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ACETYLENE
and
CARBON MONOXIDE
CHEMISTRY

by

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and

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REINHOLD PUBLISHING CORPORATION
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Dr H Mark and Dr H S Kaufman, Polytechnic Institute of Brooklyn, very graciously granted permission to publish their x-ray diffraction data on cyclooctatetraene Dr S T Gross of General Aniline and Film Corporation wrote the section on molecular configuration of cyclooctatetraene Dr D L Fuller of the same company was of material assistance in writing the chapter on "Explosive Decompositions of Acetylene"

Foreword

At the outset of World War II, it was known that the Germans were studying the reactions of acetylene and carbon monoxide, primarily for the manufacture of synthetic rubber. It was not until Germany was defeated that the results of their investigations were learned.

Teams of American and British experts visited Germany and published their findings through such agencies as the Field Information Agency, Technical (*FIAT*) and the British Intelligence Objective Sub-Committee (*BIOS*). One such team, consisting of Dr. G. M. Kline, U. S. Bureau of Standards, Dr. Walter E. Gloor, Hercules Powder Company, Mr. John M. DeBell, DeBell and Richardson, and Dr. William C. Goggin, Dow Chemical Company, was primarily interested in plastics. In gathering documentary evidence and interviewing German chemists, they learned that Dr. Julius Walter Reppe was the leading scientist in the field of acetylene chemistry.

Recognizing that the interviewing team barely touched Dr. Reppe's massive store of information on acetylene chemistry, it was believed that Dr. Reppe should be requested to write about his life's work in detail.

On July 6, 1945, the American Chemical Society suggested that the Chemical Corps enlist Dr. Reppe's services so that the knowledge of acetylene chemistry could be enlarged and brought up to date. In response to this suggestion, a cable was addressed to the Chemical Corps in the European Theatre requesting that steps be taken to have Dr. Reppe