding an equivalent of aqueous sodium sulphite to copper sulphate solution. They state that this catalyst is more active than the red-violet variety made as above or by adding aqueous ammonium sulphite saturated with sulphur dioxide to copper sulphate. With cupro-cupric sulphite they made 1 : 2-, 1 : 4-,

1 : 6-, 1 : 7-, and 2 : 6-dinitronaphthalene from the corresponding nitro-1-diazonaphthalenes and 6-nitro-2-diazonaphthalene.

Addition of diazonium fluoborates as a thin aqueous suspension to an excess of saturated aqueous sodium nitrite having finely-divided copper in suspension can also afford good yields of some nitro-compounds.[15] For each molecular proportion of the fluoborate Starkey uses sodium nitrite (1·14 mol.) and copper (2·52 atoms). 2-Nitroanthracene has thus been made via anthracene-2-diazonium fluoroborate.[14] Copper powder has also been used by Veselý and Dvorák,[8] who added aqueous solutions of diazonium salts into alkaline nitrite having the copper in suspension; they said that the results are as good as those with cupro-cupric sulphite.

A most effective variation of Hantzsch and Blagden's method in which both diazo-compound and nitrito-group are combined in a single complex is the use made by Hodgson and Marsden [17] of the diazonium cobaltinitrites, which are decomposed in aqueous sodium nitrite in presence of cuprous oxide and cupric sulphate. As is shown in Table XXXIII, it is essential with diazo-compounds not having substituents which induce positivity in the carbon atom to which the diazo-group is attached to use both cuprous oxide and cupric sulphate, thus linking with the observations of Contardi,[9] who used cupric salts as catalysts for a number of replacements. The preparation of the cobaltinitrite and its decomposition are carried out thus :—

The amine (0·1 g. mol.) is diazotised in aqueous hydrochloric or sulphuric acid with sodium nitrite (7·0 g.), the volume being kept as small as possible; the diazo-solution is neutralised with calcium carbonate and filtered. To the clear solution is added sodium cobaltinitrite $[Na_3Co(NO_2)_6]$ with stirring, and the precipitated aryldiazonium cobaltinitrite, $(ArN_2)_3$, $Co(NO_2)_6$, is collected as yellow to orange crystals; those derived from the chloro- and nitro-anilines are stable when dry, those from the toluidines, anisidines, and naphthylamines are less stable. The finely-powdered cobaltinitrite (10 g.) is added in portions at room temperature to a well-stirred solution of sodium nitrite (10 g.) and crystalline copper sulphate (10 g.) in water (60 g.), in which is suspended cuprous oxide (4 g.). After the evolution of nitrogen is complete (twelve hours may be required) the nitro-compound is recovered by steam distillation or solvent extraction.

Hodgson and Marsden regard the mechanism of the reaction as analogous to that of the Sandmeyer reaction, the feebly-linked anionoid nitrito-group attacking the cationoid carbon to which the diazo-group is attached, the function of the copper compounds being to remove the nitrogen, while the nitrite replenishes the cobaltinitrite complex which has given up nitrito-groups to form the nitro-compound.

In Table XXXIII on p. 296 are set out the yields of nitro-compounds obtained from some diazo-compounds by the cobaltinitrite and fluoroborate methods.

As with replacement by halogen, the Körner–Contardi reaction is only effective with diazo-compounds having the necessary negative

substituents. Körner and Contardi [7] made isomers of 1 : 3 : 5-trinitrobenzene and 2 : 4 : 6-trinitrotoluene from amines such as 2 : 6- and 2 : 4-dinitroaniline and 2 : 6-dinitro-*m*-toluidine

$$[2 : 6 : 1 : 3\text{-}(NO_2)_2C_6H_2Me{\cdot}NH_2],$$

which they diazotised with nitrous gases in nitric acid, sp. gr. 1·4, then

TABLE XXXIII

Replacement of the Diazo-Group by the Nitro-Group.

Diazo-compound from :	Diazocobaltinitrite decomposed by : Cuprous oxide, NO_2-compound, %.	Cuprous oxide, cupric sulphate, NO_2-compound, %.	Diazofluoborate decomposed by copper. NO_2-compound, %.
Aniline	75·5	—	—
o-Nitroaniline	67·4	—	33 (33–38 [16])
m- ,,	72·0	—	43
p- ,,	75·0	—	64 (67–82 [16])
p-Chloroaniline	82·5	—	15 (64 [3])
α-Naphthylamine	20·0	68	<10 (25 [3])
β- ,,	16·9	60	—
p-Toluidine	—	69	10
p-Anisidine	—	68	—
o-Toluidine	—	61 *	—
o-Anisidine	—	63 *	—
Ethyl *p*-aminobenzoate	—	—	50

* On the weights of amine diazotised; the cobaltinitrite is unstable and is used moist.

isolated the diazonium nitrate by dilution with water, and decomposed it as moist filter-cake with aqueous sodium nitrite in presence of cupric chloride or sulphate.

Hantzsch and Blagden [2] attempted to replace the diazo-group by the nitroso-group but failed.

Replacement by the Amino-Group.—Böhmer [25] reduced dibromodiazophenol to dibromoaminophenol and ammonia by means of zinc and acetic acid, but in general the reagents which regenerate the amine from a diazo-compound are ammonia and its substituted derivatives. Thus recovery of a part of the amine from which the diazo-compound was originally prepared can be brought about by adding the solution to hydroxylamine in presence of caustic alkali; apparently an O-azo-compound is formed under these conditions, and then splits up in two ways :—

$$ArN_2{\cdot}Cl + OH{\cdot}NH_2 \longrightarrow ArN{:}N{\cdot}O{\cdot}NH_2 \begin{cases} \rightarrow ArN_3 + H_2O \\ \rightarrow ArNH_2 + N_2O \end{cases}$$

Mai [26] demonstrated the presence of the nitrous oxide and separated the arylamine from the arylazide with dilute acid. He recovered 60% of *p*-toluidine from *p*-toluenediazonium chloride.

Griffin,[27] when investigating the action of alcohols on diazotised *p*-toluidine-*m*-sulphonic acid, found that the amine is regenerated when the diazo-compound is acted on by methanol containing dissolved ammonia. Diazoamino-compounds are often produced by the action of ammonia on diazo-compounds, as the latter immediately combines with the amine as soon as it is regenerated. An example is the formation of the dye Clayton Yellow (C.I. 813), which is a diazoamino-compound, and can be obtained by diazotising dehydrothiotoluidine sulphonic acid and adding ammonia, when nitrogen is given off and the dyestuff is formed by coupling of the undecomposed diazo-compound with the freshly-formed amine.[32]

1-Diazoanthraquinone-6-sulphonic acid (believed by Wacker [28] to be the 2-sulphonic acid) is abnormally sensitive to ammonia, easily regenerating the original amine. If hydroxylamine or hydrazine is used instead of ammonia the nucleus is hydroxylated at 4 in addition to regeneration of the amino-group, the product being 1-amino-4-hydroxyanthraquinone-6-sulphonic acid.[28] Wacker extended the work to 1 : 5- and 1 : 8-tetrazoanthraquinone, which with ammonia afford a mixture of the regenerated diamines mixed with 1 : 5- and 1 : 8-dihydroxyanthraquinone, while with hydroxylamine regeneration, deamination, and hydroxylation occur in the same molecule, so that 1 : 5-tetrazoanthraquinone affords 1-amino-4 : 8-dihydroxy- and 1 : 5-diamino-4 : 8-dihydroxyanthraquinone; analogous compounds are obtained from 1 : 8-tetrazoanthraquinone and hydroxylamine.[29] Acid wool dyes are made by treating dry 4-halogeno-1-diazoanthraquinone-2-sulphonic acid with amines, such as aniline, in presence of the metals copper, zinc, or magnesium.[30] The products of this last reaction are for the most part mixtures. Lynas-Gray and Simonsen [31] acted with primary aromatic and aliphatic bases on 1-diazoanthraquinone-2-sulphonic acid and on 4-anilino- and 4-bromo-1-diazoanthraquinone-2-sulphonic acid, and separated the products by chromatographic absorption on alumina. For example, treatment of the last-named with aniline affords 4-bromo- (20%), 4-anilino- (10%), 1 : 4-dianilino anthraquinone-2-sulphonic acid (30%), and 1-anilinoanthraquinone-3-sulphonic acid (40%).

Replacement by the Carbimido-Group [35, 36].—Phenylcarbimide is formed as a floating oil when a concentrated aqueous solution of potassium cyanate is mixed with one of benzenediazonium sulphate and copper powder is added to the solution; the oil that floats up as formed is skimmed off, dissolved in ether, dried, and distilled (yield, 2 g. from aniline, 10 g.). A larger yield is obtained from *o*-toluidine, but the method is only of academic interest, as the usual mode of preparation from a primary arylamine and phosgene is more satisfactory.

The Formation of Azo-compounds by Reactions other than Coupling.—The action of certain mild reducing agents on some diazo-

compounds leads to the formation of azo-compounds, part of the total diazo-nitrogen being lost. In the present state of knowledge it is convenient to classify this reaction as a replacement of the diazo-group, the replacing group being the diazo-radical itself. Nor at present can the reaction be considered as general, though a better understanding of its mechanism may reveal conditions making possible its extension to a greater range of diazo-compounds.

Two different types of azo-compounds are produced in this way, (*a*) symmetrical azo-compounds, and (*b*) benzeneazodiphenyl, $Ph{\cdot}N_2{\cdot}C_6H_4Ph$, or its homologues; when members of type (*b*) are formed they are accompanied by a proportion of type (*a*), but the reverse is not true.

The reaction of type (*b*) was first observed by Griess,[40] who treated an aqueous solution of diazobenzene with potassium ferrocyanide, and in the yellow product identified (i) azobenzene, (ii) an oil, (iii) a yellow substance which Locher [41] showed to be benzeneazodiphenyl. Ehrenpreis [45] also repeated these experiments, and further obtained an oil and a yellow solid by acting on *o*- and *p*-diazotoluene with ferrocyanide. Börnstein [43] also obtained benzeneazodiphenyl mixed with diphenyl sulphide by the action of cuprous sodium thiosulphate on a neutral solution of diazobenzene.

Lange [42] first observed the occurrence of the reaction of type (*a*) among diazo-compounds of the naphthalene series when he found that the diazonaphthalenes and their sulphonic acids do not form diazosulphonates by interaction with sulphite, but are instead reduced to symmetrical azo-compounds with loss of half of the diazo-nitrogen; he said that the yield of azo-compound is almost quantitative (cf. p. 148), but Bogolovski [51] has made symmetrical azo-compounds by the rapid decomposition of aryldiazonium chlorides with cuprous chloride (cf. p. 285).

Vörlander and F. Meyer,[44] in experiments on the action of ammoniacal cuprous oxide on diazo-compounds of the benzene series, found that *asym.* *m*-xylidine ($1:2:4\text{-}NH_2{\cdot}C_6H_3Me_2$) and *ψ*-cumidine afford symmetrical azo-compounds in high yield, whereas those diazo-compounds substituted by chlorine or carboxyl afford either small yields of the azo-compounds or none, producing instead the symmetrical diaryl (cf. p. 310). Some of their results for azo-compounds are shown in Table XXXIV below. They maintained that the cuprous oxide must be in solution, and that cuprous oxide in alkaline suspension is not effective. Hydroxylamine was Vorländer and Meyer's reagent for the reduction of the ammoniacal cupric sulphate; they mention reduction by sulphur dioxide, but give no account of experiments in which it was used. Cumming and Muir [48] showed decisively that the choice of reducing agent for the copper is not a matter of indifference, for if ammoniacal copper sulphate reduced with sulphur dioxide interacts with 1 : 4-, 1 : 5-, or 1 : 8-diazonaphthalenesulphonic acid the diazo-group is replaced by hydrogen, but if hydroxyl-

amine is the reducing agent for the copper, then the same diazo-compounds afford the corresponding azonaphthalenesulphonic acids, as do also 1 : 2- and 2 : 6-diazonaphthalenesulphonic acid, though the yield from the last is much less than that from the 1-diazonaphthalenesulphonic acids. 2 : 1-Diazonaphthalenesulphonic acid affords only 2 : 2′-dinaphthyl-1 : 1′-disulphonic acid.

Cumming and Muir's tetrammino-cuprous sulphate is made as follows :—

Crystallised copper sulphate (20 g.) is dissolved in water (150 c.c.) with aqueous ammonia, *sp. gr.* 0·88 (23 c.c.), and to this is added a solution of hydroxylamine hydrochloride (9 g.) and caustic potash (7 g.) in water (100 c.c.); after effervescence has ceased a pale green solution results. It is sufficient for interaction with 10 g. of diazonaphthalenesulphonic acid.

Hodgson and his co-workers,[49] on the other hand, added an acid solution of a diazonium sulphate to freshly precipitated cuprous oxide suspended in water, and obtained symmetrical azo-compounds in high yield from diazo-compounds of the naphthalene series, whilst phenols or naphthols and compounds in which the diazo-group is replaced by hydrogen (" deaminated product ") also appear, especially among diazo-compounds of the benzene series. The temperature rises during the reaction, the cuprous oxide being dissolved and oxidised to cupric sulphate.

The results of the procedures of Vorländer and F. Meyer and of Hodgson and his co-workers are compared in Table XXXIV on p. 300.

Azobenzenediarsonic acids have been reported as derivatives of the diazobenzenearsonic acids. Thus azobenzene-2 : 2′-diarsonic acid appears as a by-product in the reaction of *o*-diazobenzenearsonic acid with phenylarsenious acid,[46] and the isomeric 3 : 3′-diarsonic acid is formed when a solution of *m*-diazobenzenearsonic acid and sodium arsenite is set aside while just acid.[47]

The formation of the ring-compound diphenyleneazone (cf. p. 266) by reduction of 2 : 2′-tetrazodiphenyl with cold aqueous cuprous bromide or with sodium arsenite is an example of the formation of an internal azo-compound when the replaced and replacing groups are both part of the same molecule.

The mechanism of the reactions by which the foregoing azo-compounds are formed is as yet obscure. As has already been suggested (cf. p. 113), the formation of azobenzene and benzeneazodiphenyl may be due to interaction of diazobenzene with free neutral phenyl radicals, produced by homolysis of part of the undissociated diazobenzene, an approach which gives a reason for the appearance of more than one product, one of the number being an azodiaryl derivative.

To account for his experimental results with cuprous oxide, Hodgson [49] suggests that on oxidation the reducing agent releases an electron to the diazonium group, which can then suffer scission into two different free radicals, (*a*) an aryl radical and nitrogen, and (*b*) a diazo-radical, $ArN{=}N\cdot$

(dots represent electrons) formed by rearrangement of the diazonium radical; these two then combine to form the azo-compound, whilst the aryl radicals also combine among themselves to form diaryls. Hodgson assumes that aryl radicals will always be formed, but that the appearance or otherwise of an azo-compound depends on the existence and stability of

TABLE XXXIV

The Formation of Symmetrical Azo-compounds

Diazo-compound from :	Reduction by :			
	Ammoniacal cuprous oxide. *sym.* Azo-compound, %.	Cuprous oxide suspension.		
		sym. Azo-compound, %.	Phenol, %.	Deaminated product, %.
Aniline	30	33	26·5	27·5
o-Toluidine	31	—	—	—
m- ,,	27	—	—	—
p- ,,	52	—	—	—
asym. m-Xylidine	85–90	—	—	—
ψ-Cumidine	90–95	—	—	—
Mesidine	41	—	—	—
o-Chloroaniline	17	80	—	—
m- ,,	7	—	28	—
p- ,,	14	70	31	—
o-Nitroaniline	—	35	—	39·5
m- ,,	—	*	—	13·0
p- ,,	—	35	13	8·0
β-Naphthylamine	—	54	—	34·0
2-Chloro-1-naphthylamine	—	65	—	25·0
1- ,, -2- ,,	—	87·5	—	trace
4- ,, -1- ,,	—	78·3	—	,,
2-Nitro-1- ,,	—	none	—	85
1- ,, -2- ,,	—	,,	—	10
4- ,, -1- ,,	—	trace	32·5	31
5- ,, -1- ,,	—	40·5	15·0	42

* Mixture of azo-compound and diaryl.

the diazo-radical, which in turn is determined by the measure of positivity induced on the carbon to which the diazo-group is attached by substituents in the nucleus. Further, if the positivity is very high, as in 2-nitro- and 2 : 4-dinitro-1-diazonaphthalene, the diazo-radical cannot exist, and hence no azo-compound is formed. In 5-nitro-1-diazonaphthalene, the chloro-diazonaphthalenes, and in α- and β-diazonaphthalene the diazo-radical is stable, and is able to exist long enough to effect combination with the aryl radical, and hence the azo-compound appears in high yield. If, however, sulphite in acetic acid solution is the reducing agent (Lange's reaction) then Hodgson, Leigh, and G. Turner [50] found that 4-nitro-1-diazonaphthalene gives 4 : 4′-dinitro-1 : 1′-azonaphthalene. For this reaction they envisage the same mechanism as above of union of aryl and diazo-radicals which under these conditions are sufficiently stable to exist and combine.

It must be noted that Hodgson's suggested method of formation of the free diazo-radicals is novel, and is as yet not supported by such a mass of evidence as that for the production of free radicals by homolysis, a process, moreover, by which two neutral radicals must always be formed (cf. p. 109).

Lange's reaction, in which no trace of a diaryl has yet been reported, makes it impossible to believe at the present time that azo-compounds of the type discussed above are always formed from diazo-compounds via free radicals. Moreover, no reason has ever been suggested as to why Lange's reaction is confined to the diazonaphthalenes, nor is one forthcoming now. The evidence above does, however, suggest that these azo-compounds are only formed from a narrow band among the tautomers of the diazo-compounds with particular reducing agents, and there evidently remains scope for interesting research in this field.

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GROUP 4. REPLACEMENT OF THE DIAZO-GROUP BY OXYGEN. FORMATION OF PHENOLS, PHENOL ESTERS, PHENOL ETHERS, AND DIAZO-RESINS.

Substances containing anionic hydroxyl attack diazo-compounds directly at the positively-charged carbon atom left by loss of the nitrogen, and thus directly replace the diazo-group. The process can be represented as follows :—

$$ArN_2^{\oplus}\cdot X^{\ominus} \longrightarrow Ar^{\oplus} + N_2 + X^{\ominus}$$

$$Ar^{\oplus} + H\overset{\ominus}{O}\cdot R \longrightarrow Ar\cdot OR + H^{\oplus} \qquad H^{\oplus} + X^{\ominus} = HX$$

Here R can be hydrogen, as in water, acyl as in acetic acid, or aryl or alkyl as in a phenol or alcohol, and the corresponding products are a phenol, a phenol ester, and a phenol ether.

Alternatively Hodgson and his school say that the anionoid reagents attack the positively-charged carbon atom to which the diazo group is attached thus ejecting and substituting the diazo nitrogen atoms.

As a side-reaction the Griess replacement can occur if the anion is chlorine (*vide infra*) or bromine and to avoid this loss it is best to work with the diazonium sulphate.

The Formation of Phenols.—Phenols are the result of the normal course of decomposition of diazonium salts in aqueous solution, a reaction which it is impossible to prevent entirely by cooling if the diazo solution is kept long enough, and one which proceeds rapidly in boiling water. Griess [1] discovered that phenol is produced by heating a solution of benzenediazonium sulphate in water. E. Fischer [2] showed that a molecule containing three amino-groups, as in rosaniline, can replace each of them by hydroxyl, whilst tetrazodiphenyl affords 4 : 4′-dihydroxydiphenyl in good yield,[5] and 4 : 4′-tetrazodiphenyl-3 : 3′-dicarboxylic acid similarly produces disalicylic acid.[11] In general, substituents do not prevent the reaction except in so far as by increasing the stability, the time and temperature necessary to attain complete conversion to the phenol may be increased. The case may be different with polydiazo-compounds, where the diazo-groups are under the influence of different substituents;

for example, the action of boiling water on 3-ethoxy-4 : 4′-tetrazodiphenyl produces 4′-hydroxy-3-ethoxy-4-diazodiphenyl, the diazo-group *ortho* to the ethoxy-group being protected,[13] but such protection by *ortho* substituents is not general.[14]

Various modifications of the technique for carrying out the operation are practised in order to avoid unwanted side-reactions and to effect the decomposition of some diazo-compounds which are stable at 100°. One such side-reaction which may proceed extensively when a large bulk of liquid is heated slowly is the formation of azo-compounds due to coupling of the undecomposed diazo-compound with the phenol already formed; Nevile and Winther[3] found that the action of hot water on 1-diazonaphthalene-4-sulphonic acid produces largely the azo-dye 1-hydroxy-2 : 1′-azonaphthalene-4 : 4′-disulphonic acid (C.I. 179) accompanied by only a small yield of 1-hydroxynaphthalene-4-sulphonic acid. Reaction time can be shortened by running cold diazo solution in a thin stream into boiling acid, or by boiling the solution of amine salt and adding a solution of nitrite slowly, when the diazo-compound is decomposed as quickly as formed. When nitric acid is present, either as such or as the anion of the diazonium salt, mono- or di-nitrophenols are produced, according to the amount of nitric acid present;[4] with one equivalent of nitric acid *p*-toluenediazonium sulphate affords a good yield of 3-nitro-*p*-cresol (3 : 1 : 4-NO_2·C_6M_3Me·OH), and with excess of nitric acid α-diazonaphthalene affords 2 : 4-dinitro-1-naphthol. Dinitrophenol is the product when aniline hydrochloride is diazotised below 0° with nitrous gases, and the product is crystallised from ethanol after half an hour.[19] If instead of running the diazo solution into boiling water it is run into a boiling salt bath containing acid, higher temperatures can be reached—sometimes so high that the phenol boils away and is preserved by removal from the reaction sphere. This principle has found several applications; Heinichen[6] made 2 : 6-dibromophenol by heating 2 : 6-dibromodiazobenzene with aqueous sulphuric acid at 150°, followed by steam distillation, guaiacol[7] boils away when *o*-methoxydiazobenzene is run into a bath of sulphuric acid and sodium sulphate at 140°, while *m*-chlorophenol is carried off with the condensate when *m*-chlorodiazobenzene[18] is run into water through which a current of steam is passing. Cain and Norman[14] said that Kalle's process for guaiacol is better than Heinichen's for dibromophenol, and they used Kalle's process[7] successfully to prepare phenols from very stable diazo-compounds, such as those from the di- and trichloro- and bromo-anilines. Diazodibenzfurans (diphenylene oxide) which are not decomposed by water at 100° are converted into hydroxydibenzfurans by mixing with syrupy phosphoric acid and dropping into a flask through which is passing a current of superheated steam, thus[23] :—

2-Aminodibenzfuran (38·6 g.) is boiled with water (300 c.c.) and 20% sulphuric acid (150 c.c.), cooled to 50—60°, and diazotised at that temperature with sodium

nitrite solution. The diazo solution is filtered, sulphuric acid, sp. gr.1·84 (250 c.c.), is added and the diazonium sulphate crystallises on cooling; it is collected, mixed with technical syrupy phosphoric acid (250 c.c.), and dropped into a flask at 200° through which a current of super-heated steam is passing. The 2-hydroxydibenzfuran distils off, and is collected and crystallised from light petroleum, m. p. 139°.

The stable diazo-compounds of the anthraquinone series can also be converted into hydroxyanthraquinones by heating the sulphuric acid solutions in which they are diazotised;[8,9] the diaminoanthraquinones, *e.g.*, 1 : 6-diaminoanthraquinone,[16] are converted similarly. Noelting and Worthmann[15] tetrazotised the diamines with nitrosyl chloride in sulphuric acid solution, then added water and boiled the solution. α- and β-Hydroxyanthraquinone are also formed when the corresponding diazonium chlorides are electrolysed at 0° in neutral solution with a mercury cathode at less than 20 volts.[17] α-Anthraquinonediazonium chloride electrolysed at more than 20 volt covers the cathode with a spongy deposit which decomposes into nitrogen, mercury, and αα′-dianthraquinonyl.

The concentration of the diazo-compound is not without influence on the yield of phenol, and it is probably true for other diazo-compounds as it is for benzenediazonium chloride that the more dilute the solution the higher the yield of phenol. Crossley, Kienle, and Benbrook,[24] to whom Table XXXV below is due, also remark that the velocity constant and

TABLE XXXV

Effect of Concentration on the Reaction Velocity Constant and the Yield of Phenol in the Decomposition of Benzenediazonium Chloride Solutions at 35°

(Velocity constants are included here to save repetition in Chapter II.)

Mols. H_2O/Mols. diazo.	k (sec.$^{-1}$) × 10^5.	% yield of phenol.
2·36	26·2	24·3
3·11	26·8	30·0
3·54	25·6	27·1
3·94	26·7	31·4
7·93	—	37·0
11·89	25·3	40·0
23·80	24·5	48·7
31·70	23·9	58·3
47·58	23·4	59·3
79·30	21·9	78·0
158·60	21·2	88·0
317·20	—	90·8
634·40	—	94·6
1268·00	19·2	95·2

yield of phenol are the same for pure benzenediazonium chloride as they are for a solution of the diazo-compound prepared in the usual way. At high concentrations of the diazo-compound where the yield of phenol is low chlorobenzene is the other substance appearing in greatest amount, possibly due to the reaction $Ph^{\oplus} + Cl^{\ominus} = PhCl$. Diphenyl and benzene

also found, indicating that free neutral radicals may also have been ned.

Replacement by hydroxyl fails with some diazo-compounds. As mples may be quoted 3 : 3′-dimethoxy- and 3 : 3′-dichloro-4 : 4′- azodiphenyl, which on heating with water afford compounds insoluble austic alkali,[12] and 1 : 1′-dinaphthyl-2 : 2′-tetrazonium sulphate, which ergoes self-oxidation with loss of half the nitrogen giving [4 : 5- phtho-1 : 2′)pyrazole-(3)]-*o*-cinnamic acid.[20, 21] More usually failure he reaction produces tar.

The Formation of Phenol Esters.—When dry diazo-compounds boiled with glacial acetic acid or acetic anhydride the diazo-group is laced by the acetoxy-group; the reaction has long been known, for llach [30] boiled 4-acetamido-*o*-toluenediazonium bromide with acetic ydride and obtained 4-acetamido-2-acetoxytoluene

(4 : 1 : 2-NHAc·C_6H_3Me·O·COMe).

ating dry diazoacetates also produces the acetoxy-compounds, but in r yield,[33] and a better result is obtained by boiling the diazonium sul- te in acetic acid. Other aliphatic acids, except formic acid, would bably afford their esters, but so far interest has centered on acetic acid, l since dry diazo-compounds are necessary, the process is most con- iently carried out with easily-isolated diazo-compounds, such as those high molecular weight; thus Meldola and East [31] boiled with acetic d the easily-isolated diazo-compound of *m*-nitrobenzeneazo-2-amino- phthalene, and converted it into the 2-acetoxy-compound. Hence ller and his co-workers have used the sparingly-soluble diazonium borates; [33, 34] *m*-chlorobenzenediazonium fluoborate gives chlorophenylacetate in 50% yield, while 3 : 4-dimethoxybenzene- zonium fluoborate affords 2-hydroxy-4 : 5-dimethoxyacetophenone, acetyl group having migrated from the oxygen to the ring, while a all quantity of 3 : 4-dimethoxyfluorobenzene appears as a by-product. e possibility of the appearance of such by-products is always present; orene-2-diazonium chloride boiled with acetic acid gives 2-acetoxy- ·1%), -hydroxy- (11%), and -chloro-fluorene (10%), while fluorenone-2- zonium chloride similarly gives 2-acetoxyfluorenone (60%), and no ier identifiable product.[35] The easily-isolated zinc chloride–diazonium orides when boiled with acetic acid also afford a mixture of products in ich the diazo-group is replaced by acetoxy and by chlorine derived m the zinc chloride. Hodgson and Foster [36] illustrate the influence of substituent *para* to the diazonium group by the following series of lds of acetoxy-compound and chloro-compound (in parentheses, in the egoing order) from the following amines: *p*-hydroxy- (70; 18·8), chloro- (49; 31), *p*-methoxyaniline (39; 29), *p*-toluidine (38·6; 33·4), d β-naphthylamine (35%; 23·5%); thus while the yield of acetoxy- npound falls that of the corresponding chloro-compound rises.

The Formation of Phenol Ethers.—The normal course of interaction of diazonium salts with alcohols is the replacement of the diazo- by the alkoxy-group; [58] the replacement by hydrogen described earlier (cf. p. 268) occurs either in diazo-compounds having negative groups *ortho* or *para* to the diazo-group, or when the alcohol is diluted with water. Thus it was early discovered that dry chlorotoluenediazonium sulphate boiled with ethanol affords chlorocresol ethyl ether,[40] and that the alkylbenzenediazonium salts, such as cumene-[46] and tetramethyl-benzenediazonium sulphate,[47] afford the corresponding ethoxy-compounds in fairly good yield; in this connexion Haller,[46] having used well-dried diazonium salt and absolute ethanol, wrote that the alcohol attacks the diazo-compound directly, and that the phenol ether is not the result of alkylation of a previously-formed phenol by alcohol and the anion of the diazonium salt. Tetrazo-compounds, such as 4 : 4′-tetrazo-3 : 3′-ditolyl, replace both diazo-groups by ethoxy,[45] and, as with other replacement reactions, it is advisable to avoid the use of the diazonium nitrate, or nitrated products may appear.[50] The sparingly soluble internal diazonium sulphonates obtained from *o*-toluidine sulphonic acid [42] and from aniline disulphonic acid [43] also give the ethoxy-compounds when boiled with ethanol.

Phenols attack diazonium salts in absence of water in the same way as the aliphatic alcohols. A mixture of dry benzenediazonium sulphate and phenol forms a syrup, which if set aside until all the diazo-compound has disappeared or warmed to the same end-point produces a small yield of diphenyl ether [41] (10 g. from 250 g. of diazonium salt). A mixture of diaryl ether with diaryl is also formed when a cold diazo solution is run on to cresol at 95° and the whole is steamed.[60]

The easily-isolated and dried diazonium chloride-zinc chloride double salts, if free from nitro-groups, afford with molten phenol a mixture of the corresponding chloro-compound, the hydroxydiaryl (by Hirsch's reaction, cf. p. 315), and the diaryl ether [62]; the proportions of these for various diazo-compounds as found by Hodgson and Foster are given below in Table XXXVI.

TABLE XXXVI

Products of Decomposition by Molten Phenol of Zinc Chloride Double Salts of Diazonium Chlorides

Diazotised amine in the double salt.	Chloro-compound, %.	Hydroxy-diaryl, %.	Diaryl ether, %.
p-Aminophenol . . .	*ca.* 40	*ca.* 41	*ca.* 11
p-Anisidine . . .	48	36	13
p-Chloroaniline . . .	41	31	15
Aniline	40	26	20
α-Naphthylamine . .	46	29	20
β-Naphthylamine . .	44	35	18

Zinc chloride–diazonium chloride double salts with methanol or ethanol in most of the cases examined by Hodgson and Foster were found to give either the hydrogen replacement or a mixture of alkyl ether with hydrocarbon; the double salts derived from *o*- and *p*-toluenediazonium chloride are two exceptions, both affording only the alkoxy-compounds in over 70% yield, just as the simple *o*-toluenediazonium sulphate with methanol gives only *o*-cresol methyl ether.[57]

Diazonium chlorides free from negative groups were shown by Hantzsch and Vock [59] to react with the propanols, as they do with methanol and ethanol, but with pentanol oxidation occurs, *i.e.*, the diazo-group is in part replaced by hydrogen. Orndorff and Hopkins [55] similarly found that *iso*pentanol heated at 100° with diazobenzene-*p*-sulphonic acid produces the *iso*amyl ether mixed with phenol-*p*-sulphonic acid and benzene. Benzyl alcohol is largely converted by diazonium chlorides into benzaldehyde. Among polyhydric alcohols glycerol affords the monophenyl ether, but mannite is not attacked; [59] 2 : 4 : 6-tribromodiazobenzene always acts as an oxidising agent to alcohols, and the diazo-group is not replaced by alkoxy.[59]

Compounds in which carboxyl is *ortho* to the diazo-group, except *o*-diazobenzoic acid, lose carbon dioxide when boiled with methanol; 3-diazophthalic acid affords *m*-methoxybenzoic acid, and 2-diazo-3 : 4-dimethoxybenzoic acid gives 1 : 2 : 3-trimethoxybenzene.[61]

The temperature usually selected for carrying out the reaction—viz., the boiling-point of the alcohol at atmospheric pressure—is not necessarily the best, and at one period American chemists were much concerned with the effect of altering the pressure on the boiling alcohol.[48, 49, 52, 53] Shober [55] took the pressure to thirty atmospheres, and at the corresponding temperature for boiling methanol found that anisole-*p*-sulphonic acid is the only compound produced from diazobenzene-*p*-sulphonic acid, whereas at lower pressures benzenesulphonic acid is present. Diazobenzene-*m*-sulphonic acid is more rapidly attacked by alcohols than is the *para* isomer, but with methanol under pressure the anisole-*m*-sulphonic acid is always mixed with benzenesulphonic acid.[56] The effect of heating *p*-diazotoluene-*o*-sulphonic acid (from 1 : 4 : 3-$NH_2 \cdot C_6H_3Me \cdot SO_3H$) with ethanol under increasing pressure is given by Remsen and Dashiell as follows [51] :—

Pressure, in mm. Hg .	120	210	300	400	500	600	700	800
Phenol ether formed, mol.-% . . .	37·2	40·6	43·4	48·7	52·8	57·7	63·2	69·8

The same authors conclude that 15% is the maximum permissible amount of water in the alcohol.

The Formation of Diazo-Resins.—The replacements considered above are all reactions of a diazonium salt. If an aqueous solution of a diazo-compound is made fully alkaline so that metallic diazotates suffer

decomposition, then coloured resinous masses, which have been called " diazo-resins " by Jolles,[70, 72] are obtained. Oddo and Indovina [71] have shown that the resins still contain nitrogen, and appear to be formed by chain condensation or coupling. As yet diazo-resins have not received any technical application.

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GROUP 5. REPLACEMENT OF THE DIAZO-GROUP WITH FORMATION OF A C·C LINK. FORMATION OF ARYL-CYANIDES, SYMMETRICAL AND ASYMMETRICAL DIARYLS, ARYLQUINONES, ARYLATED UNSATURATED AND HETEROCYCLIC COMPOUNDS.

The Formation of Aryl Cyanides (Aryl nitriles).—The replacement of the diazo-group by the cyanido-group is a typical Sandmeyer reaction, in which replacement is by an anion derived from the solution through the agency of a metallic complex. Although Griess Ref. 1, p. 291 had treated diazoaminobenzoic acid with hydrogen cyanide, and had thus obtained cyanobenzoic acid and aminobenzoic acid, the reaction was without significant value for synthesis until Sandmeyer [1] showed that benzenediazonium chloride is converted into phenyl cyanide (benzonitrile) through the agency of potassium cuprocyanide :—

Crystallised copper sulphate (25 g.) is dissolved in water (150 c.c.) to which is then added potassium cyanide (28 g. of 96%). A precipitate is formed, but soon dissolves with evolution of cyanogen, and at 90° a solution of benzenediazonium chloride is allowed to flow in slowly. The latter is made from aniline (9·3 g. = 0·10 mol.) dissolved in water (80 c.c.) and hydrochloric acid, sp. gr. 1·17 (21 c.c.), and diazotised with a solution of sodium nitrite (7 g.). When all the nitrogen is disengaged the whole is distilled, the oily layer in the distillate is collected, washed with dilute caustic soda, then with dilute sulphuric acid, and distilled. The yield is 6·3 g., b. p. 184° uncorr. = 61% on the aniline.

Sandmeyer [2] made the three nitrophenyl cyanides, the preparation of *o*-nitrophenyl cyanide being afterwards improved,[4] and Ahrens [3] made the three hydroxyphenyl cyanides and the replacement by the cyano-group has come to be a useful transformation of the diazo-compounds, as subsequent hydrolysis affords carboxylic acids. Generally the yields are not so good as those from other replacements, because only the labile diazocyanide reacts, and many of these rearrange rapidly to the stable

diazocyanide, which does not undergo the replacement reaction; hence the yield of arylcyanide is the product of a race between replacement and rearrangement. The technique of carrying out the reaction is varied only in detail; for example, the sparingly soluble diazonaphthalene-sulphonic acids, having been collected and washed on the filter, are added in portions to the hot cuprocyanide solution, from which the cyanide is subsequently salted, as in the case of 1-cyanonaphthalene-8-sulphonic acid [8, 12] or by evaporation to dryness and extraction with alcohol, as for 1-cyanonaphthalene-3-, -6-, and -7-sulphonic acid.[7] Cyanides of the anthraquinone series are made in the same way,[5, 6] and diamines, such as 4 : 8-dichloro-1 : 5-diaminoanthraquinone, can be tetrazotised and converted into biscyanides.[10] Ruggli and Caspar [11] tetrazotised *m*-xylylene-4 : 6-diamine [1 : 3 : 4 : 6-$C_6H_2Me_2(NH_2)_2$], isolated the tetrazonium fluoborate, and converted it into 4 : 6-dimethyl*iso*phthalyl cyanide.

An interesting aspect of the cyanide replacement is that copper is not the only metal able to form a complex which will supply the necessary cyanide ions, for potassium nickelocyanide has also been found effective, and Korczynski and Fandrich [9] state that it affords aryl cyanides of better purity than the cuprocyanide; among many other metal cyanides tested no other was effective. Using potassium nickelocyanide, Storrie [13] has prepared 2 : 4-dinitrophenyl cyanide as follows :—

A solution of potassium cyanide (35 g.) in water (150 c.c.) is added to a solution of nickel chloride (16·5 g.) or nickel sulphate (30 g.) dissolved in water (50 c.c.), the whole is diluted with water (300 c.c.), and sodium carbonate (150 g.) is added. 2 : 4-Dinitroaniline (18·3 g.) is diazotised by Hodgson and Walker's method by dissolving in acetic acid (175 c.c.) and adding to a solution of sodium nitrite (7·7 g.) in sulphuric acid, sp. gr. 1·84 (55 c.c.). This diazo solution is run with stirring into the potassium nickelocyanide solution, and during the addition water (300 c.c.) and sodium carbonate (*ca.* 50 g.) are added to maintain neutrality; the temperature is allowed to rise, and reaches 30—35°. The whole is then stirred at 90° for half an hour, the solid is collected, washed with warm water, then with dilute caustic soda, dried, and boiled with light petroleum b.p. 60—80° to remove *m*-dinitrobenzene, and crystallised from ethanol. The yield of 2 : 4-dinitrophenyl cyanide, m. p. 103—104°, is 85% (16·49 g.).

Barber [14] has given a process for the preparation of pure, dry cuprous cyanide, but it is rarely needed in this form for diazo-reactions.

The Formation of Symmetrical Diaryls.—From time to time a number of investigators have reported that reducing agents of the kind which replace the diazo-group by hydrogen also simultaneously produce symmetrical diaryls in smaller amount. Griess [20] noticed that diphenyl is produced by the action of alcoholic caustic potash on diazobenzene, whilst Oddo [24] obtained a mixture of diphenyl and aniline with alcoholic sodium ethoxide. The diazo-compound, the reducing agent, and the conditions can, however, be so chosen that the diaryl is the chief product, the reducing agent being used in suspension or solution in a solvent for the diazo-compound with which, under the conditions chosen, the latter does not react. The mechanism of the reaction may be either Type II or Type

III. When the reducing agent is an ammoniacal solution of cuprous oxide the transient insoluble complex may centre on the insoluble diaryl itself as it separates from the solution on formation.

The use of finely-divided copper as the reducing agent was introduced by Gattermann,[23] and the reaction is commonly named after him. He carried out the reaction as follows :—

Aniline (31 g.) is dissolved in water (150 c.c.) and sulphuric acid (*sp. gr.* 1·80; 40 g.) and diazotised at 0—3° with sodium nitrite (23 g.) dissolved in water (55 c.c.). To the diazo solution is then added alcohol (100 g. = 125 c.c.), then copper (50 g.) (prepared by precipitation from copper sulphate solution with zinc dust). Nitrogen is given off freely, and the temperature rises to 30—40°; an hour later the solution is steam-distilled. Alcohol goes over first, then an oil immiscible with water (? benzene), then the solid diphenyl. The yield is 6—7 g., *i.e.*, 24—28% on the aniline.

Gattermann also effected the reduction with zinc dust and with iron filings. Friebel and Rassow,[32] using zinc dust (300 g.) and alcohol (800 g.) to reduce benzenediazonium sulphate (from 2·45 mols. of aniline), obtained a 27·8% yield of diphenyl (50 g.). Oddo [24] also obtained diphenyl by stirring a solution of benzenediazonium chloride into a zinc–copper couple suspended in chloroform.

Gattermann included the alcohol, which is likely to produce benzene as a by-product, because he believed it to be the actual reducing agent, the copper acting as an activator. Hantzsch was also of opinion that Gattermann's copper acts "catalytically," whereas cuprous salts bring about transformations by intermediate compound formation. The reaction is, however, essentially one of reduction by the copper, and copper ions are always found in the solution after the reaction. Beeson [25] obtained diphenyl from benzenediazonium nitrate and zinc dust in methanol, and Chattaway [27] converted naphthalene-β-diazonium chloride into ββ′-dinaphthyl in very poor yield with zinc dust, but copper has the advantage that it can be freshly prepared in active form by precipitation with zinc. Niementowski,[29] who insisted on the latter condition, introduced the latter reagent for preparing 2 : 2′-dinitrodiphenyl from *o*-nitrodiazobenzene thus :—

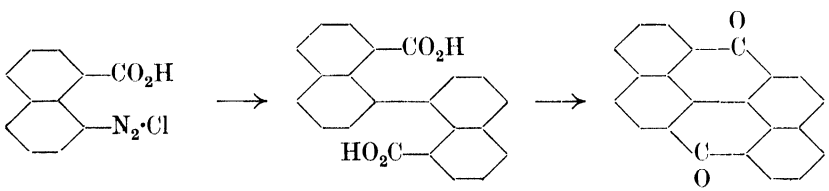
o-Nitroaniline (276 g. = 2·0 mol.) which has been passed through a fine sieve is suspended in water (2 l.) with hydrochloric acid (*sp. gr.* 1·18; 700 c.c.) and diazotised with sodium nitrite (143 g.) dissolved in water (500 c.c.), the solution being kept at 12—15° with ice. Meanwhile zinc dust (260 g.) is added to a stirred solution of copper sulphate crystals (1 kg. = 4 mols.) in water (2·5 l.) allowing the temperature to rise to 95—100°; the sludge of copper is washed by decantation, and then the diazo solution is run on to it with strong agitation in a large crock. The temperature may rise to 30°. When the evolution of nitrogen has ceased and all diazo-compound has disappeared from the solution, the solid is collected, dried, and freed from *o*-chloronitrobenzene by washing with ethanol then extracted several times with boiling benzene, from which the 2 : 2′-dinitrodiphenyl cystallises on concentration. Yield 145—150 g. = approx. 60%, m. p. 128°.

Niementowski also tried (i) zinc with a little copper as activator, (ii)

cuprous chloride, (iii) the diazonium sulphate instead of the chloride, and (iv) ethanol as solvent, but all gave much inferior yields. Macrae and Tucker [45] said that the yield increases as the scale of working increases, while Dennett and Turner [43] obtained a better yield by Ullmann's reaction with *o*-chloronitrobenzene than from *o*-nitrodiazobenzene.

Knoevenagel [26] suspended dry benzenediazonium sulphate in acetic anhydride, and on adding copper powder a 50% yield of diphenyl separated. Scholl and Kunz [35] extended this technique to the anthraquinone series, converting 2-methyl-1-diazoanthraquinone into ββ-dimethyl-αα-dianthraquinonyl, and the process has been patented for the manufacture of dianthraquinonyls.[36, 37, 38] αα-Dianthraquinonyl is also formed by electrolysis of anthraquinone α-diazonium chloride at over 20 volts with a mercury cathode and carbon anode.[40]

Vorländer and Meyer [33] showed that an ammoniacal solution of cuprous oxide also converts diazobenzene substituted by the nitro, cyanido, aldehydo, carboxyl, or sulphonic acid group into the corresponding diaryls, and that the most active reagent is obtained when the cuprous salt is prepared by reducing a cupric salt with hydroxylamine (cf. p. 299). Atkinson and his co-workers [49, 50, 52] have studied the preparation of diphenic acid, diphenyl-2 : 2′-dicarboxylic acid, with a number of reducing agents under various conditions, and obtained a 90% conversion with the above reagent. Cuprous oxide suspended in aqueous ammonia converts diazotised 4 : 6-dichloro-anthranilic acid (2 : 3 : 5 : 1-$NH_2 \cdot C_6H_2Cl_2 \cdot CO_2H$) into *dl*-4 : 6 : 4′ : 6′-tetrachlorodiphenic acid in 60% yield. The most important technical application of the reaction is in the naphthalene series, where 1-diazonaphthalene-8-carboxylic acid is converted by ammoniacal cuprous oxide into 1 : 1′-dinaphthyl-8 : 8′-dicarboxylic acid, an intermediate from which by ring closure with sulphuric acid there is obtained anthanthrone, the parent of a series of vat dyes [45] :—



Anthanthrone.

1-Diazonaphthalene-8-sulphonic acid does not undergo the same reaction, but instead affords 1 : 1′-azonaphthalene-8 : 8′-disulphonic acid (cf. p. 297) though 8-nitronaphthalene-1-diazonium sulphate with a neutral suspension of cuprous oxide gives 8 : 8′-dinitro-1 : 1′-dinaphthyl. Under the same conditions 4 : 8-dinitronaphthalene-1-diazonium sulphate behaves anomalously, and the product is 4 : 8 : 4′ : 8′-tetranitro-1 : 1′-dinaphthylamine, $NH[C_{10}H_5(NO_2)_2\text{-}1 : 4 : 8]_2$,[46] a type of substance not commonly

derived from a diazo-compound, though diphenylamine-2 : 2′-dicarboxylic acid is obtained as a by-product, together with diphenic acid, when diazobenzene-*o*-carboxylic acid is reduced with hydrated cuprous oxide suspended in dilute aqueous ammonia.[50]

Ullmann and his co-workers[30, 31, 34] published papers describing the production of diaryls by running a solution of cuprous chloride in dilute hydrochloric acid into the solution of a diazo-compound, especially ones having a nitro-group *ortho* to the diazo-group, but other workers have failed to reproduce their results, the diazo-group being instead replaced by chlorine.[43, 49] Some light is thrown on these contradictions by Hodgson and his co-workers,[51] who say that if a solution of cuprous chloride so diluted with water that the cuprous chloride is just about to precipitate is added *to* a solution of benzenediazonium chloride below 10°, the product is chlorobenzene with a considerable amount of diphenyl and 4-hydroxydiphenyl. From this they draw the conclusion that, since if the order of mixing the solutions is reversed chlorobenzene is the only product, the products of reaction are different according to whether the complex salt or the diazo-compound is in excess.

Diphenyl appears as a by-product in many reactions, suggesting that part of the diazobenzene readily undergoes homolysis. Culmann and Gasiorowski[22] tried to produce it by the reaction :—

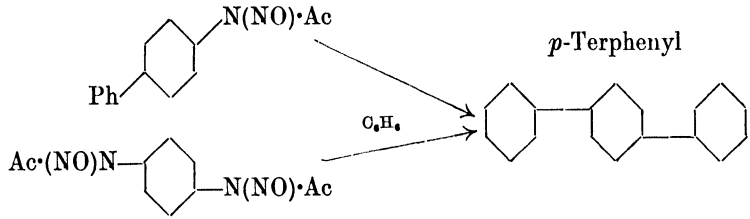
$$2PhN_2{\cdot}Cl + SnCl_2 = Ph_2 + SnCl_4 + 2N_2$$

They obtained only a small yield of diphenyl mixed with benzene, chlorobenzene, phenylazide, phenol, and aniline, evidently due to random combination of phenyl radicals as well as Type I reactions. Yet under certain conditions free phenyl radicals, if once formed, can link with each other until there are formed not only di-, but also ter-, quater-, and quinque-phenyl, all links being *para* to each other. Suggestions as to how such molecules are formed have already been made (cf. p. 113). These polyaryls have been isolated by Gerngross and his co-workers[41, 42] from the products of reaction of diazobenzene with copper in glacial acetic acid or a mixture of acetic and formic acid or benzenediazonium sulphate and copper in ethanol; the yields are small and the separation is laborious. Both *p*- and *m*-terphenyl can be produced in much better yield by an extension of Bamberger's synthesis of diphenyl from a solution of nitroso-acetanilide in benzene.[28] As already explained, this is a typical free radical reaction :—

$$PhN{:}N{\cdot}O{\cdot}COMe = Ph^* + N_2 + {}^*O{\cdot}COMe \qquad Ph^* + C_6H_6 = PhPh + H^*$$

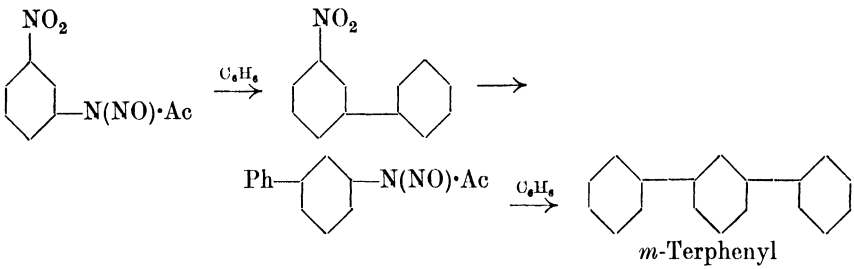
The expelled protons eventually escape as hydrogen molecules, while the acetate radicals decompose into carbon dioxide and methyl radicals, which may form ethane or attack the benzene to form toluene or combine with protons to form methane. Thus France, Heilbron, and Hey[47, 48]

obtained terphenyl by dissolving 4-nitrosoacetamidodiphenyl or *p*-di-(nitrosoacetamido)benzene in benzene :—



Nitrous fumes are passed into a solution of 4-acetamidodiphenyl (15 g.) dissolved in glacial acetic acid (250 c.c.) and acetic anhydride (50 c.c.) at 8° ; the yellow nitroso-compound (17 g.) is precipitated by pouring on ice, washed, and air-dried overnight, then dissolved (16 g.) in benzene (400 c.c.), stirred for 1½ hr. at 20°, evaporated to dryness, and sublimed at 190—200°/15 mm., giving *p*-terphenyl (7 g. = 43% on 4-acetamidodiphenyl).

If anisole is used in place of benzene a mixture of 2- and 4-methoxy-*p*-terphenyl is obtained, whilst *m*-terphenyl is produced by first combining *m*-nitronitrosoacetanilide with benzene to form 3-nitrodiphenyl, which is in turn reduced, acetylated, converted into the nitroso-compound, and combined with benzene :—



Copper acetylide [39] reduces aqueous benzenediazonium sulphate to diphenyl, though the chief reaction products are tetraphenylethane and acetylene, apparently produced by the overall equation :—

$$4PhN_2{\cdot}SO_4H + 2Cu_2C_2 = Ph_2HC{\cdot}CHPh_2 + C_2H_2 + 4N_2 + 4CuSO_4$$

On the other hand, a solution of benzenediazonium chloride or *p*-nitrobenzenediazonium chloride with copper acetylide gives chlorobenzene and *p*-chloronitrobenzene respectively.

Diphenyl is also produced as a special case of the Gomberg reaction (cf. p. 316) when aqueous sodium benzenediazotate decomposes in the presence of benzene.

The Formation of Asymmetric Diaryls, Arylquinones, Arylated Unsaturated, and Heterocyclic Compounds.—Asymmetric or asymmetrically-substituted diaryls are produced by Type II reactions, in which free aryl radicals, formed by homolytic decomposition of a diazo-

ıpound, combine with a hydrocarbon or substituted hydrocarbon. A racteristic of such reactions which marks them out as being due to free icals is that the radical enters an aromatic nucleus already containing a stituent in the *ortho* or *para* position to that substituent, no matter ıt its usual directive effect (cf. p. 109).

Hodgson [123] denies that asymmetric diaryls are formed by combination ree radicals. In his view the active reagent is the diazonium ion of ch a small concentration remains even under caustic alkaline conditions of the Gomberg ction. As shown in Fig. 1 (dots represent trons) this attacks the other component, for mple benzene, at an anionoid carbon atom, sing the attached covalent hydrogen atom to ome cationoid so attracting the anion of the zonium salt. Release of an electron from the hydrogen permits ıination of molecular nitrogen with consequent formation of diaryl anion the aryl cation with the aryl anion; acid or water, HX, is ultaneously eliminated.

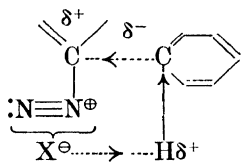


FIG. 1.

One of the simplest means of synthesis is that due to Oddo and atolo,[77] who mixed aniline and *p*-toluidine (equal mols.), diazotised the ture, and dropped the diazo-solution into alcoholic sodium ethoxide, overing benzene, toluene, and 4-methyldiphenyl. Aniline and *o*-toluıe similarly afford 2-methyldiphenyl, whilst 4 : 6-dichlorodiphenic d is produced from a mixture of diazotised anthranilic acid and zotised 3 : 5-dichloroanthranilic acid (2 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2Cl_2{\cdot}CO_2H$) uced with ammoniacal cuprous oxide.[119]

The reaction is, however, usually carried out by some device akin to the mberg reaction, by which the diazo-compound generates free radicals a solvent with which it is to combine. Hirsch [70] extracted diazoızene from water with phenol using slightly acid conditions to suppress pling; on heating, the phenol solution nitrogen was given off, and on tillation he recovered a mixture of 2- and 4-hydroxydiphenyl and henyl ether in yield up to half the weight of aniline taken. Colbert l Lacey [120] say that they obtained 2- and 4-hydroxydiphenyl by this ction in yields of 1·8% and 5·9% respectively on the aniline; in a ies of experiments their best yield was 27·8% of 3-chloro-2-hydroxy henyl from diazobenzene and *o*-chlorophenol. Norris, Macintire, and se [84] added a solution of diazobenzene to phenol and a little water at , and obtained 2- and 4-hydroxydiphenyl in 2% and 27% yield, pectively. Catechol similarly affords a dihydroxydiphenyl, but orcinol does not, while quinol gives *p*-hydroxyphenyl ether. Chatter- [95] made asymmetric diaryls by adding diazo-compounds to hot cresol, ilst 1-diazopyridine and phenol afford a mixture of α-(*o*′- and -hydroxyphenylpyridine.[87] Aniline can be used in place of phenol in

Hirsch's process when 2- and 4-aminodiphenyl are obtained,[71] a reaction reminiscent of Heusler's synthesis of the same compounds from diazoaminobenzene (cf. p. 161).

In the above cases the diazo-compound may be presumed to be removed from the water by virtue of compound formation with the solvent, and Hirsch did indeed suppose that an intermediate *O*-azo-compound or a diazoamino-compound is formed, especially as he failed to extract from the acid solution any diazo-compound with liquids such as benzene, nitrobenzene, or ethyl benzoate. Gomberg and his co-workers,[88, 89, 118] however, introduced a vital improvement in the technique by diazotising the amine in the smallest possible quantity of water, then mixing with the selected liquid with a powerful agitator while dropping in cold concentrated caustic soda solution to form the diazotate. Sooner or later the diazo-reaction disappears from the aqueous phase, and, on distilling, the non-aqueous phase products formed by union with aryl radicals are found to be present. This method of producing diaryls is generally known as the Gomberg reaction. The yields are rarely good since, although this is a Type II reaction, no reducing agent is present to control reaction by giving up electrons, and hence tar is formed by random chain combination of the free radicals. Whether the diazo-hydroxides are extracted as such by the solvent, or whether they first decompose into free radicals, is not known. Waters (private communication) says that if a fresh benzene surface is exposed to a solution of a diazotate, bubbles are seen to form at the interface, suggesting that this is the site of the formation of free radicals. Hey [107] and his co-workers have shown that the caustic soda can sometimes be replaced with advantage by sodium acetate, and the effect on yield in the preparation of some diaryls is compared in Table XXXVII below.

TABLE XXXVII

Diaryls Formed from Diazo-Compounds and Benzene by the Gomberg Reaction

Diazo-compound from :	Product.	Yield.	
		NaOH.	NaOAc.
Aniline	Diphenyl	22 %	16 %
o-Nitroaniline	2-Nitrodiphenyl	21	45
m- ,,	3- ,,	18	45
p- ,,	4- ,,	26	60
o-Chloroaniline	2-Chlorodiphenyl	25	38
m- ,,	3- ,,	25	13
p- ,,	4- ,,	40	35
p-Bromoaniline	4-Bromodiphenyl	44	12
p-Toluidine	4-Methyldiphenyl	22	11
p-Anisidine	4-Methoxydiphenyl	25	4
p-Phenetidine	4-Ethoxydiphenyl	29	11
β-Naphthylamine	2-Phenylnaphthalene	16	25

Diazo-compounds can be combined with solid, low-melting hydrocarbons such as naphthalene and diphenyl; for example, diazotised methyl anthranilate forms methyl *o*-α-naphthyl benzoate with naphthalene.[97] Solvents cannot be used to dissolve such solids, for the solvents are also attacked by the diazo-compound, and under the Gomberg conditions diazobenzene attacks carbon tetrachloride, forming chlorobenzene. Diazotised methyl anthranilate also combines with benzene to give methyl diphenyl-2-carboxylate, which, after hydrolysis to the acid, can be ring-closed to fluorenone.[98]

The Gomberg technique is not the best means of bringing about the union of aryl radicals with pyridine; for example, only a poor yield of phenylpyridine is obtained from aqueous sodium benzenediazotate and pyridine,[88] but Haworth, Heilbron, and Hey [103] found that if *p*-nitrodiazobenzene is added *to* excess of pyridine at about 40°, a 70% yield of mixed *p*-nitrophenylpyridines is produced which can be resolved through the picrates into pure α-, β-, and γ-*p*-nitrophenylpyridine in 24%, 9%, and 4·5% yield, respectively. If pyridine is added to aqueous *p*-nitrobenzenediazonium chloride no reaction occurs until all free and combined acid has been removed; if only enough pyridine is added to form a compound $p\text{-}NO_2\cdot C_6H_4\cdot N_2\cdot NC_5H_5\}Cl$ and the solution is stirred with benzene, then 4-nitrodiphenyl is obtained just as in the Gomberg reaction. Union of *p*-nitrophenyl radicals with the pyridine only begins when enough base has been added to produce undissociated *p*-nitrobenzene hydroxide, which then forms free radicals by homolysis. The single-phase reaction with pyridine is general, and has been extended to a number of diazo-compounds,[104, 105, 106] including those derived from Bz-aminoquinolines [115] and tetraminophthalocyanine.[108] 1-Hydroxylamidoanthraquinone-5-diazonium sulphate, made from 1 : 5-tetrazoanthraquinone and hydroxylamine, on treatment with pyridine gives 5-N-pyridyl-1-azohydroxylamidoanthraquinone.[86]

Instead of relying on the extractive effect of the solvent to remove the diazohydroxide or free radicals from water, dry metallic diazotates may be stirred with the solvent and treated with organic acid chlorides or anhydrous organic acids. Kühling [74] carried out this reaction with sodium *p*-nitrobenzene *iso*diazotate and benzoyl chloride in benzene, hoping to make the benzoyl derivative of the diazotate under more favourable conditions than in aqueous solution (cf. p. 38). Doubtless a diazobenzoate is formed, but it at once decomposes, and the product is 4-nitrodiphenyl. Reaction occurs similarly in toluene with acetyl chloride in place of benzoyl chloride, 4-nitro-4′-methyldiphenyl being formed; Kühling [76] similarly combined the *p*-nitrophenyl radical with benzaldehyde, acetophenone, and ethyl benzoate, but said the yields are very poor, though Jacobson and Loeb [85] made 3-nitrodiphenyl (21% yield) from moist potassium *m*-nitrobenzene *iso*diazotate suspended in benzene

and treated with acetyl chloride. Bamberger [75] showed that Kühling's reaction can be brought about by adding one equivalent of an anhydrous organic acid to the *iso*diazotate followed by the second component; thus *o*-nitrobenzene*iso*diazotate affords 2-nitro-2′ : 5′-dimethyldiphenyl when treated with *p*-xylene and acetic acid.[96] The reaction can be carried out at raised temperatures, for Kühling [78] prepared α-*p*-nitrophenylnaphthalene from sodium *p*-nitrobenzene *iso*diazotate and molten naphthalene. Bamberger also showed that *p*-nitrodiazobenzene methyl ether reacts with benzene [75] to form 4-nitrodiphenyl, whilst diphenyl derivatives are formed from benzene and diazoanhydrides [80] and diazosulphides.[79]

Another way of making asymmetric diaryls is that due to Möhlau and Berger,[72, 73] who added aluminium chloride to a suspension of a dry diazonium chloride in liquids such as benzene, diphenyl, thiophen, pyridine, and molten naphthalene; the yields of arylated derivatives are small. Stabilised diazo-compounds, especially the zinc chloride double salts and triazens, which have the advantage over *iso*diazotates and dry diazonium chlorides in being more easily prepared, have been used similarly.[100] The freshly-prepared zinc chloride double salt of *o*-toluenediazonium chloride is collected, washed with acetone, then with benzene, and suspended in benzene and treated with aluminium chloride; after one hour the mass is poured on ice and hydrochloric acid, when distillation of the benzene layer affords 2-methyldiphenyl. Or the triazen made from 3 : 4-dichlorodiazobenzene and dimethylamine is dissolved in nitrobenzene at 90°; passage of dry hydrochloric acid gas decomposes the triazen, and the diazonium chloride at once reacts, forming 3 : 4-dichloronitrodiphenyl. A still simpler process equivalent to the above is to pass nitrous acid gases into a solution of the arylamine in the substance which it is desired to arylate. Elks and Hey [112] have examined the process based on the scission of a dimethyl triazen, $ArN_2 \cdot NMe_2$, with the results as in table XXXVIII.

Hodgson and Marsden [101] decomposed suspensions of diazonium salts stabilised as naphthalene-α-sulphonates and naphthalene-1 : 5-disulphonates in benzene and nitrobenzene in presence of acetic acid, sodium acetate, and water, but the yields of diaryls were not high. They also noticed that if the zinc chloride double salts of the diazo-compounds are used some chlorinated derivatives are always formed.

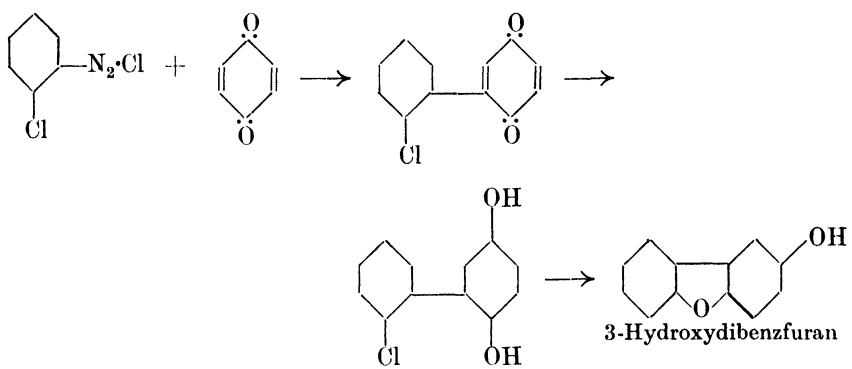
Aqueous solutions of diazo-compounds, brought near the neutral point by addition of acetate, combine directly with benzoquinone, naphthaquinones,[92, 111] and quinone oximes; [81, 83] initially the quinone is usually dissolved in alcohol or acetic acid, and, on adding the diazo-compound with stirring, nitrogen is given off, and in about twenty-four hours at room temperature all diazo-compound has disappeared. The arylquinone is precipitated, and can be collected, usually in good yield.

TABLE XXXVIII

Production of Diaryls or Arylpyridines by the Decomposition of Solutions of Triazens

Base used for preparation of triazen	Second component.	Decomposing agent.	Product.	Yield, %.
Aniline	Benzene	HCl	Diphenyl	25
,,	,,	AcOH	,,	37
,,	Nitrobenzene	HCl	2- and 4-Nitrodiphenyl	35
,,	Pyridine	,,	α-, β-, γ-Phenylpyridine	51
p-Nitroaniline	Benzene	,,	4-Nitrodiphenyl	52
,,	Pyridine	,,	α-, β-, γ-4-Nitrophenylpyridine	50
m- ,,	Benzene	,,	3-Nitrodiphenyl	53
,,	,,	AcOH	—	0
Methyl anthranilate	2-Methoxynaphthalene	HCl	Methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate	25
,, ,,	,, ,,	AcOH	,, ,, ,,	29
Anthranilic acid	Benzene	HCl	—	0
β-Naphthylamine	,,	AcOH	2-Phenylnaphthalene	36
,,	Pyridine	HCl	2-Pyridylnaphthalenes	41
5-Aminoquinoline	Benzene	,,	5-Phenylquinoline	13
4-Aminophthalimide	,,	,,	4-Phenylphthalimide	very small
,,	Pyridine	,,	4-Pyridylphthalimides	49
Methyl 4-aminophthalate	Benzene	,,	Methyl 4-phenylphthalate	66

By taking two equivalents of diazo-compound, two aryl radicals can be introduced.[102] This reaction is the basis of a technical process for the production of 3-hydroxydibenzfuran, starting from *o*-chlorodiazobenzene and benzoquinone :—



2-Chloro-2′ : 5′-dihydroxydiphenyl

3-Hydroxydibenzfuran

Non-quinonoid 1 : 2-unsaturated carbonyl compounds, both cyclic and open chain, are also arylated by diazo-compounds;[94, 99] the reaction is carried out in acetone in presence of a cupric salt, usually cupric chloride and an acetate buffer. This reaction has come to be known as the

Meerwein reaction. Thus a solution of *p*-nitrodiazobenzene diazonium chloride is added all at once to a solution of coumarin in acetone, together with sodium acetate; evolution of nitrogen is complete within an hour, when the acetone is removed, leaving a crystalline mass of crude 3-*p*-nitrophenylcoumarin. Similarly, *p*-chlorodiazobenzene and benzalacetone afford 1-acetyl-*p*-chlorostilbene; from carboxylic acids the carboxyl-group may be removed, and thus *p*-chlorodiazobenzene and cinnamic acid give *p*-chlorostilbene :—

$$p\text{-}C_6H_4Cl\cdot N_2\cdot Cl + Ph\cdot CH{:}CH\cdot CO_2H \longrightarrow Ph\cdot CH{:}CH\cdot C_6H_4Cl\text{-}p + N_2 + HCl + CO_2$$

A curious point concerning the Meerwein reaction is that only diazonium bromides or chlorides arylate 1 : 2-unsaturated compounds; sulphates and nitrates are ineffective.

Meerwein and his co-workers believed that in their reaction the aryl radical is always attached to the 1-carbon of the 1 : 2-unsaturated compound, but Koelsch [113] combined diazo-compounds under Meerwein's conditions with vinyl cyanide (acrylonitrile) and with methyl acrylate, and proved that the aryl radical attaches itself to the 2-carbon. The intermediate hydrochloro-compounds can usually be isolated in fair purity, the unsaturated compound being formed by boiling for five minutes in diethylaniline :—

$$PhN_2\cdot Cl + CH_2{:}CH\cdot CN \longrightarrow \underset{\text{1-Chlorohydrocinnamyl cyanide.}}{CH_2Ph\cdot CHCl\cdot CN} \longrightarrow \underset{\text{Cinnamyl cyanide.}}{CHPh{:}CH\cdot CN}$$

$$p\text{-}C_6H_4Me\cdot N_2\cdot Cl + CH_2{:}CH\cdot CO_2Me \longrightarrow \underset{\text{Methyl 1-chloro-}p\text{-methylhydrocinnamate.}}{p\text{-}C_6H_4Me\cdot CH_2\cdot CHCl\cdot CO_2Me} \longrightarrow \underset{\text{Methyl } p\text{-methylcinnamate.}}{p\text{-}C_6H_4Me\cdot CH{:}CH\cdot CO_2Me}$$

Extending the work, Koelsch and Boekelheide [114] found that 2 : 4-dichlorobenzenediazonium chloride and crotonic acid afford methyl α-chloro-β-2 : 4-dichlorophenylbutyrate :—

$$2:4:1\text{-}C_6H_3Cl_2\cdot N_2\cdot Cl + Me\cdot CH{:}CH\cdot CO_2Me \longrightarrow 2:4\text{-}C_6H_3Cl_2\cdot CHMe\cdot CHCl\cdot CO_2Me$$

But dienes such as cinnamalacetic acid and sorbic acid with benzenediazonium chloride afford 1 : 4-diphenylbutadiene and 1-phenylpenta-1 : 3-diene, respectively :—

$$PhN_2\cdot Cl + CHPh{:}CH\cdot CH{:}CH\cdot CO_2Me \longrightarrow CHPh{:}CH\cdot CH{:}CHPh$$

$$PhN_2\cdot Cl + CHMe{:}CH\cdot CH{:}CH\cdot CO_2H \longrightarrow CHMe{:}CH\cdot CH{:}CHPh$$

From the above it is seen that whereas the crotonic acid is arylated at 2, the dienes are arylated at 1.

For these reactions Koelsch and Bockelheide suggest a mechanism depending on the formation of free radicals by homolysis of the aryldiazo-

tate formed by the action of the sodium acetate on the diazonium oride and reduction-oxidation of the cupric chloride :—

1. $ArN_2^+ + AcO^- \rightleftharpoons Ar{\cdot}N{:}N{\cdot}OAc \longrightarrow Ar^* + N_2 + MeCO_2^*$
2. $Ar^* + RCH{:}CHR' \longrightarrow ArCHR{\cdot}\overset{*}{C}HR'$ (I).
3. (I) $+ Cu^{++} \longrightarrow Cu^+ + ArCHR{\cdot}\overset{+}{C}HR'$ (II).

3*a*. $Cu^+ + MeCO_2^* \longrightarrow Cu^{++} + MeCO^-$.

4. (II) $+ Cl^- \longrightarrow AcCHR{\cdot}CHClR'$.

4*a*. (II) $\longrightarrow H^+ + ArCR{:}CHR'$.

Bergmann and Schapiro, however, suggest that the reaction is ionic.

Bergmann and his co-workers [110, 116, 117, 122] have used the Meerwein ction to make substituted stilbenes and 1 : 4-diarylbutadienes; thus, itro-1-diazonaphthalene and cinnamic acid afford 1-styryl-4-nitrophthalene, $CHPh{:}CH{\cdot}C_{10}H_6{\cdot}NO_2$-4, and cinnamylideneacrylic acid and itrodiazobenzene give 1-phenyl-4-*p*-nitrophenylbutadiene,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2\text{-}p.$$

Quaterphenyl $Ph{\cdot}(C_6H_4)_2{\cdot}Ph$, can be made by combining diazotised minodiphenyl with cinnamalacetic acid then decarboxylating the adduct maleic anhydride with the 1-phenyl-4-diphenylylbutadiene so formed.[117]

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GROUP 6. REPLACEMENT OF THE DIAZO-GROUP BY GROUPS IN WHICH ATTACHMENT IS BY SULPHUR, SELENIUM, OR TELLURIUM.

The Formation of Arylthiocyanates and Arylselenocyanates.—The diazo-group is replaced by the thiocyano-group by either the Type I reaction or by the Type III reaction, which latter is catalysed by a number of metals. Billeter [1] brought about the Type I reaction by adding a concentrated solution of benzenediazonium sulphate to one of thiocyanic acid and steam distilling, when phenylthiocyanate is carried over. Kuhn and Eichenberger [9] add a solution of a diazo-compound of the benzene or naphthalene series to a concentrated solution of an alkali thiocyanate or ammonium thiocyanate, and claim a yield of 54% from *o*-toluenediazonium chloride. Gattermann and Haussknecht [2] obtained a better yield than Billeter by the same procedure, using cupric thiocyanate instead of thiocyanic acid, while Müller [3] used a mixture of cupric and potassium thiocyanate with *o*-nitrodiazobenzene; *m*-nitrophenylthiocyanate is made similarly.[5] Interaction of anthraquinone-1-diazonium sulphate and potassium thiocyanate affords a solid diazothiocyanate, which on heating in suspension in water slowly becomes pure yellow, as it gives off nitrogen and is converted into 1-thiocyanoanthraquinone;[4] Gattermann also noted that 1-nitro-4-diazoanthraquinone with excess of potassium thiocyanate affords 1 : 4-dithiocyanoanthraquinone. Korczynski and his co-workers [6] showed that by interaction of benzenediazonium chloride

with cobalt chloride and potassium thiocyanate (3 mols.) a malachite-green double salt, $(PhN_2 \cdot SCN)_2CO(SCN)_2$, is formed, which gives phenylthiocyanate on distillation with steam in better yield than from cupric thiocyanate. A solution of *m*-nitrobenzenediazonium chloride poured into a solution of potassium thiocyanate with a salt of the metal under examination gave the following percentage yields (in brackets) of *m*-nitrophenylthiocyanate with metals in order of rising atomic weight: Cr (6·6), Mn (10), Fe (80), Co (53), Ni (30), Gattermann's Cu (60), Zn (3·0), Mn (0), Sn (0), W (20·0), and U (20·0).[7] Similar treatment with *o*-nitrobenzenediazonium chloride,[8] which affords easily decomposed double thiocyanates, gave the results shown below :—

TABLE XXXIX

Yields of o-*Nitrophenylthiocyanate by the Action of Metallic Salts on* o-*Nitrobenzenediazonium Chloride and Potassium Thiocyanate*

Salt.	Yield at 15–20°, %.	Yield at 60–70°, %.
Nil	51	33
$MnSO_4$	56	64
$Cr_2(SO_4)_3$	55	59
$FeCl_3$	76	51
$NiSO_4$	53	51
$CoCl_2$	58	56
Cu	51	40
$ZnSO_4$	2	48
$CdSO_4$	56	51
$SnCl_4$	56	55
WCl_6	66	69
$UO_2(NO_3)_2$	51	56

Anthraquinone-1-diazonium sulphate and potassium selenocyanate afford an unstable red diazoselenocyanate which loses nitrogen at room temperature giving orange 1-selenocyanoanthraquinone.[15] *p*-Chloro- and *p*-bromophenylselenocyanate and *p*-tolylselenocyanate [16] and *m*-carboxyphenylselenocyanate [17] are made similarly by the direct action of the diazonium sulphates on potassium selenocyanate in presence of sodium acetate.

The Formation of Thiophenols, Diaryl Sulphides, Arylthioglycollic Acids, Sulphinic, and Sulphonic Acids.—The S-azo-compounds formed by combination of diazo-compounds with substances containing the thiol-group have already been mentioned, and attention has been called to the fact that many of them are explosively unstable (cf. p. 155). By controlling the decomposition of such S-azo-compounds or by selecting such compounds as can be controlled during decomposition, loss of nitrogen is accompanied by union of carbon with sulphur, and there are obtained thiophenols, diaryl sulphides, arylthioglycollic acids, and similar substances. Griess [25] obtained a heavy, evil-smelling, yellow

y interaction of benzenediazonium chloride with aqueous potassium
ıide, gas being evolved; he obtained the same substance by treating
;old or silver salt of diazobenzene hydroxide in aqueous suspension
hydrogen sulphide, but found that if hydrogen sulphide is passed
the dry gold salt it explodes unless in very small quantities in a thin
, while the silver salt explodes in even the smallest quantity. Griess
ed that his compound was not a thiol, and later Graebe and Mann [27]
nued the work, cautiously adding a solution of benzenediazonium
ıate to one of hydrogen sulphide or ammonium sulphide in a large
cooled with ice chips; the reddish-yellow precipitate, which can
ıpose explosively in the liquid, decomposes slowly at room tem-
ıure, and a yellow oil collects in the centre of the dish, is filtered from
ıur, and on distillation affords diphenyl sulphide in good yield with a
l amount of diphenyl disulphide as by-product. Diphenyl disulphide,
d with benzeneazodiphenyl, is also formed by the action of sodium
ɔthiosulphate on neutral diazobenzene; [44] on the other hand,
ous solutions of diazonium chlorides only afford dark resins on inter-
n with cupric sulphide.[61] Diphenyl sulphide is, however, produced
ıe direct action of dry benzenediazonium chloride on sulphur under
ı acetone; selenium under the same conditions gives diphenyl
ide, and tellurium in the cold is converted into diphenyltellurium
oride.[69] Stadler [28] made phenyl ethyl sulphide, Ph·S·Et, by the
ıposition of the explosive S-azo-compound, Ph·N_2·SEt, formed from
enediazonium chloride and ethyl thiol; the less dangerous *p*-sulphonic
p-$HO_3S{\cdot}C_6H_4{\cdot}N_2SEt$, obtained from diazotised sulphanilic acid and
l thiol, loses nitrogen when boiled in ethanol, and the diazo-group is
ced forming thiophenol-*p*-sulphonic acid ethyl ether,

$$p\text{-}EtS{\cdot}C_6H_4{\cdot}SO_3H.$$

andsberg,[30] by acting on diazotoluene sulphonic acid with aqueous
ssium sulphide, replaced the diazo-group by the thiol-group in 30%
, but a notable improvement in this replacement was made by
ardt,[31] who examined the interaction of diazo-compounds with
ɔances such as the salts of thiosulphuric acid, thiocarbonic acids,
ormic esters, and the alkali xanthates. All these form S-azo-com-
ds which can be broken down to give thiophenols or their derivatives,
vhereas the yields from the first three are poor, that obtainable from
ast is outstandingly good, and the production of thiophenols or their
ethers from diazo-compounds and xanthates is known as the
ardt reaction. The reaction follows the course :—

$$ArN_2{\cdot}Cl + KS{\cdot}CS{\cdot}OAlkyl \xrightarrow{70^\circ} ArS{\cdot}CS{\cdot}OAlkyl + N_2 + KCl$$

$$ArS{\cdot}CS{\cdot}OAlkyl \xrightarrow{Heat} Ar{\cdot}S{\cdot}Alkyl + COS$$

$$ArS{\cdot}CS{\cdot}OAlkyl \xrightarrow{aq.\ KOH} Ar{\cdot}SK + KS{\cdot}CO{\cdot}OEt \xrightarrow{Acid} Ar{\cdot}SH$$

r

The reaction has been, and is, much used to make thiols, and among typical examples are thiophenol-*o*-sulphonic acid,[57] *m*-nitrothiophenol,[60] and 3 : 5-dichloro-4-aminothiophenol [67] [by diazotisation of 2 : 6-dichloro-*p*-phenylenediamine (cf. p. 23)], but 3-diazopyridine [63] does not undergo the reaction, and 5 : 8-dichloro-1-diazonaphthalene, beside the xanthate, gives *SS'*-di-5 : 8-dichloro-1-naphthyl dithiocarbonate.[73]

The general conditions for interaction of a diazonium compound with potassium ethyl xanthate are :—

The arylamine is best diazotised in aqueous hydrochloric acid, and brought to faint acidity to congo with aqueous sodium carbonate.

For each molecule of diazo-compound there is taken 1·4 molecule, *i.e.*, 200 g., of xanthate dissolved in 2 l. of water.

The minimum temperature for reaction is 40°, and 60—70° is usually the best temperature, but the optimum must be found by trial experiments with about 0·01 mol.; if the temperature is too low the addition compound floats and may decompose explosively, and the nitrogen must be evolved rapidly to avoid danger.

The product is usually an oil, which is washed with water and hydrolysed by boiling for some hours with 15% aqueous caustic soda (4 mols.); a small amount of sodium sulphide may be added to prevent oxidation.

Instead of xanthate Lustig [34] used the red solid obtained by digesting solid caustic potash with excess of carbon disulphide; this with aqueous benzenediazonium chloride affords an oil with loss of nitrogen, and on steam distillation of the oil thiophenol and diphenyl disulphide pass over. A reaction analogous to Leukardt's also occurs with sodium alkyl dithio-carbamates, the products being aryldialkyldithiocarbamates : [64]

$$ArN_2\cdot Cl + Alkyl_2N\cdot CS\cdot SNa \longrightarrow Alkyl_2N\cdot CS\cdot S\cdot N_2\cdot Ar + NaCl \longrightarrow Alkyl_2N\cdot CS\cdot SAr + N_2$$

Thus diazobenzene and sodium dimethyldithiocarbamate gives phenyl-dimethyldithiocarbamate, $Me_2N\cdot CS\cdot S\cdot Ph$; when *p*-nitrodiazobenzene is used, the unstable explosive S-azo-compound can be isolated.

Thiophenols are also made by adding nearly neutral solutions of diazo-compounds to aqueous solutions of polysulphides having a greater proportion of sulphur than corresponds with Na_2S_2 or CaS_2.[58] The product is the disulphide ArS·SAr, which is reduced to the thiophenol, and may then be converted into the arylthioglycollic acid (*vide infra*). The diazo-group attached to anthanthrone is replaced by the thiol-group on treatment with potassium hydrosulphide or with thiourea at 70°.[59] Benzenediazonium chloride and thiourea in acetone afford the hydrochloride of an unstable S-azo-compound, but only formamidine disulphide dihydrochloride can be identified among the scission products [66] :—

$$PhN_2\cdot Cl + NH_2\cdot C(:NH)\cdot SH \longrightarrow NH_2\cdot C(:NH)\cdot S\cdot N_2Ph,HCl \longrightarrow [NH_2\cdot C(:NH)\cdot S]_2,2HCl$$

Busch and Schulz [66] found, however, that thiophenols are formed as end-products of the decomposition of S-azo-compounds derived from substituted thioureas, which here also react in the *iso*-form; for example,

benzenediazonium chloride and 1 : 4-diphenylthiosemicarbazide in acetone combine to form an S-azo-compound, which decomposes into S-phenyl-1 : 4-diphenyl*iso*thiosemicarbazide, which is in turn hydrolysed by alkali into thiophenol and semicarbazide :—

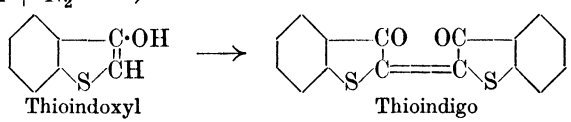
$$NHPh{\cdot}NH{\cdot}CS{\cdot}NHPh + PhN_2{\cdot}Cl \longrightarrow NHPh{\cdot}NH{\cdot}C(:NPh){\cdot}S{\cdot}N_2{\cdot}Ph \longrightarrow$$
$$NHPh{\cdot}NH{\cdot}C(:NPh){\cdot}S{\cdot}Ph \xrightarrow{\text{aq. KOH}} NHPh{\cdot}NH{\cdot}CO{\cdot}NHPh + PhSK$$

Evidence that free radicals may be concerned in this reaction is that part of the S-phenyl-1 : 4-diphenyl*iso*thiosemicarbazide is oxidised to the red azo-compound $Ph{\cdot}N{:}N{\cdot}C(:NH){\cdot}S{\cdot}Ph$.

Thiocarbanilide does not interact with benzenediazonium chloride, but with *p*-nitrobenzenediazonium chloride it affords NN′-diphenyl-S-*p*-nitrophenyl*iso*thiocarbamide, $NHPh{\cdot}C(:NPh){\cdot}S{\cdot}C_6H_4{\cdot}NO_2$-*p*, also easily hydrolysed to *p*-nitrothiophenol.

Diazo-compounds are one of the starting materials for the preparation of the arylthioglycollic acids which are the proximate intermediates for the manufacture of many thioindigo dyes. The synthesis of *o*-carboxyphenylthioglycollic acid has been specially studied because it ring-closes with loss of water and carbon dioxide to form thioindoxyl, the intermediate for Thioindigo (C.I. 1207), made by oxidising two molecules of thioindoxyl :—

$$o\text{-}CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl + HS{\cdot}CH_2{\cdot}CO_2H \longrightarrow o\text{-}CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H \longrightarrow$$
$$o\text{-}CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H + N_2 \longrightarrow$$



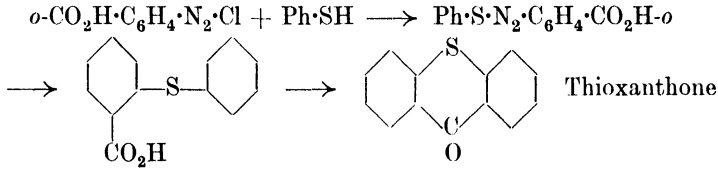
Thioindoxyl Thioindigo

Other arylthioglycollic acids are also used to make thioindigoid dyes; for example, *p*-chlorophenylthioglycollic acid on treatment with chlorosulphonic acid is converted into Thioindigo Red BG (C.I. 1209).

Several different routes for the manufacture of the arylthioglycollic acids have been described. Friedländer and Chwala [54] combined diazo-compounds with thioglycollic acid, and decomposed the unstable S-azo-compounds by heating with water or an inert liquid, a process patented for making *o*-carboxyphenylthioglycollic acid; [45] copper may be added to bring about decomposition at 20—40°,[47] or the medium may be aqueous alkali.[48] Or diazotised anthranilic acid is treated with aqueous sodium sulphide, thus replacing the diazo-group by the thiol-group to form thiosalicylic acid, and chloroacetic acid is added forthwith to the solution, when *o*-carboxyphenylthioglycollic acid is at once formed.[53] Thiosalicylic acid can also be made from diazotised anthranilic acid and sodium polysulphide,[49, 71] especially the disulphide Na_2S_2 which is better than Na_2S, or by passing hydrogen sulphide into the diazo-compound, then collecting the red precipitate and charging it while moist into aqueous

sodium carbonate, and heating until a test portion with hydrochloric acid gives a pure white precipitate. It is easily oxidised by air to dithiosalicylic acid, which Henderson [39] obtained in 50% yield by adding diazotised anthranilic acid to a cold saturated solution of sulphur dioxide, having copper in suspension. Arylthioglycollic acids are also made technically by converting diazo-compounds into thiols by the Leukhardt reaction, and then condensing with chloroacetic acid.

Diazotised anthranilic acid and thiophenol yield *o*-carboxydiphenyl sulphide, which can be ring-closed to thioxanthone [35] :—



The selenophenols behave similarly; *p*-methoxydiazobenzene chloride added under carbon dioxide to selenophenol dissolved in caustic soda and in presence of copper gives 4-methoxydiphenylselenide [62] without isolation of the Se-azo-compound.

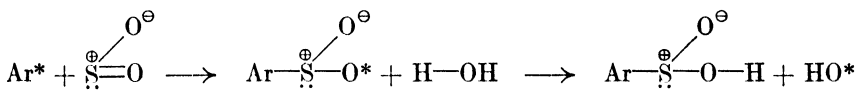
Interaction of diazo-compounds with sulphurous acid in presence of copper,[37, 40] or of cuprous oxide,[38] cuprous hydroxide,[38] red cuprous sulphite,[38] or cuprous sulphide,[50] results in the evolution of nitrogen and formation of arylsulphinic acids; the yields are generally good, and the reaction occurs with most diazo-compounds, including 1-nitro-8-diazonaphthalene,[65] a compound in which steric forces sometimes hinder reaction. Gattermann said that it is preferable to use the diazonium sulphate because if diazonium halides are used some aryl halide is formed. He also used commercial copper-bronze (" Naturkupfer C "); in order to obtain the best result, Haworth and Lapworth [56] washed the copper first with alcohol, then with ether. Diazosulphites, made by acting on diazonium chlorides with alkali bisulphite, are also converted into sulphinic acids by small amounts of copper or of copper salts in the presence of alcohol.[41] Bisulphite and alcohol alone convert diazo-compounds into sulphazides, $ArSO_2{\cdot}NH{\cdot}NHAr$, which are hydrolysed by alcoholic alkali into arylsulphinic acid, hydrocarbon, and nitrogen.[42] Arylsulphinic acids are also made by treating sulphazides with alcoholic sulphur dioxide and a copper salt, or from triazens, *e.g.*, *o*-diazotoluenepiperidide, with alcoholic sulphur dioxide alone.[43] Thomas [55] discovered that the isolation of sulphinic acids from the reaction solution is easily accomplished through the sparingly-soluble ferric salt and he isolated benzenesulphinic acid, prepared by Gattermann's method, as follows :—

Aniline (10 g.) is dissolved in water (150 c.c.) and sulphuric acid, *sp. gr.* 1·84 (20 g. = 11 c.c.) and diazotised at 3—6° with sodium nitrite (8 g.) dissolved in water (30 c.c.); a cooled solution of sulphuric acid, *sp. gr.* 1·84 (40 g. = 22 c.c.) in water (30 c.c.) is added, and sulphur dioxide is passed in until 20—25 g. has dissolved with external ice cooling.

Then copper paste (50—60 g.) is added, and after the evolution of nitrogen is complete the solution is filtered, and concentrated ferric chloride solution is added until there is no further precipitation of the bright orange ferric benzenesulphinate; it is collected, washed, and dried. Yield 16 g. The free acid is obtained by treating with dilute ammonia, filtering, and precipitating with hydrochloric acid.

The diazo-group can also be replaced by the sulphonic acid group. Landsberg,[30] by adding a solution of benzenediazonium sulphate to a solution of freshly precipitated cuprous oxide in aqueous sulphurous acid, obtained benzenesulphonic acid in 11·8% yield. Hence, if it is desired to replace the diazo-group by the sulphonic acid group, it is better to make the thiophenol or the sulphinic acid and oxidise. A special case is that of naphthalene-1 : 2-diazo-oxide and its derivatives having chlorine, bromine, nitro, or sulphonic acid at 6 with sulphonic acid at 4. These compounds combine with alkali sulphite to form an unstable orange substance, which may be a diazosulphonate, and this rapidly loses nitrogen and replaces the diazo-group by the sulphonic acid group, giving 2-naphthol-1-sulphonic substituted as above.[68, 70]

Union of free radicals formed by homolysis of the S-azo-compounds in the solid phase is most probably the mechanism in the Leukardt and similar reactions, while Waters [71] suggests that sulphinic acids are also formed by union of aryl radicals with sulphur dioxide thus :—



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GROUP 7. REPLACEMENT OF THE DIAZO-GROUP BY ARSENIC, ANTIMONY, BISMUTH, AND PHOSPHORUS

Diazo-compounds interact with both inorganic and organic derivatives of trivalent arsenic containing the groups $\cdot As(OM)_2$, where M is a monovalent cation or its equivalent, giving a water-soluble salt, or $\cdot AsO$ to give derivatives of pentavalent arsenic having a C·As link in place of the diazo-group. Thus, diazobenzene and aqueous sodium arsenite afford benzenearsonic acid and nitrogen by the overall equation :—

$$PhN{:}N\cdot OH + Na_2HAsO_3 = PhAsO_3Na_2 + N_2 + H_2O$$

The reaction requires an alkaline medium with careful control of pH,[43] and was discovered by Bart,[3, 23] by whose name it is usually known. Previous investigators had noticed only the reducing action of arsenites on diazo-compounds in strongly alkaline solution, Gutmann [2] having used the reaction to differentiate normal from *iso*diazotate, though Koenig's [1] mention of the cherry-red coloration produced on mixing diazobenzene with arsenite makes it probable that some benzenearsonic acid was formed. Such a cherry-red coloration is often seen in the opening stages of a Bart reaction starting with a diazonium salt, but not with a diazotate.

Bart's reaction is a general one for diazo-compounds, but substituents have a considerable effect on the yield, and also on the pH at which the yield is maximum. Thus *o*- and *p*-nitrodiazobenzene are converted in good yield into the corresponding nitrobenzenearsonic acids, but from *m*-nitrodiazobenzene the yield is poor,[16] while diazobenzene-*p*-sulphonic acid [37] and its amide [42] only afford the corresponding arsonic acids in 28% and 25% yield, respectively. As negative substituents increase in the benzene ring, so the optimum pH falls, and 2 : 4-dinitrodiazobenzene only affords the arsonic acid in acid solution.[10, 29] Among diazo-compounds in which the reaction occurs may be mentioned 2-chloro-1-diazo- and 1-chloro-2-diazonaphthalene,[34] diazotised 1 : 4-diaminoanthraquinone, which affords 1-aminoanthraquinone-4-arsonic acid,[15] and the diazophenols, such as 4-nitro-2 : 1-diazophenol, which on warming with arsenite in strongly alkaline solution affords 4-nitrophenol-2-arsonic acid.[9] Bart described various ways of carrying out his reaction; he introduced the use of copper powder or copper salts [4, 11] as catalysts, and a little copper sulphate is usually added in making benzenearsonic acid on the large scale.[17] Mouneyrat [18] patented the conjoint use of a reducing agent, such as hypophospite or hydrosulphite, with a copper salt. Benzenearsonic acid can also be made from normal benzenediazotate and sodium arsenite in absence of free alkali; [8] *iso*diazotates, such as the sodium salt of *p*-nitrobenzene*iso*diazotate, also give the arsonic acids under conditions of reduced alkalinity.[3, 24] Diazonium fluoborates can be used in the Bart reaction.[48]

A typical Bart reaction is carried out with *o*-nitrodiazobenzene as follows [16] :—

o-Nitroaniline (100 g.) is ground with water (250 c.c.) and hydrochloric acid, *sp. gr.* 1·16 (250 c.c.), chilled to 0—2° and diazotised with sodium nitrite (55 g.) in water (120 c.c.); after 10 minutes the solution is filtered, poured into 25% caustic soda (550 c.c.), keeping the temperature at less than 0°. The alkaline solution is added to a solution of sodium arsenite (135 g.) in water (1250 c.c.), and the whole is heated to 60—70° for 1½ to 2 hours, acidified with acetic acid, stirred with charcoal, filtered, and the filtrate is made strongly acid with hydrochloric acid; *o*-nitrobenzenearsonic acid crystallises as a heavy, pale-yellow, powder. The yield is 110 g.

An alternative method of isolation used by Karrer [13] for toluene-*o*-

arsonic acid and by Bauer [14] for 4-nitro-2-hydroxybenzenearsonic acid is to oxidise all excess of arsenic to the pentavalent state with hydrogen peroxide, add magnesia mixture, filter, and warm when the insoluble magnesium arsonate is precipitated.

The nitro-group in the nitrobenzenearsonic acids is preferentially reduced by alkaline ferrous sulphate; on diazotisation a second arsonic acid group can be introduced, and o-,[21] *m*-,[22] and *p*-benzenediarsonic [3, 22] acid have been made in this way. Lieb [22] reported that if in the last case the solution becomes acid the product is azobenzene-4 : 4′-diarsonic acid.

Benzenearsonic acid is easily reduced by sulphur dioxide or bisulphite in presence of a little hydriodic acid to arsenosobenzene (phenylarsenious oxide), PhAsO, in which the arsenic is trivalent; this dissolves in aqueous caustic soda as sodium phenylarsenite, $Ph{\cdot}As(ONa)_2$, which will again combine with diazobenzene with oxidation to pentavalent arsenic thus forming diphenylarsonic acid, Ph_2AsO_2H :—

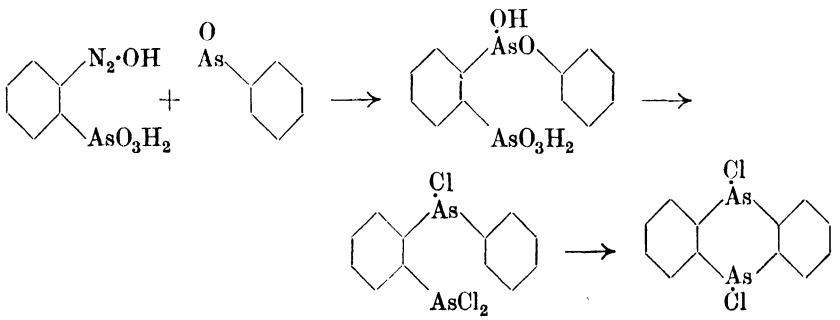
$$PhAsO_3H_2 \xrightarrow{SO_2/HI} PhAsO \xrightarrow{\text{aq. NaOH}} PhAs(ONa)_2 \xrightarrow{PhN_2{\cdot}OH} Ph_2AsO_2H$$

Bart [3] thus made di(*p*-nitrophenyl)arsonic acid, $(p\text{-}NO_2{\cdot}C_6H_4)_2AsO_2H$, from *p*-nitrodiazobenzene and *p*-nitroarsenosobenzene (*p*-nitrophenylarsenious oxide). The synthesis of diphenylarsonic acid by the ' double Bart ' reaction is the last stage but two in the manufacture of diphenylarsine chloride, Ph_2AsCl (D.A., Blue Cross, Clark I, Sternite), which is used in chemical warfare, and is made by reducing the diphenylarsinic acid *via* bisdiphenylarsine oxide :—

$$2[PhAsO_2H] \xrightarrow{2SO_2 + H_2O} (Ph_2As)_2O \xrightarrow{HCl} 2Ph_2AsCl$$

For large-scale manufacture of diphenylarsine chloride the Bart reaction is carried out in ordinary wooden azo-dye units, starting with a charge of 3 kg. mol. of aniline.[17]

Naturally both aryl nuclei in a diarylarsonic acid need not be the same. Kalb [21] combined *o*-diazobenzenearsonic acid with arsenosobenzene to produce phenylarsonobenzene-*o*-arsonic acid as the first stage in the synthesis of arsanthrene chloride :—



Bart [3] suggested that the arylarsonic acids are formed through an unstable O-azo-compound :—

$$Ar{\cdot}N{:}N{\cdot}OH + As(OK)_3 \longrightarrow Ar{\cdot}N{:}N{\cdot}O{\cdot}As(OK)_2 + KOH \longrightarrow Ar{\cdot}AsO(OK)_2 + N_2$$

Schmidt [19] accounted for the oxidation of the arsenic by postulating a pentavalent As-azo-compound, $PhN_2{\cdot}As(OH)_3OK$, which loses nitrogen and water spontaneously.

Waters [35] has, however, pointed out that the reaction shows evidence that free radicals may be concerned, since the arsenic is oxidised, and diphenyl derivatives are always found in small quantity among the by-products.[19, 23] Földi [26] said that the formation of a diazonium arsenite is the first step in Bart's reaction. He made a colourless granular double salt of arsenic trichloride and *p*-toluenediazonium chloride which couples, showing that it contains the active diazo-compound, but which on treatment with aqueous alkali at once undergoes Bart's reaction. Scheller [27] dissolved an arylamine in a solvent, such as acetic acid, methanol, or carbon tetrachloride, added one equivalent of arsenic trichloride with a copper salt as catalyst, then diazotised with aqueous sodium nitrite, drawing off the water-layer if present, leaving the diazonium-arsenic trichloride double salt in the solvent layer; on evaporation of the solvent and treatment of the residue with hot water the arylarsonic acid is formed with liberation of nitrogen. Binz and v. Schickh [33] give for the reaction the equation :—

$$ArN_2AsCl_4 + 3H_2O = ArAsO_3H_2 + N_2 + 4HCl$$

The Scheller reaction has been used to make *p*-ethylthiolbenzenearsonic acid, p-$EtS{\cdot}C_6H_4{\cdot}AsO_3H_2$, and *p*-thiocyanobenzenearsonic acid, p-$CNS{\cdot}C_6H_4{\cdot}AsO_3H_2$.[31]

Arsenic can also be attached by this method to the pyridine ring in place of a diazo-group at 3 or 5;[32, 33] 3-pyridylarsine dichloride is made as follows [33] :—

3-Aminopyridine (50 g.) is dissolved in hydrochloric acid, *sp. gr.* 1·19 (200 c.c.), cooled with ice, and arsenic trichloride (200 g.) and cuprous chloride (8 g.) are added; then sodium nitrite (82 g.) dissolved in water (82 c.c.) is added at 0°, and the whole is kept for eight hours at 35—40° and filtered from sodium chloride and some 3-pyridylarsine dichloride hydrochloride. The main product in the filtrate is precipitated by adding potassium iodide and passing sulphur dioxide; the yield of 3-pyridylarsine dichloride hydrochloride is 111 g.

Doak [45] found that the Scheller process fails with sulphanilic acid and with *vic.* *m*-xylidine ($1:2:6\text{-}NH_2{\cdot}C_6H_3Me_2$), though the latter gives a 30% yield of the arsonic acid by Bart's reaction.

Metallic arsenic is directly attacked by the free radicals formed by homolysis of benzenediazonium chloride in warm acetone in presence of chalk; by evaporating the acetone and extracting the residue with hot water, Waters [38, 40] obtained triphenylarsinephenoxyhydroxide,

$Ph_3As(OPh)\cdot OH$, of which triphenylarsine dichloride is the probable precursor.

Arylstibonic acids, $ArSbO_3H_2$, are formed by Schmidt's reaction [6, 20] by adding a solution of a diazo-compound to a strongly alkaline solution or suspension of an antimonate, and the reaction is therefore analagous to Bart's. The combination of diazobenzene with *m*-aminostibinosobenzene [12] also provides a reaction analogous to the double Bart reaction :—

$$PhN_2\cdot OH + m\text{-}NH_2\cdot C_6H_4\cdot SbO \longrightarrow m\text{-}NH_2\cdot C_6H_4\cdot SbPh\cdot O_2H$$

Another method of preparation, also due to Schmidt,[20] is to act on May's diazonium chloride-antimony trichloride double salt with alkali; the amino-group in *p*-aminobenzenesulphonamide has thus been changed for stibonic acid by interaction of the diazo-derivative with trivalent antimony compounds.[46] A still more comprehensive synthesis of arylantimony compounds starting from May's salt has been patented by Gibson and Kingan.[49] In this process trivalent antimony compounds are treated with a diazonium halide or its zinc chloride double salt in an organic solvent in presence of copper or a cuprous salt, giving pentavalent aryl antimony compounds. The product of this stage can be reduced back to an arylstibine dichloride, and the operation of combining with the diazo-compound can be repeated twice more, if desired, with an intermediate reduction; it is not necessary to isolate the intermediate stages. The ultimate product is the triarylantimony dichloride. For the second and third stages Gibson and Kingan give the equations :—

$$2ArSbCl_2 + [Ar'N_2]_2ZnCl_4 \longrightarrow 2ArAr'SbCl_3 + 2N_2 + ZnCl_2$$
$$2ArAr'SbCl + [Ar''N_2]_2ZnCl_4 \longrightarrow 2ArAr'Ar''SbCl_2 + 2N_2 + ZnCl_2$$

They prepare triphenylantimony dichloride as follows :—

Aniline (18·6 g.) is diazotised in hydrochloric acid and the diazo solution is added to a solution of antimony trioxide (29·2 g.) in hydrochloride acid, sp. gr. 1·16 (198 g.); the precipitated May salt, PhN_2SbCl_4, is collected, washed, and added to ethanol (158 g.) containing cuprous chloride (1 g.). Decomposition sets in at once, and is allowed to continue for forty minutes, when the whole is heated to 60° for five minutes and cooled, giving a clear solution of phenylstibinic chloride, which still contains some antimony trichloride. To convert the latter, the double salt $[PhN_2]_2ZnCl_4$ [made from aniline (15 g.) diazotised and added to zinc oxide (6·6 g.) dissolved in hydrochloric acid, sp. gr. 1·16 (35·2 g.)] is added with stirring. When evolution of nitrogen is finished, reduction is carried out by passing sulphur dioxide for one hour at less than 10° in presence of a little iodine, and after air-blowing and neutralising with chalk (30 g.), another charge of $[PhN_2]_2ZnCl_4$ [made as above from aniline (28 g.)] is added, and after forty minutes the whole is heated to 60° for five minutes, producing a clear solution of diphenylantimony trichloride. If desired this can be converted into diphenylstibonic acid by pouring the solution as a thin stream into 5N-NaOH (71·2 c.c.) diluted with hot water (2 l.). Alternatively the solution is reduced as above, air-blown, neutralised with chalk, and treated with a third charge of $[PhN_2]ZnCl_4$ (made as the second). Reaction is completed by heating on the water-bath, the solution is filtered and concentrated when the triphenylantimony dichloride crystallises.

Naturally by using different diazo-compounds at each stage mixed

arylantimony compounds can be made as shown in the general equations above.

A single-stage process affording a mixture of arylantimony compounds is used by Nesmejanov and Kocheshkov,[50] who add May's double salt to a strongly-stirred suspension of zinc dust in ethyl acetate, when there are formed the triarylantimony dichloride, the stibosoaryl (arylstibine oxide), ArSbO, and stibinosodiaryl (diarylstibine hydroxide), Ar_2SbOH; the proportions vary with the substituents in the aryl nucleus.

Like arsenic, powdered antimony is attacked by benzenediazonium chloride or its zinc chloride double salt in acetone in presence of chalk, and the product is triphenylantimony dichloride; 4-chloro-toluenediazonium chloride similarly gives tri-(4-chloro-*o*-tolyl)stibine and its zinc chloride double salt affords di-(4-chloro-*o*-tolyl)stibine chloride.[40]

Arylbismuth compounds are made by reduction of bismuth chloride-diazonium chloride double salts with copper in an inert solvent. Gilman and Svigoon [43] thus made tri-*p*-tolylbismuth in small yield with acetone as the medium. Gilman and Yablunky [47] obtained arylbismuth dichlorides and diarylbismuth chlorides by the action of copper bronze (4 equivs.) on the double salts in ethanol and these are reduced by hydrazine to triarylbismuths; the two operations can be carried out in one step. The yields are not high, triphenylbismuth being obtained in only 22% yield; the side-reactions produce chiefly chlorobenzene, benzene, and azobenzene. The reaction in alcohol fails when the nucleus contains water-solubilising groups.

Nijk [25] reported that he was unable to replace the diazo-group by phosphorus, but Plets [36] has described the preparation of arylphosphinous acids from hypophosphite and diazo-compounds, though these may in fact be aryl esters of hypophosphorous acid as Plets represents the reaction as :—

$$NaH_2PO_2 + ArN_2{\cdot}Cl \longrightarrow H_2\underset{\underset{O}{\|}}{P}{\cdot}O{\cdot}N{\cdot}N{\cdot}Ar \longrightarrow H_2\underset{\underset{O}{\|}}{P}O{\cdot}Ar + N_2$$

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GROUP 8. REPLACEMENT OF THE DIAZO-GROUP BY METALS

The double salts of the diazonium halides with those of mercury, tin, and lead can be reduced to give organo-metallic compounds having carbon attached directly to metal in the position previously occupied by the diazo-group. The Russian school of chemists led by Nesmejanov have been the principal workers in the field, and the greater number of the derivatives known are compounds of mercury. Nesmejanov [8] considers that synthesis via the diazo-compounds is the best method of preparation of many organo-metallic compounds. So easily does the replacement of the diazo-group by mercury occur that McClure and Lowy [4] produced arylmercuric chlorides by strongly agitating the mercury cathode during the electrolytic reduction of diazonium chlorides in aqueous solution :—

$$ArN_2{\cdot}Cl + Hg = ArHgCl + N_2$$

Yields by this process vary from 20% to 70%, the latter being reached with *o*-tolylmercuric chloride from *o*-toluenediazonium chloride. Evolu-

tion of nitrogen begins at once when benzenediazonium fluoborate suspended in acetone is added to finely-divided mercury produced by stirring mercuric chloride with stannous chloride in acetone–water; when evolution of nitrogen ceases, the whole is boiled for ten minutes, filtered, the insoluble is washed with acetone, and the filtrate deposits crystalline phenylmercuric chloride in 60% yield.[12]

Benzenediazonium tri- and tetraiodomercuriate, $PhN_2 \cdot HgI_3$ and $(PhN_2)_2HgI_4$, made by adding potassium iodide and mercuric iodide to benzenediazonium chloride in methanol at $-10°$, decompose when kept at room temperature, giving small yields (10% and 3% respectively) of diphenyliodonium tri-iodomercuriate $[Ph_2I]HgI_3$.[1] If the iodomercuriates are reduced by copper powder the chief product is phenylmercuric iodide.[2] The more stable diazonium-metallic double chlorides always require a reducing agent operating in a non-ionising solvent, such as acetone or ethyl acetate, circumstances which point to the probability that these are free radical reactions. Nesmejanov [9] finds copper to be the best reducing agent, but stannous chloride gives fair results.

The diazo-compounds having positive substituents and which form double salts of the type ArN_2HgCl_3 are most easily reduced, and according to the proportion of copper used there are formed either arylmercuric chlorides [2] or mercury diaryls,[3] according to the overall equations :—

$$ArN_2HgCl_3 + 2Cu = ArHgCl + N_2 + 2CuCl$$
$$2ArN_2HgCl_3 + 6Cu = HgAr_2 + 2N_2 + 6CuCl + Hg$$

The first reaction is probably pure homolysis of the unstable salt ArN_2HgCl left when the copper has removed two atoms of chlorine, followed by union of radicals :—

$$ArN_2HgCl_3 \xrightarrow{2Cu} ArN_2HgCl \longrightarrow Ar^* + {}^*HgCl + N_2 \longrightarrow ArHgCl$$

The second reaction is more complicated, and probably involves the further action of the reducing agent on the arylmercuric chloride in presence of the products of homolysis of the first reaction.

When the aryl radical contains negative substituents the double salts have the constitution $(ArN_2)_2HgCl_4$, and the products of reduction are chiefly the halogenoaryls and the hydrocarbons. The arylmercuric chlorides can, however, be made by adding the double salt to copper (3 atoms), strongly agitated in the solvent at $-10°$ to $-20°$; again acetone is usually the best solvent, but ethyl acetate is best for the preparation of *o*- and *p*-nitrophenylmercuric chloride.[7] Another device is to mix an equivalent of mercuric chloride with the double salt, so that the mixture has the same empirical composition as that of the positively substituted double salts.

Stannic chloride double salts [11, 13] can be reduced with copper, zinc, or tin, the last being the best; the metal powder is stirred with ethyl acetate,

and the double salt is sprinkled in fast enough to keep the ester boiling, the reaction being energetic. The chief product is the diaryl stannic chloride, Ar_2SnCl_2, produced by the overall equations :—

$$ArN_2SnCl_6 + 2Sn = Ar_2SnCl_2 + N_2 + 2SnCl_2$$

If the chlorides are oily and difficult to crystallise, they can be isolated as the diarylstannic oxides, Ar_2SnO. Like mercury, tin is directly attacked in acetone by benzenediazonium chloride, and the product is diphenylstannic chloride, Ph_2SnCl_2.[15]

The lead double salts $(PhN_2)PbCl_6$ and $PhN_2{\cdot}PbCl_3$ are reduced by copper or zinc in boiling acetone, ethyl acetate, or ether, the chief products being benzene, diphenyl, and phenol, but small amounts of triphenyl lead chloride, Ph_3PbCl, and diphenyl lead dichloride, Ph_2PbCl_2, isolated as the oxide, Ph_2PbO, have been found.[11, 14]

Treatment of benzene-, *o*- and *p*-nitrobenzene-, and *o*-toluenediazonium fluoborate in dry benzene or toluene with copper powder produces a small yield of the copper aryl, CuAr, which is held in solution in the hydrocarbon solvent.[18, 19] These substances are unstable, being decomposed by water and by air, but they can be isolated as a blue pyridinium compound $ArCu(C_5H_5N)_3$ by adding dry pyridine to the hydrocarbon solution, and are purified by precipitation from ethanol with ether.

The attempt to produce aryl silver compounds by the above reaction failed.[18]

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CHAPTER IX

THE ANALYTICAL DETERMINATION OF DIAZO-COMPOUNDS

DETERMINATION OF ARYLAMINES BY DIAZOTISATION—DETERMINATIONS WITH DIAZO-COMPOUNDS, GENERAL, BIOCHEMICAL—DETERMINATION OF NITROUS ACID—THERMOCHEMISTRY—DIAZO-COMPOUNDS AS EXPLOSIVES—MISCELLANEOUS APPLICATIONS OF DIAZO-COMPOUNDS.

ANALYTICAL METHODS

Qualitative Determination.—The coupling reaction is the readiest means of showing the presence of a diazo-compound, since the formation of an intensely coloured azo-compound is unmistakable. The test is conveniently carried out by putting a drop of the diazo solution and a drop of the coupling component side by side on filter-paper; if a diazo-compound is present a coloured line appears where the two drops meet. As coupling components 1 : 8-aminonaphthalenesulphonic acid (Peri-acid) and 1 : 8 : 3 : 6-aminonaphtholdisulphonic acid (H-acid) are commonly used as the azo-compound formed is clearly visible, being purple or blue. β-Naphthol or a 2 : 3-hydroxynaphthoic arylamide dissolved in dilute caustic soda can also be used, and since these substances with many diazo-compounds afford insoluble or sparingly soluble azo-compounds, extraneous impurities can be washed out of the paper, leaving the coloured azo-compound. Alkaline β-naphthol can be used to identify many diazo-compounds because the melting points of the azo-compounds so formed have been recorded for that purpose.

Diazo-compounds in presence of coloured extraneous substances can also be determined by adding to a solution of resorufin (7-hydroxy-phenoxaz-2-one) in aqueous sodium carbonate (0·2 g. of each in 100 c.c.). The resorufin solution shows a red fluorescence, which it loses on coupling, hence extinction of the fluorescence with formation of a brown precipitate indicates the presence of a diazo-compound. This test is due to Eichler.[19]

Tests for the qualitative differentiation of the normal and *iso*diazotates have already been given (cf. p. 132).

Quantitative Determination.—The methods available for the quantitative determination of diazo-compounds are :—

1. By the nitrometer.
2. By titration with reducing agents.
3. By titration with coupling components.

1. *The Nitrometer Method.*—In this method an acid aqueous solution of a diazo-compound is heated, and the nitrogen produced by its decom-

position is swept into a nitrometer by a stream of carbon dioxide, and its volume is measured. This method was first used by Tiemann and Ludwig [1] to determine the nitrogen in the stannic chloride double salt of benzaldehyde-*m*-diazonium chloride, it was used by Hantzsch,[5] and by all investigators except Hirsch and Schwalbe, for determining the velocity of decomposition of diazo-compounds in acid solution. It is, of course, useless where side-reactions prevent complete evolution of nitrogen, as, for example, under alkaline conditions when coupling and resinification occur. Schmidt [7] by cautious heating decomposed dry diazo-compounds in a stream of carbon dioxide and collected the nitrogen.

Diazo-compounds which are slow couplers, and therefore not susceptible to determination by titration, can sometimes be rapidly determined by the nitrometer if means of accelerating their decomposition can be found. Thus the industrially important naphthalene-1 : 2-diazo-oxide-4-sulphonic acid is accurately and quickly determined by treating with sodium arsenite, when its nitrogen is immediately evolved quantitatively.[16] Golosenko [23] has reported that adding a solution of *p*-phenylenediamine to acid solutions of diazonium salts has the same effect. Shaefer and Becker [27] add stable diazo-compounds, such as diazodinitrophenol, to a large excess of titanous chloride and measure the evolved nitrogen, whilst Spencer and Taylor [28] bring about the decomposition by irradiation.

The nitrometer method is sometimes useful when the problem is to determine an arylamine which is a constituent of a mixture of substances. The amine is diazotised, and if no other constituent of the mixture evolves nitrogen on heating, the amine can be thus determined.

2. *Titration with Reducing Agents.*—This method is due to Knecht,[11] and is an application of his researches with titanous chloride as a reducing agent in volumetric analysis. Titration is carried out in cold acid solution using H-acid as an external indicator to show the end-point of the complete reduction of the diazo-compound. Only two equivalents of reducing agent are necessary because the diazo-compound reacts with the hydrazine produced :—

$$2PhN_2Cl + 4TiCl_3 + 2HCl = Ph{\cdot}N{\cdot}(N{:}NPh){\cdot}NH_2 + 4TiCl_4$$

Sodium hydrosulphite can also be used as the reducing agent, with Acid Green as an internal indicator, and here the reduction goes completely to the hydrazine :—

$$PhN_2Cl + 2Na_2S_2O_4 + 4H_2O = PhNH{\cdot}NH_2,\ HCl + 4NaHSO_3$$

The reduction method cannot be used indiscriminately with diazo-compounds containing other reducible groups beside the diazo-group—for example, the large class of nitrodiazo-compounds, unless the diazo-nitrogen is separately determined.[27] Knecht, however, showed that

sodium *p*-nitrobenzene*iso*diazotate ("Nitrosamine Red," see p. 135) could be accurately titrated with alkaline hydrosulphite, using Safranine or Rosinduline as internal indicator. The diazo-group is reduced before the indicator and the indicator before the nitro-group :—

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}ONa + 2Na_2S_2O_4 + 3NaOH = NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2 + 4Na_2SO_3$$

Titanous chloride brings about complete reduction of "Nitrosamine Red" to *p*-phenylenediamine and ammonia.

3. *Titration with Coupling Components.*—Titration against standard solutions of coupling components may be regarded as a supplement to the nitrometer method for use in cases where the reaction solution is alkaline or acid with organic acids. In such solutions diazo-compounds couple quickly and completely. To obtain accurate and consistent results requires some practice, which may be the reason why it has been alleged that the method is not accurate. In skilled hands it is quite as accurate as the nitrometer, and is largely used for industrial purposes.

The method was used by Hirsch and by Schwalbe in their work on the stability of diazo-compounds to determine the amount of remaining diazo-compounds after decomposition had proceeded for a determined period. The accuracy obtainable depends on a number of factors, including a standardised end-point against fresh H-acid solution, and the choice of the correct coupling component. Hirsch used Schäffer acid (2-naphthol-6-sulphonic acid) to combine with the diazo-compound; Yamamoto [13] used 1-naphthol-5-sulphonic acid; Schwalbe [6, 8] used β-naphthol. The disadvantage of β-naphthol is that it yields insoluble azo-compounds with diazo-compounds not containing water-solubilising groups, and inaccurate results may be obtained because uncombined naphthol is occluded in the grains of precipitated azo-compound. Rostovzeva [14] has given full details for preventing this by the use of protective colloids, particularly gum arabic or gelatin, which prevent the precipitation of the insoluble azo-compound. To-day phenylmethylpyrazolone sulphonic acid is much used,[26] the coupling being carried out in acetic acid solution. The sparingly soluble azo-compound formed from this component does not occlude unused component, while it gives a sharper end-point than R-salt which Vaubel [4] said is also carried down by the azo-compound on salting. The determination is carried out by adding an aliquot portion of the diazo-solution to excess of a standard solution of phenylmethylpyrazolonesulphonic acid mixed with sodium acetate solution. Coupling at once proceeds to completion, after which the precipitation of the azo-compound is completed by salt, and the excess of coupling component is back-titrated with a standard diazo-solution, usually N/20 *p*-nitrodiazobenzene.

In some cases the coupling method can be used differentially to determine the proportion of either of two different primary aryl amines in

a mixture or of primary arylamines in admixture with other amines. Thus, if aniline is mixed with the nitroanilines, its amount can be determined by diazotising the mixture, making alkaline with caustic soda, and titrating with N/20 β-naphthol, when only the diazobenzene couples.[5, 21] If concordant results are to be obtained, standardised conditions must be observed, particularly in the matter of alkalinity, as too little alkali will not entirely inhibit the coupling of the nitrodiazobenzenes, while too much will commence destruction of the diazobenzene. As another example, aniline mixed with monomethylaniline can be diazotised and its amount determined by titration with standard R-salt.[3] A similar method has been used by Japanese chemists.[16] Each case where it is proposed to use this method requires examination on its own merits.

Gutmann [10] determined normal sodium benzenediazotate in alkaline solution by mixing with standard arsenite, passing carbon dioxide to remove the benzene formed, and back-titrating the excess of arsenite with standard iodine.

Golosenko [25] has proposed to determine diazo-compounds by an electrical oxidation-reduction method.

Determination of Arylamines by Diazotisation.—Since arylamines which are soluble in cold dilute acid are quantitatively diazotised by nitrous acid, they can be determined by titration with a standard solution of nitrite, using starch-iodide as either internal or external indicator. Green and Rideal [2] standardised the nitrite solution against permanganate and said that for the highest accuracy the titration should be carried out under hydrogen or carbon dioxide. E. Müller and Dachselt [12] showed that the end-point can be found potentiometrically, thus dispensing with starch-iodide and Singh and Ahmed [24] have also used the potentiometric end-point.

Ueno and Sekiguchi [17] made a notable contribution to the technique of this titration when they showed that speed and accuracy, using starch-iodide indicator, is greatly improved if potassium bromide is added to the solution.

Determinations with Diazo-compounds.

(A) *General.*—Standard diazo-solutions are easily prepared, and can be used for the determination of compounds able to couple. *p*-Nitroaniline and *p*-chloroaniline are the amines usually chosen because they are solids easily obtained in high purity. They are made up into N/4 solution in hydrochloric acid, diazotised with slightly more than one equivalent of N/2 sodium nitrite in presence of potassium bromide, and diluted to give an N/10 or N/20 diazo-solution, which is kept in ice-water shielded from direct sunlight. Such solutions have for long been used in the control of the manufacture of dyestuffs, and Bucherer [36] has described their use for the determination of amino- and hydroxy-compounds of the

benzene and naphthalene series. Lee [37] recommended the use of *p*-diazotoluene for the determination of H, γ, J, and S-acid. Korolev and Rostovzeva [42] add gum arabic when titrating components such as β-naphthol which give insoluble azo-pigments, while easily oxidised substances, such as *p*-phenylenediamine, are titrated in presence of thiosulphate. Butadiene, and other conjugated diolefines which couple with diazo-compounds, are determined in admixture with other hydrocarbons by titrating with standard *p*-nitrodiazobenzene.[39] Butadiene can be detected in admixture with other gaseous products by passage through a solution of tetrazotised *p*-phenylenediamine which becomes yellow.[43]

Qualitatively resorcinol is detected in admixture with phenol or cresol by 4-diazophenol-3 : 5-disulphonic acid in presence of ammonia when a red colour is produced if resorcinol is present, whereas neither phenol nor cresol couple with this diazo-compound.[38] Diazonium naphthalenesulphonates can also be used for this purpose and give concordant results because they can be obtained crystalline and free from excess of amine or nitrous acid.[47] Tritolylphosphate is detected in edible oils by hydrolysing, and coupling the cresol produced with standard *p*-nitrodiazobenzene.[46] E. Fischer and Penzoldt [35] tried to determine aldehydes with diazo-compounds, but they are of little use for this purpose.

The sulphonamide drugs can be differentiated by the colours they give on diazotisation in trichloroacetic acid followed by coupling with α-naphthylamine.[48]

Lastly, Dwyer has shown that certain diazoamino-compounds are delicate reagents for the qualitative detection of magnesium ions. Diazoamino-compounds having a nitro-group *ortho* or *para* to the triazen nitrogen atoms are adsorbed on magnesium hydroxide in alkaline solution giving characteristic colours. The following diazoamino-compounds are used as 0·1% solution in ethanol, and the colour with magnesium ions is shown in parentheses : 4 : 4′-dinitrodiazoaminobenzene (heliotrope), 4-nitrobenzenediazoamino-4′-nitronaphthalene (sky blue), 4-nitrodiazoaminobenzene (cornflower blue), 4-nitronaphthalene-4-aminoazonaphthalene (blue). No other hydroxide except that of magnesium gives a colour with the last compound.[40] Cadmium ions are detected, also in alkaline solution, by diazoamino-derivatives of aminoazo-compounds. Dwyer [41] proposed the name Cadion reagents for these substances. To carry out a spot test one drop of the 0·02% 2N-alcoholic caustic potash solution of Cadion, 4-nitrobenzenediazoaminoazobenzene

$$(4\text{-}NO_2\cdot C_6H_4\cdot N_2NH\cdot C_6H_4\cdot N_2\cdot Ph),$$

is placed on filter-paper, on it is placed a drop of the solution to be tested acidified with acetic acid, followed by a drop of 2N-KOH. If cadmium ions are present a bright pink centre is formed surrounded by a violet-blue ring. Ions of silver, mercury, copper, nickel, iron, cobalt, chromium, and

ammonium cause interference and must be removed. Cadion 2B is 4-nitronaphthalenediazoaminobenzene-4′-azobenzene

$$(4\text{-}NO_2\cdot C_{10}H_6\cdot N_2\cdot NH\cdot C_6H_4\cdot N_2\cdot Ph),$$

and Cadion 3B is benzenediazoaminobenzene-4-azonitrobenzene

$$(Ph\cdot N_2\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot N_2C_6H_4\cdot NO_2\text{-}4).$$[44]

These are dissolved in ethanol (0·01 g. per 100 c.c.) containing two or three drops of 2N-KOH; five to ten drops are added to the test solution (5 c.c.), which is then made alkaline with 2N-KOH. Cadion 2B gives scarlet with low concentrations of cadmium ions and blue with high concentrations; Cadion 3B gives red-violet to bluish-purple. Both reagents also react with magnesium ions, giving blue and greenish-blue respectively. Cadion 2B gives a pink spot with blue rim by the spot test, and detects one part of cadmium in ten thousand of lead and fifty thousand of zinc. Cadmium and magnesium can be detected in the same sample by adding Rochelle salt to the solution, then several drops of Cadion 2B solution, then making alkaline with 2N-KOH. The presence of cadmium is shown by a pink colour, the magnesium reaction being inhibited by Rochelle salt in the cold; on heating, the pink colour is destroyed and a greenish-blue develops if magnesium ions are present.[45]

(B) *Biochemical.*—The diazo-compounds have for long proved useful reagents in the hands of the biochemist and pathologist. They are used in two ways. The first and oldest use is to detect the presence of compounds able to couple with diazo-compounds to form azo-derivatives recognisable by their colour. In the second way compounds containing diazotisable amino-groups are diazotised and coupled with selected azo-dye components.

Ehrlich [50, 52, 57] discovered that a substance able to couple with diazobenzene-*p*-sulphonic acid is present in the urine of typhoid fever. " Ehrlich's diazo-reaction " invariably appears in typhoid fever, but subsequent observations have shown that substances able to couple also appear in the urine, though not invariably, in other pathological conditions, including measles and phthisis. The appearance of such substances can naturally be expected whenever protein metabolism has been disturbed. They also appear as the breakdown products of drugs, especially those containing phenolic nuclei. One way of carrying out Ehrlich's reaction is as follows [65] :—

A solution (10 c.c.) of sulphanilic acid (5 g.) in water (1 l.) with hydrochloric acid, *sp. gr.* 1·19 (50 g.), is mixed with four drops of a solution of sodium nitrite (0·5 g.) in water (100 c.c.), followed by urine (10 c.c.) and 25% aqueous ammonia (3 c.c.). The froth becomes pink on shaking if the reaction is positive. In typhoid fever the reaction appears on the second to sixth day and ceases on the first day of remission.

p-Acetoxydiazobenzene, sometimes known as Friedenwald's reagent,[59] made by diazotising *p*-aminoacetophenone, is also used in place of diazobenzene-*p*-sulphonic acid because it gives a froth of brighter red;

dichlorodiazobenzene has also been recommended [70a, 70b] Spiethoff [55] pointed out that Ehrlich's reagent must not be used in any but low concentrations otherwise normal urine affords coupling products, and Penzoldt [51] showed that glucose in urine causes the appearance of a yellow-red colour when solid diazobenzene-*p*-sulphonic acid is added. G. Hunter [74] introduced a variation of Ehrlich's reaction carried out in alkaline solution :—

To 1·1% aqueous sodium carbonate (5 c.c.) is added diazo-reagent (2 c.c.) and the contents of the tube are shaken without inversion; after one minute one drop of urine is added. Normal urine gives the yellow observed by Spiethoff, and this slowly intensifies to a pale orange which occasionally shows a pink or markedly red tinge. The urine of typhoid fever or measles gives a bright orange-red, which quickly disappears, and the normal slow intensification of a yellow is seen.

Petri [54] first set out to find the cause of Ehrlich's reaction, a theme later taken up thoroughly by Japanese biochemists.[76, 77, 92, 95] They examined the urines of typhoid fever, scarlet fever, measles, and phthisis, and found present a number of compounds able to couple, chiefly antoxyproteic acid, a substance already said to give Ehrlich's reaction,[61] oxyproteic acid, and histamine., They said that the antoxyproteic acid present in all the above diseases seems to be the same chemically. Sachs [93] isolated a solid crystalline azo-dye from the products of Ehrlich's reaction, but at the present time there is no firm consensus of opinion as to the exact nature of the substance, giving the red coupling product with diazo-compounds in Ehrlich's diazo-reaction.

Continuing his studies, Ehrlich [53] found that bilirubin, the red colouring matter of the bile, which is present in icteric urine, couples with diazobenzene-*p*-sulphonic acid, and showed that under the correct conditions the test is specific, since none of the other bile pigments couple with diazo-compounds. Here there is no question as to the nature of the substance with which the diazo-compound is coupling, for both monoazo- and bisazo-derivatives of bilirubin have been prepared in the solid state.[58, 62, 69] The azo-pigment is soluble in concentrated hydrochloric acid to a deep blue colour, and the urine may either be treated directly with the diazo-reagent or the bilirubin may be first extracted with chloroform. The chloroform layer is then shaken with an equal volume of the diazo-reagent and acidified with hydrochloric acid, when the aqueous layer becomes deep blue if bilirubin is present. Various modifications of the reagent [56] and the method of testing have been described. Greco [85] used Daddi's reagent, a 0·5% aqueous solution of potassium *p*-nitrobenzene*iso*diazotate :—

The precipitate formed in fresh acid urine (7 c.c.) with 10% barium chloride solution is centrifuged, washed several times, then treated with 0·1N-alcoholic caustic potash (2 c.c.), centrifuged, and to the liquid which has been decanted from the precipitate is added Daddi's reagent (six drops) and sulphuric acid, sp. gr. 1·86 (0·5 c.c.). Bilirubin down to 1 p.p.m. is shown by a sudden reddish-purple coloration turning purple in four seconds and becoming more intense over fifteen minutes.

All variations can be made quantitative by using standard conditions and matching the colours against previously prepared charts. Barac [112] reports that the diazo-reagent method and direct photometry give the same values for bilirubin in urine. Urobilinogen is also determined in urine with Ehrlich's reagent.[115]

In icteric disease bilirubin is also present in the blood, in which it can be quantitatively determined colorimetrically by coupling with diazobenzene-*p*-sulphonic acid, a test introduced by van den Bergh.[67] The results are reliable at concentrations of bilirubin down to 1 p.p.m., and the test can be carried out with 0·25 c.c. of clear serum.

The reagent is freshly made by adding 0·5% sodium nitrite solution (0·75 c.c.) to 0·1% sulphanilic acid solution (25 c.c.), followed by hydrochloric acid, sp. gr. 1·18 (15 c.c.). The blood serum is treated with alcohol (2 vols.), centrifuged, then the supernatant liquid is taken up in a pipette, and to it is added the diazo-reagent (0·25 vol.). If bilirubin is present the liquid becomes red with a violet tinge.

Daddi [91] uses an equal volume of an 0·1% of potassium *p*-nitrobenzene *iso*diazotate, then acidifies with acetic acid; bilirubin gives a pink to red colour.

van den Bergh's test has been much used, and has a considerable literature.[68, 70, 71, 80, 83, 86, 87, 89, 97a, 106a] It can be used to detect latent jaundice.[75, 94] Moreover, with the aid of the diazo-reagent, G. Hunter [80] first showed that bilirubin can be carried in the blood in two states. In cases of obstructive jaundice the bilirubin couples at once, and may be present as sodium hydrogen bilirubinate or combined with serum albumin.[104] In haemolytic jaundice the coupling is delayed either by a lipoid solvent or by combination of bilirubin with globin,[105] the breakdown of haemoglobin being not yet complete,[116] and coupling does not occur until alcohol or acetone has been added. Fowweather [88] said that crystalline bilirubin from gall stones gives the delayed van den Bergh reaction. The general inference of the latest work on the van den Bergh reaction [117, 118, 120] seems to indicate that in the indirect reaction the diazo-compound has to remove a substituent from a coupling position in the bilirubin.

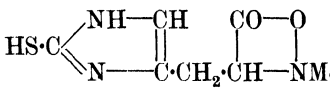
Blood serum also reacts with Ehrlich's reagent in uraemia, a test due to Andrewes.[72]

Alcohol (2 vols.) is added to serum (1 vol.), and after centrifuging the supernatant layer is drawn off, diluted with alcohol (0·5 vol.), then the diazo-reagent (1 vol.) is added. In uraemia a brownish-buff colour slowly develops.

Nakayama [90] said that the cause of Andrewes diazo-reaction in kidney deficiency is urochromogen.

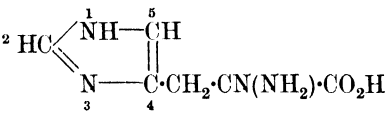
Leimdörfer [73] found that normal mammalian and human blood contains a substance, present only in the erythrocytes, which is able to couple; it is obtained by boiling with dilute acetic acid, extracting with ethanol, and precipitating with alcoholic cadmium chloride. Nakayama [90] suggested

that the substance responsible is ergothioneine, and said further that in diseases in which Ehrlich's diazo-reaction is strong in the urine the diazo-reaction of the blood falls off or disappears. Ergothioneine is β-2-thiolglyoxaline-4(5)-propiobetaine or " thiohistidine betaine " :—



It can be determined in simple solution or in blood filtrates by Hunter's test,[78] in which the liquid is mixed with aqueous sodium carbonate and acetate and added to the diazo-reagent. A clear yellow colour develops in acid solution in presence of ergothioneine, turning red on making alkaline. Hunter [82] has shown that this test is general for 2-thiolglyoxalines, having displaceable hydrogen or carboxyl at 4(5), and is also given by thiol urocanic acid and by 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylic acid, but not by derivatives in which the thiol hydrogen is substituted.

Histidine, 1-amino-2-4′-glyoxinyl- [or -iminazolyl]propionic acid,



of which it is seen that ergothioneine is a derivative, is of widespread biological occurrence as a breakdown product of complete proteins, and is recognised by Pauly's diazo test.[60] The solution to be tested is made alkaline with sodium carbonate, then diazotised sulphanilic acid is added, when a cherry-red colour turning pure orange in acid is produced if histidine is present. The sensitivity is 1 in 10^5. Tyrosine must be absent. The reaction is given by histamine and other histidine derivatives also by benzoylhistidine, but not by dibenzoylhistidine.[63] The technique can be varied by extending the dye on butanol,[84] and it has been used to determine histidine in beer and wort.[96] Koessler and Hanke [66] used standards made up from Congo Red, with or without Methyl Red, for the micro-determination of glyoxalines colorimetrically. Pauly [64] found the coupling product of histidine with diazobenzene-*p*-sulphonic acid too soluble for easy isolation, but was able to isolate the azo-derivative from diazobenzene-*p*-arsonic acid.

Beyer [106] has plotted the absorption spectra of the extracts in butanol of the coloured products formed by combination of diazonium salts in aqueous solution, especially *p*-nitrodiazobenzene, with sympathomimetic amines. Any given amine can thus be placed in one of three groups, (*a*) those having no hydroxyl in the benzene ring but having a primary aliphatic amino-group, *e.g.*, β-phenylethylamine, benzedrine, or γ-phenylpropylamine (these presumably form triazens), (*b*) those coupling with a

monohydric phenol residue, *e.g.*, β-(*p*-hydroxyphenyl)-β-hydroxyethyl methylamine, and (*c*) those coupling with a catechol residue, *e.g.*, β-(3 : 4-dihydroxyphenyl)-β-hydroxyethylamine.

Vitamin B, couples with Friedenwald's *p*-acetoxydiazobenzene, giving a red precipitate,[101, 102, 113] and the reaction can be used for quantitative determinations as can the purple colour given with *p*-acetamidodiazobenzene,[119] but this method is said to be inferior to the fluorometric method of determining vitamin B in animal tissues. γ-Tocopherol is determined colorimetrically after coupling with *p*-nitrobenzenediazonium chloride, with which α- and β-tocopherol do not react.[107]

The process of diazotising the substance to be determined and coupling to form an azo-dye is applied to drugs or their scission products in tissues and body-fluids. This method is in universal use for the determination of the sulphonamide drugs, which on administration always contain the necessary primary amino-group, since they are of the general constitution p-$NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NHX$, where X is, for example, the benzene, pyridine, thiazole, or pyrimidine nucleus. The prepared tissue extract or body-fluid is acidified, treated with nitrite, and added to a coupling component under standard conditions. The key to success is to choose a component which couples strongly, preferably in dilute acid, to form an azo-compound freely soluble in acid medium to a deep, bright shade easily compared against a standard in a colorimeter or having a sharp absorption spectrum. Fuller[97] used β-naphthol and thymol, Marshall[98, 99] used dimethyl-α-naphthylamine, while the use of H-acid was patented;[100] N-acetyl H-acid has also been used.[104] None of these is entirely satisfactory, either because they couple best in alkali or because the dye is too sparingly soluble in cold dilute acid. The special coupling component most widely used is N-α-naphthylethylenediamine, $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_{10}H_7$-α, introduced by Marshall[103] and his co-workers. It affords a deep reddish-purple (absorption max. 550 mμ), and owing to the β-aminoethyl group, the dye is readily soluble in dilute acid. Rose and Bevan[108] introduced sulphatoethyl-*m*-toluidine, m-$C_6H_4Me \cdot NH \cdot CH_2 \cdot CH_2 \cdot O \cdot SO_3H$, which, although it only gives an orange-red dye, has the advantage of a sharp absorption spectrum (absorption max. 507·5 mμ) suitable for reading with a spectrophotometer,[111] whilst it is also not affected by nitrous acid so that any excess remaining from the diazotisation need not be destroyed.

Some drugs can be broken down by hydrolysis, thus affording diazotisable amines, whose determination gives a measure of the drug present in tissues or body-fluids. This is the case with antimalarial drugs, which are pyrimidines having a *p*-chlorophenylguanidino side-chain or are diguanides of the type of Paludrine,[110, 111] p-$C_6H_4Cl \cdot NH \cdot C(:NH) \cdot NH \cdot C(:NH) \cdot NHPr^{\beta}$. These, on autoclaving with acid, afford *p*-chloroaniline, which is determined by diazotisation and coupling. Concentrations of drug down to

1×10^{-6} g. (1γ)/5 c.c. in blood or plasma can be accurately determined. The following are the outlines of the analysis of blood :—

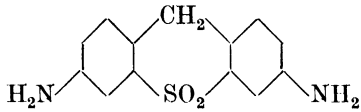
Blood (1—7·5 ml.) in a glass-stoppered bottle is diluted with an equal volume of water, then with half its volume of 40% sodium hydroxide. The mass is warmed at 50° for thirty minutes, allowed to cool, and benzene-ethanol (50 : 1) is added (10, 12, 15, 18, 20, or 30 ml. for 1, 2, 3, 4, 5, or 7·5 ml. of blood). The mixture is shaken for five minutes, transferred to a tube, and centrifuged until the emulsion has separated. Then as large an aliquot as possible of the solvent is transferred by vacuum pipette to a glass-stoppered centrifuge tube, N/2 hydrochloric acid (1·3 ml.) is added, and the tube is shaken for five minutes, then centrifuged for five minutes. The aqueous layer is transformed by a capilliary pipette to an ampoule, which is sealed and autoclaved at 20—35 lb. per sq. in. for six hours. After opening the ampoule 1 ml. is pipetted into a tube graduated at 2 ml., partly neutralised by adding 15% sodium hydroxide (0·1 ml.) then the dye is formed by adding 0·1% sodium nitrite (0·1 ml.), followed after fifteen minutes by 1% sulphatoethyl-*m*-toluidine (0·2 ml.) and 30% sodium acetate (0·3 ml.). After coupling has proceeded for ten minutes the yellow colour is changed to red with concentrated hydrochloric acid (4 drops), and the volume is made up to 2 ml. with distilled water, and the solution is read in a colorimeter, using a filter with maximum transmission at 510 mμ. The concentration of drug is obtained from a standard curve made by hydrolysing as above solutions containing known concentrations of drug, for example 1, 3, 5, 7, 10, and 20, and diazotising and coupling as above.

The three aminobenzoic acids and *p*-aminobenzenesulphonamide can be differentiated by coupling tests on their diazo-derivatives.[114]

Detection and Determination of Nitrous Acid with Diazo-compounds.—The diazotisation reaction occurs even in the most dilute solutions when nitrous acid is present, so that by adding a primary arylamine to a liquid containing nitrous acid, and coupling the resultant diazo-compound to give an azo-dye, the presence of nitrous acid, even in minute amounts, is visually demonstrable. Griess[120] used *m*-phenylenediamine for this purpose, since by diazotisation and concurrent self-coupling it affords the reddish-brown tinge of Bismarck Brown. Hahn[126] used test papers containing α-naphthylamine oxalate; these can be made pure white and give a pink spot with nitrous acid affording a clear mark at 0·1γ per ml. Later, however, Griess[121] found that a mixture of sulphanilic acid and α-naphthylamine dissolved in dilute hydrochloric acid is a still more delicate reagent than *m*-phenylenediamine, affording a reddish-purple colour on adding even so dilute a solution of nitrous acid as saliva. The method was still further refined by Ilosva,[123] who used aqueous acetic acid and dissolved the two components separately, and by Lunge,[124] who used a solution of both components (0·5 g. of sulphanilic acid and 0·1 g. of α-naphthylamine in 150 g. dilute acetic acid). The reagent is generally known as the Griess-Ilosva reagent, and Lunge said that it detects 1 part of nitrous acid in 10^9 of water. The reagent is useful for determining nitrous acid in potable water,[130] and with a good photometer is an accurate means of determining nitrous acid in brines and cured meats.[132] It can also be used to detect nitrous acid in urine.[133]

Some diazo-compounds are known which are intensely coloured (cf. p. 382), and these can themselves be used as reagents for detecting

nitrous acid. Meldola [122] found that the diazo-derivative of 4-amino-4′-dimethylaminoazobenzene, $NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NMe_2$, gives an intense blue solution, especially if made neutral or slightly alkaline with ammonia. The colour of this diazo-compound is well known to dyers of cellulose acetate, as bases of the above type are used to develop a black by diazotising and coupling with 2 : 3-hydroxynaphthoic acid. Stein [125] discovered that the least trace of nitrous acid produces an intense transient blue when added to an aqueous solution of the hydrochloride of 3 : 6-diaminothioxanthone-S-dioxide (" *p*-diaminodiphenylmethane sulphone "),



A solution of the hydrochloride dried on filter-paper affords a pure blue spot with nitrous acid, but it is not so sensitive as starch-iodide, and fades in about half a minute, though it has the advantage over starch-iodide that it does not mark with concentrated mineral acid.

Since the detection of nitrous acid is so important in determining the end-point in the diazotisation reaction, it is worth mentioning that nitrous acid can also be detected by its action on the almost colourless disulphuric ester of leuco indigo, which it oxidises to indigo,[127] by the similar oxidation of leuco methylene blue to methylene blue,[130] and by its discharging the fluorescence of Magdala red [128, 129] (C.I. 857). Sulphite ions also give the last reaction.

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Thermochemistry of the Diazo-compounds.—Berthelot and Vieille [1] studied the thermochemistry of benzenediazonium nitrate, and showed that it is an endothermic compound, their determination of the heat of formation of the solid salt from its elements being —47·4 kg.-cal.

Though no similar determinations have been made for other diazo-compounds, it is probable that nearly all diazo-compounds of the benzene series are endothermic.

Vignon [2] commenced the study of the thermochemistry of the diazo-compounds in aqueous solution, and pointed out that although heat is given out to the amount of about 32 kg. cal./mol. on diazotisation by the direct method, the heat arises from the formation of water and sodium chloride, the heat of formation of the diazo-compound itself being negative. The determination of the heat effects in the various transformations of the diazo-compounds is a subject which has been studied for many years by Swientoslawski and the Polish school of physical chemists.[3]

No laws have been discovered which permit calculation of the heat effects in specific instances when basic values of certain changes are known, in the same way that heats of formation can be calculated from the number of atoms in a molecule and their linkages. As it is impossible here to compress into a sufficiently small space the immense mass of figures which has been published, the reader must refer to the original papers for detailed information. Wojeiechowski [4] has, however, published the figures, as determined by the method of Swientoslawski, for the diazotisation of *p*-chloroaniline and nine transformations of *p*-chlorobenzenediazonium chloride and its derivatives. These are reproduced in Table XL because they give an idea of the magnitude of the heat changes pertaining to each reaction.

TABLE XL

Heat changes in the Diazotisation of p-*Chloroaniline and in Transformations of* p-*Chlorobenzenediazonium Chloride*

Reaction [Ar = p-C_6H_4Cl·].	Heat change (kg.-cal./mol.).
1. $ArNH_2 + HCl = ArNH_2,HCl$	6·94
2. $ArNH_2,HCl + NaOH = ArNH_2 + NaCl + H_2O$	6·71
3. $ArNH_2 + HNO_2 = Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot OH + H_2O$	16·74
4. $Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot OH + HCl = Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot Cl + H_2O$	11·39
5. n-$ArN_2\cdot OH + NaOH = ArN_2\cdot ONa + H_2O$	3·95
6. *iso*-$ArN_2\cdot OH + NaOH = iso$-$ArN_2\cdot ONa + H_2O$	9·44
7. $Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot Cl + NaOH = Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot OH + NaCl$	2·31
8. n-$ArN_2\cdot ONa + HCl = n$-$ArN_2\cdot OH + NaCl$	9·50
9. *iso*-$ArN_2\cdot ONa + HCl = iso$-$ArN_2\cdot OH + NaCl$	4·26
10. $Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot OH \longrightarrow n$-$ArN{:}N\cdot OH$	0·50
11. $Ar\overset{\cdot\cdot}{N}\overset{\cdot\cdot}{N}\cdot OH \longrightarrow iso$-$ArN{:}N\cdot OH$	−2·39
12. n-$ArN_2\cdot OH + \beta$-$C_{10}H_7\cdot OH$(solid) $= Ar\cdot N_2\cdot C_{10}H_7\cdot OH + H_2O$	31·04

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Diazo-compounds as Explosives.—It has been sought to turn to account the instability of diazo-compounds by using them as explosives. Berthelot and Vieille [1] found benzenediazonium nitrate to be an explosive in the same class with mercury fulminate, being more sensitive to percussion, more sensitive to heat, and giving a higher pressure on detonation. Griess and Caro [10] patented the diazonium chromates for use as explosives, Seidler [11] patented the diazoarylsulphonic acids and Herz [12] the diazonium perchlorates but the only diazo-compound which has found any general use is 4 : 6-dinitrobenzene-2 : 1-diazo-oxide, the substance produced by diazotising picramic acid [4 : 6 : 2 : 1-$(NO_2)_2{\cdot}C_6H_2(NH_2){\cdot}OH$], also used in considerable quantity for making *ortho*dihydroxyazo-dyes. Whereas the dye-maker uses the diazo-compound as an aqueous suspension, the makers of explosives require the substance as a free-flowing powder in the dry state, and with one exception [17] they use variants of the inverted process of diazotisation,[20, 21, 23] for example, by adding the acid with an air or gas-operated atomiser to a solution or suspension of sodium picramate and nitrite.[22] .

A complete account of the properties of 4 : 6-dinitro-2 : 1-diazo-oxide as a detonating explosive has been published by Clark.[2] This substance explodes when heated to 180°, detonates when struck, but it is less sensitive to friction than mercury fulminate or lead azide, though in strength as an explosive it is twice as strong as either as measured by sand crushed in a sand-test bomb, and it is equal to lead azide as an initiator and superior to mercury fulminate; it cannot be detonated under water with an electric detonator. Herz [14] first patented its use for making percussion caps, claiming it to be less sensitive to moisture than mercury fulminate and safer to handle. Dehn mixed it with potassium chlorate to make a detonating composition,[15] and compounded percussion mixtures under water, and subsequently dried them.[15] It has been used as a component of mixtures for percussion caps,[18, 19] one such mixture being given as comprising 4 : 6-dinitrobenzene-2 : 1-diazo-oxide (45%), *p*-phenylenediamine dipicrate (15%), barium nitrate (20%), and powdered glass (20%).

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11	Seidler	—	—	46,205	—
12	Herz	27,198/12	—	—	450,897
13	Howles	125,600	—	—	—
14	Herz	—	—	373,426	—
15	Dehn	—	1,404,687	—	—
16	*Idem*	—	1,428,011	—	—
17	*Idem*	—	1,460,708	—	—
18	Hercules Powder Co.	—	1,852,054	—	—
19	Remington Arms Co.	—	1,862,295	—	—
20	Hercules Powder Co.	—	1,952,591	—	—
21	*Idem*	—	2,103,926	—	—
22	*Idem*	—	2,155,579	—	—
23	Olin Industries, Inc.	—	2,408,059	—	—
24	Atlas Powder Co.	—	2,422,043	—	—

Reactions and Properties of Diazo-compounds not classifiable Elsewhere.—Richard [1] immersed woollen yarn in cold dilute aqueous nitrous acid for twenty-four hours, and, after washing-off, found that colours were developed in the yarn by immersing in solutions of azo coupling components, an alkaline solution of β-naphthol, for example, affording a garnet shade. Silk behaves in the same way. Groot [2] repeated Richard's work using a wider range of coupling components. He noted that the diazotised fibre is sensitive to light. Taken at their face value, these experiments indicate that wool and silk contain a diazotisable amino-group or groups, but the diazo-compound has unusual properties. The diazo-compound is not completely destroyed by boiling in dilute acid, and moreover Waterman and Groot [5] found that there is no loss of total nitrogen on boiling diazotised wool, and that the boiled fibre continues to take up H-acid. They concluded that the reaction is more probably an absorption of nitrous acid rather than a true diazotisation. Morel and Sisley [3] diazotised silk fibroin in the dark at 10—12° for twenty-four hours, and found that it then coupled with a limited number of azo-components to give bright shades altered by acid and alkali. They connected this slow generation of a diazo-compound with the action of nitrous acid on the tyrosine units in the fibroin, suggesting that the nitrous acid first forms an *o*-quinone oxime, converted by the long-continued action of excess nitrous acid into the diazonium nitrate. Tyrosine itself, p-$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, when treated in the dark with cold nitrous acid for thirty-six hours, affords a substance which affords two azo-derivatives with β-naphthol, α-amino-, and α-hydroxy-β-(3-β-naphtholazo-4-hydroxyphenyl)propionic acid, the latter having the constitution $OH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$.[4] Silk fibroin diazotised as above apparently contains a nitroso-group attached to an aromatic nucleus, for on reduction with stannous chloride it affords an aminofibroin which diazotises rapidly in the normal way.[4]

Diazo-compounds, especially those derived from aminoazo-compounds,

combine on the fibre with leuco vat dyes of the indigoid, anthraquinone, and sulphur groups. Thus, cotton yarn impregnated in the vat with leucotetrabromoindigo is squeezed, rinsed in a bath of cold dilute alkaline sodium hydrosulphite, and dyed black-brown by immersion in a bath of diazotised benzeneazo-α-naphthylamine.[6] Many other vat dyes similarly afford various shades of brown, but no suggestion has been made as to the constitution of the colouring matters.

Diazo-compounds have been claimed as a means of detecting flaws in protective coatings on metals.[8] The surface is soaked for some hours in a solution of a diazo-compound, rinsed, then treated with a solution of a coupling component, when flaws appear as coloured lines.

3-Diazocarbazole has antiseptic action against *staphylococcus aureus* and *Es. coli*, though the action is reduced in presence of serum.[7] Treatment of diphtheria antitoxin with diazotised sulphanilic acid or *p*-aminobenzenesulphonamide decreases its toxicity without affecting its power to combine with the toxin.[9, 10] This may be a differential coupling. Diazotised *p*-aminobenzenesulphonamide can be isolated in stable form by combining with benzenesulphonic acid, and the powder can be dusted on wounds to remove toxic substances.[10]

Fibrous sheets can be impregnated with a solution of a diazotisable heterocyclic amine [11] or a sulphonated arylamine,[12] an ionisable nitrite, an inorganic salt as electrolyte and a coupling component in alkaline medium, and when the impregnated sheet is made the anode for a current nitrous acid is generated, the amine is diazotised and couples with the coupling component, so forming an azo-dye throughout the mass of the sheet. Similarly in facsimile recording a travelling band impregnated with azo-dye components passes through an electrolytic cell the anode of which is a printer bar. Acid conditions prevail at the bar so where it touches the strip an azo-compound is formed with special rapidity if the coupling component is the morpholine salt of chromotrope acid

$$[1:8:3:6\text{-}(OH)_2C_{10}H_4(SO_3H)_2].^{13}$$

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CHAPTER X

THE ACTION OF LIGHT ON DIAZO-COMPOUNDS. DIAZOTYPES

A QUITE casual practical acquaintance with the diazo-compounds will indicate that they are sensitive to light, although in widely varying degrees. A solution of a diazonium salt standing in sunlight is seen to give off nitrogen bubbles more rapidly than a portion of the same solution in a shaded place, and a specimen of a solid diazo-compound will sooner or later become discoloured where it is illuminated. Berthelot and Vieille [1] noted that solid benzenediazonium nitrate is turned rose-red in sunlight. Closer observation has shown that diazonium salts are decomposed by light with evolution of nitrogen and the formation of different products according to conditions. On the other hand, the normal diazotates are but little influenced by light,[9] whilst the isodiazotates are converted back into the normal salts.[29] Similarly, the stable forms of the diazosulphonates and diazocyanides are converted back into their labile forms, though Ciusa [8] reported that labile 2 : 4 : 6-tribromobenzenediazocyanide is converted by light into the stable form. Proof that irradiation in ionising solvents generally brings about the change from stable to labile diazocyanide has been provided by Stephenson and Waters,[44] who dissolved the stable diazocyanide in alcohol with silver nitrate and irradiated, whereupon the precipitation of silver cyanide commenced, all the stable diazocyanide being eventually decomposed, leaving a clear solution of the diazonium nitrate. The reaction does not occur in the dark. Both the labile diazocyanide and the diazonium cyanide precipitate silver cyanide from silver nitrate, but it is probable that the stable diazocyanide is first converted into the labile form by light, and not directly ionised to the diazonium cyanide, as Hartley in measuring the absorption spectra of diazocyanides (cf. Ref. 17, p. 147) found that the change from stable to labile diazocyanide occurs on irradiation in benzene. The equilibrium in alcohol of the labile form is small, for addition of silver nitrate to a solution which has been irradiated gives at first only a slight turbidity. Long-continued irradiation of the stable diazocyanide in alcohol or acetone produces nitrogen and other decomposition products identical with those of the labile diazocyanides, but irradiation under non-ionising solvents, such as benzene or carbon tetrachloride, brings about no evolution of nitrogen.

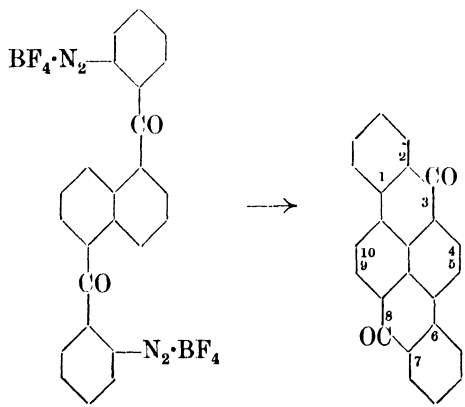
Diazonium salts irradiated in aqueous solution are decomposed into phenol and nitrogen, a fact first demonstrated by Andresen [3] in the case of α- and β-diazonaphthalene, light bringing about the same reaction as heat. The otherwise comparatively stable diazo-oxides are, like the diazonium salts, rapidly decomposed by light, Meldola [5] and his co-workers

first observing this for 3-bromo-5-nitrobenzene-1 : 2-diazo-oxide, and members of this class have become important in photography. Irradiation can, indeed, be more effective than heat in bringing about controlled decomposition, for Orton, Coates, and Burdett,[7, 9] by irradiation with sunlight in glass vessels, obtained 2 : 4 : 6-tribromophenol in quantitative yield from 2 : 4 : 6-tribromobenzenediazonium sulphate, a reaction which cannot be brought about by heat except to a trifling degree. Moreover, they found that if the same diazonium sulphate is irradiated in methanol or ethanol, the products are 2 : 4 : 6-tribromoanisol or -phenetol mixed with some tribromobenzene, whilst in acetic acid there is obtained 2 : 4 : 6-tribromophenol acetate :—

$$C_6H_2Br_3\cdot N_2\cdot HSO_4 + Me\cdot CO_2H = C_6H_2Br_3\cdot O\cdot COMe + N_2 + H_2SO_4$$

Irradiation in formic acid produces tribromobenzene, the diazo-group being replaced by hydrogen. 2 : 4 : 5 : 6-Tetrabromo-, 2 : 6-dibromo-, and 2 : 4 : 6-tribromo-3-nitrodiazobenzene and 3 : 5-dibromo-*o*- and -*p*-diazotoluene undergo analogous reactions, but the method is useless for diazo-compounds of lower stability to heat because effective action by the light is soon prevented by the light-absorbent power of coloured decomposition products. The thermally stable diazo-derivative of sulphanilic acid is suitable for irradiation, and Seywetz and Mounier [14, 15] found that the liberation of nitrogen is proportional to the exposure up to 90% decomposition. Irradiation of solid dry diazonium salts may lead to replacement of the diazo-nitrogen by the anion, especially if it is halogen. Thus Hantzsch [4] found that 2 : 4 : 6-trichlorobenzenediazonium chloride placed in sunlight for two days in a desiccator was converted into 1 : 2 : 4 : 6-tetrachlorobenzene.

If the diazonium group is suitably situated destruction on irradiation can lead to ring closure, for example, by tetrazotising 1 : 5-di(*o*-aminobenzoyl)naphthalene, precipitating as the fluoborate and exposing the solid suspended in water to sunlight a double Pschorr reaction occurs with production of 1 : 2 : 6 : 7-dibenzpyrene-3 : 8-quinone [186] :—



To study the sensitivity to light of diazonium salts, especially carbazole-3-diazonium chloride (for numbering cf. p. 263), which they proposed for use in photography, Ruff and Stein [6] painted strips of paper with equimolecular solutions of diazonium salts, and exposed successive portions to daylight for a series of fixed periods, so as to produce a cumulative effect at one end of the strip graded down stepwise to the unexposed residue at the other. The undestroyed diazo-compound was fixed by coupling, and the shade of the azo-compound so formed on each step were compared. Spencer [13] reduced Ruff and Stein's results to a common basis, and constructed the following table showing the relative times needed for complete destruction of the diazo-compounds derived from the amines listed.

TABLE XLI

Decomposition of Diazo-compounds by Direct Sunlight

Amine diazotised.	Time, units.
p-Toluidine	200
o- ,,	200
p-Chloroaniline	175
p-Aminobenzoic acid	150
m-Toluidine	125
p-Nitroaniline	125
p-Aminophenol	100
Benzidine	75
Diaminocarbazole	32
Diaminofluorene	29

Ljaschenko and Kirzner [26] used the light of a mercury vapour lamp and irradiated diazo-solutions at 0° in both glass and quartz vessels. These were agitated by a stream of carbon dioxide during irradiation, and the nitrogen resulting from the decomposition was collected and measured in a nitrometer. In Table XLII below are given the percentage molar decompositions occurring in three hours.

TABLE XLII

Decomposition of Diazo-compounds in Solution in Glass and Quartz by Mercury Vapour Light

Amine diazotised :	Glass (mol.% decomp.).	Quartz (mol.% decomp.).	Difference.
Anthranilic acid	3·7	17·0	13·3
Aniline	9·0	22·0	13·0
m-Nitroaniline	9·5	23·5	14·0
m-Aminobenzoic acid	9·7	24·0	14·3
Metanilic acid	13·0	27·0	14·0
m-Toluidine	15·0	29·0	13·5
o- ,,	19·0	33·5	14·5
o-Chloroaniline	21·0	34·0	14·5
o-Nitroaniline	26·8	40·5	13·2
o-Anisidine	27·0	41·0	14·0
m-Aminophenol	30·4	44·0	13·6

Schmidt and Maier [21] prepared naphthalene-1 : 2-diazo-oxide-4-sulphonic acid and investigated the constitution of many of its salts and irradiation products (see below), and also prepared [22] diazonium chlorides of substituted *p*-phenylenediamines of the types used in photography, notably *asym*-dimethyl- and -diethyl-*p*-phenylenediamine

(p-$NH_2 \cdot C_6H_4 \cdot NMe_2$, p-$NH_2 \cdot C_6H_4 \cdot NEt_2$),

and their double salts with mercurous, ferric, cadmium, and zinc chlorides. They measured the nitrogen evolved on irradiation of acid diazonium salt solutions with sunlight, sweeping out the nitrogen with a stream of carbon dioxide and collecting in a Dumas nitrometer.[21] Volumes of nitrogen close to the theoretical were obtained for naphthalene-1 : 2-diazo-oxide-4-sulphonic acid, the zinc chloride, and mercuric chloride double salts of *p*-diazodiphenylamine and the internal salt of 2 : 6-dibromodiazobenzene-4-sulphonic acid. The same method has been used by Spencer and Taylor [60] as a method of analysis employing a carbon arc lamp to effect decomposition. Lastly, Brown [53] has used a technique similar to that of Ruff and Stein to compare the sensitivity to light of fifty diazobenzene derivatives. Each amine at a concentration of 0·01 mol.% in acid was diazotised, the solution thickened with starch, coated on paper, and dried in the dark. Portions were then exposed to white (Osira quartz mercury vapour lamp), red, yellow, blue, and ultra-violet light, and the minimum time found for loss of the coupling reaction with β-naphthol. Stability of the diazo-compound to storage was determined by keeping strips in the dark for a week and again measuring sensitivity. Red and yellow light have no appreciable effect on any diazonium salt, and white, blue, and ultra-violet light were used for the experiments affording the results shown in Table XLIII and Table XLIV.

TABLE XLIII

Relation of Sensitivity to Position of Substituent

Substituents.	Order of decreasing sensitivity to :		
	Blue.	Ultra-violet.	White light.
Br . . .	*o*, *m*, *p*	*o*, *m*, *p*	*o*, *m*, *p*
OMe . . .	*o*, *m*, *p*	*o*, *m*, *p*	*o*, *p*
SO_3H . . .	*o*, *m* = *p*	*o*, *p*, *m*	*m*, *p*, *o*
CO_2H . . .	*m* = *p*, *o*	*o*, *m* = *p*	*m*, *p*, *o*
Cl . . .	*o*, *m*, *p*	*o*, *m*, *p*	*o*, *m*, *p*
NEt_2 . . .	*m*, *p*, *o*	*p*, *m*, *o*	*m*, *p* = *o*
Me . . .	*o*, *m*, *p*	*o*, *m*, *p*	—

The second table is especially interesting, since it shows that when substituents are arranged in order of polar strength, sensitivity falls off from the most positive as far as the end of the *o*-, *p*-directing group and increases again to the most negative. The arrows in the margin of

Table XLIV indicate the directions of increasing sensitivity. From these two tables Brown concluded that desirable diazo-compounds for use in photography (see below) have positive polar substituents, as these confer high sensitivity to light with stability to storage, and that the substituents must be *ortho* or *para* to the diazonium group.

Green, Cross, and Bevan,[2] who prior to Andresen's work on diazo-

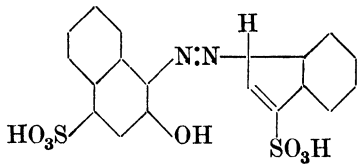
TABLE XLIV

Relation of Sensitivity to Polar Strength of Substituent

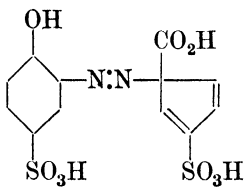
Substituents.	Exposure times in mins. for isomers to blue light.		
	Para.	Meta.	Ortho.
Most positive NEt_2	2	1	3
OH	10	—	—
OMe	120	25	13
Me	60	60	40
Br and Cl (average)	110	75	40
CO_2H	35	35	40
SO_3H	20	20	18
Most negative NO_2	?10	—	—

naphthalene had shown that the nitrogen is liberated quantitatively from irradiated diazo-Primuline, were not certain as to the nature of the residual molecule, for they disclosed the fact, which has never been satisfactorily explained, that this diazo-compound, which, like diazo-dehydrothiotoluidinesulphonic acid, is of high stability both to light and heat, is only markedly affected by light when in close association with a colloid such as gelatin or cellulose. Exposure in a thin film, whether wet or dry, as, for example, by smearing some of the precipitated diazo-compound on glass or cotton cloth, is accompanied by little or no action. On the other hand, Primuline which has been dyed on cotton and then diazotised on the fibre is rapidly decomposed by light. It would appear, therefore, that for rapid decomposition by light water is necessary, and, in some cases at least, extension on a colloid is also necessary. Possibly water could be replaced by other ionising solvents. Schmidt and Maier [21] said that naphthalene-1 : 2-diazo-oxide-4-sulphonic acid on irradiation by sunlight in acid solution is quantitatively converted into 1 : 2-dihydroxy-naphthalene-4-sulphonic acid, whilst Seywetz and Mounier [15] also said that the products of decomposition of diazotised aniline, sulphanilic acid, 1-amino-2-hydroxynaphthalene-4-sulphonic acid, and *p*-aminophenol are the same both for heat and light, but different for the nitrodiazobenzenes and diazobenzene-*p*-carboxylic acid. But if naphthalene-1 : 2-diazo-oxide-4-sulphonic acid is irradiated in solution less acid than that used by Schmidt and Maier then strongly coloured substances are produced, and Süs [54] found that these are not azo-compounds formed by coupling of

unchanged diazo-oxide with 1 : 2-dihydroxynaphthalene, but that the substituted ring is rearranged to a five-membered ring, the product being 1-carboxyindene-3-sulphonic acid, which couples at 3 with elimination of carbon dioxide, so that the coloured azo-compound has the constitution :—



Similarly, diazo-oxides of the benzene series are converted into *cyclo*-pentadiene derivatives; for example, irradiation of benzene-1 : 2-diazo-oxide-5-sulphonic acid produces the dye :—



1-Carboxyindene-3-sulphonic acid is also the product of irradiation of naphthalene-2 : 1-diazo-oxide-4-sulphonic acid.

Light of wave-lengths in the blue and near ultra-violet are most effective in bringing about decomposition of diazonium salts; Eder [17] gives the relative sensitivity of the range blue : green : red as 90 : 0·6 : 0. No means of extending the sensitivity towards the red has been found analogous to the sensitisation of silver salts by dyes. Light of wave-length 450—400 mμ attacks many benzene- and naphthalene-diazonium salts,[24, 27] and hence the markedly destructive effects of the mercury lines at 436 mμ and 405 mμ.[28] Schröter [7] and Fukushima and Horio [19, 20] found the quantum yield of decomposition products to be independent, within wide limits, of other conditions, including temperature and concentration, so that the reaction under steady illumination proceeds at constant velocity, though at higher temperatures the effects of thermal decomposition are noticeable. The quantum yields are poor compared with silver salts. Schröter gives the quantum efficiency, ϕ, as 0·40 at $\lambda = 436$ mμ for the decomposition of naphthalene-1 : 2-diazo-oxide-4-sulphonic acid by a bleaching method, and as 0·35 by the nitrometer. In methanol or ethanol ϕ becomes 0·50. The foregoing means that for each light quantum absorbed statistically at most only one out of two molecules of the diazo-oxide is decomposed. For the photolysis of diazobenzene-*p*-sulphonic acid $\phi = 0{\cdot}16$ for light of $\lambda = 366$ mμ,[20] and Eggert,[33] comparing various light-sensitive systems, gives $\phi = 0{\cdot}50$ for the reaction :

$$p\text{-NHPh}\cdot C_6H_4\cdot N_2\cdot SO_4H + H_2O + h\nu = N_2 + NHPh\cdot C_6H_4\cdot OH + H_2SO_4$$

Goodeve and Wood [38] for the same reaction give $\phi = 0{\cdot}34$ for $\lambda = 365$ mμ, in unbuffered solution at pH 4·2 to 4·7, nor is it altered at pH 6·0 but ϕ rises to unity at pH 10. They also report that the rate of decomposition is not altered by adding a Tartrazine-type (yellow) dye as an internal light-filter.

X-rays do not liberate nitrogen from solid diazo-compounds although their appearance is altered.[8]

Though the range of spectral sensitivity of diazo-compounds cannot be altered, yet apparently ϕ can be increased by adding ketonic substances to diazotype emulsion layers.[334] In this patent it is stated that a film containing the internal salt of diazotised 4-aminophenetol-3-sulphonic acid [4 : 1 : 3-$NH_2{\cdot}C_6H_3(OEt){\cdot}SO_3H$] is fifteen times more sensitive when disodium anthraquinone-2 : 7-disulphonate is present, and the low sensitivity of diazophenols is increased by mixing with substances having strong light-absorption at 330—440 mμ, for example, polynuclear aromatic hydrocarbons.[347]

Diazotypes and Other Uses of Diazo-Compounds in Photography.

The application of the photo-sensitivity of diazo-compounds has become a distinct part of photographic technology, and the list of patents appended to this chapter shows that a degree of intricacy has been reached which can only be fully appreciated by those skilled in the art. From time to time summary papers [10, 13, 16, 17, 23, 25, 32, 36, 43, 46, 48, 50, 51, 55] have appeared tracing the evolution of diazotypes, and these, with the patent specifications and the Intelligence Objectives Reports on German industry,[57, 58, 59] are the main sources of published information. Since it is neither possible nor desirable to discuss this mass in detail in this work the patents have been coded, according to subject-matter (cf. p. 372), thus allowing them to be discussed in blocks. Chemists interested in detail can thus easily trace the original sources for further information.

Emulsions prepared with diazo-compounds do not compete with those prepared from silver salts, since they are too insensitive for taking pictures nor are they suitable for making prints behind an ordinary silver negative because they do not reproduce half-tones. In photographic terms their γ is high. While attempts have been made to overcome this,[45, 285] and some diazotype emulsions can be used with half-tone screens, *e.g.*, Ozalid M (cf. p. 367), the consequence is that the main use for diazo-emulsions is for reproducing or copying objects of high contrast such as drawings or prints. Such reproductions are known as diazotypes. Diazo-emulsions are also used on cine films [40, 41, 135, 160, 196] to reproduce line drawings for cartoons and educational purposes, and have the advantage that they are cheaper than silver emulsions, whilst, like all diazo-emulsions, no dark room is needed, and processing is quick. Levkojev and Petrov [41]

say the film can become clouded after exposure to light, possibly due to the liberation of bubbles of nitrogen in the emulsion layer.

Diazo-emulsions can be used to make either positive or negative prints on textiles, paper, gelatin or other colloid films, or metals, the picture being fixed by converting the diazo-compound into an azo-compound by coupling with a phenol or amine, the azo-compound being substantially insoluble in water.

The majority of diazotype processes utilise the destructive power of the light to remove the diazo-group in those areas which are illuminated. Subsequent to irradiation the undestroyed diazo-compound is fixed by coupling, and thus a positive is produced direct. Green, Cross, and Bevan [2, 102] first appreciated the possibilities of the technique, and applied it to the printing of cloth with Primuline. The cloth was dyed with Primuline, a diazotisable direct cotton dyestuff, treated with nitrous acid and exposed to light under stencils. After exposure the cloth was run through a developing solution of β-naphthol or similar coupling component, when full development occurred only at those points which had been shielded from the light. By varying the period or intensity of the exposure the contrast with the fully developed shade could be made as sharp as desired, down to complete destruction of the diazo-compound on the exposed portions. Cellulose acetate which has been impregnated with an arylamine can be printed in the same way.[142]

The established technique of continuous printing of textiles by means of engraved rollers was never seriously threatened by the diazotype process, which laboured under the disadvantages that it must perforce be intermittent, as even in bright sunlight or under an arc lamp the cloth must remain stationary for at least half a minute during irradiation, and, as it could only print in monochrome, it offered no particular inducement to the more exclusive hand-block printing trade. From the very outset, however, it opened up prospects of improvement in the means of copying drawings and documents, though many difficulties had to be overcome before the present ascendency over the blue-print was attained. A copying paper which could be kept some time in the dark was prepared by Green, Cross, and Bevan by surfacing paper with Primuline solution, diazotising, and drying. After exposure under a transparency the copy was developed by brushing with a solution of β-naphthol or α-naphthylamine, and washed. The print was thus developed in red or purple on a yellowish ground.

While this process was indeed the precursor of those at present in use, it needed much improvement, because users demand at least four chief desiderata in a diazotype paper :—

1. Reproduction in black or dark colours, developing quickly and fast to light and water.

2. Clear whites.

3. The sensitive diazo-layer must not be unduly perishable nor have any effect on the paper.

4. The process of operation must be simple and especially should avoid the necessity for drying the print.

The diazo-compounds which have been used to meet the above requirements can be arranged in six groups :—

1.	Diazo-oxides and diazo-imides . . Code ref. (cf. p. 372)	D1
2.	Diazo-compounds having dialkylamino or similar substituents	D2
3.	,, ,, ,, arylamino	D3
4.	,, ,, ,, alkoxy with or without acylamido	D4
5.	Other diazo-compounds	D5
6.	Diazosulphonates	DS

The copying papers made from the above fall into two broad classes :—

Class 1. Those employing the principle of Green, Cross, and Bevan, in which the diazo-compound alone is present in the emulsion and development is accomplished by treating the paper after exposure with a coupling component.

Class 2. Those papers in which both the diazo-compound and the coupling component, actual or potential, are present in the same layer and coupling is prevented prior to development, either by the nature of the diazo-compound, by control of the acidity or by protection of the phenol until the time of development.

Class 1. For making diazotype papers of this class diazo-compounds are needed which will give monoazo-compounds of shade approaching black and this need is supplied almost entirely by substances which can be looked on as derivatives of asymmetrically N-substituted *p*-phenylenediamine (D2 and D3 references). They are incorporated in the film as diazonium salts, though they may be stabilised with metallic double salts or as fluoborates.[126] 3-Diazocarbazole was tried by Ruff and Stein, but present-day commercial papers contain diazotised *p*-aminoalkylanilines,[116] and diazotised *p*-aminodiphenylamine (sometimes known as "ZA").[31, 122, 244] Substances of the type of 4-benzamido-2 : 5-diethoxyaniline [178] (D4 references) are also used, and mention has been made of halogenated benzylarylenediamines.[216] Diazotised casein also forms a light-sensitive layer.[47, 250, 265] Mixtures of diazo-compounds can also be used, especially when reproducing drawings having areas of different colour density.[127]

Chief among the compounds used for development is phloroglucinol, both because it couples quickly, even with weakly coupling diazo-compounds such as some of the above, and because it affords deep shades which appear as blacks if sufficiently heavy. Resorcinal is used, and tends to give brown prints, often quite pleasing in shade. 2 : 3-Dihydroxy-

naphthalene [277] and esters and amides of 2 : 3-hydroxynaphthoic acid having basic groups in the ester [320] or amide [329] group are also used, especially in papers of Class 2.

The papers of this class are handicapped in competition with those of Class 2, in that to fix the print it must be treated with a solution of the coupling component, and special apparatus has been devised to facilitate handling of the exposed prints, passing them through the developing bath with great expedition.[32] A bath and paper have been devised from which, after development, the paper emerges dry to the touch, fillers having been precipitated into the paper to prevent its holding the developing solution.[238] It has also been proposed to retain the developer in a jelly on which the exposed paper is pressed,[151] or to develop with the vapour of arylamines that can couple.[207]

As the developing solution must be alkaline, its removal presents a problem, as alkali is harmful to paper on long contact. As an alternative components are selected which will couple under faintly acid conditions,[222] diazotised *p*-aminodiphenylamine being one compound which has this property. Acid layers can also be placed under the emulsion to neutralise alkalis.[165]

A problem common to papers of both classes is that of keeping the whites clear, and for this purpose thiourea has come into general use.[137, 180] It has also been proposed to keep the whites clear with reducing agents such as polyhydroxy-compounds [124] applied in the layer or hypophosphites [146] applied after development.

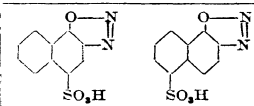
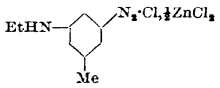
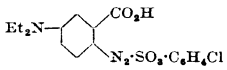
Class 2. The papers of Class 2 are used more widely than those of Class 1. Kögel was largely responsible for their invention, and the firm of Kalle has marketed them as Ozalid papers. An account of the components used in making these papers has been published,[56] and Table XLV has been assembled from this source.

Premature coupling of the diazo-compound with the coupling component present in the layer is prevented in two ways. In Ozalid M there is used naphthalene-2 : 1-diazo-oxide-4- or -5-sulphonic acid, since diazo-oxides and diazo-imides do not couple except when the ring has been opened by alkali. This was the earliest of the successful devices for two-component emulsions.[106, 109] In the other papers coupling is prevented by an organic acid or a salt having an acid reaction. The beneficial effect of titanium [115] and other salts [107, 230] was early discovered, and their use in some papers has remained standard practice.

On exposure to light under a tracing, the diazo-compound is destroyed, and development is brought about by bringing the paper into an alkaline medium, whereupon the undestroyed diazo-compound couples with the phenol present and the drawing is reproduced. An advantage over papers of Class I is that development can be brought about without wetting, as moist air, preferably warm, and charged with ammonia [108] brings about

TABLE XLV

Materials used in Ozalid Diazotype Papers

Brand.	Base.	Diazo component.	Coupling component. Other substances.	Notes.
Ozalid M	Paper		Phloroglucinol $NiSO_4$ Tartaric or citric acid	Red line. Can be used for half-tone work
Blue F	Paper	$NHPh{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_4H$ $(NHPh{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl)_2,ZnCl_2$	R-Salt $Al_2(SO_4)_3$	Blue line. Has best general keeping qualities
Blue G	Paper	*ditto*	*ditto*	Umbelliferone at back to prevent copying [275]
TS	Paper	$(OH{\cdot}[CH_2]_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl)_2,ZnCl_2$	2 : 3-$C_{10}H_6(OH)_2$ Thiourea or 1 : 2 : 6-$C_{10}H_5(SO_3H)_3$ Organic acid	Black line. Poor keeping quality
Air Mail	Special paper	As M, F or TS		
BGT	Paper		Resorcinol Phloroglucinol	Brown line. Used for architectural work
Half-tone B	Photographic paper	*ditto*	*ditto*	Keep 8 to 9 months
Half-tone A	Paper coated with cellulose acetate		2 : 3-$C_{10}H_6(OH)_2$ Organic acid stabilisers	Black line
BG	Transparent paper	$(p\text{-}Me_2N{\cdot}C_6H_4{\cdot}N_2Cl)_2,ZnCl_2$	Resorcinol Thiourea $Al_2(SO_4)_3$	Brown line
Sepia	Very thin paper	As for BG		
VST	Paper lacquered with cellulose acetate	*ditto*	Ethyl resorcylate [1 : 3 : 4-$(OH)_2C_6H_3{\cdot}CO_2Et$]	Red-brown line
Tracing cloth	Cloth	*ditto*	Resorcinol	Brown line
Foil A	Cellulose acetate		Resorcinol with a little phloroglucinol	Brown line
Foil B	Regenerated cellulose	As for M	Phloroglucinol Titanium borofluoride Tartaric acid	Blue line

coupling, and after a few minutes in a developing chamber the print emerges ready for use and free from added reagents.

Although the process of development with ammonia is universally used, it can be troublesome and unpleasant to operate so that the target before the makers has been a paper that can be developed by heat alone. There have been two approaches to the problem. In one the emulsion layer contains substances which will generate alkali when heated, such as the salt of a strong alkali with a weak volatile acid,[124] or the salt of a weak alkali and weak volatile, acid, such as the acetates or formates of lead, zinc, or cadmium,[267] or a mixture of an alkali fluoride and a salt of a strongly basic metal, such as aluminium. The other approach is to rub in the coupling component as a dry powder into a dry paper of Class 1; [235, 249, 252] after exposure moist heat brings about development. It is said that prints made in this way are flat in quality.[58]

Inventors have sought to prevent premature coupling, which is the great stumbling-block in making papers of Class 2, by a number of other devices than those given above. Thus phloroglucinol may be prevented from coupling with a diazonium salt in acid medium by converting it into the oxime of its tautomeric ketonic form, whilst phenols have been acetylated to prevent coupling before being acted on by the alkaline developer.[118] Another line which has been much explored is to keep the diazo-compound and coupling component in separate layers, for example, by dusting on the coupling component in the dry state [231, 240, 249] or rubbing it in mixed with a vehicle.[235] Another means is to spray the component with a binder in a volatile organic solvent.[302]

Besides the papers of Class 1 and 2 there are other ways in which the development of the photographic image may be carried out. Prints can be obtained when the sensitised layer contains a diazo-compound alone if it can couple with the phenol formed by its own decomposition in presence of the moisture in the layer. This was the principle underlying an early patent by Schoen,[104] who used diazotised *o*-aminosalicylic acid, and the same principle has been used since, chiefly with diazo-oxides, and with diazotised 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid).[130] Alternatively, the diazo-compound may be so chosen that it affords on irradiation a phenol which is oxidised to a coloured compound by unchanged diazo-compound, or by a second diazo-compound added for the purpose,[205, 228] whilst copper salts may be added to the layer. Short exposure of such a paper under a negative gives a positive, but prolonged exposure gives a negative. Papers of this kind can also be developed by an oxidising solution such as bichromate or hydrogen peroxide.[201]

An increasing amount of diazotype paper is used for copying print by the reflex process [30] (R patent references). In this procedure the diazotype paper is placed on top of and with the emulsion upwards over the page to be copied, and the whole is irradiated. Where the ink absorbs

the light, decomposition of the diazo-compound is not so rapid as in the whites, and on development of the sensitised surface a copy of the print is obtained. Scattering of the light prevents the copies being as sharp as those made through a tracing paper, but it is claimed that a fine line screen placed between the paper and source of light improves the result.[221, 247]

While the copying of drawings and print accounts for the bulk of the present usage of diazotype emulsions, other uses have been patented, and of these some may have a future. Entwistle [328] coats metal or wood with a diazotype emulsion, and then copies a master-drawing or template directly on the surface, a procedure which can save much time in setting out intricate work. Another possibility is in the production of micro-print, since in order to cope with the ever-growing literature of science and the ever-shrinking living-space of the greater number of scientists, together with the need to conserve paper, the demand for a decrease in bulk, especially of the present journal literature, will grow. In micro-print books a convenient number of ordinary pages, usually one hundred, each reduced photographically to the size of a postage stamp, is assembled as a " matrix " and copied on paper surfaced with a diazotype emulsion.[52] For reading, the matrix is projected, or may be read with a low-power wide-angle microscope. Further, it is known that gelatin mixed with a diazo-compound can be hardened on irradiation, especially by diazo-compounds such as the zinc chloride salt of diazotised 6-aminoanilino-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene.[208] Paper, metal, or glass surfaced with such an emulsion and irradiated behind a tracing can thus afford reliefs which may be coloured.[308] Where the light falls the gelatin is hardened, while the emulsion which has been shielded can be washed away. Anodised aluminium plates taking ink and capable of making 300,000 impressions have been prepared on this principle.[42, 55, 57] Line drawings can also be copied on to plastic surfaces. The hardening of sound records [232] by incorporating a diazo-compound and irradiating after the impression has been received is another application of the same principle.

All the diazotype emulsions so far mentioned have been made with diazo-compounds which are " active " in the sense in which the term is applied to stabilised diazo-compounds. But emulsions can also be prepared from mixtures of passive stabilised diazo-compounds with coupling components. On irradiation, the light activates the passive diazo-compound, and the active form so generated at once couples. The result is a negative print, which is fixed by washing away those portions of the other components which have not been irradiated. It is the diazosulphonates which lend themselves best to this process, because they are soluble in water and entirely without the power to couple, even on long storage, until light produces the active diazo-compound. Feer [101] used diazosulphonates in this way to make the first diazotype paper, and

they have since been the subject of a number of patents. For example, positive or negative prints can be obtained from layers containing diazosulphonates mixed with active stabilised diazo-compounds;[189] probably the light decomposes the diazo-compound to a phenol with which the activated diazosulphonate couples. Diazosulphonates have also been used in an emulsion which gives a paper designed to be developed to a positive print by heat alone.[313] In this emulsion there are used diazosulphonates derived from diazo-compounds of such low coupling energy that they are destroyed by light before they can couple—for example, the diazosulphonate derived from 4-diethylamino-2-ethoxyaniline

$$[1:4:2\text{-}NH_2\cdot C_6H_3(NEt_2)\cdot OEt].$$

After irradiation the paper is heated to about 150°, when the undecomposed diazosulphonate becomes sufficiently activated to couple. The apparent defects of the process are that the time required for irradiation is long, and the high temperature of development damages the paper by embrittlement.[58]

Because the whole spectrum is covered by azo-compounds made by coupling diazo-compounds with coupling components, inventors have been attracted to experiments with diazotype processes for the multi-colour printing of textiles,[105, 141] for printing coloured pictures [114, 121, 284, 293] and films,[194, 239] but these have led to little practical result, because they are not so simple as other processes achieving the same end.

Diazo-compounds can, however, be used in various ways to convert silver images formed from light-sensitive silver salts into coloured images. Lierg [131] added dye components to a silver salt emulsion and developed the coloured image after the silver image, but it was later discovered that if a silver image produced in the ordinary way is bleached by conversion into the chloride and treated with an aqueous solution of an *iso*diazotate, the latter is precipitated on the image as an insoluble silver *iso*diazotate, and, after washing, a coloured picture is developed with a selected coupling component in weakly acid medium.[190] The *iso*diazotate may also contain a group having affinity for silver—for example, the *iso*diazotate derived from aminothiolbenzthiazole.[289] Precipitation of *iso*diazotates by silver halide is the basis of a patent [253] for developing multi-layer colour films. Other processes depend on the precipitation of diazonium salts on silver halides. In Murray and Spencer's process [23, 184] each of the three colour-separation records of a coloured picture is printed on a silver emulsion, developed, bleached by conversion into chloride, and then immersed in a bath of diazo-diphenylamine containing citrate and potassium iodide; the latter produces silver iodide on which the diazo-compound is taken up, and, after washing, the red image is developed with J-acid, the blue with H-acid, and the yellow with *m*-cresol, and the three are superposed in register. A further step in progress allows the three colour-separation records to be printed in succession in register on the same silver halide

emulsion layer thus: (*a*) the layer is exposed under the first negative, (*b*) the positive is bleached to a silver ferrocyanide image, (*c*) treatment with aqueous zinc bromide gives a zinc ferrocyanide image and active silver bromide, (*d*) the silver bromide is desensitised with an oxidising agent, (*e*) the film is bathed with a solution of a diazonium salt which is taken up only on the zinc and is then developed with a coupling component, (*f*) the washed film is resensitised with a reducing agent, exposed under the next record, and the process of development repeated.[335] In another process a coupling component is incorporated with alkali in the silver salt emulsion layer; after exposure the silver image is developed, unexposed silver is removed, and the washed film is treated with a solution of a diazonium salt, and thiourea in acid medium, so that coupling does not occur. The diazo-compound is destroyed in presence of the silver image, and washing with dilute aqueous sodium carbonate causes development of a reversed colour image.[318]

Prints can be obtained on paper coated with an emulsion containing a water-soluble silver salt not sensitive to light and a diazo-compound which produces a reducing agent on irradiation; the black or brown positive obtained from a negative is fixed with aqueous thiosulphate.[199] In a recent development which may become important the light sensitive system consists of a diazonium salt and a salt of mercury. On exposure a negative image is formed and can be developed or intensified, the diazonium salt and its decomposition products being washed away. The sensitivity is greater than that of the usual diazotype papers.[61]

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PATENTS.

It is impossible within the scope of this work to discuss all the patents listed, and they are therefore grouped under the code designations shown below, which, placed against each entry, indicate the subject matter. More than one code letter may be used, *e.g.*, D4, S, AM, indicates a light-sensitive surface made with diazo-compounds containing an alkoxy-group and developed in a special machine.

Diazo-compounds used for diazotype layers :—

Diazo-oxides and diazo-imides	D1
Diazo-compounds with dialkylamino or similar substituents	D2
,, ,, ,, arylamino substituents	D3
,, ,, ,, alkoxy substituents, with or without acylamido . .	D4

Other diazo-compounds D5
Diazosulphonates . . . . . DS
Coupling components. C
Preparation of sensitised surfaces . . . . . S
Increasing sensitivity of diazotype emulsions . . . . . SS
Developing processes . . . . . A
Multi-colour processes . . . . . AC
Apparatus for developing . . . . . AM
Copying technique with diazotypes, including reflex copying . . . . R
Uses of diazo-compounds in silver photography . . . . . P

Patents of addition, other than British patents, are entered immediately beneath the chief patent without repetition of patentee's name.

		Code.	B.P.	U.S.P.	D.R.P.	F.P.	Sw.P.
101	Feer	DS	—	—	53,455 (*Fr.*, 2, 558)	—	—
102	Green, Cross, E. J. Bevan	D5	7,453/90		56,606 (*Fr.*, 2, 559)	—	—
103	Andresen	D5	—	—	82,239	—	—
104	Schoen	D1	—	—	111,416	—	—
105	Valette, Feret	DS, AC	—	—	—	457,446	—
106	Kalle	D1	210,862	1,444,469	376,385 379,998 381,551 383,510	—	—
107	Kalle	D1	—	—	386,433 386,434	—	—
108	Kalle	A	—	—	419,987	—	—
109	Kalle	D1	234,818	—	422,972	—	—
110	Schwickert	S	—	—	—	628,286	—
111	Deutsche Werke Kiel A.-G.	AM	—	—	440,528	—	—
112	Winkler, Volkmann	AM	—	—	441,888	—	—
113	Reden & Köhne	AM	—	—	443,263	—	—
114	Langguth, Hummel	A	274,129	1,710,455	—	—	—
115	Kalle	S	280,593	1,853,462	462,399 596,104	647,273 41,314	—
116	van der Grinten	D2	281,604	—	514,084	—	—
117	Gay	DS	282,894	—	545,486	616,562	122,999
118	Gay	DS	283,274	—	—		125,635
119	Schwickert	S	284,253	—	—	—	—
120	Kalle	S	287,063	—	466,111	—	—
122	Zaidan	D3	290,565	1,971,966	—	—	—
123	Kalle	S	294,247	—	—	657,851	—
124	van der Grinten	S	294,972	—	—	633,319	130,917
125	van der Grinten	A	295,993	—	—	—	—
126	Kalle	D1	296,008	—	461,603	—	—
127	Kalle	D5	296,725	1,760,780	467,090	—	—
128	Kalle	AC	—	—	467,162	—	—
129	I.G.	D5	—	—	473,445	—	—
130	Kalle	D5	297,363	1,936,957	502,663	—	—
131	Lierg	P	298,979	—	—	—	—
132	Kalle	—	—	—	—	664,528	—
133	Emdé	D3	—	—	—	676,317 37,318	—
134	Kalle	AC	299,010	—	—	—	—
135	Film Ozaphane	S	301,879	—	—	—	—
136	Kalle	D1	302,184	1,811,029	470,088	665,132	—

		Code.	B.P.	U.S.P.	D.R.P.	F.P.	Sw.P.
137	Kalle	S	306,408	1,803,906	526,370	687,956	144,321
138	Gay	D4, S	—	1,751,318	—	—	—
139	Brown Line Co.	D5	—	1,752,174	—	—	—
140	Kalle	A	308,653	1,837,679	523,259	671,984	—
141	Haendel	DS, R	309,166	—	—	—	—
142	Brit. Celanese	R	310,773	—	—	—	—
143	Kalle	S	311,196	1,756,400	470,731	—	—
144	van der Grinten	AM	312,261	—	—	—	—
145	Kalle	S	316,563	1,807,761	487,148	679,484	—
146	Murray, Norton and Gregory	A	317,199	1,753,059	—	—	—
147	Lehmann	D3	—	1,753,708	487,247	—	—
148	Kalle	S	318,108	1,807,761	488,148	—	—
149	Kalle	A	—	—	493,834	—	—
150	Renker	A	—	—	500,658	—	—
151	Neulipa	A	—	—	506,412	—	—
152	Kalle	S	—	—	507,171	—	—
153	Kalle	D2	—	—	512,614	—	—
154	Kalle	A	—	—	522,636	659,749	—
155	Kalle	DS	—	—	524,978	—	—
156	Kalle	A	—	—	528,638	—	—
157	Kalle	D5	—	—	530,850	—	—
158	Kalle	S	—	—	531,792	660,087	—
159	Kalle	S	—	—	535,913	—	—
160	Film Ozaphane	S	318,511	—	492,856	673,765	—
161	Kalle	AM	—	—	548,558	—	—
162	Kalle	A	—	—	559,795	—	—
163	Gay	DS, S, A	—	—	—	670,076	—
164	Kalle	S, D3	—	—	558,343	—	—
165	Murray, Norton & Gregory	S	320,395	1,770,352	—	—	—
166	*idem*	S	320,603	—	—	—	—
167	Halden	A	324,048	—	—	—	—
168	Murray, Spencer	AC	325,924	—	—	—	—
169	Kalle	C	331,459	—	490,387	683,504	—
170	Ozalid Co.	AM	331,823	—	—	—	—
171	van der Grinten	A	332,552	—	591,969	674,434	—
172	Frangialli, Freyss	D5	—	—	—	695,006	—
173	Cellophane Soc.	AM	332,631	—	—	—	—
174	Ozalid Co.	AM	334,555	—	—	—	—
175	Frangialli & Co.	C	340,166	1,857,920	—	684,881	—
176	Starostin	S	—	—	—	689,318	—
177	van der Grinten	S	344,721	1,861,330	559,596	696,478	—
178	Kalle	D5	347,430	1,816,989	590,107	693,032	—
179	Kalle	AM	—	—	—	700,196	—
180	Renker	S	353,486	—	—	—	—
181	Frangialli	A	—	—	—	705,622	—
182	van der Grinten	A	358,814	—	—	708,057	—
183	Kalle	D5	362,735	1,870,930	558,343	709,669	—
184	Murray, Spencer	P	363,616	—	—	—	—
185	van der Grinten	S	—	1,821,281	—	—	—
186	I.G.	X	364,739	—	546,226	—	160,084
187	Kalle	A	364,989	—	—	—	—
188	Kalle	D5	—	—	563,240	—	—
189	Kalle	DS	382,483	—	547,062	—	—
190	I.G.	P	387,197	—	—	—	—
192	van der Grinten	A	—	1,926,322	—	708,057	—
193	Shiraeff, F. Jacobs	A	—	1,972,323	—	—	—
194	Kalle	P	390,616	—	—	732,442	—
195	Gay	AM	—	—	—	711,153	—

		Code.	B.P.	U.S.P.	D.R.P.	F.P.	Sw.P.
196	Film Ozaphane	A	—	—	—	727,710	—
197	Kalle	A	—	—	—	734,231	—
198	Philips	S, A	391,052	—	—	745,438	—
199	Kalle	S, A	391,677	—	601,676 640,233	744,706	—
201	Kalle	S, A	391,963	—	571,825	—	—
202	Kalle	AM	—	2,009,962	—	—	—
203	van der Grinten	R	—	2,022,014	—	—	—
205	Philips	S, A	391,970	1,973,788 2,034,508 2,083,285	—	737,377 42,120 —	—
206	Kalle	A	—	—	578,362	—	—
207	Kalle	C, A	398,671	1,966,755	581,394	747,172	—
208	Kalle	A	401,898	2,100,063	581,697	747,246	—
209	Frangialli, Lantz	DS	402,883	—	—	735,718 42,925	—
210	Harding	S	403,203	—	—	—	—
211	Frangialli, Lantz	S	—	—	—	750,080	—
212	Kalle	C	405,880	1,989,065	588,994	757,863	—
213	Philips	A	—	—	—	768,261	—
214	Mason & Sons	AM	411,544	—	—	—	—
215	Kalle	DS, A	—	—	597,450	—	—
216	Kalle	D2	415,081	—	605,553	768,539	172,751
217	Gaspar	S, AC	417,588	—	—	—	—
219	Halden	S	418,976	—	—	—	—
220	Kalle	AM	424,868	—	—	—	—
221	van der Grinten	R	425,126	2,026,292	—	768,394	178,250
222	Harding	D5	425,235	—	—	779,716	179,782
223	van der Grinten	R	425,434	—	—	—	—
224	Gaspar	P	426,260	—	—	—	—
225	Kalle	AM	426,922	—	—	—	—
226	F. Post Co.	S	—	2,027,229	—	—	—
227	F. Post Co.	SS	—	—	—	—	Can. P. 339,065
228	Philips	S, A	427,732	2,083,285	—	779,512	182,083
229	Philips	S	—	—	—	783,321	—
230	Philips	D1	—	—	—	783,415	—
231	Harding	D5	427,962	—	—	—	—
232	Kögel	X	—	2,068,919	—	802,420	—
233	Philips	D1	433,586	—	—	—	—
234	Philips	S	—	—	—	794,590	—
235	Philips	S	433,999	2,113,193	704,070	796,027	—
236	Dietzgen	S	—	2,113,944	—	—	—
237	Philips	A	434,761	—	—	—	—
238	Harper, Powell	A	435,874	—	—	—	—
239	I.G.	P, AC	436,587	—	—	—	—
240	Harding	D2	438,805	—	—	—	—
241	Philips	S	439,005	—	—	785,041	181,833
242	St. Denis	DS	440,144	—	—	760,784	—
243	Philips	S	443,611	—	—	—	—
244	Halden	D3	443,955	—	—	—	—
245	I.C.I.	D5	444,193	2,110,973	—	794,776	185,988
246	Kalle	A	—	—	624,534	—	—
247	van der Grinten	R	445,438	2,051,582-6	—	—	—
248	Kalle	D4	449,341	—	645,267	—	—
249	Halden	S	450,817	—	—	—	—
250	Waterman, Borgesius	D5	454,137	—	—	—	—
251	Halden	D4	454,665	—	—	—	—
252	Philips	S	454,814	2,178,771	—	—	—
253	I.G.	P	464,398	—	—	809,319	—
254	van der Grinten	A	464,613	2,114,468	—	810,413	—

		Code.	B.P.	U.S.P.	D.R.P.	F.P.	Sw.P.
255	C. F. Pease Co.	A	—	2,141,103	—	—	—
256	Kalle	D4	467,145	2,151,532	676,394	813,263	—
257	Kalle	S	467,313	—	716,383	—	—
258	Renker, Belipa	S	—	—	630,389	—	—
259	Renker, Belipa	S	—	—	633,166	—	—
260	I.G.	D5	—	—	636,971	—	—
261	Kalle	C	—	—	639,125	—	—
262	Kalle	DS	—	—	642,223	—	—
263	F. Post Co.	A	—	2,157,206	—	—	—
264	Kalle	D5	471,614	2,158,836	—	—	—
265	Waterman, Borgesius	D5	473,244	—	—	—	—
266	Kalle	S	476,122	2,205,991	674,144	815,400	—
					680,268	—	—
267	Kalle	S	477,754	2,216,137	—	—	—
268	Kalle	AM	—	—	654,809	—	—
269	Powell	D4	—	—	—	—	Can. P. 367,405
271	Mason	D4	489,214	—	—	—	—
272	Kalle	C	491,095	2,150,565	651,145	819,627	—
273	Clement	AC	—	—	—	820,837	—
274	Kalle	A	—	—	670,371	—	—
275	Kalle	R	492,795	2,162,456	—	—	—
276	Philips	A	—	2,172,783	—	—	—
277	Kalle	C	496,090	2,196,950	676,899	834,896	—
278	Bucherer	C	—	—	677,685	—	—
279	Kalle	R	503,996	—	697,744	—	—
280	Halden	S	505,359	—	—	—	—
281	Harding	D4	507,153	—	—	—	—
282	van der Grinten	C, A	510,407	2,199,925	—	845,563	—
283	Harding	D4	510,874	—	—	—	—
284	Bertrand	DS, AC	511,134	—	—	—	—
285	Philips	S	511,816	2,183,447	705,957	—	—
286	Kalle	R	513,029	—	—	—	—
287	Kalle	S, A	—	—	684,334	—	—
288	van der Grinten	A	—	—	684,620	—	—
289	I.G.	P	513,244	2,177,257	—	835,971	—
290	Kalle	S, R	513,560	—	—	—	—
291	Kalle	DS	518,129	2,197,456	—	—	—
292	Kalle	DS	518,162	—	694,078	—	—
293	Polgar, Halmos	S	—	—	—	847,596	—
294	Mason & Sons	D4	520,304	—	—	—	—
295	Harding	D4	521,492	—	—	—	—
296	Dietzgen	D4	—	2,198,827	—	—	—
297	Ozalid Co.	AM	—	2,200,996	—	—	—
298	Dietzgen	S	—	2,209,087	—	—	—
299	Kalle	C	523,922	2,212,959	697,051	849,407	210,212
300	Frangialli	S	30,407/39	2,313,288	—	853,868	219,164
301	Dietzgen	D4	—	2,215,739	—	—	—
302	Philips	S	524,786	2,239,704	714,560	—	—
303	Murray, Norton & Gregory	D4	532,958	2,277,409	—	—	—
304	Dietzgen	A	—	2,228,562	—	—	—
304a	Polgar, Halmos	SS				854,354	
305	Kalle	D2, S	—	2,233,038	703,086	861,685	214,631
306	Poser, Scherer, Süs	R	—	2,245,628	—	—	—
307	Kalle	R	—	2,246,425	—	—	—
308	Philips	S	534,341	—	—	863,089	—
309	Film Ozaphane	S	536,714	—	—	—	—
310	Murray, Tyrrell	D4	538,869	—	—	—	—
311	Mason & Sons	D4	539,031	—	—	—	—
312	Philips	S	539,314	2,318,352	—	864,737	—

		Code.	B.P.	U.S.P.	D.R.P.	F.P.	Sw.P.
313	Kalle	DS, A	544,702	2,217,189	734,302	—	—
314	Kalle	C	—	—	691,283	—	—
315	van der Grinten	AM	544,882	—	—	—	—
316	Spang	S, A	—	—	692,393	—	—
317	Renker, Belipa	A, AM	—	—	695,570	—	—
318	Chromogen, Inc.	P	—	2,271,176	—	—	—
319	Kalle	S	—	—	700,252	—	—
320	Kalle	C	—	—	703,086	861,685	—
321	Kalle	C	—	2,286,656	703,254	—	—
322	Halden	AM	553,508		—	—	—
323	Kalle	D4	—	2,286,701	—	—	—
324	Philips	S	—	—	704,070	—	—
325	Kodak	D2	554,921	2,298,444	—	—	—
326	Kodak	D2	554,998	—	—	—	—
327	Spang	D1	—	—	709,074	—	—
328	Entwistle	A	563,547	—	—	—	—
329	Kalle	C	—	—	—	—	224,979
330	Gen. Aniline	AM	—	2,302,277	—	—	—
331	Gen. Aniline	AM	—	2,308,130	—	—	—
332	van der Grinten	A	—	—	—	—	Dutch P. 48,339
333	Hall, Harding	S	563,804	—	—	—	—
334	Kalle	S	—	2,322,982	—	868,365	217,787
335	Union Research Corp.	P	—	2,333,359	—	—	—
336	Kodak	D2	—	2,336,309	—	—	—
337	Hall, Harding	A	570,027		—	—	—
338	Hall, Harding	S	571,802	—	—	—	—
339	Kalle	D1	—	—	718,321	—	—
340	Kalle	S	—	—	720,364	—	—
341	Kalle	C	—	—	720,917	—	—
342	Kodak	D2	—	2,350,843	—	—	—
343	Gen. Aniline	S	—	2,354,088	—	—	—
344	Bruning & Co.	AM	—	2,373,040	—	—	—
345	Gen. Aniline	S	—	2,374,563	—	—	—
346	Keuffel & Esser	D4	—	2,375,366	—	—	—
347	Schmidt, v. Poser	SS	—	2,378,583	—	—	—
347a	Gen. Aniline			2,381,984			
348	Marconi Wireless	C	34,639/45	—	—	—	—
349	Kalle	S	—	—	752,852	—	—
350	Kalle	D1	—	—	762,522	—	—
351	Kalle	D1	—	—	763,388	—	—
352	Gen. Aniline	C	—	2,416,021	—	—	—
353	Gen. Aniline	S	—	2,416,773	—	—	—
354	Gen. Aniline	C	596,048	—	—	—	—
355	van der Grinten	C	607,334	—	—	—	—
356	Kodak	S	—	2,418,623	—	—	—
357	Gen. Aniline	C	—	2,431,190	—	—	—
358	Gen. Aniline	A	—	2,432,549	—	—	—
359	Gen. Aniline	C	—	2,432,593	—	—	—

CHAPTER XI

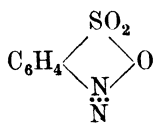
THEORIES OF THE CONSTITUTION OF THE DIAZO-COMPOUNDS

No controversy in organic chemistry has been longer sustained than that regarding the constitution of the diazo-compounds. Over a period of some fifty years there has grown up a huge body of literature on this subject, much of it, unhappily, presenting the features of a morass in which the inexperienced reader may often feel the sensation of sinking helplessly in search of a solid basis of truth. Confusion would certainly result in the mind of the reader of a purely historical survey tracing every stage by which the accumulation has been formed. Not a few of the statements which have been made have been proved to be false, and the critical reader may well doubt others. That controversy has abated during the past decade is due not to general acceptance of any particular solution of the problem, but to recognition that solution must await further development of the electronic theory of valency as applied to compounds of nitrogen. For while that theory has made pointless much of the old debate resting on a valency theory of rigidly fixed bonds, yet it has not itself produced a satisfactory answer to the problems posed.

Little serious interest was shown by chemists in the question of the constitution of the diazo-compounds until the 1890's, when the progress of discovery brought to light the three families of the diazo-compounds: the diazonium salts, the normal diazotates and the *iso*diazotates (cf. p. 126). The acute problem then arose of offering an explanation as to how the constituents of a system consisting of an aromatic nucleus united with two nitrogen atoms can arrange themselves so as to function over the acid pH range as a strong base, and over the alkaline range in two separate weakly acidic forms. The object is this chapter is, therefore, to state the general problem and to condense to the most concise form possible an account of the theories which have been put forward to assign a constitution to the members of each family.

The Diazonium Salts.—To the first question—that of the constitution of the strong base—a satisfactory answer had been given years before and forgotten. The circumstances were these. Griess named the substances he had discovered the "diazo"-compounds, because he believed two hydrogen atoms in the benzene ring to have been substituted by nitro-

gen atoms.[1] He wrote the radical $C_6H_4 \cdot N_2^-$, and believed it to be a weak base forming salts by addition, $C_6H_4 \cdot N_2 \cdot HX$; he used this constitution for a number of years.[3, 5] The question of the constitution of the diazo-compounds at once aroused the interest of Wurtz,[2] Butleroff,[2a] and Erlenmeyer.[2b] Griess later speculated on the possibility of one pentavalent and one trivalent nitrogen atom in a chain, $C_6H_4 \cdot N{:}N{:}N,HX$.[9] Kekulé first perceived that these are strong bases forming salts by direct union with anions, and he suggested that they have the same form as their best-known derivatives, the azo-compounds, the constitution of which had by then been determined. Adopting the latter configuration, he wrote the diazo-compounds $Ar \cdot N{:}N \cdot X$.[4] He differed from Griess in another particular, in that he believed the two nitrogen atoms to have but one point of attachment to the benzene ring, his reason being that the transformation products of the diazo-compounds are so often mono-derivatives of benzene, *e.g.*, chlorobenzene. The matter was later clinched when the penta-substituted aniline, 2 : 4 : 5 : 6-tetrabromoaniline-3-sulphonic acid, was found to diazotise without loss of any substituent.[13, 14] But whereas the azo-compounds are substances of great stability, the diazo-compounds are notoriously unstable, so that it was protested that the diazo-compounds must differ essentially in constitution from the azo-compounds. Strecker,[7] Erlenmeyer,[8] and Blomstrand [6] took this view; independently, and in a short space of time, they put foward the same proposal. Priority belongs to Blomstrand, and his proposition was based on the premise that for salt formation by substitution a pentavalent nitrogen atom must be present, exactly as in the ammonium salts. He therefore wrote the diazo-compounds as $Ar \cdot \underset{\overset{\cdot\cdot}{N}}{\overset{\cdot\cdot}{N}} \cdot X$, where X is the ion of a strong monovalent acid or its equivalent. Strecker further pointed out that the salt-forming capacity of the pentavalent nitrogen atom might be just as well satisfied by an acidic group actually contained in the same molecule as the diazo-group, *e.g.*, in the diazo-compound of sulphanilic acid :—



Unfortunately Blomstrand published his idea in a book which did not have a large circulation, and where it remained forgotten for twenty-six years, while when first proposed it was somewhat summarily pushed into the background because E. Fischer was unable to reconcile a substance having such a constitution as being the parent by reduction of phenylhydrazine. The full extent of the labile nature of the diazo-compounds had not yet been revealed, and it was asserted at that period that a nitrogen atom once pentavalent remained pentavalent in such compounds.

Hence it was argued that reduction of Blomstrand's compound must proceed as follows :—

$$\mathrm{Ph\underset{\underset{\cdot\cdot}{N}}{N}\cdot Cl} + 2H_2 \longrightarrow \mathrm{Ph\underset{NH}{\underset{\cdot\cdot}{N}}H_2,HCl} \longrightarrow \mathrm{Ph\underset{NH}{\underset{\cdot\cdot}{N}}H_2}$$

Fischer proved that phenylhydrazine must be, not the above isomer, but $Ph{\cdot}NH{\cdot}NH_2$,[12] and nineteen years elapsed before Blomstrand parried with the remark that a completely reduced substance cannot contain a double bond, and that the reduction in question can be formulated[36] :—

$$\mathrm{Ph\underset{Cl}{\underset{\cdot\cdot}{N}}:N} + 2H_2 \longrightarrow \mathrm{Ph{\cdot}NH{\cdot}NH_2\atop HCl} \longrightarrow \mathrm{Ph{\cdot}NH{\cdot}NH_2}$$

In 1895 Blomstrand's constitution was almost simultaneously rediscovered by Bamberger[30] and by Hantzsch,[33] who at once recognised how correctly it interpreted the facts. By analogy with the ammonium radical, Hantzsch proposed the name " diazonium " radical, a proposal which was immediately accepted, and to this day Blomstrand's constitution containing the pentavalent nitrogen atom is known as the " diazonium " form, although Blomstrand himself suggested the clumsier name " azo-ammonium." This constitution has entirely displaced those such as v. Pechmann's, which denoted diazobenzene as the anilide of nitrous acid,[17] or that of Walther,[29] who had the same basic idea, or of Sieber,[98] who viewed the diazonium compounds as substituted ammonium nitrite.

The analogy of the diazonium with the ammonium salts cannot be pushed much beyond common possession of basic properties due to pentavalent nitrogen, for in the manner of their reactions the two classes diverge widely,[65] and Hantzsch preferred to compare the diazonium radical to a complex alkali metal. Goldschmidt's cryoscopic evidence that pure diazonium salts are electrically dissociated into two ions has already been mentioned (cf. p. 100), and Hantzsch found the degree of ionic dissociation to be about the same as that shown by potassium or sodium salts. He compared, moreover, the electrical conductivities of solutions of metallic salts with complex ammonium salts and diazonium salts, finding such complete analogy that the basic idea of the diazonium radical has never since been questioned. The large number of double salts which have been described also bear witness to the presence of a radical able to act in combination with other ions in the same way as a metallic ion.

Bamberger, although it was he who had first emphasised the positive nature of the diazonium radical, objected to a thorough-going comparison with the alkali metals because, he said, it cannot be denied that the properties of the diazonium salts are altered, sometimes more, sometimes less, by every substituent attached to the aromatic nucleus,[38] whereas an alkali metal is an invariable entity. But this argument is not valid, because a distinction must be drawn between the effects due to compensations of internal strains set up by substituents and the general

behaviour of the remaining valency by which the radical maintains contact with outside anions, and it is in respect of the general behaviour of this valency that the analogy with the alkali metals subsists.

On the other hand, Schoutissen has maintained that the diazonium group behaves as a powerful negative, *i.e.*, electron-attracting, substituent in its behaviour to its fellow-substituents in the aryl nucleus, the effect being as great as that of two nitro-groups in the *o* : *o*- or *o* : *p*-positions. The evidence for this is (*a*) the difficulty in nitrating benzenediazonium salts, the *ortho* and *para* positions being deactivated by the diazonium-group,[3, 92] (*b*) the single coupling in concentrated acid solution of *m*- [126] and *p*-tetrazobenzene [124] (cf. p. 196), where the negative effect of one diazonium group has the same activating effect on the other as the two nitro-groups have on the diazonium-group in 2 : 4-dinitrobenzenediazonium sulphate, and (*c*) the condensation in the cold of benzaldehyde-*p*-diazonium sulphate to form triphenylmethane-*p*-diazonium sulphate.[125] Here again the diazonium-group exerts the effect of a negative group, for arylaldehydes combine with benzene only when the aldehyde-group is activated by a negative group, as in *p*-nitrobenzaldehyde.

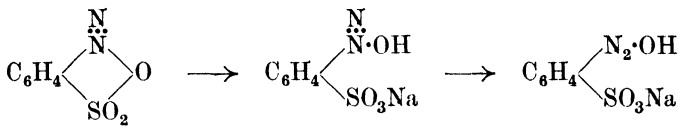
If the analogy of the diazonium salts to the ammonium salts and to the alkali metals is to be complete, then a diazonium hydroxide must exist analogous to ammonium hydroxide or the caustic alkalis. But treatment of the diazonium salts with one equivalent of alkali brings about far more deep-seated changes than the liberation of the required hydroxide, and a hydroxide having the constitution $Ar{\cdot}\overset{\cdot\cdot}{N}{=}\overset{\cdot\cdot}{N}{\cdot}OH$ has never been isolated, nor can it be certain that it has been obtained free from tautomers in solution. To obtain such a hydroxide Hantzsch [56] acted on a pure diazonium chloride in dilute aqueous solution at 0° with a slight excess of moist silver oxide :—

Benzenediazonium chloride (0·7 g.) is dissolved in water (50 c.c.) at 0°, and moist silver oxide (0·8 g.) mixed with ice is added. After thorough shaking the solution, from which silver chloride has been filtered, is found to be strongly alkaline. Coupling with β-naphthol is instant and the solution darkens rapidly even at 0°.

Hodgson and Marsden [131] say that the diazonium hydroxide prepared by the above method decomposes into phenol, which at once couples with the *n*-diazohydroxide, into which part of the diazonium hydroxide tautomerises, so that a considerable quantity of di- and tribenzeneazophenol is formed.

Hantzsch and his co-workers carried out extensive researches to demonstrate by conductivity measurements [57] the existence of diazonium hydroxides in solution. They found the affinity constant of benzenediazonium hydroxide at 0° to be seventy times that of ammonium hydroxide, whilst the effects of substituents in the ring have been closely studied.[62] Battegay and Béhar [95] made anthraquinone-α- and -β-diazo-

nium hydroxide by acting on the diazonium sulphate with barium hydroxide, a method Curtius [15] used much earlier with benzenediazonium sulphate. The anthraquinone-α-diazonium hydroxide is more stable than the β-isomer, the solution of both in water being alkaline to Methyl Red and Clayton Yellow, but they become acid in a few minutes as tautomerisation to the *iso*diazohydroxide takes place. Wistar (private communication) says that the alkaline reaction is due to slow precipitation of the barium salt which, while still in solution, gives the alkaline reaction. Yet another example of such rearrangement was contributed by Hantzsch and Gerilowski,[34] who added one equivalent of alkali to diazotised sulphanilic acid; the originally neutral solution becomes alkaline, and then neutral again due to the changes :—



Neutral. Alkaline, passing on standing to: Neutral.

Bamberger [40] said that the reactions are not so clear-cut as presented above.

Attempts have been made to obtain some light on the constitution of the diazonium salts from the fact that some are coloured, though derived from colourless bases. This is especially the case with some acylated *p*-diamines, such as 4-benzamido-1-naphthylamine, which affords a yellow diazonium salt. Morgan and his co-workers [83, 84, 85] examined this question, and reached the conclusion that the colour is connected with changes in the aromatic nucleus induced by the diazonium group rather than by any alteration in the constitution of the latter. An extreme case which may be mentioned is Meldola's blue diazoazo-compound (cf. p. 350).

The Normal Diazotates.—As has already been explained in describing their preparation, the normal diazotates are the first product of the action of excess of alkali on the diazonium salt, and they are formed by rearrangement of the unstable diazonium hydroxides. Concerning their constitution there is by no means general agreement among chemists, and on them and on the *iso*diazotates, centres the controversy as to the constitution of the diazo-compounds. The instability of the normal diazotates and the still greater instability of the corresponding hydroxides make it difficult to prepare and examine them in a state of purity, and hence arguments as to their constitution are based on such foundations as their reactions and the known constitution of their derivatives.

The diazohydroxides, having the empirical formula $ArN_2{\cdot}OH$, can take part in reactions involving either the hydrogen atom or the hydroxyl group. The metal salts, unstable and hydrolytically dissociated, are the result of reaction in the acidic form, but since greater energy loss occurs

when the hydroxyl group is eliminated, the *n*-diazotates react more readily with substances from which the necessary proton can be acquired to permit the elimination of water with formation of a covalent compound containing the azo link :—

$$ArN{:}N{\cdot}OH + HA = ArN{:}N{\cdot}A + H_2O$$

In reactions in which the diazotates disengage their nitrogen atoms they also act as oxidising agents, since two electrons must be acquired from the environment. But, as the discussion of the various theories will show, there are reasons why the above simple constitution, ArN:N·OH, though convenient and often used, is not an accurate picture of the constitution of the *n*-diazohydroxides.

On the point of nomenclature arising from the above, it is worth noting that at one time Hantzsch proposed that the term " diazo " should be dropped for a whole group of covalent derivatives of the diazo-compounds, such as the diazocyanides and diazosulphonates, and that they should all be called azo-compounds, *e.g.*, azocyanides, azosulphonates. For a time he employed this nomenclature in his writings.[66] The proposal is logical (and had also been made by Blomstrand), but it has never overcome the inertia of tradition, which baulks at naming as an azo-compound a substance, such as a labile diazocyanide, which is still able to form another azo-compound by coupling with a phenol. As a result of this conservatism, the possibility of confusion arising from the use of the term diazo-compound both as a generic term and as a name for certain specific molecular species—namely, the normal and *iso*diazo-compounds—has never been removed. There is also want of agreement as to the name to be applied to the diazohydroxides. English usage since 1903 has adhered fairly consistently to the name diazohydroxide, which has therefore been used in this book; but more logical writers have sometimes used the term " hydrogen diazotate," while the Germans consistently use the term " diazohydrate " for the same substances.

The *iso*Diazotates.—The consideration of the constitution of the normal diazotates cannot be divorced from a parallel consideration of the *iso*diazotates, the second and final result of the change wrought on diazonium salts by the action of excess of alkali. As the *iso*diazotates are so much more stable than the normal salts, so the parent *iso*diazohydroxides might be expected to reach a sufficient degree of stability to permit their isolation and examination. A description has already been given (cf. p. 134) of the fruitless attempts made by Hantzsch and his co-workers to isolate *iso*diazohydroxides in a state of purity and the criteria used to distinguish them from the primary arylnitrosamines, Ar·NH·NO. The place to be allotted to the latter substances has proved difficult, but there has been a considerable school of thought which agreed that neither of the diazohydroxides can have this constitution, as it represents a substance which

should be neutral and incapable of direct salt-formation—a point on which Hantzsch was always inflexible. Consequently, if such substances have ever been obtained from an *iso*diazotate, they must have arisen by isomerisation of an acid form which can combine with a metal cation. It is unfortunate that the primary arylnitrosamines have not been prepared by any other route, so that an equilibrium with the *iso*diazotates cannot be approached from that side. The foregoing therefore militated against another school, which accepted the face-value of the evidence that the metal salts of the *iso*diazohydroxides may have the constitution of nitrosamine salts, Ar·NM·NO. In addition, a number of chemists mistrusted and set aside evidence pointing in this direction, the cause for distrust being that while alkylation of the sodium salt of " Nitrosamine Red," $NO_2 \cdot C_6H_4 \cdot N_2 \cdot ONa$, gives the N-ether, similar treatment of the silver salt gives the O-ether. Less ambiguous appeared the result of the acetylation by acetic anhydride of alkaline solutions of diazobenzene. Here v. Pechmann and Frobenius obtained a 30% yield of nitroso-acetanilide, PhN(NO)·Ac, a fact from which they were led to declare that in cold moderately alkaline solutions of diazobenzene a metal salt of the constitution Ph·NM·NO exists.[17] Indeed, it was the view of v. Pechmann that just as an equilibrium exists between the diazonium hydroxide and the *n*-diazohydroxide, so another equilibrium, determined by the concentration of alkali, exists between the salts of the *n*-diazohydroxide and the *iso*-form, which he regarded as the nitrosamine.[16] As will be explained (cf. p. 390), Hantzsch taught that this direct explanation is not a true account of the mechanism of the change, which, though often proceeding spontaneously from normal to *iso*diazotate, in the reverse is accomplished only through the diazonium salt. v. Pechmann and Frobenius' view was further disturbed when Bamberger [18] said that alkaline hydrolysis of nitrosoacetanilide gives the normal diazohydroxide, whereas the slowly-coupling *iso*diazotate would be expected according to the equation :—

$$PhN(NO)\cdot Ac + 2NaOH = Ph\cdot NNa\cdot NO + NaOAc + H_2O$$

This result may be due either to the nitrosoacetanilide reacting in its tautomeric form or to change of the *iso*diazotate first formed into the normal diazotate. Hantzsch explained it in the case of nitrosobenzanilide as proceeding through addition and subsequent scission.

Dobbie and Tinkler found that the absorption spectrum of the potassium salt of benzene *iso*diazotate is different from that of the potassium salt of benzene normal diazotate,[70] and closely resembles that of phenylmethylnitrosamine, while later Hantzsch and Lifschitz [87] found similar differences between the normal and *iso*diazotates, thus reinforcing the chemical evidence for the separate identity of the two forms.

The foregoing gives an idea of what are some of the loose pieces of

the jigsaw puzzle which framers of theories have essayed to piece together, and explains why there have been put forward such a variety of proposals for the constitution of the diazo-compounds, since avoidance of the nitrosamine constitution for the metal salts of the *iso*diazotates entails propounding some other less obvious structure which will explain or adequately represent the differences between the normal and *iso*diazo-compounds.

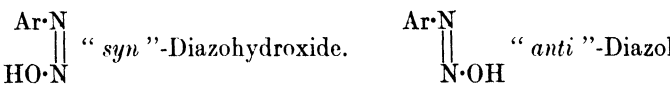
The stage is now set for a review of these theories, but before proceeding farther, the issue can be much clarified by setting out in tabular form the various constitutions which have been put forward from time to time (cf. Table XLVI). Since interest in many of these theories is now only historical, a number are discussed in very brief form or not at all, but the reader who is interested can elucidate the details by search of the appended references.

The Theory of Hantzsch.

Pride of place must be given to Hantzsch, not only for the break-away from current thought which marked his original contribution, but also for the resource with which for nearly forty years he sought experimental proof in defence of his thesis. In 1894 he published a paper [19] in which he compared the diazo-compounds with the oximes, the properties of which had been proved by Werner and himself to be due to the existence of stereoisomerides made possible by the immobile C:N bond, thus :—



Hantzsch reared the whole of his theory from the fundamental proposition that the difference between the oximes and the diazo-compounds lies merely in the substitution of nitrogen for carbon, and that the normal and *iso*diazotates are derived from two stereoisomeric diazohydroxides. Hantzsch called the two possible stereoisomers the " *syn* "-form and the " *anti* "-form, representing the two parent hydroxides thus :—

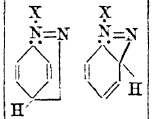
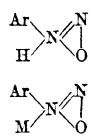
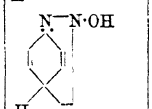


Angeli [27] has also left a record that he discerned the possibility of the same explanation independently of Hantzsch, but he did not pursue the idea.

Hantzsch said that the *n*-diazohydroxides are represented by the *syn*-configuration because it represents a molecule rendered unstable by internal strain, whether arising from the mere mass of two groups compelled to lie close together, or from the effects of chemical attraction or repulsion between them. The *iso*diazohydroxides are represented by the more stable *anti*-configuration, in which strain has been relieved by the

TABLE XLVI

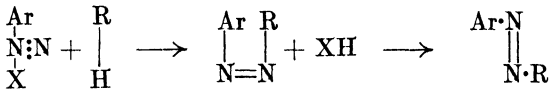
Constitutions Proposed for the Diazonium Compounds and Diazotates

Investigator:	Hantzsch.	Bamberger.	Hodgson, Marsden.	Bruhl.	Armstrong, Robertson.	Cain.	Swientoslawsky.	Angeli.	Oddo.	Sarkar.
Basis of theory:	Stereoisomerism	Structural isomerism		Optical properties	Colour	Quinonoid tautomerism.	"Deformed" nitrogen	Reactions of azoxy-compounds		Electronic theory of valency
Diazonium salts	$ArN{:}N{:}X$	$ArN{:}N{:}X$	$ArN{:}N{:}X$					$ArN{:}N{:}X$	$ArN{\equiv}N{\cdot}X$	$[Ar{-}N{:}{:}N]^{+}{\cdot}X^{-}$ $[Ar{-}N{:}{:}N]X^{-}$
Normal diazohydroxides and diazotates	*syn*-Diazohydroxide $Ar{-}N(OH){=}N$ $HO{\cdot}N$	$ArN{:}N{\cdot}OM$ $ArN{:}NH$ (O) $ArN{:}NH$ (O)	Solid: $ArN{:}N{\cdot}OM$ Solution: $ArN{:}N{\cdot}OM \rightleftharpoons ArN{:}N{\cdot}OH \rightleftharpoons ArN{:}N\}OH^{-}$		Labile diazo-compounds, *e.g.*, $ArN{\cdot}SO_3M$ (N) $ArN{\cdot}OM$ (N)		$ArN{:}N{\cdot}OH$	$[Ar{\cdot}N{:}N(O)]^{-}\ H^{+}\ \text{or}\ M^{+}$ $[Ar{\cdot}N{:}N(O)]^{-}\ H^{+}\ \text{or}\ M^{+}$	$ArN{\equiv}N{\cdot}OM$	$Ar{-}N{:}{:}N{:}\overset{\rightarrow}{\underset{\cdot\cdot}{X}}$
*iso*Diazohydroxides and *iso*diazotates	*anti*-Diazohydroxide $Ar{-}N(OH){=}N{\cdot}OH$	$ArN{:}N{\cdot}OH$	Solid: Ion pair $Ar\overset{-}{N}(NO){\cdot}M^{+}$ Solution: $ArN{:}N{\cdot}O\overset{-}{M}^{+}$ $Ar\overset{-}{N}(NO)\}M^{+}$	$ArN{:}N{\cdot}OM$	Stable compounds: $ArN(OH){\cdot}NH(OH)$ $ArN{-}NH$ (O) $ArNH{\cdot}N(OH)$ $ArNH{\cdot}NO$	$ArN{:}N{\cdot}OH$ $ArN{:}N{\cdot}OM$	$Ar{-}N(OH){=}N{\cdot}OH$ Nitrogen atoms have lost a plane of symmetry	$ArN{:}N{\cdot}OH$ $[ArN{:}NO]^{-}\ K^{+}$ *	$ArN{=}N{\cdot}OM$	$Ar{-}N{:}{:}N{-}X$ Dots here represent electrons
Neutral isomers	Nitrosamine $Ar{-}NH{\cdot}NO$	$Ar{\cdot}NH{\cdot}NO$								
Chief references	19, 33, 34, 42, 51, 56, 60, 62, 68	18, 22, 26, 30, 40	131, 135	53–55	71	72, 75, 78, 78A, 89	91, 96, 109, 121, 122	93, 94, 97, 99, 100, 101, 102, 103, 104, 111, 113, 115, 116–120, 133	127, 130	128

M = atom of a monovalent metal or its equivalent. X = a monovalent anion. * Private communication by Dr. Z. E. Jolles.

acquisition of sufficient space for each group, while distance has diminished the effects of mutual physical forces. Since energy is dissipated in the relief of strain, it follows that the *anti*-form must be at a lower energy level than the *syn*-form, from which it thus differs in lower reactivity and lower sensitivity to agencies, such as heat and shock. A further corollary is that the change from *syn*- to *anti*-form should take place with evolution of heat.

Hantzsch conceived of all derivatives of the diazo-compounds as being formed through the *syn*-form, and therefore that the reactions of the diazonium salts, except their decomposition to phenols in acid solution,[68] must be indirect, and he accordingly adopted the following scheme, which represents the general reaction as occurring by a particular mode of addition from which the requisite *syn*-form alone results by scission [65] :—



He used this mechanism to explain the formation of the *syn*-diazotates, -diazosulphonates, and -diazocyanides and their subsequent rearrangement to the stable *anti*-forms.

Hantzsch was never able to prove his theory by the same conclusive means that Mills and Bain [84] used to prove the geometrical isomerism of the oximes, and its present wide acceptance has been achieved more by careful co-ordination of many facts all pointing in the same direction. In building up this body of evidence he sought support from three classes of compounds :—

1. The diazocyanides.
2. The diazobenzenesulphonic acids.
3. The diazosulphonates.

Hantzsch [19] also claimed to have discovered two stereoisomeric forms of diazoaminobenzene but Bamberger [23] showed that his supposed new form was in fact v. Pechmann's bisdiazoaminobenzene, $Ph{\cdot}N(N_2{\cdot}Ph)_2$.

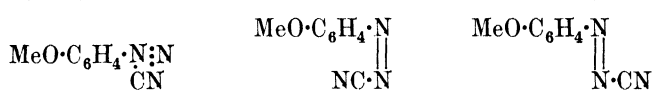
A brief *résumé* of the evidence Hantzsch produced under the above three headings and of his views on the primary arylnitrosamines will now be given, followed by some account of the criticisms to which the theory has been subjected.

The Diazocyanides.—In describing the reactions of the diazo-compounds it has been remarked that when they react with cyanides in aqueous solution, coloured precipitates result, and that two modifications, labile and stable, of such diazocyanides can usually be shown to exist. Their physical properties and reactions show that they cannot be diazonium compounds, and Hantzsch therefore said that they are the *syn*- and *anti*-compounds, as demanded by his theory. But he said that it is reasonable to suppose that there should also be capable of existence a

diazonium cyanide which should be colourless and highly ionised and, the diazonium radical being a compound alkali metal, such cyanides would resemble an alkali cyanide. A clue to their existence was discovered when it was found that diazonium chlorides, on treatment with silver cyanide, give, in addition to the insoluble yellow diazocyanide, a soluble colourless double cyanide with silver cyanide.[52] Alkali cyanides cannot be used for this reaction because their invariable accompaniment by hydroxyl ions causes isomerisation of any diazonium cyanide formed to the diazocyanide. Since hydrocyanic acid is so weak an acid, difficulty was experienced in finding a case where a solid salt could be isolated, but eventually, by evaporating *p*-methoxybenzenediazonium hydroxide with excess of hydrogen cyanide *in vacuo* at room temperature, a double cyanide was obtained of the constitution :—

$$p\text{-MeO}\cdot C_6H_4\cdot N_2\cdot CN, HCN, 2H_2O$$

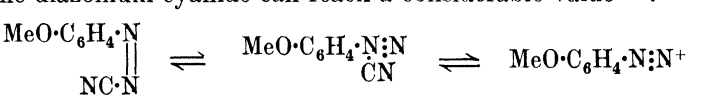
This was found to have the properties expected of a diazonium salt, being a colourless crystalline solid ionised in aqueous solution and giving the typical yellow precipitate of the diazocyanide when treated with alkali.[67] Also it has a different absorption spectrum to that of the *syn*- and *anti*-diazocyanides which are identical.[87] Hantzsch could therefore point to a group of three isomers as demanded by his theory : —



Diazonium cyanide — *syn*-Diazocyanide — *anti*-Diazocyanide

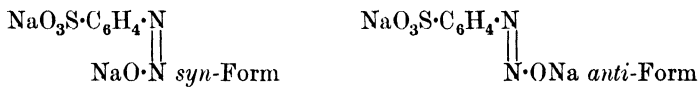
The achievement afforded strong support for the stereochemical theory, but was still not a proof.

There are only two other cases in which the complete group of the three expected isomers can be isolated in the solid state (p. 389), and there is little possibility of the existence of many more. This is because hydrocyanic acid occupies an anomalous place among the acids, and its constitution and behaviour have only been satisfactorily explained on the electronic theory.[112] Acids stronger than hydrocyanic afford only the diazonium salts; with weaker ones only the diazo-compounds exist. Only strongly positive substituents in the benzene ring are favourable to the diazonium cyanide so that when *p*-methoxybenzene diazocyanide or ψ-cumene diazocyanide is dissolved in water the equilibrium concentration of the diazonium cyanide can reach a considerable value [67] :—



Nevertheless, the most weakly negative substituents influence the equilibrium so greatly in favour of the diazo-forms that, in general, it is only the *syn*- and *anti*-diazocyanides which can be isolated.

The Isomeric Diazobenzenesulphonic Acids.—Owing to its insolubility in water, the inner anhydride of diazobenzene-*p*-sulphonic acid had long been known before Hantzsch confirmed for it the diazonium constitution shown above (cf. p. 382). Moreover, before Hantzsch published his theory, Bamberger had prepared the *iso*diazotate by the usual method heating with excess of caustic alkali. The normal or labile isomer necessary to complete the group of isomers was prepared by Hantzsch and Gerilowski [34] by acting on diazotised sulphanilic acid or orthanalic acid [47] with caustic alkali at 0°. Both the sodium and potassium salts were made, the former as white needles crystallising with four molecules of water, the latter anhydrous and passing more easily into the *iso*-form. For purity and ease of preparation this is by far the most satisfactory group of isomers. Conductivity measurements of the normal sodium salt showed the acid to be weaker than that giving rise to the *iso*-salt, which gave values agreeing well with those for sodium salts of other dibasic acids, whilst both salts gave three ions. Hantzsch and Gerilowski [42] regarded these facts as evidence that the isomerism of the two diazotates is spatial, and represented their constitutions by the structures :—



Against this it should be noted that in the same paper Hantzsch and Gerilowski reported that the *syn*-oximes are stronger acids than the *anti*-oximes. Angeli [97] in regard to this point has noted that *cis*-cinnamic acid, *i.e.*, the acid having the carboxyl group nearer to the phenyl radical, is more acidic than the *trans*-acid. Since this agrees with the order of acidity of the oximes, the *syn*-diazotate appears to be anomalous in being less acidic than the *anti*-diazotate.

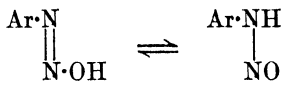
The Isomeric Diazosulphonates.—The diazosulphonates are known only in the two modifications, the preparation and properties of which have already been described (cf. p. 147). No substance having the properties to be expected of a diazonium salt of sulphurous acid has ever been discovered to complete the group of isomers. When Hantzsch discovered the labile form of the diazosulphonates he brought these compounds forward as evidence for the stereoisomerism of the diazo-compounds. The following were the basis for his assertion :—

1. The more deeply coloured isomer has the power to couple with β-naphthol, and on keeping in solution changes into the stable form, which cannot couple, and therefore must be a member of the *anti*-series. Therefore the labile coloured form is the *syn*-isomer.

2. The measurements of absorption spectra, made first by Dobbie and Tinkler [70] and later repeated by Hantzsch and Lifschitz, showed the

absorption curves of both labile and stable diazosulphonates to be the same, and hence their molecular structure must be the same. Hodgson and Marsden [132] say, however, that the labile benzenediazosulphonate changes so rapidly into the stable form that its absorption spectrum has not been plotted.

The *iso*Diazotates and the Primary Arylnitrosamines.—An account has already been given of the attempts made by Hantzsch to prepare the free *iso*diazohydroxides. As the result of these he held the opinion that as soon as the metal in an *iso*diazotate is replaced by hydrogen, a labile molecule results setting up the equilibrium :—

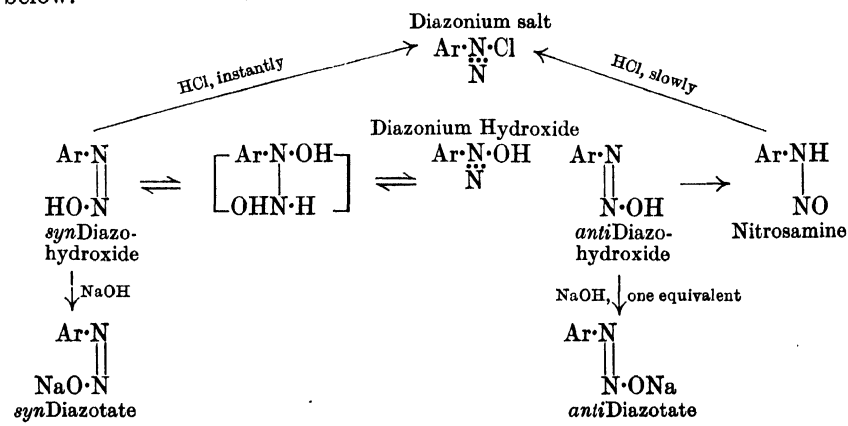


The equilibrium can move so that the nitrosamine is the only form, and the aryl nucleus and its substituents determines which way the equilibrium moves. The criteria Hantzsch employed to decide which of the two isomers was in hand were the following, from which it is evident that they are widely different in character :—

*iso*Diazohydroxides are electrolytes of acid reaction with definite affinity constants, forming salts with dry ammonia and reacting directly with phosphorus halides and acyl halides.

Primary nitrosamines are non-conductors, without action on indicators, without measurable affinity constants, and not reactive at room temperature with phosphorus halides and acyl halides. They are *pseudo*-acids—that is to say, they will combine with an alkali, but only after undergoing tautomeric change, and thus produce a neutral salt—the *anti*diazotate. It follows, therefore, according to Hantzsch, that as the nitrosamines are not acids, the metallic *iso*diazotates cannot possess the nitrosamine constitution.

Hantzsch summarised his conclusions as to the constitution and relationships of the diazo-compounds in the well-known diagram shown below.



Criticisms of the Theory of Hantzsch.—As has been remarked, Hantzsch secured a wide measure of recognition for his theory, not by any incontrovertible proof, but by the accumulation of small pieces of evidence, and also possibly because the basic idea bears the stamp of *prima facie* probability. Opponents have not been lacking, but, the evidence being piecemeal, the attack has likewise been of necessity scattered and unable to gain a decisive victory. The opposition has chiefly concentrated on facts pointing to structural isomerism among the diazocyanides and the diazosulphonates; these arguments are set out below in discussing the theories of Bamberger and of Hodgson and Marsden. The latter also remark *inter alia* that Hantzsch's theory does not explain the endothermic formation of *iso*diazotates from diazobenzene or from *o*- or *p*-diazotoluene as compared with the ready and exclusive formation from *p*-nitrodiazo-benzene, and also that no stereoisomeric diazoethers have ever been prepared.

Because of the inherent possibility of isomerism in molecules containing cyanide and sulphite radicals, v. Pechmann examined the benzenediazo-sulphones (cf. p. 94). He could find no evidence of isomerides, nor did Hantzsch and Singer,[50] whilst Hantzsch and Dybowski proved that a supposed case of isomerism in the diazothiosulphonates had no basis in fact. Hantzsch said that the failure to find the expected isomers is because such compounds can exist only in the *anti*-form, which is almost certainly true because they are really azo-compounds.

Among the theories that chemists at the present day consider as likely to be demonstrated finally and conclusively as representing the constitutions of the diazotates, that of Hantzsch continues to hold a high place, though many keep an open mind as to which isomer represents the labile and the stable form. So the possibility remains that in the fulness of time the daring postulates of Hantzsch may take their place in the long line of inspired guesses which have so notably advanced the science of chemistry.

The Theories of Bamberger and of Hodgson and Marsden.—In his efforts to elucidate the problem of the constitution of the diazo-compounds, Bamberger studied their chemical reactions and attempted syntheses which would give unequivocal evidence of structure, whereas Hantzsch supplemented his chemical studies by physical measurements. In dealing with compounds so labile as the diazo-compounds, Bamberger was at some disadvantage—a disadvantage which was accentuated because he did not start from such a firmly held basic hypothesis as did Hantzsch. Consequently, although he contributed much to the knowledge of the reactions of the diazo-compounds, he changed his opinion as to their constitution more than once, and indeed for a time was in agreement with Hantzsch.[86] It may be said that it was he who compelled Hantzsch to hammer out his theory of the stereoisomerism of the diazotates, because in alliance with v. Pechmann and Frobenius he represented

the school which held that the diazotates are structural isomers. He accepted Blomstrand's constitution for the diazonium salts having been largely instrumental in its rehabilitation, though for some time he held that diazonium hydroxides combine directly with cations to form metallic diazotates.[31]

Bamberger [22, 24] insisted that the coupling power of the labile diazosulphonates, as well as their oxidation by iodine, is reasonably explained if they have the sulphite constitution, whereas the stable isomers, which undergo neither of these reactions, are sulphonates :—

$Ph{\cdot}N{:}N{\cdot}O{\cdot}SO_2K$	$Ph{\cdot}N{\cdot}N{\cdot}SO_3K$
Potassium diazobenzenesulphite	Potassium diazobenzenesulphonate
Normal or *syn*-salt	*iso*- or *anti*-salt

Claus [48] reached the same conclusion, though he reached it from the belief that potassium sulphite can exist in the form $KO{\cdot}SO_2K$, while the instability of the normal or labile form tallies with the known instability of the azo-group when attached to oxygen, as in the diazo-ethers.

Hodgson and Marsden [132] interpret the behaviour of the products formed by coupling *p*-nitrodiazobenzene with the two forms of benzenediazosulphonate in the same sense. The product (I) below, formed from the stable isomer, couples with β-naphthol to give exclusively *p*-nitrobenzeneazo-β-naphthol, while the regenerated stable diazosulphonate remains in solution. Now, (I) can only have the constitution :—

$PhN_2{\cdot}SO_2{\cdot}O{\cdot}N_2C_6H_4{\cdot}NO_2$ otherwise expressed as $PhN_2{\cdot}\overset{\ominus}{S}O_3\}\overset{\oplus}{N}_2{\cdot}C_6H_4{\cdot}NO_2$

and it couples on account of the breaking of the N·O link. But the product from the labile isomer gives a mixture of benzeneazo-β-naphthol and *p*-nitrobenzeneazo-β-naphthol, the latter appearing because the normal isomer is never free from the stable form. Hence, if coupling is preceded by breaking of an N·O link, the normal isomer must contain the group $Ph{\cdot}N{:}N{\cdot}O$ in order to give benzeneazo-β-naphthol, and hence it must have Bamberger's sulphite constitution.

The nitrosamine structure for the *iso*diazotates has always been the first choice of the believers in the structural isomerism of the diazotates, whilst the structure $Ar{\cdot}N{:}N{\cdot}OM$ has been favoured for the normal diazotates. Bamberger at first supported the school which held the above view and which drew its chief arguments from the facts of the acetylation of alkaline diazo solutions and the formation of hydrazones in coupling reactions. But, as the result of attempts to determine the constitution of the *iso*diazotates by synthesis, he was led to alter his view. He devised the synthesis of benzene diazotates from nitrosobenzene and hydroxylamine [32] :—

$$PhNO + H_2N{\cdot}OH = Ph{\cdot}N{:}N{\cdot}OH + H_2O$$

Although his product coupled instantly with β-naphthol, he considered that only traces of the normal compound had been formed as the first

product of reaction, and he therefore gave the above constitution to the *iso*-form. Hantzsch [69] said the reaction produces the normal diazotate, which must therefore have the *syn*-structure, arrived at by addition of the reactants followed by scission of a complex.

Undoubtedly Bamberger's most subtle attempt to come at the structure of the *iso*diazo-compounds was his synthesis from *o*- and *p*-hydroxybenzylaniline, which has already been described (cf. p. 131). The synthesis proceeds according to the scheme :—

$$p\text{-OH}\cdot C_6H_4CH_2\cdot NHPh \longrightarrow p\text{-OH}\cdot C_6H_4CH_2\cdot N(NO)Ph \longrightarrow p\text{-OH}\cdot C_6H_4CH_2\cdot OH + PhN{<}^{NO}_{K}$$

He considered that the nitrosamine salt thus produced has only a transitory existence, and that it isomerises into the *iso*diazotate, Ph·N:N·OK.

Faced with difficulties surrounding the constitution of the *n*-diazotates, he could not reach a fixed conclusion, but suggested the various forms shown in Table XLVI. One of these forms, $PhN{\nearrow}^{O}{:}NH$, later became the choice of the Italian school under Angeli.

Hodgson and Marsden [134] have adopted and modified Bamberger's and v. Pechmann's early views on the diazotates, in the attempt to circumvent the objections to Hantzsch's theory. They use the constitution Ar·N:N·OM for solid *n*-diazotates, while stressing that in aqueous solution the free diazohydroxide is in equilibrium between an ionised and unionised form :—

$$Ar\cdot N{:}N\cdot OH \rightleftharpoons Ar\cdot \overset{\oplus}{N}{:}N\}\overset{\ominus}{O}H$$

The *iso*diazotate they represent as an ion-pair * with the nitrosamine constitution $Ar\overset{\ominus}{N}(NO)\}\overset{\oplus}{M}$, which in dilute alkaline solution may give the equilibrium :—

$$Ar\overset{\ominus}{N}(NO)\}\overset{\oplus}{M} \rightleftharpoons ArN{:}\overset{\ominus}{N}O\}\overset{\oplus}{M}$$

Since Hodgson regards the undissociated *n*-diazohydroxide as the coupling reagent (cf. p. 234), the above explains why the *iso*diazotates will not

* For the definition of an ion-pair Hodgson and Marsden refer to Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., 1940, p. 40. "Ion Pairs, Triplets, etc.—The breakdown of the crystal into ions on solution need not be complete. It is probable that even aqueous solutions of ionic substances contain ion pairs, *i.e.*, pairs of ions of opposite charge held together by the electrostatic attraction due to their charge, but the concentration is so low that it is difficult to establish their presence with certainty. They are, however, easily shown to be present in liquid ammonia and the proportion is large in solvents of low dielectric constant. . . . In spite of the fact that the ion pair is a molecule of the salt it is impossible to write a useful structural formula for it. The structural formula is indissolubly bound up with the concepts of definitive links and of valence forces that exhibit the property of saturation. These characteristics are those of shared electron bonds; the electrostatic attraction involved in the formation of ion-pairs behave in an entirely different fashion. There is no saturation of valence, no definite linkage between the atoms of different ions; the ion pair is only one of a large number of equally important intermediates between ion and crystal."

couple in strongly alkaline solution, but in dilute alkali are converted by weak acids, including phenols, into the undissociated diazohydroxide, which at once couples. Further, the fact that alkaline stannite does not reduce *iso*diazotates is explained as due to the stability of the ion-pair which resists attack whereas the *n*-diazotates hydrolyse to an equilibrium with the diazonium hydroxide which is reduced by the alkali stannite.

Thus the characteristic of these latter views is not any fundamentally new proposal for the actual constitution of the diazotates, but an appreciation, lacking from the more rigid concepts of the earlier workers, of the facility with which by a small change of conditions one form passes into another form of the same or a different family of the diazo-compounds, these derived forms then taking part in reaction.

Hodgson and Marsden further believe the isomerism of the diazocyanides to be structural. Orton [67a] early suggested, but without any evidence, that the properties of the *syn*- and *anti*-diazocyanides could be well explained if they are *iso*cyanide and cyanide respectively :—

Ar·N:N·NC	Ar·N:N·CN
Labile or *sym*-diazocyanide	Stable or *anti*-diazocyanide

Hodgson and Marsden [134] produce as evidence for this view the interaction of labile diazocyanides with methylmagnesium iodide to give a complex which on hydrolysis affords aldehydes, a reaction parallel to the known behaviours of *iso*cyanides.

The evidence for the structural isomerism of the diazocyanides as against Hantzsch's theory has been carefully surveyed by Anderson, Le Fèvre, and Savage,[137] who repeated Hodgson and Marsden's work, and they concluded from the evidence of dipole moments, infra-red absorption spectra,[138] and magnetic optical rotation [139] that the diazocyanides are not structural isomerides, but behave like geometrical isomerides, and, indeed, on the evidence brought forward, the diazocyanides remain the most solid bastion for Hantzsch's theory and hence the most active centre of controversy.[140-4]

The Theory of Angeli.—There is a close relation between the diazo-compounds and the azoxy-compounds, one aspect of which Bamberger demonstrated by showing that a diazotate is produced by mild oxidative scission of *p*-azoxyphenol.[61] Angeli, who proved that oxidation of asymmetric azo-compounds affords structurally isomeric azoxy-compounds, $\begin{matrix}\text{Ar·N:N·Ar'}\\ \downarrow\\ \text{O}\end{matrix}$ and $\begin{matrix}\text{Ar·N:N·Ar'}\\ \downarrow\\ \text{O}\end{matrix}$, concluded [93, 94] that their analogy with the diazohydroxides, is so close that the diazohydroxides must also be structural isomerides of which four possibilities exist :—

Ar·N:N·OH	$\begin{matrix}\text{Ar·N:NH}\\ \downarrow\\ \text{O}\end{matrix}$	$\begin{matrix}\text{ArN:NH}\\ \downarrow\\ \text{O}\end{matrix}$	Ar·NH·NO

As the guiding reaction to decide which of the above is to be selected as the normal and which as the *iso*-diazotate, Angeli [97] used the alkaline hydrolysis of benzeneazoxycarbonamide, which he had already shown to be hydrolysed by cold caustic alkali to give a solution which contains benzene *n*-diazotate. Benzeneazoxycarbonamide is made by oxidation with hydrogen peroxide of benzenediazocarbonamide, $Ph{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$ (cf. p. 146), and Pieroni [93a] could not find evidence that more than one isomer is produced, though it has four possible constitutions, the last having been suggested by Hodgson :—

$$\underset{\downarrow\ \text{O}}{\text{PhN:N}{\cdot}\text{CO}{\cdot}\text{NH}_2}\ (1) \qquad \underset{\downarrow\ \text{O}}{\text{PhN:N}{\cdot}\text{CO}{\cdot}\text{NH}_2}\ (2) \qquad \text{PhN}{\cdot}\text{NO}\ \text{CO}{\cdot}\text{NH}_2\ (3) \qquad \text{PhN:N}{\cdot}\text{CO}{\cdot}\text{NH}{\cdot}\text{OH}\ (4)$$

The third compound is known, and is the very unstable nitrosophenylurea, while the fact that benzeneazoxycarbonamide cannot be nitrated at once rules out the second and last compounds, for among the isomeric asymmetric azoxy-compounds nitration is the chief means of discovering to which nitrogen atom the oxygen is attached, since, like the nitro-group, it diminishes the possibility of nitration of the nucleus to which it is attached. The constitution of benzeneazoxycarbonamide is thus determined as $\underset{\downarrow\ \text{O}}{\text{PhN:N}{\cdot}\text{CO}{\cdot}\text{NH}_2}$, and hence it is difficult to escape the conclusion that the sodium benzene *n*-diazotate formed from it by alkaline hydrolysis has the constitution $\underset{\downarrow\ \text{O}}{\text{PhN:N}\}^{\ominus}\text{Na}^{\oplus}}$. As is to be seen from Table XLIV, this constitution was first put forward by Bamberger, but later abandoned by him, whilst Walther,[29] from a study of diazoamino-compounds, was also led to formulate the diazohydroxides as containing pentavalent nitrogen in a form which would have the present-day notation $\underset{\downarrow\ \text{O}}{\text{PhN:NH}}$. Another piece of evidence pointing to the same constitution as Angeli's appeared quite unexpectedly when Farrar and Gulland [133] discovered that condensation products made by them from Chloramine T (sodio-*p*-toluenesulphonchloroamide, $p\text{-}C_6H_4Me{\cdot}SO_2NClNa$) and arylnitroso-compounds and named by them azoxysulphones, when boiled for a few seconds with an aqueous alcoholic solution of β-naphthol affords a good yield of the arylazo-β-naphthol :—

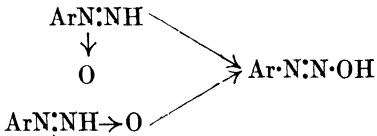
$$\underset{\downarrow\ \text{O}}{\text{ArSO}_2{\cdot}\text{N:N}{\cdot}\text{Ar}} + \text{H}_2\text{O} \longrightarrow \text{Ar}{\cdot}\text{SO}_3\text{H} + \underset{\downarrow\ \text{O}}{(\text{ArN:N})^{\ominus}} + \text{H}^{\oplus}$$

Angeli thought that the *n*-diazohydroxides may have either of

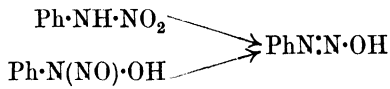
two constitutions which contain what he called "twinned double bonds" :—



On his theory the formation of the *iso*diazo-compounds is brought about and the reactivity at the same time diminished, by the nitrogen passing into the tervalent state, and hence the reason why so drastic a means as caustic fusion is often necessary :—

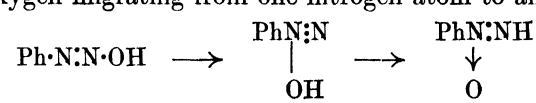


This constitution for the *iso*diazohydroxide agrees with Bamberger's, and is in line with his production of *iso*diazotates by the reduction of both phenylnitroamine and nitrosophenylhydroxylamine :—



Angeli is careful to explain that the above constitutions are those of the diazohydroxides, and that the metallic diazotates, especially in the solid state, may not have the same constitution, but that the characteristic reactions of the *n*-diazotates are essentially those of the diazohydroxides produced by hydrolytic dissociation of the metal salts even in dilute alkaline solution.

Angeli's constitution for the *n*-diazotates explains why their normal mode of reaction is to behave as oxidising agents, and a considerable number of such reactions have been examined by the Italian chemists, and have been noted elsewhere in this book. Cambi and Szegö [100] examined and compared the absorption spectra of diazotates with arylnitramines and arylnitrosohydroxylamines, and reached the conclusion that in the *n*-diazohydroxides the nitrogen is pentavalent. The difference in both structure and valency of the nitrogen, of course, at once explains why the normal and *iso*diazohydroxides differ in their reaction to certain reagents such as sodium stannite (cf. p. 132) or nitrohydroxylamine, which Bigiavi [110] found not to attack *iso*diazotates, but to give nitrosobenzene from benzene *n*-diazohydroxide. The same chemist explained the change back of the *iso*-diazohydroxide into the normal form, a change usually supposed to go through the diazonium form, and always requiring a diminution of alkalinity, as being analogous to the Beckmann transformation, oxygen migrating from one nitrogen atom to another [105] :—



Angeli's constitution for the *n*-diazohydroxides compelled him to represent many reactions of the diazo-compounds as addition reactions, followed by scission of the complex first formed. Thus, coupling and diazo-ether formation are represented as [93, 94] :—

$$\begin{array}{lllll} \mathrm{Ar{\cdot}N{:}NH} + \mathrm{PhOH} & \longrightarrow & \mathrm{Ar{\cdot}N(OH){\cdot}NH{\cdot}OPh} & \longrightarrow & \mathrm{Ar{\cdot}N{:}N{\cdot}OPh} \longrightarrow \mathrm{Ar{\cdot}N{:}N{\cdot}C_6H_4OH} \\ \downarrow\,\mathrm{O} & & & & \\ \mathrm{Ar{\cdot}N{:}NH} + \mathrm{Alk{\cdot}OH} & \longrightarrow & \mathrm{Ar{\cdot}N(OH){\cdot}NH{\cdot}OAlk} & \longrightarrow & \mathrm{Ar{\cdot}N{:}N{\cdot}OAlk} + \mathrm{H_2O} \\ \downarrow\,\mathrm{O} & & & & \end{array}$$

Present knowledge of the coupling reaction (cf. p. 230) suggests that such a mechanism as the above is unlikely, but if a compound $\mathrm{ArN{:}NH}$ is a
$\downarrow\,\mathrm{O}$
n-diazohydroxide or the immediate precursor of one having Hantzsch's or Hodgson's constitution, $\mathrm{Ar{\cdot}N{:}N{\cdot}OH}$, then there is no escape from the conclusion that in the diazohydroxides an oxygen atom is easily able to change its attachment from one nitrogen atom to the other. Pieroni [93a] apparently took such a migration for granted when he represented the hydrolysis of *p*-bromobenzeneazoxycarbonamide by cold aqueous caustic potash to give a compound coupling with β-naphthol by the stages :—

$$\begin{array}{lllll} p\text{-}\mathrm{C_6H_4Br{\cdot}N{:}N{\cdot}CO{\cdot}NH_2} & \longrightarrow & \mathrm{C_6H_4Br{\cdot}N{:}N{\cdot}CO_2H} & \longrightarrow & \\ \downarrow\,\mathrm{O} & & \downarrow\,\mathrm{O} & & \\ & & \mathrm{C_6H_4Br{\cdot}N{:}NH} & \longrightarrow & \mathrm{C_6H_4Br{\cdot}N{:}N{\cdot}OH} \\ & & \downarrow\,\mathrm{O} & & \end{array}$$

Cambi [111] frankly declared that oxygen associated with the group ·N:N· can easily migrate from one nitrogen atom to the other, but, as Farrar and Gulland remark, there is neither analogy nor experimental support for belief in such a migration, and at the present time some Italian chemists represent the undissociated *n*-diazohydroxide as $(\mathrm{Ar{\cdot}N{:}NH}) \rightarrow \mathrm{O}$ thus leaving open the question of the point of attachment of the oxygen while indicating its oxidising properties.

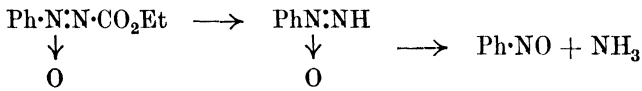
Angeli's theory has also run the gauntlet of criticism, especially by Hantzsch, who called in question the interpretation of the absorption spectra.[102] Other criticisms may be condensed as follows :—

1. That salts of the *n*-diazohydroxides have the metal attached to oxygen, and not to nitrogen, as must be the case in a compound of the constitution proposed by Angeli. In this the defect of the nitrosamine constitution reappears and it was the central point in his polemics with Hantzsch.[99]

2. Normal benzenediazotates are oxidised in alkaline solution to salts of phenylnitroamine, $\mathrm{PhNH{\cdot}NO_2}$, which would be impossible on Angeli's constitution.

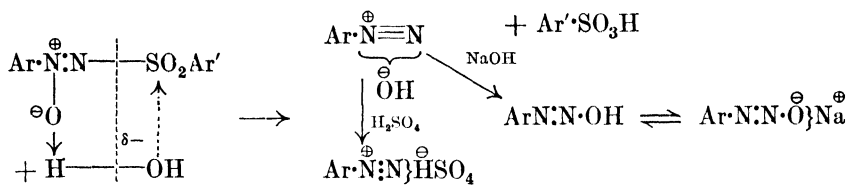
3. Angeli's constitution cannot explain the isomerisation of normal to *iso*diazo-compounds which takes place even in the solid state, as the change would require the migration of an oxygen atom, whereas, according to Hantzsch, the change is merely one of position, and so can take place without the substance being dissolved.[120]

4. The substance having Angeli's constitution for the *n*-diazohydroxide would be iminonitrobenzene, and it can be formed by hydrolysis of benzeneazoxycarbonic ester, a process in which nitrosobenzene and ammonia are said ultimately to appear :—



No diazo-compound has ever been observed to decompose in the above way and therefore the supposed intermediate, if it is a diazo-compound, cannot have such a constitution as the above.[113, 120] Farrar and Gulland [133] say that this criticism, which has carried much weight, is possibly beside the point, since the experiments were carried out with compounds which may not have been pure.

5. Hodgson and Marsden [135] have suggested that the hydrolysis of the azoxysulphones can take place in such a manner than an aryldiazonium hydroxide is formed and passes into a diazonium salt or a diazotate, according as the solution is acid or alkaline :—



Thus no intermediate of Angeli's constitution is formed, and the question of the migration of oxygen does not arise.

There are few chemists who to-day would dismiss the work of Angeli as having nothing to contribute to the solution of the riddle of the constitution of the diazo-compounds, and it is likely to stay the course until the truth is finally known.

Diazo-Compounds and the Electronic Theory of Valency.— In its evolution up to the present time (1947) the electronic theory of valency has not been able to produce any general principle on the basis of which the question of the constitution of the diazo-compounds can be settled. Hence the electronic constitutions due to Sarkar,[128] and set out in Table XLIV, really amount to giving electronic interpretation to constitutions already arrived at by the older methods, though at the same time the electronic theory is unable to refute the claims of the alternative forms.

For the diazonium salts Sarkar accepts the established constitution, but assigns two electron formulae, which he holds to be indistinguishable in which he agrees with Waters and Stephenson but it is a point on which the work of Schoutissen on the coupling of tetrazo-compounds throws doubt.

He rejects Hantzsch's stereochemical theory, holding, with Bamberger and Angeli, that the *n*-diazotates, on account of their close resemblance to the diazonium salts, must contain a pentavalent nitrogen atom, but it cannot be agreed that his method of escape from Bamberger's dilemma—*viz.*, that the same hydroxide cannot be both a base and an acid—is a happy one. The instability of the *n*-diazotates he ascribes to disproportionate sharing of electrons between the nitrogen atoms which his formula indicates. To the *iso*diazotates he accepts the constitution of Angeli and of Bamberger.

This attempt to apply the electronic theory of valency cannot be regarded as more than a preliminary exercise in the problem, for a full solution must include provisions for explaining the effects of substituents on stability not only of the normal and *iso*diazotates but also for diazocyanides, and diazosulphonates and the problems of their isomerism.

CONCLUSION

The foregoing account of the chemistry of the aromatic diazo-compounds may be likened to a small-scale map of a piece of country, and this map, however crude its cartography, is offered to all fellow-chemists of every nationality who wish to visit and explore the country of the diazo-compounds. Sprung from the legacy of Peter Griess to humanity, this country has been created entirely by the intellect and skill of man, for although founded on the laws of Nature, and existing only in obedience to them, the diazo-compounds are not found in the free state in Nature. The topography of the diazo-country includes grimy industrialised valleys where men work for their living, some pleasant uplands of refreshing academic contemplation, and some as yet unscaled aiguilles. Where the limits of the diazo-country are to be drawn remains as yet undiscovered. This book merely attempts to mark and sign-post the major roads traversing the country, and the smallness of the scale may in some places lead to error or confusion. To have made a much larger scale map would have been easier for the author, but that would have made it difficult for readers to see the country as a whole. Finally, at the confines of this country, there are set barriers which only those willing to undergo an intellectual discipline of study may pass, while for those who would explore there is only one point of departure—that from which Peter Griess originally effected his entry—the laboratory bench.

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AUTHOR INDEX

Abt, 249
Abel, 48
Abraham, 60
Abrams, 66
Adams, 81, 104
Acree, 293
Agfa, 22, 23, 83, 97
de Aguiar, 250
Ahmed, 342
Ahrens, 309
Ainley, 220
Albanesi, 138
Albert, 43, 60
Albrecht, 192
Alcock, 43, 401
Alexander, 272
Algerino, 155, 177
Alink, 372
Allen, 238
Allied Chem. & Dye Corp., 9, 69
Altschul, 5, 50
Ambühl, 176, 238
American Cyanamid Co., 15, 60, 172, 179
Ammelburg, 119
Ampola, 68
Anan'ina, 20
Andersen, 351
Anderson, D., 144, 145, 394
Anderson, L. C., 31, 34
André, 352
Andresen, 357
Andrewes, 346
Angeli, 60 127, 146, 186, 233, 275, 285, 385, 389, 394, 395, 396, 397
Angelico, 60
d'Angelo, 43, 60
Arkhipov, 81
Armstrong, 286, 401
Arnoldi, 43
Asano, 322
Atlas Powder Co., 355
Atkinson, C. M., 245
Atkinson, E. R., 312,
v. Auwers, 218, 238, 240
Avenarius, 258
Avery, 104, 117, 138, 153, 177, 330
Ayling, 230

Bär, 226
Babbitt, 352
Bachmann, 261, 322
Back, 265
Bader, 97, 235
Badl, 176
Baeyer, 42, 169
Bailar, 271
Bailey, 148
Bain, 387
Baker, 34
Balle, 258
Balz, 80, 277, 283
Bamberger, 19, 20, 22, 31, 33, 39, 45, 50, 51, 60, 61, 124, 126, 127, 128, 131, 133, 134, 139, 140, 145, 149, 156, 169, 179, 180, 181, 185, 189, 215, 223, 228, 238, 246, 252, 271, 318, 380, 382, 384, 387, 389, 391, 392, 393
Barac, 352
Barbaro, 308
Barber, 310, 336
Barbieri, 238
Bardach, 176
Barger, 258
Barnard, 372
Barrensheen, 351
Bart, 80, 331, 332, 333
Bartlett, 230, 231
B.A.S.F., 22, 28, 35, 124, 135, 139, 236, 322
Batko, 351
Battegay, 14, 33, 43, 81, 116, 124, 239, 301, 322, 371, 381
Baudisch, 145, 182, 401
Bauer, C., 200, 225
Bauer, H., 176, 335
Baum, 35
Bayer, 9, 14, 22, 50, 68, 84, 85, 116, 186, 237, 251, 292, 329, 330
B.D.C., 308
Bean, 104
Beccari, 351
Becker, P., 42, 83
Becker, W. W., 351
Beckh, 176
Bedwell, 145, 402
Beekmann, 292
Beeson, 275, 311
Béha, 43, 81, 308, 322, 381
Behrend, 60
Belipa, 376, 377
Bell, 238
Benati, 267, 293
Benbrook, 20, 63, 64, 304
Benda, 22, 23, 43, 124, 335
Bennett, 330

Berger, 286, 318
van den Bergh, 346
Bergmann, E., 239, 321
Bergmann, F., 323
Bergstrom, 127
Berlin Aniline Co., cf. Agfa
Bernthsen, 169
Berry, 330
Bertheim, 292
Berthelot, 352, 354, 357
Bertrand, 376
Bevan, E. J., 361, 364, 373
Bevan, H. G. L., 348
Beyer, C., 237
Beyer, K. H., 347
Beysen, 14
van Biema, 238
Bigiavi, 132, 396
Biginelli, 44
Billiter, 323
Binder, 80, 164
Bindewald, 239
Bini, 138
Binz, 333
Birtwell, 30, 31, 34, 115, 273, 279, 281, 322
Bischler, 186
Blagden, 280, 294, 296
Blangy, 12, 44, 116
Blankenburg, 233, 402
Blas, 336
Blaszkovska, 354
Bleier, 261
Blomstrand, 39, 149, 379, 380
Blumberger, 64, 66, 67, 229, 240, 330
Böcking, 35
Böeseken, 46
Böhmer, 32, 115, 289, 296
Börnstein, 298, 330
Bössneck, 249
Böttger, 17
Bodenstein, 239
Boehler, 14, 117, 301
Boehringer, 356
Boekelheide, 320
Bogolovski, 298
Bolth, 338
Bondzýnski, 351
Booth, 292
Borgesius, 372, 375, 376
Borghaus, 26, 149
Borsche, 238, 239, 243, 322
Bowers, 336
Boyd, S. N., 245
Boyd, W. C., 236
Boxer, 236
Bradfield, 181
Bradford, 372
Bradley, 227
Brandsma, 46
Brandt, 402
Brass, 192, 239
Bratton, 352
Braun, E., 238
Braun, P., 371
Bremer, 60
Breslow, 231
Bressel, 60
Brewster, 272
Briner, 18
British Celanese, 60, 374
Brodski, 186
Bromwell, 309
Broun, 308
Brown, 360, 361
Browning, 356
Brown Line Co., 374
Brühl, 40, 386, 400
Brütsch, 237
Bruning & Co., 377
Büchner, 322
Bülow, 23. 155, 210, 308
Bürkle, 240
Bucherer, 9, 90, 102, 132, 136, 139, 147, 223, 239, 240, 293, 294, 342, 376
Buckow, 258
Buehler, 138
Burawoy, 226
Burchfield, 292
Burdett, 358
Burge, 272
Burger, 32
Burgess, 52
Burns, 92
Burr, 237
Busch, 177, 237, 238, 244, 326
Busoni, 111, 274
Buss, 240
Busson, 352
Butleroff, 379
Butterworth, 323
Butterworth-Judson Corp., 117

Cain, ix, 61, 62, 66, 196, 303, 386, 401
Cairns, 267
Calco Chem. Co., 179, 238
Calderbank, 402
Calico Printers Assoc., 238
Cambi, 397
Cameron, F. K., 275
Cameron, J. M. L., 265
Camiglieri, 67, 130
Campbell, 238, 250
Cantzler, 291, 301
Capuano, 60
Carey, 53
Caro, 42, 354
Carter, 60
Caspar, 26, 81, 193, 310
Cassella, 28, 35, 75, 292, 321, 335
Cauffmann, 275
Cellophane Soc., 374
Chabrol, 352
Challenger, 81, 329

Chamberlain, 270
Charonnat, 352
Charrier, 81
Chattaway, 50, 77, 154, 155, 192, 235, 311
Chatterjee, 315
Cherkasskiĭ, 100
Cherline, 336
Chervinskaya, 9
Chromogen, Inc., 377
Chwala, 43, 193, 327
Ciusa, 147, 357
Claas, 43, 94
Claborn, 308
Claisen, 237
Clark, 354
Clayton Aniline Co., 254, 330
Claus, 11, 13, 149, 392
Cleage, 37
Clemens, 351
Clement, 376
Clemo, 124, 292
Clifford, 330
Coates, 358
Cockburn, 124, 292
Coffey, 237
Colbert, 315
Collins, 351
Conant, 230, 234
Consden, 154
Contardi, 277, 293, 295, 296
Cook, A. H., 228
Cook, J. W., 257
Corbellini, 308
Corbishley, 104, 138, 237
Corse, 315
Couzens, 401
Craig, 288
Crook, 322
Cross, 361, 364
Crossley, 20, 63, 64, 304
Crowe, 237
Crymble, 239
Culbransen, 356
Cullinane, 262, 263
Culmann, 186, 191, 275, 313
Cumming, 288, 290, 298
Cunze, 147
Curatolo, 315
Curtius, 126, 176, 187, 382
Cyriax, 233

Dachselt, 342
Daddi, 346
Danziger, 147
Darling, 265
Dashiell, 309
Davey, 263
Davidson, C. S., 352
Davidson, W. B., 33, 77, 400
Davies, G. R., 27, 246
Davies, J. S. H., 92
Davies, W., 183, 184
Daur, 237
Debenedetti, 308
de Degiorgi, 81
Degering, 238
Dehn, 169, 354, 355
De Jonge, 372
Demidova, 238
Demuth, 253
De Montmollin, 192
Dennett, 312
Desai, 152, 372
Deutsche Werke Kiel, 373
Dey, 124
Deybeck, 40
Dietzgen, 375, 376
Dieckmann, 237
Dijkstra, 372
Dilthey, 233, 402
Dimant, 323
Dimroth, 36, 43, 141, 159, 160, 165, 166, 169, 192, 232, 233, 267
Dinger, 258
Dippel, 372
Diserens, 104
Doak, 333
Dobbie, 265, 267, 293, 384, 389
Dolder, 372
Dombrowski, 351
Dorst, 372
Dostrovsky, 240
Dovey, 92
Dresel, 12
Drumm, 46
Duden, 238
Dunbar, 92
Dunkel, 322
Dunker, 81, 338
Dunn, J. T., 193
Dunn, R., 352
Du Pont, 9, 50, 69, 93, 117, 178, 179, 236, 292
Durand & Hugenin, 179
Durmaschkina, 372
Dutt, 192
Duval, 216
Dvorák, 295
Dwyer, 162, 168, 169, 343
Dybowski, 95, 391
Dziewonski, 239

Eagle, 236
Earl, 47, 158, 159, 167
East, 305
Eastman Kodak, 9, 253
Eberle, 18
Ebersole, 156
Ebert, 192
Eble, 165
Eckert, 308
Eder, 362
Effront, 274

Eggert, 362
Ehrenpreis, 298
Ehrhardt, 321
Ehrlich, 344, 345
Eibner, ix, 138, 238, 271
Eichenberger, 276, 323
Eichhorn, 352
Eichler, 339, 352
Eickel, 258
Ekbom, 95, 298
Elderfield, 258
Elias, 9
Elion, 15
Eliot, 238
Elliott, 27, 235
Elkins, 228
Elks, 318
Elsey, 292
Engel, 239
Engler, 132, 134, 135, 401
Entwistle, 369, 377
Emdé, 373
van Emster, 322
Epifansky, 338
Epstein, 25
Erban, 7
Erber, 15
Erdmann, 250, 285, 286
Erlenmeyer, 379
Ernert, 60
Erzberger, 250
Eskin, 338
Esser, 377
Evelyn, 352
Evens, 35, 124, 235, 273
Everatt, 235, 272
Ewers, 95
Eynon, 51
Eyre, 119
Euler, 62, 65, 102, 140, 401

Fabrique de Thann & Mulhouse, 83
Faldino, 236
Falta, 372
Fandrich, 310
Farmer, 226
Farrar, 128, 156, 295, 396
Favrel, 237
Feasley, 238
Fedorova, 309
Feer, 79, 83, 369
Feitler, 285
Feret, 373
Fernelius, 177
Fichter, 329
Field, 352
Fierz-David, 44, 104, 192, 207, 232
Fieser, 235, 238
Fiessinger, 352
Filippytschew, 224
Film Ozaphane, 373, 374, 375, 376
Finger, 253
Finke, 242
Finzi, 22
Fischer, B., 176, 178
Fischer, E., xi, 50, 148, 183, 191, 241, 302, 343, 379, 380
Fischer, I. H., 351
Fischer, O., 39, 40, 51, 200, 225, 261
Fisher, 237
Flegontov, 338
Fleischner, 238
Fletcher, 193
Földi, 77, 333
Fones, 290
Forgan, 321
Forster, Sir M., 60, 154, 166, 192
Forsyth, 322
Foster, 270, 305, 306
Fowweather, 346
Fox, 265, 267, 293
Frahm, 92
France, 39, 313
Francolor, 247
Frangialli, 374, 375, 376
Frankland, 235
Freese, 193
Frehden, 240
Frei, 238
Freimann, 235, 238
Frentzel, 322
Freri, 235, 238, 239
Frey, 44
Freyss, 374
Fridman, 372
Friebel, 311
Friedemann, 37, 43, 142
Friedenwald, 351
Friedheim, 356
Friedländer, 11, 43, 69, 124, 192, 193, 271, 327
Friedman, 236
Fries, 254
Friese, 238
Friswell, 163
Fritsch, 239
Fröhlich, A., 92, 138, 301
Fröhlich, E., 155
Frobenius, 40, 129, 133, 139, 140, 160, 384, 391
Fry, 267
Fuchs, 15
Fuller, 348
Fukui, 40
Fukushima, 362
Funk, 80
Fussler, 372

Gabriel, 143, 247
Gad, 35
Gadamer, 258
Gaess, 119
Gajdos, 352
Gajewski, 236

Galpern, 238, 351
Gardikas, 352
Gardner, 352
Garforth, 92
Garland, 166
Garton, 81, 192
Gasirowski, 186, 191, 274, 275, 277, 313
Gaspar, 375
Gattermann, 11, 22, 28, 192, 236, 275, 287, 301, 311, 323
Gatti, 261
Gauge, 265, 267, 293
Gaus, 245
Gay, 373, 374
Gebauer-Fülnegg, 142, 221, 351
Gehren, 292
Geigy Co., 35, 116, 235, 236, 237, 330
Gen. Aniline & Film Corp., 139, 179, 239, 377
General Aniline Works, 179
Gerilowski, 137, 382, 389
Gerngross, 313
Giannini, 138
Gibbs, 148
Gibson, 334
Giguère, 323
Gil, 352
Gilman, 9, 81, 335
Gipp, 338
Girard, 19, 20
Glogauer, 94
Gluschnev, 338
Glutz, 148
Godden, 249
Godfried, 352
v. Goldberg, 247
Goldberger, 138
Goldschmidt, 102, 163, 165, 166, 196, 197, 229, 233, 380
Golosenko, 340, 342
Gomberg, L. L., 238
Gomberg, M., 60, 316
Goodeve, 363
F. B. Goodrich Co., 179
Gortner, C. V. and R. A., 228
Gorvin, 230
Goske, 169
Govindachari, 124
Grässler, 96
Grachev, 101, 351
Graebe, 161, 261, 262, 263, 264, 325, 330
Graham, 275
Grandmougin, 35, 184, 191, 192, 235, 238, 246
Gray, C. H., 352
Gray, W. H., 43, 81
Greco, 345
Green, 163, 254, 301, 342, 361, 364
Greiner, 60
Grieshammer, 177
Griesheim, 139, 182
Griess, xi, 1, 2, 7, 12, 16, 17, 22, 23, 25, 26, 27, 42, 51, 61, 76, 126, 128, 133, 143, 148, 153, 157, 159, 160, 169, 186, 187, 197, 201, 223, 236, 248, 268, 271, 276, 277, 290, 298, 302, 309, 310, 324 325, 349, 354, 378, 379
Grieve, 39, 109, 322
Griffin, 275, 297
van der Grinten, 373, 374, 375, 376, 377,
van der Grinten, jun., 372
Grist, 133
Groggins, ix
Groot, 355
Grube, 253
Gruhl, 165
Gross, 253
Gueffroy, 292
Guitermann, 238
Gulland, 128, 395, 396
Gunzert, 152
Guppy, 177
Gusman, 81
Gutmann, 132, 335, 342

Hähle, 321
Haager, 40
Hadler, 67
Haendel, 153, 374
Haggerty, 67
Hahn, 349
Halberstadt, 262
Halden & Co., 374, 375, 376
Halévy, 329
Hall, 148
Hall, Harding, Ltd., 377
Haller, 305, 306
Hallmann, 238
Halmos, 376
Hamilton, 336
Hammett, 232, 393
Hammick, 401
Hanby, 115
Hanke, 347
Hanson, 235
Hantzsch xi, 19, 24, 26, 33, 38, 39, 41, 45, 46, 48, 51, 60, 62, 64, 66, 77, 78, 94, 95, 101, 102, 125, 127, 129, 132, 133, 134, 135, 140, 141, 143, 144, 145, 149, 153, 154, 168, 182, 185, 193, 226, 239, 271, 280, 284, 294, 296, 309, 311, 340, 358, 380, 381, 382, 383, 384, 385, 387, 388, 389, 390, 393, 397, 398
Harberts, 402
Harding, 375, 376, 377
Harington, 236
de la Harpe, 350
Harper, 375
Harris, 9
Harrison, 240
Hartley, G. S., 147, 228, 357
Hartley, H., 239
Hartmann, 232

Hartung, 336
Haselhorst, 351
Hass, 9
Hathway, 30
Haussknecht, 323
Hauser, 231
Hausser, 62
Haworth, J. W., 317
Haworth, R. D., 258, 328
Hay, 118
Hayduck, 293, 308
Heath, 322
Heaton, 178, 179
Heertjes, 25, 402
Heidelberger, 177, 335
Heidlberg, 25
Heilbron, Sir I., 39, 261, 313, 317
Heilmann, 239
Hein, 27
Heinichen, 303
Heinrich, 351
Heller, 143, 197, 225, 253, 291
Henderson, 328
Hendrickson, 352
Henrich, 237
Henriques, 238, 372
Henry, 169
Hepburn, 41, 89, 90, 91
Herbert, 243
Hercules Powder Co., 355
Hermanns, 351
Herschmann, 176
Herz, 60, 354
Heumann, 176
Heusler, 176, 292
Hewitt, 238
Hey, 39, 109, 111, 113, 114, 134, 261, 313, 316, 317, 318
Heyden, 335
Hickinbottom, 202, 236
Hidegh, 197
Hilgenberg, 293
Hill, 235
Hills, 47
Himmat, 92
Hindenburg, 251
Hinkel, 230
Hinman, 51
Hird, 38
Hirsch, B., 19, 43, 125
Hirsch, R., 62, 176, 308, 315
Höbold, 43
Hölzle, 330
Hobson, 256
Hodgson, 13, 24, 26, 27, 30, 31, 34, 41, 43, 67, 77, 101, 113, 146, 149, 150, 156, 197, 225, 229, 231, 232, 234, 254, 269, 270, 271, 273, 274, 276, 279, 280, 281, 283, 285, 291, 294, 295, 299, 300, 302, 305, 306, 313, 315, 318, 381, 390, 391, 392, 393, 394, 398, 402
Hoffman, 323
v. Hofmann, A. W., xi, 247, 250, 308
Hofmann, K. A., 43
Hoffmeister, 308
Hollmann, 51
Hollemann, 292
Holliday & Co., 28
Holliday, T. and R., 69
Holm, 165
Holm-Hansen, 322
Holzach, ix, 236
Holzer, 351
Hooker, 236
Hoover, 9
Hopff, 238
Hopkins, 307
Horio, 362
Houston, 20
Howis, 179
Howles, 355
Hromatka, 258
Hübner, 147
Hubalek, 40
Huber, L., 40
Huber, M., 290
Huber, W. F., 293
van der Hulst, 402
Hummel, 373
Hunter, G., 345, 346, 347
Hunter, L., 167, 228
Hunter, R. F., 53
Hunter, W. H., 265
Hurd, 60, 236
Hurtley, 330
Huthwelker, 402
Huysers, 372

Iacoubovitch, 336
I.C.I., 15, 35, 93, 97, 153, 178, 179, 235, 239, 323, 375
I.G., 9, 15, 22, 23, 25, 28, 44, 60, 68, 75, 93, 96, 98, 117, 139, 150, 151, 153, 171, 178, 179, 235, 236, 237, 238, 239, 247, 261, 265, 275, 292, 301, 308, 322, 330, 336, 356, 373, 374, 375, 376
Ikuta, 24, 51
Illgen, 251, 265
Ilosva, 349
Inamura, 239
Indovina, 66, 138, 308, 372, 402
Ingold, 273
Inouye, 351
Interchem. Corp., 98, 179
Irschick, 238
Ivanova, 238, 351
Iwamoto, 9

Jäger, 42, 51, 169
Jänicke, 40
Jackson, 237
Jacobs, F., 374
Jacobs, W. A., 177, 335
Jacobson, 11, 24, 40, 254, 275, 317

Jadassohn, 44, 236
Jaeckel, 258
Jambuserwala, 218
Janssen, 254
Japhe, 323
Japp, 210
Jean, 237
Jenisch, 210
Jenkins, 81, 338
Jörgensen, 240
Jochem, 19, 275, 309
Joffe, 221, 239
Johnsen, 177
Johnson, E. S., 235
Johnson, P., 69
Johnson, T. B., 20
Jolles, 67, 68, 111, 113, 130, 186, 275, 308, 401
Jonas, 18, 322
Jones, D. G., 240,
Jones, E., 275

Kačer, 14
Kahn, 81, 338
Kalb, 237, 302, 332
Kaljanov, 236
Kalle, 22, 35, 97, 116, 117, 254, 303, 330, 373, 374, 375, 376, 377
Kamedo, 322
Kaminski, 81, 329
Kanesaka, 350
Kapeller-Adler, 236
Karrer, 22, 202, 233, 236, 331
Kastle, 20
Kauffmann, 44
Kaufler, 19, 22, 44, 293
Keefer, 351
Kehrmann, 14
Keimatsu, 329
Keiser, 20
Kekulé, 33, 197, 248
Kekwick, 352
Keller, 240
Kench, 352
Kendall, 267
Keneford, 245
Kenner, 47, 48, 113, 167
Kenyon, 154
Keppeler, 240
Kershaw, 269
Keuffel, 377
Keuning, 372
Key, 192
Kidd, 163
Kiefer, 309
Kienle, 20, 63, 64, 304
Kienzle, 117
Kimball, 322
Kimich, 238
Kindlmann, 184
Kingan, 334
Kinne, 60
Kinzelberger, 75
Kirzner, 359
Kischner, 104
Klason, 330
Klausing, 177
Klemenc, 33
Klett, 244
Klimova, 338
Klingemann, 210
Klingler, 258
Klug, 240
Knapp, 117, 275
Knecht, 16, 65, 340
Kniatovna, 81, 329
Knoevenagel, 17, 312
Knorr, 60
Kögel, 366, 375
Köhler, 236
König, A., 253
König, W., 236, 239
Königs, *see* Koenigs
Körner, 277, 293, 296
Kocheshkov, 81, 335, 338
Kodak, 377
Koechlin, 69
Koelsch, 320
Koenigs, E., 24, 60, 322
Koenigs, W., 186, 331
Koessler, 347
Kohn, 338
Kolb, 25
Kolbe, 1
Komori, 351
Konink, 19
Kopp, 9
Kornfeld, 244
Korolev, 343
Kortright, 275
Korczynski, 77, 310, 323
Kozlov, 28, 30, 81, 330
Krasova, 104
Kratz, 253
Kraus, 35, 124, 156, 322
Krebser, 330
Kretschmer, 152
Krishnamurthy, 18, 308
Krokiewicz, 351
Krollpfeiffer, 238
Krugliakoff, 138
Kühling, 317, 318
Küster, 237
Kuchenbecher, 182
Kuhara, 40
Kuhlemann, 237
Kuhlmann, 98, 124, 139, 178, 179
Kuhn, 216, 226, 267, 323
Kunz, J., 51, 312
Kunz, M. A., 322
Kusnetzov, 351
Kvalnes, 322

Lacey, 315

Ladenburg, 250
Lambert, 236, 323
Lampl, 236
Lamplough, 68
Landsberg, 325, 329
Landsteiner, K., 182, 205, 236
Lange, M., 27, 153, 298
Lange, W., 81
Langfurth, 400
Langguth, 373
Lantz, 35, 90, 375
Lapworth, 328
Laue, 238
Lauer, 239, 240
Laurence, 47
Lauth, 11, 51
Lawlor, 322
Lawson, 7, 249
Lecco, 186
L'Ecuyer, 323
Lee, 343
Le Fèvre, 142, 144, 145, 167, 240, 372, 394
Lehmann, 374
Leichtlin, 36, 43, 142
Leigh, 275, 300
Leimdörfer, 346
Leitch & Co., 236
Lellmann, 78, 280
Lenhardt, 238
Lenz, 182, 292
Lesser, 35
Lesur, 65
Leuck, 235
Leukardt, 325
Levi, 236
Levin, 51, 92, 104, 138
Levinstein & Co., 23
Levinstein, H., 238, 322
Levkojev, 363, 372
Levy, 216
Lewis, E. E., 258
Lewis, J. H., 352
Ley, 292
Lichty, 330
Lieb, 302, 332
Liebermann, C., 195
Liebermann, H., 237
Lierg, 370
Lifschitz, 384, 389
E. Lilley & Co., 352
Limpricht, 186, 191
Linstead, 213
Lions, 237
Litchfield, 352
Ljaschenko, 359
Locher, 298
Lodi, 352
Loeb, 317
Loewenhof, 239
Longo, 247, 261, 322
Lothrop, 14, 235
Lowitsch, 40
Lowy, 186, 336
Ludwig, K., 9
Ludwig, R., 340
Lunge, 349
Lustig, 326
Lutzenko, 338
Lynas-Gray, 297
Lythgoe, 236

Macciotta, 147
Macintyre, 315
Macmillan, 262
Macrae, 312
Madden, 60
Magis, 352,
Mahadevan, 15, 292, 301
Mai, 192, 271, 296
Maier, 25, 35, 77, 360, 361
v. Majewski, 192
Makarova, 51, 338
Makin, 115
Mallet, 261
Malloy, 352
Manchot, 60
Mangini, 168, 169, 189
Mann, E., 23
Mann, F. G., 162
Mann, W., 323
Manning, 323
Manoszan, 354
Manske, 237
Manteufel, 238
Manuf. Lyonaise Mat. Col., 68
Manzelius, 292
Marias, 60
Marconi's Wireless Telegraph Co., 356, 377
Margot, 44
Marini-Bettòlo, 323
Marino, 322
Markowitsch, 226
Marriott, 66, 85
Marsden, 24, 41, 43, 67, 101, 146, 148, 149, 150, 197, 225, 240, 271, 295, 318, 381, 390, 391, 392, 393, 394, 398
Marshall, 348
Martin, 372
Martius, 4
Mascarelli, 22, 261, 267, 293
Mason, ix, 218, 227
Mason & Sons, 375, 376, 377
Maué, 182
May, 81
May Chem. Corp., 75, 179
Mayer, 235, 258
Mazzara, 235
McCleland, 336
McClure, 186, 336
McCollum, 352
McCombie, 262
McNee, 351

Mebus, 7, 10
Meerwein, 320
Mehner, H., 168, 225, 253, 351
Mehta, 152, 372
Meimberger, 271
Meisenheimer, 252, 294
Meldola, 35, 51, 118, 119, 120, 164, 305, 350, 357
Melnick, 352
Melnikov, 81
Merz, 117, 240, 275
Metcalf, 309
Metzler, 43
v. Meyer, E., 95
Meyer, F., 298, 312
Meyer, H., 253
Meyer, K. H., 217, 219, 226, 233, 238
Meyer, L., 147
Meyer, R., 237
Meyer, V., 176, 186, 209, 238
Michaelis, F., 238
Michaelis, H., 178
Michaelis, L., 50, 51, 60, 81
Michel, 35, 192, 247
Michels, 117
Mickelthwait, 27, 38, 43, 176, 236, 250, 401
v. Migray, 352
Millar, 176
Miller, H. F., 261
Miller, S. E., 239
Mills, 100, 121, 387
de Milt, 14
Ming Chow, 291
Misslin, 12, 26
Mitchell, 238
Mitra, 292
Mitscherlich, 195
M.L.B., 9, 28, 75, 116, 124, 176, 182, 308, 330, 335
Möhlau, E., 136
Möhlau, R., 16, 186, 238, 286, 318
Moale, 275
Modlin, 32
Moelwyn-Hughes, 62, 63
Mohr, 60
Molinari, 165, 166
de Montmollin, 267
Moore, ix
Morel, 355
Morgan, C. R., 323
Morgan, Sir Gilbert, xi, 22, 25, 27, 29, 33, 36, 37, 38, 43, 52, 124, 133, 147, 176, 201, 236, 246, 249, 250, 273, 382
Morpeth, 352
Morrow, 60
Mouneyrat, 331
Mounier, 358, 361
Mowry, 293
Mrozinski, 329
Müller, A. H. R., 177
Müller, E., 81, 321, 342
Müller, F. H. S., 329
Müller, H. A., 323
Müller, J., 138, 237, 239
Müller, P. J., 60
Müller, R., 60
Müller, W., 239
Münzer, 237
Muhlert, 235
Muir, 288, 290, 298, 321
Mullen, 237
Muller, 62
Murray, 370, 372, 374, 376, 377
Musanti, 60

Nakayama, G., 346
Nakayama, S., 352
Nametkin, 81
National Aniline Co., 139, 153, 179
Nawiasky, 156
Neogi, 292
Nesmejanov, 51, 81, 335, 336, 337
Neulipa, 376
Neunhoffer, 235
Nevers, 322
Nevile, 303
New, 401
Newman, 289, 290
Nicholson, 153
Nicoll, 62, 196
Niementowski, 262, 263, 311
Nietzki, 21, 238
Nijk, 335
Nölting, 9, 15, 25, 124, 164, 191, 192, 236, 247, 249, 304
Nötzel, 235
Noelting, *see* Nölting
Norman, 177, 303
Norris, 315
Northcott, 147, 372, 402
Norton & Gregory, 374, 376
Noyes, 291

Oberst, 272
Oddo, 62, 66, 138, 177, 191, 288, 308, 310, 311, 315, 372, 402
Oehler, 28
Oekonomides, 176
Olin Industries, Inc., 355
Oliveri, 292
Olivier, 323
Oneto, 336
Oppenheimer, 258
Orlow, 177
Orndorff, 235, 274, 275, 307, 351
Orsati, 138
Orton, 120, 132, 135, 147, 181, 235, 272, 301, 358, 394
Ostroshinskaya, 350
Ostro Research Labs., 235
Overwien, 177
Ozalid Co., 374, 376

Paal, 40, 152
Pabst, 19, 20
Paden, 238
Padfield, 263
Palmer, 308
Panek, 351
Parkes, 81, 192, 237
Parks, 309
Parsons, 271
Pask, 92
Paterno, 292
Patrascanu, 177
Patzig, 294
Pauling, 187, 236
Pauly, 205, 236, 347
de Pay, 44
C. F. Pease Co., 376
v. Pechmann, 38, 94, 129, 133, 139, 140, 160, 210, 214, 380, 384, 391
Penzoldt, 343, 345
Perdue, 372
Perkin, A. G., 254
Perkin, F. M., 176, 239
Perkin, W. H., 258
Pernert, 322
Peters, 90, 329
Petersen, 17
Peterson, 230, 234
Petri, 345
Petrov, 363, 372
Pharma Chem. Corp., 178, 179
Philips Lamp Co., 375, 376
Phillips, 34
Pickard, 22, 38
Pieroni, 138, 146, 395, 396
Pierron, 236
Pillarsky, 81
Pinner, 176, 191
Pinnow, 321
Pirelli, 179
Pirosky, 356
Plachut, 322
Plant, 265
Platt, 65
Plets, 335
Pohl, 135
Poje, 272
Polgar, 376
Pollack, 221
Polonovski, 352
Polverini, 401
Ponzio, 147
Popp, 60
Porai-Koshits, 101, 239
Porter, 29
Poser, 376
F. Post Co., 375, 376
Powell, 375, 376
Power, 275
Pozzetto, 235
Pray, 66
Prebluda, 352
Preston, 265
Priestley, 60, 236
Pröscher, 351
Pschorr, 254, 255, 257
Purgotti, 186
Pyman, 322

Quaife, 352
Quilico, 60, 235, 238, 239, 401

" R.A.", 10, 186
Radio Corp. of America, 356
Raiford, 272
Rajagopalan, 124
Ralph, 49
Rankin, 258
Rappaport, 352
Rapson, 258
Rassow, 311
Rast, 245
Räth, 330
Rauch, 239
Ray, 235
Read, E. R., 322
Read, H. N., 25
v. der Recke, 132, 147, 301
Reddelien, ix
v. Reden, 308
Reden & Köhne, 373
Reed, 124, 401
Reilly, 46, 53, 60, 236
Reinders, 176
Reissert, 253
Reitz, 254
Remington Arms Co., 60, 355
Remsen, 274, 308
Remy, 78, 280
Renauld, 192
Renker, 374, 376, 377
Renshaw, 236
Renoll, 293
Resinotrust, 178
Reumuth, 10
Reverdin, 12, 119, 350
Rheinische Kampfer Fab., 192
Richard, 355
Richardson, 198
v. Richter, 237, 243
Rideal, 342
Ridge, 270, 271
Ritchie, 43, 60
Rjazancev, 60
Römer, 49, 148, 183
Roberge, 323
Robertson, 401
Robinson, G. M., 231
Robinson, Sir R., 220, 227, 231, 237, 258
Rodionov, 309
Roedel, 31, 34
Rohner, 9, 236
Rolf, 335
Rolfes, 236, 275, 322

Rolfs, 192
Rondelli, 352
Rose, 348
Rosenhauer, 163
Ross, 239
Rossi, 323
Rossow, 293
Rostovtzeva, E., 47, 341
Rostovtzeva, K., 47, 343
Roth, 43
Rotter, 176
Rowe, 25, 51, 90, 104, 138, 237
Royle, 321
Rügheimer, 50
Ruddy, 336
Rudolph, 248
Ruff, 359, 365
Ruge, 351
Ruggli, 26, 44, 81, 116, 193, 256, 273, 310
Ruhl, 51, 81
Rupe, 192
Ruppelt, 24, 322

Saccardi, 146
Sachs, 351
Sakelarios, 81
Sako, 263, 267
Sakurai, 372
Salcher, 176
Salkowski, 9
Sandin, 267
Sándor, 239
Sandmeyer, 277, 280, 286, 294, 309
Sandoz, 98, 235
Sarauw, 176
Sarkar, 398
Saunders, C. E., 155
Saunders, K. H., 115
Savage, 144, 394
Scarborough, 262
Scavuzzo, 372
Schäfer, 60
Schäffner, 238
Schaarschmidt, 13, 28, 192
Schachnow, 322
Schaffer, 308
Schaeling, 177
van der Schalk, 321
Schall, 43
Scharvin, 236, 322
Schapiro, 323
Schaum, 177
Schedler, 321
van der Scheer, 236
Scheid, 286
Scheller, 333
Schemjakina, 322
Scherer, 376
Schering-Kahlbaum A.G., 60, 322
Scheuer, 22, 38
v. Schickh, 333
Schiemann, 81, 124, 277, 283
Schiff, 192
Schild, 352
Schimpf, 237
Schinzel, K. and L., 9
Schlein, 35
Schleissing, 125
Schlittler, 258
Schlösser, 238
Schlotterbeck, 237
Schmachtenburg, 155
Schmid, 47, 96
Schmidlin, 290
Schmidt, C., 128, 129, 135
Schmidt, H., 333, 334
Schmidt, J., 25, 35, 43, 77, 360, 361
Schmidt, M., 9
Schmidt, M. P., 151, 372
Schmidt, O., 51, 238, 322, 350
Schmiedel, 149
Schmitt, 17, 35, 148, 236, 292
Schneider, G., 18
Schneider, R., 351
Schöller, 238
Schöpf, 250
Schoeler, 258
Schoen, 368
Schofield, 243, 244
Scholl, 14, 17, 312
Schonlau. 329
Schoutissen, 12, 19, 25, 26, 27, 46, 47, 102, 186, 196, 197, 234, 381
Schraube, 128, 129, 135, 239
Schröter, 362
Schroeter, 83, 84
Schschetinina, 350
Schümann, 45, 46, 48, 134
Schuler, 351
Schultess, 330
Schultz, 15, 308
Schultze, 143
Schulz, 326
Schulze, 236
Schwalbe, 9, 64, 65, 341
Schwarz, 292
Schwechten, 81, 262, 277, 283, 289
Schweizer, 237
Schwickert, 373
S.C.I., 9, 15, 28, 35, 75, 93, 97, 98, 116, 117, 139, 178, 182, 235, 237, 239, 265, 330, 356
Seide, 60
Seidler, 13, 354
Sekiguchi, 342
Semard, 104
Sendju, 351
Senn, 253
Seywetz, 358, 361
Shaefer, 340
Sharp, 258
Shedden, 275
Sheppard, 144, 402
Shinda, 258

Shiraeff, 374
Shober, 309
Shorygin, 20
Shreve, 60
Sibbald, 77, 276, 281
Siebert, 254
Siddle, 92
Sidgwick, 192, 401
Sieber, 49, 65, 380
Silberbach, 258
Silberrad, 176
Silbermann, 117
Silberstein, 120
Siller, 253
Simon, 236
Simonet, 176
Simonov, 38
Simonovskaya, 81
Simonsen, 297
Simpson, 242, 243, 244
Singer, 94, 391
Singh, 342
Sisley, 355, 372
Skorodumova, 81
Skvirskaya, 350
Smiles, 239, 330
Smith, C., 165, 221, 238
Smith, D. E., 236
Smith, L. E., 308
Smith, L. I., 238
Smith, W., 19
Smythe, 125
Snow, 64
Socony-Vacuum Oil Co., 179
Solvay Process Co., 20, 179
Sommer, 239
Soulez, 352
Späth, 258
Spang, 377
Specht, 142
Spence, 124, 292
Spencer, 340, 359, 360, 370, 374
Spiegelberg, 400
Spiethoff, 345
Spinks, 352
Spruson, 237
Squibb & Sons, 60
Stählin, 258
Stadler, 325
Staedel, 176, 261
Staehling, 235
Stafford, 138
Starkey, 81, 295, 336, 338
Starostin, 374
Staub, 256
St. Denis, 153, 239, 375
Stelzner, 247
Stein, O., 43, 350
Stein, V., 359, 365
Steinkopf, 60
Stenhouse, 16
Stepanov, 28
Stephens, 35, 124
Stephenson, 100, 111, 147, 242, 357, 372, 402
Stoermer, 242
Stoll, 40
Stollé, 25, 132, 152
Stolz, 60
Storch, 180
Storrie, 310
Strache, 186
Strasser, 147, 401
Streatfeild, 120, 164
Strecker, 148, 183, 379
Stricker, 352
Strohbach, 238
Stuart, 239
Stuckwisch, 9
Stursa, 239
Süs, 361, 376
Suais, 238
Suchannek, 44
Suizi, 177
Sunder, C. and H., 10
Supniewsky, 77
Sutherland, 144, 402
Sutton, 401
Suzuki, 46, 329
Svigoon, 81, 335
Swarts, 292
Swientoslawski, 353, 386, 401
Szegö, 401
Szpilfogel, 179

Tabone, 352
Täuber, 21, 25, 44, 262, 263
Tafel, 176
Tama, 92
Tanuma, 372
Tassilly, 45, 46
Tassinari, 330
Taylor, F. J., 340, 360
Taylor, T. W. J., 34, 258
Teegan, 53
Teeple, 351
Tepper, 92
Terentiev, 238, 350, 351
Thannhauser, 351
Thiele, 60, 132, 238
Thode, 253
Thomas, J., 291, 328
Thomas, W., 237
Thompson, K. J., 65
Thompson, L., 186, 350
Thosar, 152, 372
Tichwinski, 186
Tiemann, 340
Tilden, 176
Tinkler, 384, 389
Tinsley, 237
Tischner, 291
Tobias, 271, 278
Tochtermann, 238

Todd, 236
Tomlins, 35
Tomlinson, F. S., 92
Tomlinson, M. L., 265
Topham, 236
Topchiev, A. V., 20
Topchiev, K. S., 301
Toropova, 338
Tottey, 352
Traumann, 60
Troeger, 95
Troschke, 191
Tschekalin, 224
Tschitschibabin, 60, 235, 322
Tucker, 265, 312, 356
Turcotte, 323
Turner, E. E., 312
Turner, G., 153, 275, 300
Turner, H. S., 13, 35, 271
Tyrell, 377

Uémura, 239
Ueno, 46, 342
Ufimtsev, 81
Ullmann, 161, 251, 253, 261, 262, 263, 264, 313
Unger, 177
Union Research Corp., 377
Upton, 37
Usines du Rhone, 308

Valentiner, 292
Valette, 373
Vanino, 237
Vannotti, 330
Van Veen, 236
Van Zandt, 14
Varma, 18, 308
Vaubel, 22, 38, 50, 176, 177, 341
Vaughan, 34
Veinberg, 92, 167
Veley, 229
Verein Chem. Met. Prod. in Aussig, 93
Veselý, 239, 292, 295
Vickers, 236
Vielan, 329
Vieille, 352, 354, 357
Vignon, 176, 353
Viktoreff, 85
Viktorov, 65
Vine, 142, 144, 167
Vinogradova, 238, 351
Vock, 41, 132, 271, 284, 309
Volkmann, 373
Vorbrodt, 254
Vorländer, 41, 298, 312
Votoček, 292

Wacker, 297
Waentig, 291
Wagner, 27
Wahl, 35, 90
Wakelin, ix
Wald, 238
Walder, 25, 44
Waldmann, 251, 258, 265
Walker, 13, 26, 27, 115, 240, 279, 280, 281, 322
Wallach, 8, 169, 170, 195, 284, 305
Wallbaum, 13
Walls, 177
Walther, 40, 167, 177, 186, 380
Walter, 291
Wang, 213
Wanka, 321
Ward, 301
Waring, 19, 66
Warren, 323
Waterman, 25, 355, 372, 375, 376, 402
Waters, 100, 108, 109, 110, 111, 112, 114, 147, 281, 282, 291, 316, 329, 333, 338, 357, 372, 402
Watson-Smith, xi
Watt, 177
Watts, 165
Waÿss, 274, 276
Weber, 177
Wechsler, 40, 124
Weddige, 253
Wedekind. 236, 275
Wedum, 236
Wegner, 186
Weida, 275
Weidenhagen, 186
Weiler, 253
Weiler-ter-Meer, 35
Weinberg, A., 236
Weinberg, Z., 323
Weise, 235
Weisz, 60
Weitzenbock, 258
Weizman, 323
Weizmann, 239
Wentzel, 374
Werner, 156, 385
Weselsky, 176
Wetter, 138
Whaley, 338
Wheelwright, 237
Whidborne, 352
White, F. D., 352
Whitehead, 192
Whitehurst, 27
Whitmore, 235
Wichelhaus, 61
Widman, 40, 242, 253
Wiesinger, 329
Wild, 308
Wilke-Dörfurt, 80
Wilkinson, J. F., 81, 352
Wilkinson, R., 261, 322
Willgerodt, 293
Williams, E. H., 237
Williams, N. H., 92

Williams, R. G., 28
Williams (Hounslow) Ltd., 236
Willis, 60
Willstätter, 40
Wilson, I. R., 402
Wilson, R. H., 336
Wimmer, 176
Windaus, 258
Winkelmüller, 292
Winkler, 373
Winston, 275
Winther, 303
Winthrop Chem. Co., 179, 336
Wise, 289, 382
Wistar, 230, 231
Witt, F. H., 177, 236
Witt, O. N., 9, 15, 16, 84, 124, 235, 236, 247
Witte, 294
Wizinger, 233
Wlodkowski, 40
Wohl, A., 38, 126, 140, 192
Wohl, (Mlle.) Anna, 177
Wojcieschowski, 130, 353
Wolbring, 237
Wolf, 178
Wolfe, 372
Wolff, 33, 223
Wood, 363
Woodberry, 69
Woolcott, 371
Wootton, 147, 401
Wormall, 192
Woroshtzov, 308, 330
Wortmann, 15, 304
Wray, 371
Wrede, 60
Wroblewski, 274
Wulz, 169, 237
Wurtz, 379
Wynne, 280, 286

Yablunky, 335
Yamamoto, 62, 67, 341, 372
Yamashita, 372
Yates, 104
Yokojima, 177
Yokota, 329

Zacharias, 253
Zahn, 226
Zaidan, 373
Zakrewski, 250
Zander, 308
Zechmeister, 228
Zeidler, 258
Zeitlin, 192
Zegelman, 238
Zellner, 237
Zenísek, 292
Ziegler, 237
Zimmermann, 117, 253, 275
Zincke, 7, 182, 239, 249
Züblin, 237
Zürcher, 236
Zucker, 351

PATENTS INDEX

British Patents

Number	Page	Number	Page	Number	Page	Number	Page
1,956/66	355	14,578/05	322	262,537	97	311,196	374
2,811/78	20	22,736/05	330	262,987	97	312,261	374
1,593/88	28	23,034/05	35	264,879	23	314,933	178
7,433/90	373	7,288/06	330	265,985	93	316,563	374
6,630/92	22	10,323/06	35	266,388	22	316,691	82
17,546/92	28	11,174/06	330	266,771	9	317,199	374
1,320/97	9	13,055/06	330	269,212	93	317,355	82
20,605/93	139	765/07	238	273,352	93	318,108	374
1,920/94	292	6,930/07	330	274,129	373	318,511	374
13,577/94	139	10,412/08	322	275,245	93	318,833	356
15,305/94	236	13,903/09	236	278,100	322	320,324	178
18,429/94	93	16,151/10	321	279,136	330	320,395	374
21,227/94	75	568/11	335	280,593	373	320,603	374
8,995/95	93	3,508/11	116	280,945	93	324,041	178
11,757/95	93	15,438/11	124	281,604	373	324,048	374
13,460/95	139	20,072/11	117	282,894	373	325,797	330
1,645/96	82	20,073/11	117	283,274	373	325,924	374
2,946/96	23	22,915/11	239	284,253	373	326,866	68
17,065/96	23	2,037/12	93	287,063	373	328,383	139
26,020/96	28	16,350/12	335	288,572	124	329,353	178
26,139/96	330	17,829/12	251	290,565	373	331,217	301
2,874/97	236	23,164/12	329	292,100	82	331,459	374
7,233/97	308	24,667/12	335	294,247	373	331,823	374
9,827/97	292	27,198/12	355	294,248	82	332,227	82
23,047/97	330	11,290/13	93	294,972	373	332,552	374
28,107/97	35	23,945/13	75	295,050	124	332,631	374
13,564/98	308	9,102/14	139	295,993	373	334,529	178
15,353/98	75	6,663/15	139	295,050	124	334,555	374
4,792/00	254	15,884/15	139	296,008	373	340,166	374
12,871/00	330	104,108	139	296,725	373	340,534	139
12,872/00	330	116,360	93	297,363	373	341,598	60
18,624/00	28	125,600	355	298,518	239	344,721	374
20,864/00	330	142,947	336	298,979	373	347,430	374
1,766/01	321	200,714	308	299,010	373	347,742	239
16,811/01	124	210,862	373	301,879	373	349,339	93
1,561/02	124	211,223	239	302,184	373	352,368	237
6,615/02	124	217,594	139	303,527	82	352,878	237
12,584/02	124	234,818	373	303,942	139	353,486	374
23,993/02	124	238,676	82	305,498	75, 82	355,464	23
16,995/03	124	238,683	237	305,787	139	355,970	44
18,283/03	28,124	238,704	93	306,408	374	358,814	374
27,372/03	124	246,181	93	306,844	178	362,735	374
4,997/04	124	246,870	93	307,890	97	363,616	374
10,235/04	35	248,230	239	307,965	139	363,950	75
15,418/04	116	249,526	139	308,653	374	364,490	93
27,373/04	50	260,682	97	308,660	178	364,739	261, 374
27,498/04	23	261,026	336	309,166	153, 374	364,989	374
82/05	28	261,133	336	309,610	178	365,759	82
10,022/05	35	262,119	15	310,773	374	372,562	9

Number	Page	Number	Page	Number	Page	Number	Page
374,497	97	427,962	375	457,763	178	512,798	92
374,498	239	429,618	178	458,808	178	513,029	376
376,143	82	429,936	15	459,342	178	513,244	376
376,307	82	430,167	97	459,766	98	513,560	376
377,207	153	430,222	97	461,051	93	513,846	82, 322
377,978	153	430,236	97	462,535	60	515,980	179
379,279	153	433,574	265	463,305	178	515,981	179
379,280	153	433,586	375	463,515	178	517,030	98
381,580	22	433,878	178	464,398	375	518,129	376
382,483	374	433,999	375	464,511	178	518,162	376
385,307	93	434,158	75	464,613	376	519,574	82, 93
387,197	374	434,416	9	465,484	178, 236	519,838	235
388,721	178	434,725	25	466,846	178	520,304	376
390,616	374	434,761	375	467,145	376	521,492	376
391,052	375	434,917	182	467,157	239	523,296	9
391,677	375	435,171	178	467,313	376	523,922	376
391,963	375	435,449	238	467,971	265	524,786	376
391,970	375	435,874	375	468,189	98	525,099	98
393,830	93	436,371	178	469,578	178	526,007	235
397,034	82	436,587	375	471,389	247	530,881	323
398,671	375	436,873	356	471,443	93	531,625	75
398,846	153	437,824	97	471,614	376	532,958	376
399,753	75	438,805	375	472,224	237	534,271	179
401,898	375	439,005	375	473,244	376	534,341	376
402,883	375	439,560	9	475,942	75	535,805	179
402,920	239	440,113	60	476,122	376	536,714	376
403,013	75	440,144	153, 375	476,143	82	538,869	377
403,203	375	440,424	28, 75	477,754	376	539,031	377
405,880	375	440,964	75	479,708	239	539,314	377
407,840	178	441,178	237	480,169	178	539,912	179
410,669	239	441,085	75	480,617	322	540,978	179
411,544	375	441,178	9, 97	481,019	178	541,912	179
413,257	68	441,590	235	481,735	139	544,702	377
414,381	9, 235	443,222	178	485,592	9	544,882	377
414,681	153	443,611	375	485,971	330	546,499	235
414,768	93	443,955	375	487,724	98	552,919	179
415,081	375	444,193	375	489,035	44	553,508	377
417,588	375	445,278	275	489,214	376	554,921	377
417,861	35	445,438	375	489,972	235	554,998	377
418,011	22, 117	446,746	60	490,958	60	558,009	323
418,976	375	447,514	182	491,095	376	563,804	377
421,971	153	447,561	15	491,398	117	569,037	336
422,195	178	449,267	98	492,795	376	570,027	377
422,488	178	449,341	375	496,678	178	571,009	179
423,587	178	450,817	375	497,407	239	571,802	377
423,736	261	452,177	98	496,090	376	576,401	179
424,868	375	452,482	178	502,309	235	580,122	236
425,126	375	454,137	375	503,996	376	587,540	356
425,235	375	454,665	375	505,359	376	587,928	82
425,434	375	454,729	236	507,153	376	587,929	82
426,260	375	454,814	375	507,260	179	587,930	82
426,403	9, 308	454,869	178	510,407	376	596,048	377
426,922	375	455,621	235	510,874	376	599,834	247
427,732	375	456,343	330	511,134	376	603,280	356
427,803	178	457,718	153	511,816	376	607,334	377

United States Patents

Number	Page	Number	Page	Number	Page	Number	Page
277,182	178	1,724,062	139	1,916,327	292	2,051,583	375
285,335	178	1,735,432	322	1,920,542	153	2,051,584	375
516,380	28	1,744,149	93	1,926,322	374	2,051,585	375
531,973	139	1,744,903	93	1,193,566	139	2,051,586	375
531,975	139	1,751,318	374	1,936,957	373	2,052,216	235
531,976	139	1,752,174	374	1,947,433	97	2,052,386	82
535,037	292	1,753,059	374	1,948,589	153	2,053,745	28
557,228	75	1,753,708	374	1,952,591	355	2,054,397	178
619,194	23	1,756,400	374	1,959,995	153	2,058,418	179
619,574	308	1,758,912	93	1,962,111	82	2,058,419	179
621,679	308	1,760,780	373	1,966,755	375	2,063,211	35
656,229	292	1,770,352	374	1,968,878	178	2,063,631	117
693,607	28	1,799,068	82	1,968,879	178	2,064,817	60
710,059	124	1,803,906	374	1,968,923	153	2,065,593	179
737,967	124	1,807,761	374	1,970,070	153	2,065,593	179
760,363	116	1,811,029	373	1,971,966	373	2,068,919	375
770,177	124	1,816,989	374	1.972,323	374	2,069,461	178
793,743	35	1,821,281	374	1,973,788	375	2,078,387	179
797,441	35	1,829,672	237	1,975,409	75	2,083,285	375
806,415	35	1,829,673	237	1,977,266	236	2,083,311	93
807,422	35	1,837,679	374	1,979,327	178	2,084,934	93
823,793	28	1,846,113	93	1,982,681	178	2,086,986	20
913,634	238	1,846,150	82	1,986,276	179	2,088,506	178
929,442	322	1,846,151	82	1,989,065	375	2,095,484	60
993,549	236	1,847,513	82	1,989,541	93	2,098,861	178
1,023,199	117	1,851,969	23	1,993,433	75	2,100,063	375
1,026,257	117	1,852,054	355	1,999,723	82	2,103,926	355
1,028,006	117	1,853,462	373	2,008,750	178	2,105,326	179
1,057,137	68	1,855,289	9	2,009,962	375	2,105,919	9
1,061,587	335	1,857,230	97	2,013,180	25	2,106,539	75
1,065,440	251	1,857,920	374	2,013.723	179	2,110,270	179
1,065,441	329	1,858,623	178	2,014,428	93	2,110,973	375
1,075,537-8	335	1,861,330	374	2,018,095	75	2,111,011	265
1,093,567	93	1,862,241	82	2,018,103	153	2,111,692	178
1,193,566	139	1,862,295	355	2,021,911	178	2,112,864	98
1,200,726	139	1,862,361	60	2,022,923	93	2,113,193	375
1,394,556	117	1,863,154	93	2,022,014	375	2,113,944	375
1,404,687	355	1,867,088	178	2,024,864	124	2,114,468	376
1,428,011	355	1,867,105	44	2,025,095	179	2,115,149	178
1,444,469	373	1,867,937	93	2,026,292	375	2,116,131	93
1,453,600	239	1,870,930	374	2,027,066	75	2,118,986	75
1,460,708	355	1,871,850	178	2,027,229	375	2,119,891	139
1,532,627	237	1,874,524	178	2,027,908	265	2,122,424	179
1,572,175	82	1,875,243	75	2,029,647	238	2,124,070	330
1,585,145	9	1,879,424	178	2,031,634	179	2,124,594	178
1,602,991	239	1,880,522	178	2,032,110	75	2,124,899	235
1,607,462	93	1,880,920	301	2,034,508	375	2,125,087	178
1,629,906	93	1,880,959	97	2,035,518	178	2,125,509	179
1,677,558	93	1,882,556	178	2,036,530	182	2,128,201	236
1,677,640	93	1,882,560	178	2,039,514	238	2,128,202	236
1,684,272	322	1,882,561	178	2,040,587	275	2,129,136	75
1,690,021	23	1,882,562	178	2,041,455	9, 97, 237	2,132,456	178
1,700,790	15	1,889,298	82	2,042,696	97	2,133,037	179
1,704,106	336	1,893,991	178	2,048,745	139	2,139,987	239
1,706,489	330	1,895,099	97	2,049,674	178	2,141,051	60
1,710,455	373	1,916,327	292	2,051,148	178	2,141,103	376
1,717,453	93	1,915,734	139	2,051,582	375	2,144,578	98

Number	Page	Number	Page	Number	Page	Number	Page
2,149,703	179	2,193,998	75, 82	2,270,756	9	2,357,226	93
2,150,565	376	2,196,950	376	2,271,176	377	2,369,307	179
2,151,532	376	2,197,456	376	2,274,551	9	2,369,308	179
2,154,405	179	2,198,827	376	2,277,409	376	2,369,309	179
2,154,470	179	2,199,003	179	2,280,504	322	2,373,040	377
2,154,509	153	2,199,925	376	2,286,656	377	2,374,563	377
2,155,579	355	2,200,926	179	2,286,701	377	2,375,012	179
2,155,942	179	2,200,996	376	2,294,380	60	2,375,132	179
2,157,206	376	2,205,417	139	2,298,444	377	2,375,366	377
2,157,797	9	2,205,991	376	2,299,244	179	2,378,276	82
2,158,836	376	2,206,611	153	2,299,245	179	2,378,305	82
2,160,882	9	2,208,096	352	2,302,277	377	2,378,583	377
2,161,622	44	2,209,087	376	2,308,130	377	2,378,646	82
2,162,456	376	2,209,985	9	2,308,675	179	2,381,145	82
2,166,681	179	2,210,369	235	2,309,946	179	2,381,984	377
2,162,960	179	2,212,959	376	2,309,982	98	2,388,260	356
2,168,800	178	2,215,739	376	2,310,012	179	2,402,106	82
2,169,736	179	2,216,137	376	2,310,013	179	2,402,611	253
2,169,737	179	2,217,189	377	2,313,233	179	2,404,893	15
2,171,976	82, 93	2,228,562	376	2,313,288	376	2,408,059	355
2,172,783	376	2,229,744	179	2,314,196	69	2,409,832	179
2,173,324	179	2,230,791	275	2,314,652	179	2,416,021	377
2,175,807	82	2,232,406	139, 179	2,318,352	377	2,416,187	179
2,177,257	376	2,233,038	376	2,319,265	82	2,416,549	179
2,178,585	51	2,234,036	239	2,322,982	377	2,416,773	377
2,178,771	375	2,237,885	82	2,333,359	377	2,418,623	377
2,183,447	376	2,239,704	376	2,336,309	377	2,419,296	356
2,185,152	179	2,245,628	376	2,339,213	50	2,421,367	356
2,185,154	179	2,246,425	376	2,339,934	179	2,422,043	355
2,186,722	117	2,257,091	179	2,350,843	377	2,431,190	377
2,188,262	179	2,257,190	179	2,353,175	235	2,432,549	377
2,189,367	308	2,266,229	75	2,354,088	377	2,432,593	377
2,190,841	179	2,267,760	179	2,356,618	82		

German Patents

6,034	20	78,225	153	89,437	82	109,699	43
14,950	97	78,874	139	89,998	93	109,932	35
25,146	16	79,055	292	92,169	93	111,416	373
39,954	28	80,263	139	92,237	93	120,504	254
40,890	178	80,652	42	93,109	75	126,802	237
45,120	330	81,039	93	93,304	236	126,961	321
46,205	355	81,134	139	93,305	93	128,619	28
51,576	22	81,202	139	94,074	236	130,119	330
52,661	22	81,203	139	94,280	93	131,538	14, 292
53,455	373	81,204	139	94,495	82	138,268	124
56,606	373	81,206	139	95,339	308	139,327	124
58,001	322	81,791	139	95,830	330	140,955	236
62,004	186	82,239	373	96,153	292	141,750	124
65,863	28	82,446	139, 236	97,688	308	143,450	14
68,303	28	83,010	139, 236	97,933	75	144,640	124
69,073	330	84,389	139	100,702	330	145,906	124
70,813	182	84,609	139	102,160	23	148,085	28, 124
72,394	22	85,387	75	103,660	28	148,882	124
75,743	236	86,367	93	103,685	28	152,661	14
77,264	182	87,970	155	108,231	43	152,879	28
77,397	182	88,949	93	108,459	308	152,926	356

Number	Page	Number	Page	Number	Page	Number	Page
155,083	35	264,268	93	479,163	23	548,558	374
156,440	124	264,924	335	484,905	93	550,711	178
156,803	182	266,944	335	487,148	374	552,283	178
156,828	28	268,172	335	487,247	374	553,787	93
157,325	124	269,205	335	488,148	374	553,942	237
158,532	124	281,055	82	490,387	374	555,406	93
160,536	124	281,098	75	491,318	82	557,298	237
161,954	50	287,086	139	492,856	374	557,658	82
162,009	124	291,076	139	493,834	374	558,343	374
163,447	186	292,118	139	495,631	82	559,421	93
164,655	116	298,236	139	496,833	68	559,596	374
167,211	308	308,666	176	499,151	330	559,795	374
168,299	28	308,909	239	499,294	93	560,797	153
171,024	35	373,426	355	500,437	178	560,798	153
172,446	35	376,385	373	500,658	374	561,424	44
175,593	35	379,998	373	502,334	178	563,061	153
176,618	116	381,551	373	502,663	373	563,240	374
176,619	116	383,510	373	506,412	374	569,205	82
176,620	116	386,433	373	507,171	374	571,825	375
178,936	35	386,434	373	508,395	322	572,268	93
181,658	330	408,505	139	510,441	178	572,269	93
181,714	35	409,564	237	512,614	374	573,180	82
184,495	322	413,145	254	513,209	178	575,024	93
186,005	292	419,987	373	514,084	373	575,832	20
189,179	35	422,972	373	515,205	75	578,362	375
193,211	236	426,033	97	519,729	44	578,648	153
194,040	330	430,621	97	518,229	301	581,394	375
199,349	330	433,276	97	522,636	374	581,697	375
201,231	330	438,743	97	522,892	336	586,354	75
201,232	330	440,528	373	523,259	374	586,355	75
204,702	238	440,802	336	523,358	275	588,212	153
205,037	22	441,888	373	524,266	139	588,994	375
205,450	330	442,075	97	524,978	374	590,107	374
206,455	116	443,263	373	525,399	178	590,321	9
206,698	116	443,284	97	526,370	374	591,213	9, 308
211,927	322	444,325	321	526,879	178	591,969	374
215,006	322	445,390	322	528,638	374	593,260	93
224,024	236	447,069	97	530,396	178	593,790	68
224,387	116	448,426	139	530,850	374	596,104	373
229,247	93	448,728	93	531,008	178	596,731	117
236,656	116	449,013	97	531,792	374	597,450	375
238,841	239	450,998	239	532,401	178	600,706	292
243,648	124	451,903	97	532,402	82	601,676	375
243,788	321	453,133	239	534,305	23	604,278	25
246,085	176	453,985	97	534,640	178	605,553	375
246,573	117	454,894	82	535,076	178	605,577	75
246,574	117	456,857	192	535,670	178	606,942	75
250,264	335	456,859	15	535,913	374	607,536	75
253,238	176	461,603	373	537,021	9	607,870	75
254,092	335	462,399	373	540,607	139	609,334	9
254,345	335	465,564	139	541,255	292	609,476	75
254,421	335	466,111	373	542,780	97	609,928	35
254,745	251	467,090	373	542,870	329	611,398	20, 75
255,340	176	467,162	373	543,288	60	611,463	28, 75
256,667	329	470,088	373	544,057	93	614,198	178
257,610	236	470,731	374	545,486	373	614,459	22
261,825	335	473,445	373	545,852	75	614,838	239
262,076	182	474,659	139	546,226	374	615,744	9
263,431	68	478,031	82	547,062	374	615,846	178

Number	Page	Number	Page	Number	Page	Number	Page
620,247	139	640,935	178	670,371	376	703,254	377
622,306	75	641,769	97, 237	670,767	265	704,070	375
623,496	275	641,874	98	671,788	178	705,957	376
624,534	375	642,223	376	673,388	265	709,074	377
624,765	178	642,716	97	673,536	236	714,560	376
625,263	117	644,070	98	674,144	376	716,383	376
626,134	124	645,267	375	676,394	376	718,321	377
629,478	75	645,934	93	676,899	376	720,364	377
630,328	182	647,667	93	677,685	376	720,917	377
630,389	376	651,105	60	680,268	376	734,302	377
630,967	182	651,145	376	682,344	238	752,852	377
633,166	376	654,447	69	684,334	376	762,522	377
633,867	336	654,448	75	684,620	376	763,388	377
636,971	376	654,809	376	691,283	377		
638,264	75	655,047	93	692,393	377		
638,486	301	656,205	117	694,078	376		
638,878	98	659,591	236	695,570	377	Anmeldungen	
639,125	376	661,225	98	697,051	376	F. 16,863	124
639,238	178	662,935	235	697,744	376	G. 80,257	124
639,288	178	663,496	98	697,804	139	I. 46,720	178
639,727	60	666,467	236	700,252	377	I. 51,562	97
640,233	375	670,099	82	703,086	376	P. 68,587	178

SUBJECT INDEX

Figures in heavy type refer to principal references.

A

ACETALDEHYDE, 146, 220, 221, 268, 271
5-Acetamido-2-aminobenzoic acid, 75
4-Acetamido-2-acetoxytoluene, 305
p-Acetamidobenzenediazonium chloride, 22
p'-Acetamidophenyl-2-naphthyl amine-1-sulphonic acid, coupling, 222
2-Acetamidothiophen, 203
4-Acetamido-*o*-tolenediazonium bromide, 305
Acetate radicals, 110
Acetoacetarylamides, coupling, 209, 215, 216
Acetoacetic acid, coupling, 211, 215
ester, coupling, 209, 215
Acetone, 271
Acetonediacetic acid, 215
Acetone dicarboxylic acid, coupling, 209
oxime, 189
sulphonic acid, 209
Acetophenone, 317
Acetophenone-ω-sulphonic acid, 209
p-Acetoxydiazobenzene, 344, 348
2-Acetoxyfluorene, 305
2-Acetoxyfluorenone, 305
Acetylacetone, coupling, 209, 210
1-Acetyl-*p*-chlorostilbene, 320
Acetyldibenzoylmethane, 232
N-Acetyl H-acid, 348
Acetylene, 314
Acetylmethylaminobenzene-4-diazohydroxide, 133
Acridine, 264
Acrylonitrile, 175, 320
Active stabilised diazo-compounds, 71
Acylhydrazines, 190
Aldehydes, 116
Aliphatic acids, effect on velocity of decomp. of diazo-compounds, 66
alcohols, effect on velocity of decomp. of diazo-compounds, 66
diazoamino-compounds, 158, 169
Alizarine, 66, 69
Alkyl hydrogen sulphates, 73
N-Alkylhydroxylamines, 188
N-Alkyl-2-methylenedihydroquinoline, 222
N-Alkyl-2-methylenetrialkylindoline, 222
Alkyl nitrites, 18, 75
Alkyl-ω-sulphonates, 171
Aluminium chloride, 279, 318
Amidines, 170, 173
tert.-Amines, sulphuric esters, 152
4-Amino-5-acetamidotoluene, 249
p-Aminoacetanilide, 133
1-Aminoanthraquinone-4-arsonic acid, 331
1-Amino-4-(3'-aminoanilino)anthraquinone-2-sulphonic acid, 203
o-Aminoazobenzene, 201
p-Aminoazobenzene, 163, 203, 204, 227
p-Aminoazo-compounds, 201, 202, 203
o-, *m*-Aminoazotoluene, 204
o-Aminoazo-*p*-toluene, 201
p-Aminobenzenediazonium chloride, 22
auric chloride double salt, 22
p-Aminobenzenesulphonamide, 349
m-Aminobenzoic acid, 189
2-Aminobenzoic-5-sulphonic acid, 175
Amino-compounds, coupling, 200–204
m-Amino-*p*-cresol, coupling, 205 *et seq.*
1-Amino-4 : 8-dihydroxyanthraquinone, 297
2-Aminodiphenyl, 161, 316
4-Aminodiphenyl, 316, 321
o-Aminodiphenylamine, 161, 250
p-Aminodiphenylamine, diazonium salts, isolation, 73
1-Amino-2-4'-glyoxinylpropionic acid, 347
Aminoguanidine, 53
1-Amino-4-hydroxyanthraquinone-6-sulphonic acid, 297
1-Amino-2-hydroxy-4-cyanonaphthalene, 227
1-Amino-2-4'-iminazolylpropionic acid, 347
3-Aminoindazole, 247
3-Amino-4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, 252
p-Aminomethyl formanilide, 133
1 : 4-Aminonaphthol, 30
1 : 8-Aminonaphthalenesulphonic acid, 339
Aminonaphtholsulphonic acids, coupling, 205 *et seq.*
1 : 2-Aminonaphthol-6-sulphonic acid, 207
2 : 1-Aminonaphthol-4-sulphonic acid, 207
1 : 8-Aminonaphthol-4- and -5-sulphonic acid, 207

2 : 8-Aminonaphthol-6-sulphonic acid, 208
2 : 5-Aminonaphthol-7-sulphonic acid, 208
1 : 2-Aminonaphthol-3 : 6-disulphonic acid, 207
1 : 8-Aminonaphthol-3 : 6-disulphonic acid, 208, 339
m-Aminophenol, 53
p-Aminophenol, 191
2-, 4-Aminophenol aryl ethers, 73
Aminoquinolines, coupling positions, 203
2-Aminoresorcinol, 44
2-Amino-4-sulphobenzoic acid, 174
Aminosulphonamides, 97
cis-, and *trans*-Aminotriarylethylene, 242
p-Aminotriphendioxazines, 43
3-Amino-4-, 4-amino-3-ureidobenzoic acid, 248
Ammonia, 160, 161
Ammoniacal cuprous oxide, 112, 298
Amyl nitrite, 18, 159
Analysis, qualitative, 339
  quantitative, 339
Andrewe's test, 346
Anethole, 220
Aniline, 158, 189, 313, 315
Aniline, coupling, 200, 203
Aniline nitrite, 47
3-Anilino-4-ketodihydrobenztriazine, 251
1-Anilinoanthraquinone-3-sulphonic acid, 297
Anisole, coupling, 218
Anisol-*p*-sulphonic acid, stabilising effect, 85
Anisole-*m*-, -*p*-sulphonic acid, 307
Anthracene-2-diazonium fluoborate, 295
Anthracene-β-diazonium fluoborate, nitration, 116
Anthanthrone, 312, 326
β-Anthranine, coupling, 203, 225
Anthranil, 189
Anthranilic acid, 75
Anthranol, coupling, 226
Anthraquinone, 50, 270
Anthraquinone-1-azide, 188
Anthraquinone-1-diazonium chloride, 233
  electrolysis, 312
Anthraquinonediazonium fluoborates, 80
Anthraquinone-1-, 2-diazohydroxide, 381, 382
Anthraquinone-1-diazonium sulphate, 183, 189, 323, 324
Anthraquinone-2-diazonium sulphate, 183
Anthraquinone-1-diazothiocyanate, 323
Antibodies, 205
Antigens, 205
Anti-knock agents, 175
Antimony, 335
  trichloride, 77, 279
Antoxyproteic acid, 345
*iso*Apiole, 220
Aporphin, 258
Arsanthrene chloride, 332
Arsenosobenzene, 332
Arsenic, 333
2-Aryl-3-acetoxy-6-keto-2 : 3 : 4 : 6-tetrahydrocinnoline, 245
Arylamine methyl-ω-sulphonates, 202
Arylamines, 188
  determination by diazotisation, 342
Arylazides, 160, **187**, 296
Arylazodiaryls, 112
1-Arylazo-2-naphthylamine, 163
Arylazoxycarboxyamides, 128
Arylazocarboxyanilides, 128
Arylbenzoquinone, 272
Arylbismuth dichlorides, 335
Arylcyanamides, 202
Aryl cyanides, 309, 310
Arylcyanoguanidines, 164
Arylhydrazines, 50, 149, **183**, 189
Arylmercuric chlorides, 336, 337
Aryl mercury compounds, 80
Arylnitramic acids, coupling, 202, 209
Aryl nitriles, 309, 310
Arylnitroamines, 96, 180, 181
Arylnitrosamines, 135, 384, 390
Arylnitrosohydroxylamines, 97
Arylquinones, 318
Aryl radicals, 299, 300, 316
Arylphosphinous acids, 335
Arylselenocyanates, 323, 324
Arylstibine dichloride, 334
Arylstibine oxides, 335
m-Aminostibinosobenzene, 334
Arylstibonic acids, 334
Arylsulphamic acids, coupling, 202, 209
Arylsulphonic acids used as stabilisers, 88, 89
Arylthiocyanates, 323, 324
Arylthioglycollic acids, 324
Ascorbic acid, 186
Asymmetric diaryls, 314 *et seq.*
Asymmetrical diazoamino-compounds, hydrogen bonding, 167
Azimides, 248
Azimines, 248
Azobenzene, 195, 298, 299, 335
cis-, and *trans*-Azobenzene, 228, 229
Azobenzene-2 : 2′-, -3 : 3′-diarsonic acid, 299
Azobenzene-4 : 4′-diarsonic acid, 332
Azobenzeneformhydroxamic acid, 146
Azo-compounds, 51, 194, 195, 196, 285, 286, 298, 299, 300, 301, 303
  attack by diazo-compounds, 224
  constitution and configuration, 225 *et seq.*
As-Azo-compounds, 333

C-Azo-compounds, 194
Cu-Azo-compounds, 283
N-Azo-compounds, 194
O-Azo-compounds, 141, 142, 194, 333
S-Azo-compounds, 192, 193, 194, 324, 325, 326, 327
Azo dyes, generation within fibrous sheets, 356
Azo Guard, 85
Azo-hydrazo tautomerism, 209, 210
Azoimides, 187, 248
Azonaphthalene, 148
1 : 1′-Azonaphthalene-8 : 8′-disulphonic acid, 312
Azophor Red, 72
Azopyrazolones, 267
Azoxybenzene, 229
cis-Azoxybenzene, 228
Azoxybenzenecarbonamide, 146
Azoxy-compounds, 394
Azoxysulphones, 128, 395, 398
Azoproteins, 175, 205
  geometrical isomerism, 205

B

Barium nitrite, 8
Bart reaction, **331**, **332**
meso-[4 : 5]-Benzacridan, 265
Benzalacetone, 320
Benzaldehyde, 146, 185, 222, 307, 317
Benzaldehyde phenylhydrazone, 215
4-Benzamido-2 : 5-diethoxybenzenediazosulphonate, **148**, 151, 152
4-Benzamidonaphthalene-1-diazonium chloride, 141
4-Benzamidonaphthalene-1-diazocyanide, 144
4-Benzamidonaphthalene-1-azo-2′ : 2′-dibenzoylpropenyl ether, 141
4-Benzamidonaphthalene-1-azo-4′-nitrophenyl ether, **141**
1 : 2-Benzanthracene-4-carboxylic acid, 257
4 : 3-Benzanthracene-1-carboxylic acid, 257
Benzedrine, 347
Benzene, 268, 272, 304, 307, 313, 315, 317, 318, 335, 338
Benzeneazo-*p*-cresol, 227
Benzenearsonic acid, 330, 331, 332
Benzeneazodiphenyl, 112, 113, 298, 299, 325
Benzeneazodiphenylnitromethane, 217
Benzeneazo-*p*-hydroxydiphenyl, 227
4-Benzeneazo-1-naphthol, 226, 227
1-Benzeneazo-2-naphthol, 227
1-Benzeneazo-2-naphthyl amine, 203, 227
Benzeneazophenol, 67
Benzeneazopropionic ester, 212
Benzeneazoxycarbonamide, 395
o-, *m*-, *p*-Benzenediarsonic acid, 332
Benzenediazoaminoazobenzene, 163, 167
Benzenediazoaminobenzene-4-azonitrobenzene, 344
Benzenediazocarbonamide, 146, 395
Benzenediazocyanide, 154
Benzenediazonium acetate, 190
  chloride, 140, 143, 183, 185, 231, 294, 313, 314, 323, 325, 326, 335, 337, 338
  chloride, effect of chlorides on decomp., 64
  chloride, velocity of decomp., 62, 63
  chloride, velocity of decomp. in solution, 304
  fluoborate, 80, **283**, 337, 338
  hydroxide, **381**
  nitrate, 153, 159, 294, 311, 352, 354, 357
  nitrite, 47
  phosphorus hexafluoride, 81
  picrate, 161
  sulphate, **19**, 158, 276, 294, 297, 302, 306, 312, 314, 323, 325, 329
Benzenediazonium salts, nitration, 12, 381
  solid, 7
Benzenediazonium tri- and tetraiodomercuriate, 337
Benzene-1 : 2-diazo-oxide-4-arsonic acid, 120
Benzene-1 : 2-diazo-oxide-5-sulphonic acid, 362
Benzenediazo-oxydiazobenzene carbimide, 143
Benzenediazopiperidide, 231
Benzene *iso*diazotate, 210
  potassium salt, **130**
Benzene *n*-diazotate, 210
  potassium salt, **126**
  barium, calcium, lead, mercury, silver, zinc salts, 126
Benzenesulphinic acid, **328**
Benzenesulphohydroxamic acid, 128
Benzenesulphonic acid, 307, 329
Benzenesulphonylbenzidine, 36
Benzene-*o*-tetrazonium chloride, 185
Benzenethiosulphonic acid, 95
Benzonitrile, **309**
Benzophenone nitrophenylhydrazone, 217
p-Benzoquinone, 227, 272, 318, 319
p-Benzoquinonebishydrazones, 227
4 : 5-Benzpyrazole, 245
3 : 4-Benzpyrene, coupling, 221
Benzthiodiazoles, 253, 254
Benztriazines, 251, 252, 253
1 : 2 : 3-Benztriazine-3-oxide, 252
Benzoylacetic acid, 175
Benzoylazobenzene, 146
3-Benzoylcarbazole, 264

Benzoylhistidine, 347
β-Benzoylphenylhydrazine, 185
Benzyl alcohol, 307
van den Bergh reaction, 346
Bilirubin, 345, 346
Bisacetoacet-*o*-tolidide, 215
1 : 4-, 1 : 5-, 1 : 8-Bisazidoanthraquinone, 189
p-Bisazidobenzene, 191
4 : 4′-Bisazidodiphenyl, 187
Bis-S-azo-compounds, 193
Bisbenzeneazobenzene, 229
Bisbenzeneazophenol, 67
Bisbenzeneazopyrone, 211
Bisdiazoamino-compounds, 158, 159, 160
  use as anti-knock agents, 175
Bisdiphenylarsine oxide, 332
2 : 4-Bis(benzeneazo)phenol, 197
Bismarck Brown, 21, 25, 229, 349
  diazotised, 25
Blood, 346, 347, 348, 349
  serum, 346
p-Bromoaniline, 159
β-Bromoanthraquinone, 290
Bromobenzene, 290
p-Bromobenzenediazocarbonamide, 146
p-Bromobenzenediazocyanide, 142, 144
p-Bromobenzenediazonium bromide, 280
  chloride, 280
  mercuribromide, mercurichloride, 283
p-Bromodiazobenzene, 155
2-, 3-Bromodibenzfuran, 262
4-Bromodiphenyl, 316
2-Bromofluorenone, 260
3-Bromofluorenone, 259, 260
4-Bromofluorenone, 259
Bromohydrocarbons, 154
4-Bromo-4′-hydroxydiphenyl, 289
3-Bromo-5-nitrobenzene-1 : 2-diazo-oxide, 358
6-Bromo-2 : 4-dinitrodiazobenzene, 14
6-Bromo-4-hydroxy-3-methylcinnoline, 243
β-Bromonaphthalene, 288, 289
4-Bromonaphthalene-1 : 2-diazo-oxide, 120
1 : 2-, 1 : 8-, 2 : 1-Bromonaphthalene sulphonic acid, 288
1-Bromo-2-naphthol, coupling, 221, 234
6-Bromo-1-naphthol, 274
1-Bromo-2-naphthol-6-, -8-sulphonic acid, coupling, 221
4-Bromo-1 : 2-naphthylenediamine, 249
p-Bromonitrobenzene, 280
3-Bromo-5-nitro-2-diazobenzoic acid, 15
p-Bromophenol, 288
3-Bromo-4-phenylcinnoline, 242
4-Bromo-1 : 2-phthalolylcarbazole, 264
p-Bromoselenophenylthiocyanate, 324
m-Bromotoluene, 288
p-Bromotoluenesulphonic acid, 287
8-Bromo-3 : 4 : 5-trimethoxyphenanthrene-9-carboxylic acid, 256
α-Bromopyridine, **288**
Butadiene, 175, 234
  coupling, 219
  determination, 343
Butanol, *iso*-, 271, 274
  n-, 269, 271, 274

C

Cadion reagents, 168, **244**, 343, 344
Cadion 2B, 3B, 344
Cadmium iodide, 5
Cadmium ions, detection, 343
Calcium chloride, 276, 279
  nitrite, 8
Carbazole, 161, 250, **263**, 264, 288
  -3-diazonium salts, 24
  chloride, 359
Carbenium salts, 232
Carboethoxy-*o*-phenylenediamine, 248
Carbon tetrachloride, 317
Carboxybenzenediazonium nitrate, 17
m-Carboxybenzenediazonium sulphate, 276
o-Carboxydiphenyl sulphide, 328
1-Carboxyindene-3-sulphonic acid, 362
γ-(2-Carboxy-3-indolyl)butyric acid, 213
m-Carboxyphenylazide, 189
m-Carboxyphenylselenocyanate, 324
o-Carboxyphenylthioglycollic acid, 327
"Carriers", for Rapidogen dyes, 171
Casein, 52, 204, 205
Catechol, 199, 315
Cellulose acetate, 173
Chelidonic acid, coupling, 211
Chloroacetone, coupling, 210
"Chloramine T", 188
Chloroamine, 187
o-, *p*-Chloroaniline, by decomp. of phenylazide, 191
p-Chloroaniline, determination in blood and plasma, **349**
Chlorobenzene, 64, 277, 304, 313, 314, 317, 335
p-Chlorobenzenearsonic acid, 287
p-Chlorobenzenediazocarbonamide, 145
p-Chlorobenzenediazocyanide, **142**, 143, 144
o-, *p*-Chlorobenzenediazonium thiocyanate, 125
p-Chlorobenzenediazonium chloride, 19
  thermochemistry, 353
p-Chlorobromobenzene, 280
2-Chloro-4-bromobenzenediazonium chloride, 125
2-Chloro-1-bromonaphthalene, 287
2-Chlorocarbazole, 264
Chlorocresol ethyl ether, 306
Chlorodiazoamino-compounds, 188

m-Chlorodiazobenzene, 175, 303
1 : 2-, 2 : 1-Chlorodiazonaphthalene, 331
4-Chloro-2-diazotoluene, stabilisation with acetylsulphanilic acid, **84**
3-Chlorodibenzfuran, 262
2-Chloro-2′ : 5′-dihydroxydiphenyl, 319
p-Chlorodimethylaniline, 201
2-, 3-, 4-Chlorodiphenyl, 316
β-Chloroethanol, 271, 274
2-Chlorofluorene, 305
2-, 3-Chlorofluorenone, 260
6-Chloro-2 : 4-dinitrodiazobenzene, 14
1-Chlorohydrocinnamylcyanide, 320
7-Chloro-2-hydroxycinnoline, 243
3-Chloro-2-hydroxydiphenyl, 315
2-Chloro-5-methoxyaniline, 201
β-Chloronaphthalene, **286**
1-Chloronaphthalene-8-sulphonic acid, 286
1-Chloro-2-naphthol, coupling, 222
1 : 8-Chloronaphthol-3 : 6-disulphonic acid, 286
1-Chloro-2-naphthylamine, 159
m-Chloronitrobenzene, 279
p-Chloronitrobenzene, 276, 278, 281, 314
3-Chloro-7-nitrodibenzfuran, 262
2-Chloro-1-nitronaphthalene, 287
p-Chloronitrosophenylhydroxylamine, 145
3-Chloro-2-nitrotoluene, **294**
m-Chlorophenol, 303
o-Chlorophenol, 315
5-Chloro-4-phenoxyacetamido-2-methoxyaniline, 73
m-Chlorophenylacetate, 305
p-Chlorophenylnitroamine, 180
1-*p*-Chlorophenyl-5-*iso*propyldiguanide, 164
p-Chlorophenylselenocyanate, 324
2-Chloro-4-, -6-picoline, 52
p-Chlorostilbene, 320
o-Chlorotoluene, 276, 280, 285, **286**
p-Chlorotoluene, 285
Chlorotoluenediazonium sulphate, 306
Chloroprene, 175
3-Chloropyridine, 52
Chromium chloride, 279
Chromotrope acid, morpholine salt, 356
Chrysene-6-carboxylic acid, 256
Chrysoidine, 201
Cinnamalacetic acid, 320, 321
Cinnamic acid, 154, 320, 321
Cinnamylcyanide, 320
Cinnolines, 241 *et seq.*
Cinnamylideneacrylic acid, 321
Clayton Yellow, 162, 297
Cobalt chloride, 279
Colloidal metals, effect on decomposition of diazo-compounds, 65
Colloidal organic substances, effect on decomp. of diazo-compounds, 66
Colour photography, application of diazo-compounds, 370, 371
Constitution of diazo-compounds, relation with pH, 99 *et seq.*
Copper, 287, 337
  acetylide, 314
  aryls, 338
  hydride, 282
Coumarin, 320
Coupling reaction, 194 *et seq.*
  coupling energy, 225
  effect of pH, 194–197, 205–208
  effect of pyridine, 224
  elimination of substituents, 221
  kinetics, 229, 230
  mechanism, 230 *et seq.*
  theory, 397
Cresidine, coupling, 200
Cresol, 343
p-Cresol, 199, 229
o-Cresol methyl ether, 307
Crotonic acid, 320
Cuba Orange, 148
Cupric chloride, 278, 279, 287, 318
  thiocyanate, 323
Cupro-cupric sulphite, 294
Cuprous bromide, 280, **288**
  chloride, 277, 278, 279, 280, 281, **285**, **286**, 313
  cyanide, 310
  oxide, 273, 298
Cyanamide, 164, 172, 175
Cyanamide carboxylic acid, 172
p-Cyanamidoazobenzene, 202
*iso*Cyanides, 146, 394
Cyanobenzoic acid, 309
Cyanogen bromide, 203
1-Cyanonaphthalene-3 : 6 : 7 : 8-sulphonic acid, 310
Cyclic ketones, coupling, 209
*cyclo*Hexanone carboxylic acid, coupling, 212
*cyclo*Pentadiene, 219, 227
  derivatives produced by irradiation, 362
*cyclo*Pentanone-2-carboxylic acid, coupling, 212

D

Dermatitis, 186
Deuterium oxide, 63, 272
Diacetyl phenylhydrazone, 212
Diacetylsuccinic ester, 232
Daddi's reagent, 345
p-Dialkylaminobenzenediazonium salts, 52
m-Diamines, coupling, 201
o-Diaminoanthraquinones, 250
p : *p*′-Diaminodiaryl disulphides, 253
p : *p*′-Diaminodiphenylmethanesulphone, action of nitrous acid, 43, 350

Diaminopyridine, 53
4 : 6-Diaminopyrimidine, coupling, 202
4 : 6-Diamino-*m*-xylene, 159
1 : 5-Diamino-4 : 8-dihydroxyanthraquinone, 297
Diammino cuprous bromide, **288**
Diamond Black PV, 200
1 : 4-Dianilinoanthraquinone-2-sulphonic acid, 297
Dianisylethylene, 220
αα′-Dianthraquinolyl, 304, 312
1 : 5-Di-β-anthraquinonylpentazdiene, 161
ββ′-Dianthrimide, 161
Diarylbismuth chlorides, 335
Diarylethylenes, 233
Diaryls, 109, 112, 134, 145, 285
Diarylstannic chloride, 338
oxides, 338
Diarylstibine hydroxide, 335
Diaryl sulphides, 192, 324
Diaryltriazens, pyrogenic decomp., 161
rearrangement to aminoazo-compounds, 162
Diazoacetates, 305
Diazoaminobenzene, 5, 20, 47, 157, 158, **159**, 163, 167, 175, 203
Diazoamino-compounds, 4, 17, 51, 134, **157–169**, 185, 284, 297
co-ordination complexes, 162
metal salts, 162
Diazoaminotoluene, 160
Diazoamino-*p*-toluene, 201
Diazo-anhydrides, 29, **133**, **134**, 318
α-Diazoanthraquinone, 287
β-Diazoanthraquinone, 161
Diazoarylsulphonates, **83**
drying, 88
standardisation, 89
Diazoarylsulphonic acids, 354
Diazoarylsulphinates, 93 *et seq.*
Diazoarylthiosulphonates, 95
m-, *o*-Diazobenzenearsonic acid, 299
p-Diazobenzenearsonic acid, 287
Diazobenzene-*p*-diazotoluenetoluidide, 160
Diazobenzene hexachlorostannate, 277
imide, 187
methyl ether, **139**, 140
perbromide, 180, 187, 290
Diazobenzenesulphonic acids, constitution, 389
Diazobenzene-*m*-sulphonic acid, 307
Diazobenzene-*p*-sulphonic acid, **10**, 307, 331, 345, **346**, 347
explosiveness, 61
Diazobenzene platinichloride, 277
Diazobenzene-2-thionaphthol ether, 192
Diazobenzene thiophenol ether, 192
m-Diazobenzoic acid, 148, 189, 205
o-, *p*-Diazobenzoic acid, 205
2-Diazobenzthiazole, 53
3-Diazocarbazole, 365
as antiseptic, 356
Diazocarbonamides, 145
Diazocarboxylic acids, 142
Diazo casein, 365
Diazo chloroiodide, 154
Diazo-compounds, as oxidising agents, 111, 114
activation energy of decomp., 63
combination with leuco vat dyes, 356
constitution, **378**
decomp. by mercury vapour light and sunlight, 359
effect of pH on velocity of decomp., 66, 67
Hantzsch's diagram, 390
nomenclature, 378, 383
stability in solid state, 61
stability in solution, 61
velocity of decomp. in solution, 62, 63, 64
use as explosives, 354
Diazocyanides, 134, 142
anti-, *syn-*, 144
cis-, *trans-*, 144
iso-, *n-*, 94, 149
labile, 149, 309
stable, 149
constitution, 387, 388, 394
Diazo-ψ-cumene, 94
p-Diazodiphenylamine, 196, 360
sulphate, 362
photolysis of metallic double salts, 360
2-Diazo-3 : 4-dimethoxybenzoic acid, 307
2-Diazodiphenyl, 291
3-Diazodiphenyl, activation energy of decomp., 63
Diazo ethers, 139–141
"Diazo exchange", 223
Diazohydroxides, 100, 112, 130, 196, 270
constitution, 382, 383, 395, 396
anti-, *syn*-Diazohydroxides, 385
n-Diazohydroxides, 233, 234, 235
Diazoiodochlorides, 187
Diazoic acids, 179
Diazo-imines, 28, 36, 248
3-Diazoindazole, 52, 53
α-Diazonaphthalene, 303
oxidation, 31, 129
β-Diazonaphthalene, 95
oxidation, 31, 129
1 : 2-Diazonaphthalenesulphonic acid, 299
1 : 4-Diazonaphthalenesulphonic acid, 298, 303
1 : 5-Diazonaphthalenesulphonic acid, 298
1 : 8-Diazonaphthalenesulphonic acid, 288, 298
2 : 1-, 2 : 6-Diazonaphthalenesulphonic acid, 299
Diazonium acetates, 42

Diazonium-antimony trichloride double salts, 77, 334
Diazonium arylsulphonates, 271
Diazonium-arsenic trichloride double salts, 333
Diazonium azides, 42
borofluorides, 277, 283
carbonates, 42
Diazonium chlorides, 72
dry, 318
order of stability in aqueous solution, 64
Diazonium chromates, 41, 42, 354
cobaltinitrites, 42, 295
Diazonium-cuprous chloride complexes, 285
Diazonium cyanides, 388
Diazonium-diazo equilibrium, 196
Diazonium-diazotates, 102
equilibrium in solid, 102
Diazonium fluorides, 41, 284
fluoborates, 80, 283, 295, 305
group, its negative effects, 381
hydroferricyanides, 42
hydroxides, 100, 381, 382
iodides, 42
ions, 231, 233
ions, transition to diazotate ions, 100, 101, 102
molybdates, 42
nitrates, 148
nitrites, 42
perchlorates, 41, 42, 354
phosphomolybdates, 42
phosphotungstates, 42
picrates, 42
Diazonium salts, **41**, **42**, 71, 73, 151, 152
action of alkali, 100, 126
colour, 382, 402
complex cyanides, 81
constitution, 378
effect of metallic salts on decomp., 65
exchange of anions with nuclear substituents, 124, 125
ionisation, 100
labile complexes, 114
precautions against explosion, 6
resonance forms, 100
solid, 17, 19, 61
Diazonium sulphates, 72, 290, 302
decomp. in solution, 64
solid, 13, 72, 74, 75, 294
sulphinates, 42, 94, 95
tetrachloroiodides, 155
thioacetates, 42
thiocyanates, 42
thiosulphates, 42
tungstates, 41, 42
Diazo-oxides, **28**, 117, 121, 122, 123, 133, 196, 273
action of light, 357
action of bromine, 32
constitution, 33
Diazo-oxides, coupling, 31
Diazoperbromides, 94, 153, 154, 290
Diazo perhalides, 153 *et seq.*
Diazo periodide, 154
p-Diazophenol, 148
sulphate, 289
4-Diazophenol-3 : 5-disulphonic acid, 343
1 : 4-Diazophenol-3-sulphonic acid, 29
2 : 1-Diazophenol-4-sulphonic acid, 29
3-Diazophthalic acid, 307
Diazoplumbichlorides, 187
4-Diazopyrazole, rate of decomp., 53
4-Diazopyrazolone, rate of decomp., 53
1-Diazopyridine, 200, 315
Diazo-radical, 299, 300, 301
Diazo-resins, 68, 307, 308
Diazo solutions, standard, 342
Diazosulphides, 109, 155, 156, 253, 318
Diazosulphonates, 134, **147**, 183, 369, 370, 390, 391
absorption spectra, 390, 391
action of light, 151, 357
constitution, 389
Diazosulphones, 93 *et seq.*
Diazo thioethers, 192, 193
Diazotates, 270, 317
absorption spectra, 384
action of light, 357
as oxidising agents, 383
anti-, 129
syn-, 127
*iso*Diazotates, 52, 94, 101, **127–137**, 143, 180, 181, 182, 185, 204, 318, 331
constitution, 383, 384, 390
in silver photography, 370
n-Diazotates, 94, 100, 101, **126**, 127, 128, 130, 143, 146, 180, 185, 331
constitution, 382
recognition, 132
Diazotisation, failure, 43
Diazotisation methods :
concentrated acid, 10
direct, 3
Griess, method of, 16, 290
inverted, 9
Knoevenagel, method of, 18
in non-hydroxylic solvents, 75
summary of methods, 3
theory of, 44
under pressure, 13
velocity, 44
Witt, method of, 15
Diazotisation of : (see also Tetrazotisation).
Acetyl-*p*-phenylenediamine, 36
p-Aminoacetanilide, 22
1-Aminoacridine, failure, 43
Diazotisation of :
5-Aminoacridine, 52, 59
3-Amino-6-alkoxypyridines, 54
4-Amino-5-anilino-3-methylpyrazole, 50

Diazotisation of:
9-Aminoanthracene, failure, 43
1-Aminoanthraquinone, 11, 13, 17
2-Aminoanthraquinone, **19**
Aminoantipyrine, 56
Aminoazobenzene, **7**, 10
p-Aminoazobenzenesulphonic acid, 7
o-Aminoazotoluene, **74**
Aminoazotoluene, 10
p-Aminobenzaldehyde, 12
p-Aminobenzylamine, 9
2-Aminobenzthiazole, **52**, 57
8-Aminocaffeine, 59
5-Amino-3-carboxy-1 : 2 : 4-triazole, 57
3-Amino-2-*p*-chlorophenyl-4 :6-dimethyl-1-*iso*butylindole, 58
2-Aminodibenzfuran, **8**, **303**
6-Amino-2 : 2′-dicarboxydiphenyl, failure, 43
3-, 4-Amino-1 : 2-dihydroxyanthraquinone, 11
5-Amino-2 : 4-dihydroxypyrimidine, 54
p-Aminodimethylaniline, 23, **24**
2-Amino-4 : 5-dimethylazobenzene, 7
5-Amino-3 : 5-dimethyl*iso*-oxazole, 57
4-Amino-3 : 5-dimethylpyrazole, 55
p-Aminodiphenylamine, 24
3-Amino-2 : 5-diphenylpyrrole, 55
4-Amino-4′-ethoxydiphenylamine, **24**
1-Amino-2-hydroxy-4-cyanonaphthalene, 30
3-Aminoindazole, 59
Aminoleucoindigotin sulphuric esters, 8
3-Amino-4-methoxyphenyl-1-trifluoromethylsulphone, 8
5-Amino-3-methyl-1 : 2 : 4-triazole, 56
1-Aminonaphthalene-8-sulphonic acid, **290**
1 : 2-, 2 : 1-Aminonaphthol, 30, 31
1 : 8-Aminonaphthol, 31
1 : 8-Aminonaphthol-4-sulphonic acid, 31
1 : 2-Aminonaphthol-4-sulphonic acid, **30**
2 : 3-Aminonaphthol-6-sulphonic acid, 30
5-Amino*iso*-oxazole, 57
3-Aminophenanthrene, 14
o-, *p*-Aminophenol, 28
m-Aminophenols, failure to form diazo-oxides, 31
1-*p*-Aminophenyl-2-aminopropane, 9
4-Amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, 56
4-Amino-3-phenyl-1 : 2-dimethyl-5-pyrazolone, 56
3-Amino-2-phenyl-1-ethyl-4 : 5-benzindole, 58
3-Amino-2-phenylindole, 58
5-Amino-1-phenyl-3-methyl-4-alkylpyrazoles, 55
Diazotisation of:
3-Amino-2-phenyl-1-methylindole, 58
4-Amino-1-phenyl-5-methyl-3-pyrazolone, 56
2-Amino-4-, -6-picoline, 52, 54
3-, 4-Aminopyrazole, 55
3-, 4-Aminopyridine, 52, 53, 54
4-Aminoquinoline, 59
Aminosalicylic acid chromium complexes, 8
Aminostyrene-maleic anhydride resins, 8
4-Amino-1-*p*-sulphophenyl-3-alkyl-, -carboxypyrazolone, 56
5-Amino-1 : 2 : 3 : 4-tetrazole, 53, 57
2-Aminothiazole, 57
2-, 3-Aminothiophen, 58
5-Amino-1 : 2 : 4-triazole, 56
3-Amino-2 : 4 : 5-triphenylpyrrole, 55
5-Aminouracil-4-carboxylic acid, 52, 54
Aniline, 5, 7, 16, 18, **19**, **283**, 284, **309**, **311**, **334**
β-Anthramine
Anthraquinone-1 : 2-*iso*oxazoles, 12
Aposafranine, 11
Arylphosphamic acids, 8
Arylsulphamic acids, 8
4-Benzamido-2 : 5-diethoxyaniline, **148**
Benzenesulphonyl-1 : 5-, -1 : 8-naphthylenediamine, 36
Benzenesulphonyl-*p*-phenylenediamine, 36
Benzidine, 21
2-Bromo-, 2-chloro-1 : 4-diaminoanthraquinone, 23
2-Chloro-3-amino-4-butylaminopyridine, 53
5-Chloro-4-amino-1-phenyl-3-methylpyrazole, 55
2′-Chloro-4′-nitro-2-amino-4-methoxy-5-methylazobenzene, 8
Chloronitroaminophenol, 16
3-Chloro-2-toluidine, **294**
4-Choro-*o*-toluidine, **5**
Diamines, 21
1 : 4-, 1 : 5-Diaminoanthraquinone, 22
1 : 4-Diaminoanthraquinone-2 : 6-, 2 : 7-disulphonic acid, 23
4 : 4′-Diaminobenzeneazo-1-naphthalene, 22
2 : 5-Diaminobenzoic acid, 23
3 : 3′-Diamino-4 : 4′-dihydroxy-1-arsenobenzene, failure, 43
2 : 2′-, 2 : 4′-Diaminodiphenyl, 21
4 : 6-Diamino*iso*phthalaldehyde, 44
Diaminomethoxycoumarin, failure, **43**
2 : 7-Diaminonaphthalene, 22
1 : 4-Diaminonaphthalene-2-sulphonic acid, 23
3 : 5-Diamino-1-phenyl-1 : 2 : 4-triazole, 57

Diazotisation of:
2 : 6-, 3 : 4-Diaminopyridine, 53
4 : 4′-Diaminostilbene, 21
2 : 4-Dibromo-6-nitroaniline, 11
2 : 3-Dibromo-, 2 : 3-dichloro-1 : 4-diaminoanthraquinone, 23
4 : 6-Dibromo-2-nitroaniline, 14
2 : 6-Dibromo-4-nitroaniline, **12**
3 : 5-Dichloro-4-aminoacetanilide, 37
2 : 5-Dichloroaniline, **7**
2 : 5-Dichloro-*p*-nitroaniline, 118
2 : 6-Dichloro-4-nitroaniline, 11, 12, 14
NN-Dimethyl-*p*-phenylenediamine, 23
2 : 6-Dichloro-*p*-phenylenediamine, 23
3 : 5-Dinitro-4-aminobenzene-1-arsonic acid, failure, 43
2 : 3-Dinitro-4-aminophenol, 119
3 : 5-Dinitro-4-aminophenol, 12
2 : 4-Dinitroaniline, **11**, 310
2 : 3-Dinitro-*p*-anisidine, 118
4 : 6-Dinitro-3-anisidine, 118
4 : 5-Dinitro-*o*-anisidine, 119
2 : 6-Dinitro-*p*-anisidine, 29
2 : 6-Dinitro-4-chloroaniline, **13**
2 : 4-Dinitro-1-naphthylamine, 11, 13, 30, **273**
1 : 6-Dinitro-2-naphthylamine, 13
3 : 5-Dinitro-*o*-toluidine, **15**
3 : 5-Dinitro-*p*-toluidine, 11
Disulphamic acids, 22
Formyl-*p*-phenylenediamine, 37
Lead aminoaryls, 8
Leuco-β-aminoanthraquinone disulphuric ester, 8
N-Methyl-*p*-phenylenediamine, 24
Naphthionic acid, 6, 10
α-Naphthylamine, 4, **180**, **191**
β-Naphthylamine, **286**, **290**
Nitramic acids, 8
3-Nitro-4-aminoacetanilide, 37
2 : 3-Nitroaminoanthraquinone, 17
3-Nitro-4-aminodiphenyl, 14
Nitroaminophenol, 16
2-Nitro-*p*-aminophenol, **29**
3-Nitro-4-aminophenol, 30
m-Nitroaniline, 20
o-Nitroaniline, **311**
p-Nitroaniline, 4, **6**, **10**, 18, 72
4-Nitro-2-cyanoaniline, 11
1-Nitro-2-naphthylamine, 118
2-, 4-Nitro-1-naphthylamine, 13
o-Nitro-*p*-phenetidine, 10
2-Nitro-*p*-phenylene diamine, 23
o-Nitro-*p*-toluidine, 10
5-Nitro-*m*-xylidine, **272**
Pentabromoaniline, 11, 43
Pentabromo-*p*-aminodiphenylamine, 24
m-Phenylenediamine-4-sulphonic acid, 26
p-Phenylenediamine, 22
Diazotisation of:
p-Phenylenediamine-2-arsonic acid, 23
p-Phenylenediamine-2-sulphonic acid, 23
Phenylguanazole, 57
Picramic acid, 16
Picramide, 12, 14, 18, 43
Sulphanilic acid, **10**, 17, **344**, **346**
p-Sulphobenzeneazo-α-naphthylamine, 18
1 : 4 : 5 : 8-Tetra-aminoanthraquinone, 22
2 : 3 : 5 : 6-, 2 : 3 : 4 : 6-Tetrabromoaniline, 13
m-Toluidine, **288**
o-Toluidine, **286**
Toluylenediaminesulphonic acid, 26
2 : 5 : 6-Tribromo-4-nitroaniline, 13
4 : 5 : 6-Tribromo-2-nitroaniline, 13
2 : 3 : 6-Tribromo-4-nitroaniline, 13
2 : 4 : 6-Trinitro-5-amino-anisol, 12
2 : 4 : 6-Trinitro-5-amino-phenetol, 12
Trinitroanisidines, 119
Weakly basic amines, 14
m-Xylidine, 8
o-Diazotoluene, 276, 280
p-Diazotoluene-*o*-sulphonic acid, 307
6-Diazo-2 : 3 : 8-trimethylquinoline, action of hydroxylamine, 32
Diazotypes, **363** *et seq.*
5-Diazo-1 : 2 : 4-triazole, rate of decomp., 53
1 : 2 : 7 : 8-Dibenzanthracene-4 : 5-dicarboxylic acid, 257
Dibenzfuran, 261
4 : 5 : 9 : 10-Dibenzpyrene, 266
1 : 2 : 6 : 7-Dibenzpyrene-3 : 8-quinone, 260, 358
3 : 6-Dibenzoylcarbazole, 264
Dibenzoylhistidine, 347
Dibenzoylmethane, 141
1 : 2 : 5 : 6-Dibenzoylnaphthalene, 260
Dibenzthiophen, 261, 262
Dibenzylaminesulphonic acid, 171
Dibromoaminophenol, 296
9 : 9-Dibromoanthrone, 226
p-Dibromobenzene, 280, 283
2 : 4-Dibromobenzenediazonium chloride, 125
4 : 6-Dibromobenzene-1 : 2-diazo oxide, 293
2 : 6-Dibromodiazobenzene, 119, 303
Dibromodiazophenol, 32, 296
2 : 6-Dibromo-4-diazophenol, 32
2 : 6-, 3 : 6-Dibromodibenzfuran, 262
2 : 4-Dibromo-1 : 2-diazophenol, 120
2 : 2′-Dibromodiphenyl, 287, **289**
3 : 5-Dibromo-4-hydroxybenzenediazonium bromide, 115
1 : 2-Dibromonaphthalene, 287
2 : 6-Dibromo-4-nitrobenzenediazonium nitrate, 293

2 : 6-Dibromo-1 : 4-dinitrobenzene, 293
2 : 6-Dibromo-4-nitrobenzenediazonium nitrate, 15
2 : 4-Dibromo-6-nitro-1-naphthol, 32
2 : 6-Dibromophenol, 303
2 : 4-Dibromophenylnitroamine, 181
3 : 5-Dibromo-*p*-toluenediazonium thiocyanate, 125
Dibutylaniline, coupling, 202
2 : 4-Dichlorobenzenediazonium bromide, 125
chloride, 320
2 : 5-Dichlorodiazobenzene, 172, 345
3 : 6-Dichlorodibenzfuran, 262
SS'-Di-5 : 8-dichloro-1-naphthyl dithiocarbonate, 326
3 : 3'-Dichloro-, 3 : 3'-dimethoxytetrazodiphenyl, 305
4 : 6-Dichlorodiphenic acid, 315
1 : 2-Dichloronaphthalene, 287
3 : 5-Dichloro-1-nitrobenzene, 270
2 : 6-Dichloro-4-nitrobenzenediazonium sulphate, 271
3 : 4-Dichloronitrodiphenyl, 318
3 : 5-Dichloro-*p*-phenylenediamine, 326
2 : 4-Dichlorophenylnitroamine, 181
2 : 4-Dichlorotoluene, 285
Di-(4-chloro-*o*-tolyl)stibine chloride, 335
Di-*iso*crotyl, coupling, 219
Dicyanodiamide, 164
m-Difluorobenzene, 283
Diformazyl, 215
αβ-Diformylhydrazine, 267
Diethanolamine, 172, 173
2 : 5-Diethoxyaniline, 200
Diethylamine, 225
β-Diethylaminoethanol, 173
αβ-Diethylphenylhydrazines, 185
Diethyl tartrate, 173
Dihydrophthalazines, 91, 92
9 : 10-Dihydrophenanthrene, 256
1 : 5-, 1 : 8-Dihydroxyanthraquinone, 297
4 : 8-Dihydroxyanthraquinone-1 : 5-tetrazonium sulphate, 183
cis- and *trans*-*pp'*-Dihydroxyazobenzene, 226, 229
o : *o*-Dihydroxybenzophenone, 259
4 : 4'-Dihydroxy-3 : 3'-dicarboxydinaphthyl, coupling, 222
4 : 4':Dihydroxydiphenyl, 302
1 : 5-Dihydroxynaphthalene, 200
2 : 3-Dihydroxynaphthalene, 365
2 : 8-Dihydroxynaphthalene-6-sulphonic acid, 207
β-(3 : 4-Dihydroxyphenyl)-β-hydroxyethylamine, 348
Dihydroxytartaric acid osazone, 215
1 : 2-Di-iodonaphthalene, 287
2 : 2'-Di-iododiphenyl, 266, 290
4 : 4'-Di-iododiphenyl, 290
2 : 5-Dimethoxyaniline, 200
3 : 4-Dimethoxybenzenediazonium fluoborate, 305
3 : 4-Dimethoxy-8-ethoxyphenanthrene-9-carboxylic acid, 255
3 : 4-Dimethoxyfluorobenzene, 305
4 : 4'-Dimethoxydiphenyl, 270
4 : 4'-Dimethoxy-*m*-ditolyl, 270
Dimethylamine, 169, 175
p-Dimethylaminopropenylbenzene, 222
p-Dimethylaminodiazobenzene chloride, 232
p-Dimethylaminoazobenzene, 163
Dimethylaniline, 202
coupling, 231
5 : 7-Dimethyl-6-azidoindazole, 246
2 : 7-Dimethylcarbazole, 263, 264
ββ-Dimethyl-αα-dianthraquinonyl, 312
αβ-Dimethylbutadiene, coupling, 219
3 : 5-Dimethyl-4-diaz*oiso*-oxazole, 53
2 : 7-Dimethyldibenzfuran, 262
4 : 4'-Dimethyl-1 : 2 : 6 : 7-dibenzpyrene-3 : 8-quinone, 260
Dimethylformamide, 4
4 : 6-Dimethyl*iso*phthalylcyanide, 310
5 : 7-Dimethylindazole, 246
Dimethyl-*o*-toluidine, 202
Dimethyl-*p*-toluidine, 201
Dimethyl-α-naphthylamine 348
Dimethyltriazen, 169
ββ'-Dinaphthyl, 311
αβ-Dinaphthylamine, 202
1 : 1'-Dinaphthyl-8 : 8'-dicarboxylic acid, 312
2 : 2'-Dinaphthyl-1 : 1'-disulphonic acid, 299
3 : 4-Dinitroanisole, 294
cis-m : *m'*-Dinitroazobenzene, 229
4 : 4'-Dinitro-1 : 1'-azonaphthalene, 148, 300
m-, *o*-Dinitrobenzene, 293
p-Dinitrobenzene, 293, 294
4 : 6-Dinitrobenzene-2 : 1-diazo-oxide, 29, 34, 61
use as explosive, 354
Dinitrodiazoaminobenzenes, dimorphism, 168
3 : 3'-Dinitrodiazoaminoazobenzene, 20
dimorphism, 168
4 : 4'-Dinitrodiazoaminobenzene, 343
silver and cuprous salts, 168
2 : 4-Dinitrodiazobenzene, 196, 218, 219, 234, 331
action of aqueous alkali, 116
2 : 4-Dinitro-1-diazonaphthalene, 300
o : *o'*-Dinitrodiphenyl sulphone, 95
p : *p'*-Dinitrodiphenyl sulphone, 94
2 : 4-Dinitro-4'-hydroxyazobenzene, 227
8 : 8'-Dinitro-1 : 1'-dinaphthyl, 312
Dinitromethane, coupling, 217
1 : 3-Dinitronaphthalene, 273
1 : 6-Dinitronaphthalene, 271, 274, 295

1 : 2-, 1 : 4-, 1 : 7-, 2 : 6-Dinitronaphthalene, 295
2 : 4-Dinitro-1-naphthol, 303
4 : 5-Dinitro-2-naphthol, 274
2 : 4-Dinitrophenol, 18, 20, 141, 191, 303
2 : 2′-Dinitrodiphenyl, **311**
Di(*p*-nitrophenyl)arsonic acid, 332
2 : 4-Dinitrophenylazide, 191
2 : 4-Dinitrophenylcyanide, **310**
p-Di(nitrosoacetamido)benzene, 314
ω-Dinitrotoluene, 146
Diphenic acid, 312
Diphenyl, 39, 134, 270, 272, 304, 310, **311**, 312, 313, 314, 316, 317, 338
Diphenylamine, 202
Diphenylarsinic acid, 332
Diphenylarsine chloride, 332
Diphenylarsonic acid, 332
Diphenyleneazone, 266, 288, 299
3 : 4-Diphenylcinnoline, 242
Diphenylamine-2 : 2′-dicarboxylic acid, 313
Diphenylantimony trichloride, **334**
Diphenyl-4 : 4′-bisdiazocyanide, 144
1 : 4-Diphenylbutadiene, 320
2 : 3-Diphenylbutadiene, coupling, 220
4 : 5-Diphenyldibenzfuran, 262
Diphenyl-2 : 2′-dicarboxylic acid, 312
Diphenyl disulphide, 112, 325, 326
Diphenylene disulphide, 262
  iodonium iodide, 266
  oxide, 261
  sulphide, 261
  sultam, 253
Diphenyl ether, 306, 315
  ether *o*-diazonium sulphate, 261
Diphenyl Fast Blue 2G, 208
β-(NN′-Diphenylformazyl)acrylic acid, 211
Diphenyliodonium tri-iodomercuriate, 337
Diphenyl lead dichloride, 338
  lead oxide, 338
Diphenylmethane-*o*-diazonium sulphate, 258
1 : 5-Diphenyl-3-methylpentazdiene, 165
Diphenylnitromethane, 217
NN′-Diphenyl-S-*p*-nitrophenyl*iso*thiocarbamide, 327
Diphenyl-*p*-phenylenediamine, 202
Diphenyl selenide, 325
Diphenylstannic chloride, 338
Diphenyl sulphide, 298, 325
Diphenyltellurium dichloride, 325
Diphtheria antitoxin, coupling, 356
Dipropenyl, coupling, 219
Disalicylic acid, 302
Disodium anthraquinone-2 : 7-disulphonate, 363
Dispersing agents, 4
  as stabilisers, 66
Distyryls, 323
Ditetrazolyltriazen, 53
1 : 4-Dithiocyanoanthraquinone, 323
1 : 5-Dithiolnaphthalene, 192
Dithioresorcinol, 192
Dithiosalicylic acid, 328
m-Ditolyl, 270
'Double Bart' reaction, 332, 334
Double diazocyanides, 143
Double diazonium salts, decomp. by heat, 289
Double salts, with complex anions, **80** *et seq.*
  with simple anions, **76** *et seq.*
  drying of, 79
*iso*Durene, coupling, 221
*iso*Durenol, 141

E

Egg albumen, 204
Ehrlich's diazo-reaction, 344, 345
Endo-azo-compounds, 216
Ergothionine, 347
Eriochrome Verdone A, 206
Ethanol, 268, 269, 270, 271, 272, 273, 274
Ethoxy Cleve's acid, 224
4-Ethoxydiphenyl, 316
α-Ethoxynaphthalene, 270
2-Ethoxy-1-naphthylamine-6-, and -7-sulphonic acid, coupling, 224
3-Ethoxy-4 : 4′-tetrazodiphenyl, 303
Ethyl acetosuccinate, 267
  benzoate, 317
  β-(2-carboxy-3-indolyl)propionate, 213
  *cyclo*hexanone-2-carboxylate, 213
  *cyclo*pentanone carboxylate, 213
  formazylcarboxylate, 215
  glutaconate, coupling, 211
  hydrogen β-ketoadipate phenylhydrazone, 213
  hydrogen α-ketopimelic acid phenylhydrazone, 213
  methylacetoacetate, coupling, 211
  nitrite, 16, 18
  1 : 2 : 3 : 4-tetrahydroacridyl-1-glyoxylate, coupling, 216
Ethylamine, 159
2-Ethylamino-5-sulphobenzoic acid, 172, 174
p-Ethylthiolbenzenearsonic acid, 333
5-N-Ethyl-4 : 5-tolylenediamine, 249
Ethylene diamine, 161
Ethylene oxide, 172
*iso*Eugenol, 220
Exchange of substituents, 117 *et seq.*
Explosive properties of diazo-compounds, 31, 61, 155, 156, 193

F

Facsimile recording, 356

Fast Blue 2B, 151
Fast Colour Bases and Salts, 70
Ferric chloride, 278, 279
Ferrous chloride, 279
Fibroin, 204
Fluorene, 258, 261
Fluorene-9-carboxylic ester, coupling, 216
Fluorene-2-diazonium chloride, 305
Fluorenone, 258, 259, 317
Fluorenone-2-diazonium chloride, 305
Fluorenone *p*-nitrophenylhydrazone, 216
Fluorobenzene, **283**, 284
Fluorobenzoic acids, 284
p-Fluorobenzenesulphonic acid, 284
α-Fluoronaphthalene, 284
Fluoronitrobenzene, 284
Fluoronitronaphthalene, 284
1-Fluoro-2 : 4 : 6-trichlorobenzene, 284
Fluosulphonates, 80
Formaldehyde, 272
Formazyl, 214, 215
Formazylazobenzene, 214
Formazylcarboxylic acid, 214
Formylmethylaminobenzene-4-diazohydroxide, 133
Formazyl methyl ketone, 215
Free radicals, 63, 66, 109–113, 134, 175, 305, 317, 320, 321, 327, 329, 333, 337
Friedenwald's reagent, 344, 348
Fowl serum, coupling, 204
Fungicides, 152

G

γ-Acid, coupling, 208
determination, 343
Gattermann reaction, 108, 311
Globin, 346
Glucose, 273, 345
Glutaconic acid, coupling, 209, 211
Glutaconic ester, coupling, 209
Glycerol, 307
Glycine, 160
Glycol, 274
Gomberg reaction, 109, 113, 259, 315, **316**
Griess-Ilosva test, 235, 349
Guaiacol, 303
Guanidine, 164
1-Guanyl-4-nitrosoaminoguanyl*iso*tetrazene, 53
Guanyltaurine, 172
Guanylurea-N-sulphonic acid, 172
Gum arabic, 341, 343

H

H-acid, 339, 341, 343, 348, 355
coupling, 208
Haemoglobin, 346
Halogenation of diazo-compounds, 115
Hemi-quinones, 90
Heterocyclic diazo-compounds, 52 *et seq.*
Heterolysis, 109
Hexamethylenetetramine, 175
Hippurylhydrazine, 189
Histidine, 204, 205, 347
Histamine, 345, 347
Homolysis, 109
Horse serum, coupling, 204
Hunter's test, 347
Hydrazine, 189, 191, 297
Hydrazinesulphonic acids, 151
Hydrazobenzene, 229
m-Hydrazinobenzoic acid, 189
Hydrazoic acid, 187, 190
Hydrocarbons, 269, 271
coupling, **219**
formation on decomp. of diazotates, 68
α-, β-Hydroxyanthraquinone, 304
Hydroxyarylazides, 188
o-Hydroxyazobenzene, 226
p-Hydroxyazobenzene, 197, 226
o-Hydroxyazoxybenzene, 131
p-Hydroxybenzaldehyde-*p'*-nitrophenylhydrazone, 200
p-Hydroxybenzenediazonium nitrate, action of hydrobromic acid, 32
3-Hydroxy-1 : 2-benzfluorenone, 259
p-Hydroxybenzoic acid, coupling, 222
o-Hydroxybenzophenone, 259
4-Hydroxy-1 : 2 : 3-benztriazine, 251
4-Hydroxy-3-carboxycinnoline, 243
α-*o*-Hydroxybenzylidene-10-carboxy-2-phenanthrylacetic acid, 257
4-Hydroxycinnoline, 244
4-Hydroxycinnoline-3-carboxylic acid, 244
Hydroxydibenzfuran, 303
2-Hydroxydibenzfuran, **304**
3-Hydroxydibenzfuran, 319
o-Hydroxydibenzyl, 256
4-Hydroxy-6 : 7-dimethoxycinnoline-3-acetic acid, 243
2-Hydroxy-3 : 4-dimethoxyacetophenone, 305
2-Hydroxydiphenyl, 315
4-Hydroxydiphenyl, 313, 315
o-Hydroxydiphenyl ether, 261
o-Hydroxydiphenylmethane, 258
4'-Hydroxy-3-ethoxy-4-diazodiphenyl, 303
2-Hydroxyfluorene, 305
1-Hydroxyfluorenone, 259
Hydroxylamine, 188, 191, 297
5-Hydroxy-6-methylhydrindene, 198
4-Hydroxy-6-methoxycinnoline-3-carboxylic acid, 244
4-Hydroxy-6 : 7-methylenedioxycinnoline-3-carboxylic acid, 244
1-Hydroxynaphthalene-2 : 1'-azonaphthalene-4 : 4'-disulphonic acid, 303
1-Hydroxynaphthalene-4-sulphonic acid, 303

2-Hydroxy-1 : 4-naphthaquinone, coupling, 196
1-Hydroxy-3-naphthoic acid, 273
2 : 3-Hydroxynaphthoic arylamides, 8, 70, 73, 97, 173, 196, 222, 339
7-Hydroxyphenoxaz-2-one, 339
m-Hydroxyphenylacetic acid, 244
m-, *o*-Hydroxyphenylazide, 188
p-Hydroxyphenylazide, 188, 191
4-*p*-Hydroxyphenylcinnoline, 242
Hydroxyphenylcyanides, 309
β-(*p*-Hydroxyphenyl) - β - hydroxyethylmethylamine, 348
p-Hydroxyphenyl ether, 315
α-(*o'*-, *p'*-Hydroxyphenyl)pyridine, 200, 315
5-Hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrazole, 267
Hydroxyproline, 172, 205
3-, 4-Hydroxypyrene, 198
Hypophosphorous acid, 271, 272

I

Ice Colours, 69, 70, 72, 74, 96, 170, 173, 199
Ice Colour bases, 170
constitution, **102, 103**
Iminonitrobenzene, 398
Immune serum, 205
Indazoles, 245, 246, 247
" Indiazones ", 252
Indigo, 350
Indene, 220
Indole, 172
Indolylpropionic acids, 213
Indoxazene, 252
Iodine trichloride, 155
Iodobenzene, 276, 291
2-Iododiphenyl, 291
Iodohippuric acid, 290
β-Iodonaphthalene, 290
4-Iodonaphthalene-1 : 2-diazo-oxide, 30
1 : 8-, 2 : 1-Iodonaphthalene sulphonic acid, 291
1 : 8-Iodonaphthol-4-sulphonic acid, 291
p-Iodonitrobenzene, 290
Ion pairs, 393
Isoprene, coupling, 219

J

J-acid, 343
coupling, 208
Jaundice, 346

K

4-Keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, 251
1-Ketohydroacridine, 216
1-Keto-1 : 2 : 3 : 4-tetrahydrocarbazole, 212
Körner–Contardi replacement reaction, 277, 282, 283, 293, 295

L

Labile diazocyanides, 142–146
Labile and stable diazocyanides, diamagnetic susceptibility, 145
dipole moments, 144
infra-red spectra, 144
interconversion, 143, 357
magnetic optical rotary power, 145
Labile and stable *p*-chlorodiazobenzenecyanides, comparison, 143
Labile diazosulphonates, 147–150
Lævulinic acid, 215
Lange's reaction, 298, 300, 301
Leukardt reaction, 325
Light, action on diazo-compounds, **357** *et seq.*
Lignocellulose, coupling, 209

M

Magdala red, 350
Magnesium ions, detection, 343
Malachite Green, 222
Maleic acid, effect in retarding decomp., 65
Malonic acid, coupling, 214
Malonic ester, coupling, 209, 210, 215
Mannite, 307
Measles, 344, 345
Meerwein reaction, 320
Mercury, 336, 337
Mercuric chloride, 279
Mercury diaryls, 337
dinaphthyls, 51
diphenyl, 51
ditolyl, 51
Mesitol, 141
Mesitylene, coupling, 221
Mesoxalic ester phenylhydrazone, 210
phenylhydrazone, 214
Metallic diazotates, stability, 67
Metanil Yellow, 6
Mercury salts in diazotype layers, 371
Methanol, 269, 270, 271, 274
Methane sulphonamide, 190
Methazonic acid, coupling, 217
o-Methoxybenzenediazonium chloride, decomp., 63
m-Methoxybenzoic acid, 307
4-Methoxydiphenyl, 316
o-Methoxydiazobenzene, 303
4-Methoxydiphenylselenide, 328
3-Methoxyfluorenone, 259
2-Methoxy-3-naphthoic acid, coupling, 218, 219
p-Methoxyphenylacetylene, coupling, 220
2-, 4-Methoxy-*p*-terphenyl, 314

Methylacetoacetic acid, 212
Methyl acrylate, 320
Methylamine, 159, 160
2-Methylamino-5-sulphobenzoic acid, 174
Methylaniline-ω-sulphonate, 202
Methylaniline-4-sulphonic acid, 171
9-Methylanthranol, coupling, 218
4-Methylazobenzene-4′-diazonium sulphate, 271
3-Methylbenzylideneamino-4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, 252
α-Methylbutadiene, coupling, 219
Methyl α-chloro-β-2 : 4-dichlorophenylbutyrate, 320
Methyl 1-chloro-*p*-methylhydrocinnamate, 320
4-Methylcinnoline-7-carboxylic acid, 242
1-Methylcarbazole, 264
2-Methylfluorene, 261
2-Methyl-1-diazoanthraquinone, 312
4-Methyl-2-diazotriazole, 52
4-Methyl-2 : 5-dimethoxyaniline, 201
2-Methyldiphenyl, 315, 318
4-Methyldiphenyl, 315, 316
Methyl diphenyl-2-carboxylate, 317
Methylene blue, 350
Methylethyl ketone, 271
3-Methylindazole, 247
Methylmagnesium iodide, 146, 160
Methyl 2-methoxy-1-phenylnaphthalene-2′-carboxylate, 319
Methyl *p*-methylcinnamate, 320
2-, 4-Methylphenanthrene-9-carboxylic acid, 256
Methyl 4-phenylphthalate, 319
Methyltaurine, 171, 174
Migration of the diazo group, 223
Mixed azo-compounds, 209
Mixed couplings, prevention, 209
Mixtures serving as stabilised diazo-compounds, 95 *et seq.*
Monobenzoyl-*o*-phenylenediamine, 201
Monochloro-*m*-phenylenediamine, 201
Monoethylaniline, 169
Monomethylaniline, 169
N-Monomethyl-*p*-nitroaniline, 128
Mononitro-*m*-phenylenediamine, 201
Mononitrosodiphenylurea, 40
Morpholine, 169

N

α-Naphthacarbazole, 265
Naphthalene, 270, 317, 318
α-, β-Naphthalenediazocyanide, 144
Naphthalene-1 : 2-diazo-oxide, 31, 329
2 : 1-diazo-oxide, 31
Naphthalene-1 : 2-, 2 : 1-diazo-oxide, reaction with phosphorus pentasulphide, 32
Naphthalene-1 : 2-diazo-oxide-4-sulphonic acid, halogenation, etc., 115, 116
effects of irradiation, 360, 361, 362
determination, 340
Naphthalene-2 : 1-diazo-oxide-4-sulphonic acid, 362, 366
-5-sulphonic acid, 366
Naphthalene-α-, -β-diazosulphonate, 148
β-Naphthaphenyliminoketotriazine, 203
Naphthalene-β-*iso*diazotate, 135
Naphthalene-1 : 5-disulphonic acid, stabilising effect, 85
Naphthalene-1 : 8-tetrazonium fluoborate, 80
Naphthalenetrisulphonic acid, 85
"Naphthalidine", 201
Naphthaquinone, 318
1 : 2-Naphthaquinone, 30
1 : 4-Naphthaquinone, 27, 30, 225
1 : 2-Naphthaquinone diazide, 181
1 : 8-Naphthasultam, 203
Naphthasultone, 286
Naphthathiodiazole, 32
2 : 1-Naphthathiodiazole, 254
Naphthatriazoles, 249, 250
Naphthionic acid, coupling, 230
Naphthol AS, 136, 166
α-Naphthol, coupling, 196, 198, 199, 207, 225
β-Napthol, 339, 348, 355
coupling, 196, 199
2-Naphthol-1-carboxylates, 222
1-Naphthol-3-sulphonic acid, coupling, 206
1-Naphthol-4-sulphonic acid, coupling, 207
1-Naphthol-5-sulphonic acid, 341
2-Naphthol-6-sulphonic acid, 341
2-Naphthol-1-sulphonic acid, 222, 329
2-Naphthol-4-sulphonic acid, 273
[4 : 5-(Naphtho-1 : 2′)pyrazole-(3)]-*o*-cinnamic acid, 305
β-Naphthoxy-ψ-urea ether hydrochloride, coupling, 219
α-Naphthylamine, coupling, 209
β-Naphthylamine, coupling, 200, 201
Naphthylaminesulphonic acids, coupling, 205 *et seq.*
1-Naphthylamine-5-sulphonic acid, coupling, 206
1-Naphthylamine-8-sulphonic acid, coupling, 230
α-Naphthylazide, **191**
o-α-Naphthyl benzoate, 317
α-Naphthylbenztriazole, 265
β-Naphthylcyanamide, 203
N-α-Naphthylethylenediamine, 348
1 : 2-Naphthylenediamine, 249
2 : 3-Naphthylenediamine, 250
1 : 5-Naphthylenediamine, coupling, 202
1 : 8-Naphthylenediamine, 248, 250

1 : 8-Naphthylenediamine, coupling, 202
α-Naphthylnitroamine, **180**, 181
Nickel chloride, 279
α-Nitramidonaphthalene, 209
Nitration of diazo-compounds, 115
Nitrazol C, 72
CF, 80
ω-Nitroacetophenone, coupling, 209
Nitroaldoxime phenylhydrazone, 217
Nitroamine ethers, 181, 182
5-Nitro-2-aminophenol, 191
o-Nitroaniline, 181
p-Nitroaniline, 161, 163, 181
2-Nitroanthracene, 295
p-Nitroarsenosobenzene, 332
cis-*p*-Nitroazobenzene, 229
Nitrobenzene, 294
Nitrobenzenearsonic acids, 331
o-Nitrobenzenearsonic acid, **331**
p-Nitrobenzeneazocarboxyamide, 128
p-Nitrobenzeneazo-α-naphthol, 228
4-Nitrobenzenediazoaminoazobenzene, 343
o-Nitrobenzenediazonium chloride, 293, 324
m-Nitrobenzenediazonium chloride, 279, 293, 324
nitrate, 20
sulphate, 12, 75
p-Nitrobenzenediazonium chloride, 175, 183, 184, 185, 203, 276, 279, 293, 314, 320, 348
chloride, action of caustic alkali, 128
fluoborate, 80
nitrate, 20
nitrate, explosiveness, 61
sulphate, 200, 280
4-Nitrobenzenediazoamino-4′-nitronaphthalene, 343
p-Nitrobenzenediazocarbonamide, 145, 146
p-Nitrobenzenediazocyanide, 142, 143, 144
p-Nitrobenzenediazosulphonate, 148, 149
p-Nitrobenzene*iso*diazotate, 223, 331
2-Nitrobutane, coupling, 217
1-Nitrocarbazole, 264
3-Nitro-*p*-cresol, 303
Nitro*cyclo*pentadiene, 219
4-Nitrodiazoaminobenzene, 343
1-Nitro-4-diazoanthraquinone, 323
m-Nitrodiazobenzene, 185
activation energy of decomp., 63
o-Nitrodiazobenzene, 331
p-Nitrodiazobenzene, 150, 155, 170, 317, 331
stabilisation, 83, 84
p-Nitrodiazobenzene methyl ether, 129, 140, 148, 318
p-Nitrodiazobenzene-2-naphthol-1-sulphonate, transformations, 90
1-Nitro-2-diazonaphthalene, 287
1-Nitro-8-diazonaphthalene, 328
4-Nitro-1 : 2-diazophenol, 331
2-Nitrodibenzfuran, 262
2-Nitro-2′ : 5′-dimethyldiphenyl, 318
2-, 5-Nitro-1-diazonaphthalene, 300
2-Nitro-1-di-*n*-butylaminobutane, coupling, 217
2-Nitrodiphenyl, 316
3-Nitrodiphenyl, 314, 317, 319
4-Nitrodiphenyl, 140, 155, 317, 318, 319
Nitroethane, coupling, 209, 217
2-Nitrofluorenone, 259
3-Nitrofluorenone, 260
Nitroformazyl, 217
Nitrogen pentoxide, 181
tetroxide, 20
trioxide, 17, 290
4-Nitro-2-hydroxybenzenearsonic acid, 332
6-Nitro-4-hydroxycinnoline, 243
6-Nitro-2 : 3-hydroxynaphthoic acid, 273
5-, 6-Nitroindazole, 246
7-Nitroindazole, 247
6-Nitro-4-keto-3 : 4-dihydro-1 : 2 : 3-benztriazine, 251
Nitromethane, coupling, 217
4-Nitro-4′-methyldiphenyl, 317
7-Nitro-5-methylindazole, 247
β-Nitronaphthalene, 294
4-Nitronaphthalene-4′-aminoazonaphthalene, 343
4-Nitronaphthalenediazoaminobenzene-4′-azobenzene, 344
4-Nitronaphthalene-1-diazonium chloride, 148
6-Nitronaphthalene-2 : 1-diazo-oxide, reaction with bromine, 32
4-Nitronaphthalene-1-diazosulphonate, 148
4-Nitro-2-naphthol, 273
coupling, 198
6-Nitro-1-naphthol, 273
6-Nitro-2-naphthol-4-sulphonic acid, 273
6-Nitro-3-(4′-nitro-2-methylbenzeneazo) indazole, 246
1 : 4-Nitronaphthylamine, 154
2 : 1-Nitronaphthylamine, 154, 181
m-Nitronitrosoacetanilide, 314
Nitroparaffins, coupling, 216, 217
p-Nitrophenol, 141, 294
4-Nitrophenol-2-arsonic acid, 331
p-Nitrophenylarsenious acid, 332
Nitrophenylazide, 155
3-*p*-Nitrophenylcoumarin, 320
Nitrophenylcyanides, 309
Nitro-*o*-phenylenediamine, 247
p-Nitrophenylhydrazine, **184**
α-*p*-Nitrophenylnaphthalene, 318
p-Nitrophenylnitroamine, 182

m-Nitrophenyl-*p*-nitrophenyltriazen, 164
α-, β-, γ-*p*-Nitrophenylpyridine, 317, 319
m-Nitrophenylthiocyanate, 323, 324
o-Nitrophenylthiocyanate, 324
2-Nitropropane, coupling, 217
N-β-Nitropropylmorpholine, coupling, 217
5-Nitro-*m*-4-xylylnitroamine, 181
Nitrosamine Red, 135, 161
Nitrosamines, 18, 128, **129**
4-Nitrosoacetamidodiphenyl, 314
Nitrosoacetanilide, 38, **39**, **40**, 109, 110, 127, 148, 180, 291, 313, 384
Nitrosoacetarylamides, **38**, 109, 160
Nitrosoacylarylamides, 28
Nitrosoacet-α-naphthalide, 40
Nitroso-β-acetnaphthalide, 127
Nitrosoacetoluidide, 133
Nitrosobenzanilide, 38
Nitrosobenzene, 51, 131, 180, 201
Nitrosobenztoluidide, 133
Nitrosobenz-*o*-toluidide, 40
Nitroso-*p*-chlorophenylhydroxylamine, 180
Nitroso-compounds, 44
5-Nitroso-4 : 6-diamino*iso*phthalaldehyde, 44
p-Nitrosodimethylaniline, 51
Nitrosoformanilide, 40
Nitroso-*o*-hydroxybenzylaniline, 131
Nitrosomethylaniline, 131
1 : 4-Nitrosonaphthol, 44
4-Nitroso-1-naphthylamine, 44, 116
Nitrosophenol, 51
p-Nitrosodiphenylamine, 51
Nitroso-oxanilide, 40
Nitroso-*m*-phenylenediamine, 44
Nitrosophenylglycine, 51
Nitrosophenylhydrazine, 50
Nitrosophenylhydroxylamine, 131, 180, 396
Nitrosophenylurea, 395
Nitrosophenylurethane, 40
Nitrososemicarbazide, 40
Nitrosyl, nitroxyl radical, 128
Nitrosyl bromide, 20
Nitrosyl chloride, 20, 39, 75, 159, 304
Nitrosylsulphuric acid, 11, **12**, 13, 72
5-Nitrotetrazole, 53
m-Nitrothiophenol, 326
p-Nitrothiophenol, 327
Nitrous acid, 6, 47, 48
  determination, Tromsdorff's method, 45
  detection and determination, 349
  effect on stability of diazo-compounds, 65
Nitrous acid gases, 16, 37, 72, 75, 318
Nitrous anhydride, 37
sym-Nitroxylene, 272

O

O-Azo-compounds, 221, 222, 232
Octyl nitrite, 19
m-Oxamidodiazobenzene, 185
Oxidation products of diazo-compounds, 179 *et seq.*
Oximes, 189
Oxonium salts, 233
Oxygen, migration in diazohydroxides, 397, 398
Oxyproteic acid, 345
Ozalid M, 363, 366
Ozalid diazotype papers, 367

P

Paludrine, 164, 348
Paradurol, 85
Paranil A, 84
Para Red, 6, 69, 72, 90, 135, 227
Passive stabilised diazo-compounds, 71, 146, 150, 151, 152, 369
Pentabromobenzenediazonium chloride, 125
  nitrate, 11
Pentamethylbenzene, coupling, 221
Pentamethylphenol, 141
*iso*Pentanol, 307
Pentaz-1 : 4-diene, 158
Peri-acid, 339
Phenacetylpyridinium bromide, coupling, 216
Phenanthrene, 254 *et seq.*
Phenanthrene-9-carboxylic acid, 255
Phenanthreno-N-methyltetrahydropapaverine, 257
Phenetole, coupling, 218
Phenol, 64, 199, 285, 294, 304, 315, 338
  coupling, 197 *et seq.*
  dis- and trisazo derivatives, 198
  formation, 302 *et seq.*
  mixtures, coupling, 199
Phenol esters, formation, 305
  ethers, coupling, 217 *et seq.*
  formation, 306
4-Phenoxyacetamido-2 : 5-dimethoxyaniline, 73
Phenylacetylene, 277
  coupling, 220
Phenylarsenious oxide, 332
Phenylarsonobenzene-*o*-arsonic acid, 332
Phenylazide, 160, 184, 187, 188, 272, 313
α-Phenylbutadiene, coupling, 220
1-Phenylbenzenesulphontriazine, 253
4-Phenyl-3-benzylcinnoline, 242
Phenylbenzyltriazen, 165
Phenylcamphoryltriazen, 166
1-Phenyl-3-carbethoxy-5-pyrazolone, 267
Phenylcarbimide, 165, 166, 297
2-Phenylchrysene, 242, 243

4-Phenylcinnoline, 242
Phenylcyanamide, 202
Phenyl cyanide, 145, **309**
1-Phenyl-3 : 4-*cyclo*hexano-5-pyrazolone, 214
Phenyldi-imide, 111, 185
1-Phenyl-4-diphenylylbutadiene, 321
S-Phenyl-l : 4-diphenyl*iso*thiosemicarbazide, 327
1-Phenyl-3 : 5-dimethyl-4-arylazopyrrazoles, 210
Phenyldimethyldithiocarbamate, 326
m-Phenylenediamine, 21, 232, 349
o-, *p*-Phenylenediamine, 21
β-Phenylethylamine, 347
Phenyl ethyl sulphide, 325
Phenylethyltriazen, 159
Phenylformazyl, 215, 217
Phenylhydrazine, **184**, 185, 189
disulphonic acid, 39
Phenylhydrazine-*p*-sulphonic acid, **184**
3-Phenylindazole, 247
1-Phenyl*iso*indazolone, 252
Phenylmagnesium iodide, 146
Phenylmercuric chloride, iodide, 337
4-Phenyl-3-methylcinnoline, 242
Phenylmethylpyrazolonesulphonic acid, 341
Phenylmethyltriazen, 159, 160, 161, 165, 166
2-Phenylnaphthalene, 316, 319
Phenyl-α-, -β-naphthylamine, coupling, 202
4-Phenyl-3-1′-naphthylcinnoline, 242, 243
Phenylnitroamine, 131, 180, 181, 396
Phenylnitromethane, 217
1-Phenyl-4-*p*-nitrophenylbutadiene, 321
1-Phenylpenta-1 : 3-diene, 320
1-Phenyl*peri*naphthtriazole, 265
Phenylphthalamic acid, 40
4-Phenylphthalimide, 319
γ-Phenylpropylamine, 347
Phenylpyridine, 317
5-Phenylquinoline, 319
Phenyl radicals, 112, 299, 313
Phenylstibinic chloride, **334**
1-Phenyl-1 : 2 : 3 : 4-tetrazole, 267
Phenylthiocyanate, 323
Phenyl-*p*-tolyltriazen, 164
Phenyltriazen, 160
1-Phenyltriazole, 263
Phloroglucinol, 199, 365
ethers, coupling, 218
Phthisis, 345
Picric acid, 141
Pinene nitrosochloride, 167
Pipecolinic acid, 169, 172
Piperazine, 172
Piperidine, 169, 175, 284
Piperidine-3-sulphonic acid, 169
Polyhydric alcohols, 25
Potassium benzene *iso*diazotate, **130**, 131, 148
benzene *n*-diazotate, **126**, 127, 148
p-bromobenzene*iso*diazotate, 134
benzenediazosulphonate, 149, 150
p-chlorobenzene*iso*diazotate, 130, 140
5-chloro-*o*-toluene*iso*diazotate, **130**
mercurinitrite, 294
nickelocyanide, **310**
p-nitrobenzene*iso*diazotate, 345, 346
tribromobenzene*iso*diazotate, 135
Primuline, 364
diazotised, effects of irradiation, 361
Printing pastes, stabilisers for, 79
Proline, 172, 205
Propanol, 307
iso-, *n*-Propanol, 269, 271, 274
o-, *p*-Propenylphenol, 200
β-Propylaminoethanol acetate, 173
Proteins, coupling, 204–205
Pschorr reaction, 108, 242, **255**, 256, **258**
Pseudo acids, 134
Py-C-methyl-1(N) : 2-pyrazoloanthraquinone, 247
Pyrazolones, 267
coupling, 209
Pyridine, 231, 232, 317, 318
3 : 4-Pyridinotriazoles, 53
5-N-Pyridyl-1-azohydroxylamidoanthraquinone, 317
3-Pyridylarsine dichloride, **333**
2-Pyridylnaphthalene, 319
4-Pyridylphthalimide, 319
Pyruvaldehyde phenylhydrazone, 210, 211
Pyruvic acid phenylhydrazone, 212

Q

Quaterphenyl, 113
lin. Quaterphenyl, 321
Quinol, 199, 272, 315
Quinoline, effect on coupling, 225
*iso*Quinoline alkaloids, 257, 258
Quinone diazides, 24, 29
oximes, 318

R

Radicals, see Free radicals.
Rapidazol dyes, 151
Rapid Fast dyes (I.G.), 137
Rapidogen dyes, 164, **171** *et seq.*
Rapidogen Developer N, 173
Reactive methylene groups, coupling, 209 *et seq.*
Reactions, classification, 105 *et seq.*
Replacement of aldehyde-, carboxyl-, keto-group during diazotisation, 15
Replacement reactions :
Type I, 108
Type II, 109
Type III, 114

Replacement reactions, mechanism, 108 *et seq.*
Replacement of diazo-group by:
amino-group, 296
antimony, 334
arsenic, 331
azo-group, 297
bromine, 287
carbimido-group, 297
chlorine, 285
fluorine, 283
halogens, 275 *et seq.*
hydrogen, 268 *et seq.*
iodine, 290
metals, 336
nitro-group, 293
oxygen, 302
Resorcinol, 343, 365
coupling, 195, 199
Resorufin, 339
Richter reaction, 243, 244
Rodenticides, 152
R-salt, 341

S

S-acid, 343
*iso*Safrole, 220
Salicylic acid, 199, 230
Sandmeyer reaction, 108, 277, 280, 281, 282, 293
Sarcosine, 170, 171, 174, 175
Scarlet fever, 345
Scheller reaction, 333
Schiff's bases, 97
Schmidt's reaction, 334
Secondary sugar amines, 172
Selenaphenols, 328
Selenium, 325
1-Selenocyanoanthraquinone, 324
Self diazotisation, 119
Silk, diazotisation, 354
dyeing, 204
Sodium acetate, 66, 69, 72
Sodium benzaldehyde-2′-nitrophenylhydrazone-ω-sulphonate-2-β-acrylic acid, 92
Silver benzene *iso*diazotate, 216, 370
Silver benzene *n*-diazotate, 126, 139
Silver photographic emulsions, 370
Sodium benzene diazotate, 39, 314, 317
Sodium benzene *iso*diazotate, **132**
Sodium benzene *n*-diazotate, 112, 126, 127, 140, 342, 395
Sodium 3-chloro-4-hydroxybenzenediazosulphonate, 152
Sodium *p*-dimethylaminobenzenediazosulphonate, 152
Sodium hydrosulphite, 340
Sodium nitrite, 4, 5
Sodium *p*-nitrobenzene*iso*diazotate, 134
determination, 341
Sodium phenylarsenite, 332
Sodium stannite, 271
Sodium *p*-toluene diazotate, 38
Solochrome Black T, 6B, 207
Sorbic acid, 320
Stable diazocyanides, 142–146
diazosulphonates, 147–150
Stabilised *p*-diazobenzenesulphonamide, antiseptic, 356
Stabilised diazo-compounds, 69 *et seq.*, 150, 151, 152, 318
Stability, variation with pH, 98, 99
Stannic chloride, 76, 279
Stabilisers, 171, 174
Starch-iodide paper, 5
Stibosoaryls, 335
Stibinosodiaryl, 335
cis-Stilbene, 228
Stilbenes, 323
Styrene, 220
1-Styryl-4-nitronaphthalene, 321
Substituents, effect on stability to irradiation, 360, 361
Sulphamic acid, 6
o-, *m*-, *p*-Sulphamidobenzenediazonium chloride, 22
α-Sulphamidonaphthalene, 209
Sulphatoethyl-*m*-toluidine, 348
Sulphazides, 184, 328
Sulphinic acids, 190, 324, **328**
p-Sulphobenzeneazo-2-naphthol-3-carboxylic acid, 227
Sulphochrysoidine, 232
Sulphonamides, 190
Sulphonamide drugs, 343
drugs, determination, 348
Sulphonation of diazo-compounds, 115
Sulphonic acids, **328**, **329**
Symmetrical diaryls, 310 *et seq.*
Symmetrical monoazo compounds, 278

T

Tar, 108, 113
Taurine, 175
Tellurium, 325
Terphenyl, 113
m-Terphenyl, 313, 314
p-Terphenyl, 313, **314**
Tetrammino-cuprous sulphate, **299**
Tetrahydrocarbazole, 172
Tetrahydroquinoline, 169, 170, 172
1 : 5-, 1 : 8-Tetrazoanthraquinone, 287, 297
m-Tetrazobenzene, 234
o-Tetrazobenzene, 196
p-Tetrazobenzene, 196, 219, 234
Tetrazodiphenyl, stabilisation, 83, 84
2 : 2′-Tetrazodiphenyl, 287
complex with potassium hexathiocyanochromiate, 81
4 : 4′-Tetrazodiphenyl-3 : 3′-dicarboxylic acid, 302
4 : 4′-Tetrazo-3 : 3′-ditolyl, 306

1 : 2 : 4 : 6-Tetrachlorobenzene, 358
2 : 2′ : 6 : 6′-Tetrachloro-4 : 4′-dinitrodiphenyl, 270
dl-4 : 6 : 4′ : 6′-Tetrachlorodiphenic acid, 312
αα-Tetramethyldiaminodiphenylethylene, coupling, 220, 233
4 : 8 : 4′ : 8′-Tetranitro-1 : 1′-dinaphylamine, 312
Tetraphenylethane, 314
Tetrazoles, 190
1 : 2 : 3 : 4-Tetrazoles, 266
Tetrazolediazonium salts, 53
Tetrazotisation of:
4-Chloro-1 : 3-diaminobenzene-5-sulphonic acid, 26
2-Chloro-1 : 4-naphthylenediamine, 27
2 : 6-Diaminoalkoxybenzene-4-sulphonic acids, 26
1 : 4-, 1 : 5-Diaminoanthraquinone, 27
Diaminomesitylene, 246
2 : 4-Diaminophenol, 26
2 : 4-Diaminophenol ethers, 26
2 : 6-Diaminophenol-4-sulphonic acid, 26
Diaminosalicylic acid, 26
2 : 6-Dibromo-, 2 : 5-dichloro-*p*-phenylenediamine, 26
2 : 6-Dichloro-*p*-phenylenediamine, 26, 73
1 : 4-, 1 : 5-, 1 : 8-, 2 : 7-Naphthylenediamine, 27
1 : 5-, 2 : 5-, 2 : 8-Naphthylenediaminesulphonic acid, 27
Nitro-*p*-phenylenediamine, 26
o-Phenylenediamine, **27**
m-Phenylenediamine, **25**, 26, **283**
m-Phenylenediamine-4 : 6-disulphonic acid, 26
p-Phenylenediamine, **26**, 73
p-Phenylenediamine sulphonic acid, 26
Trichloro-*p*-phenylenediamine, 26
1 : 3 : 5-Trinitro-2 : 6-diaminobenzene, 26
Tetrazoxylene, 193
Textile printing, 41, 135, 150, 151, 152, 170, 171, 173
Theory of:
Angeli, 386, **394**
Armstrong and Robertson, 386
Bamberger, 386, **391**
Brühl, 386
Cain, 386
Hantzsch, **385**
Hodgson and Marsden, 386, 393
Oddo, 386
Sarkar, 386, 398
Swientoslawsky, 386
Thermochemistry of diazo-compounds, 352
Thioacetic acid, 193
1-Thiocyanoanthraquinone, 323
p-Thiocyanobenzenearsonic acid, 333
o- and *p*-Thiocyanobenzenediazonium chloride, 125
Thiohistidine betaine, 347
Thioindigo, 327
Red BG, 327
Thioindoxyl, 327
4-Thioketo-1 : 2 : 3-benztriazine, 251
Thiolacetic acid, 193
β-2-Thiolglyoxaline-4(5)-propiobetaine, 347
2-Thiol-4(5)-methylglyoxaline-5(4)-carboxylic acid, 347
Thionylphenylhydrazine, 51
Thiophen, 318
Thiophenols, 324, 325, **326**, 327
Thiophenol-*o*-sulphonic acid, 326
Thiophenol-*p*-sulphonic acid ethyl ether, 325
Thiosalicylic acid, 327
Thiourea, 366
l-Threonic acid, 186
Thymol, 348
Titanous chloride, 16, 340, 341
α-, β-, γ-Tocopherol, 348
p-Tolylazide, 189
4-*p*-Tolylcinnoline, 242
p-Tolyldi-imide, 186
m-Tolylenediamine, 25
sulphonic acid, 26
4 : 5-Tolylenediamine, 249
o-Tolylmercuric chloride, 336
1-*p*-Tolyl-1′ : 2′-naphthatriazole, 250
p-Tolylselenocyanate, 324
p-Tolylnitrososulphamic acid, 40
Toluene, 315
o-Toluenearsonic acid, 332
3-*o*-Toluenazoindazole, 246
p-Toluenazo-β-naphthylamine, 164
o-Toluenediazonium chloride, 307, 336
p-Toluenediazonium chloride, 296, 307
p-Toluenediazonium sulphate, 185, 303
n-Toluene-*p*-diazotate, 133
α-, β-*p*-Toluene sulphonamidonaphthalene, 203
m-Toluidine, 200
p-Toluidine, 159, 189, 296
2 : 4 : 6-Triaminobenzene, 27
Triazen, 157
Triazens, 39, **157** *et seq.*, 202, 204, 223, 224, 232, 248, 318, 328, 343
applications, 170–175
geometrical isomerism, 167
scission *in vivo*, 205
use for making sponge rubber, 175
use in therapeutics, 175
Triazoles, 21, 201, **247**
2 : 4 : 6-Tribromoanisol, 358
N-Tribromoarylhydrazines, 154
Tribromobenzene, 358
2 : 4 : 6-Tribromobenzenediazocyanide, 144, 357

2 : 4 : 6-Tribromobenzenediazonium chloride, 125
fluoride, 125
nitrate, 120
sulphate, 293
sulphate, action of light, 358
2 : 4 : 6-Tribromodiazobenzene, 217, 307
1 : 2 : 4-Tribromonaphthalene, 154
2 : 4 : 6-Tribromonitrobenzene, 293
2 : 4 : 6-Tribromophenetol, 358
2 : 4 : 6-Tribromophenol, 358
acetate, 358
2 : 4 : 6-Trichlorobenzenediazonium chloride, action of light, 358
2 : 4 : 6-Trichlorodiazobenzene, 196, 217
2 : 4 : 5-Trichloro-1-iodobenzene, 118
Tri-(4-chloro-*o*-tolyl)stibine, 335
Triethanolamine, 172, 196
Tri-iodobenzenediazonium chloride, 125
1 : 2 : 3-Trimethoxybenzene, 307
3 : 4 : 5-, 3 : 4 : 7-Trimethoxyphenanthrene-9-carboxylic acid, 255
ααβ-Trimethylethylene, coupling, 219
Trinitrodiazobenzene, 49
2 : 4 : 6-Trinitrodiazobenzene, 196, 221, 224
Trinitromethane, 146
Triarylantimony dichloride, 334, 335
Triarylbismuth, 335
Triarylethylenes, 323
Triphenylantimony dichloride, **334**, 335
Triphenylarsinedichloride, 334
Triphenylarsinephenoxyhydroxide, 333
Triphenylbismuth, 335
Triphenyl lead chloride, 338
Triphenyltriazen, 169
Tri-*p*-tolylbismuth, 335
Tritolylphosphate, 343
Tris-benzeneazomethane, 214
Trisbenzeneazophenol, 67
Tryptophane, 204
Twinned double bonds, 396
Typhoid fever, 344, 345
Tyrosine, 52, 204, 205, 347, 355

U

Uraemia, 346
Urea, 6
Urine, 344, 345, 346, 347, 349
Urochromogen, 346

V

Vacanceine Red, 69
Variamine Blue, 150
Vinyl cyanide, 320
Vitamin B, 348

X

Xanthates, 193
X-rays, effect of, 363
p-Xylidine, 200

W

Widman-Stoermer reaction, 242, 243, 244, 245
Wool, 52
diazotisation, 354

Z

"ZA", 365
Zein, 204, 205
Zinc chloride, 76, 77, 78, 79, 279
Zinc chloride-diazonium chlorides, 78, 305, 306, 307
Zinc diethyl, 185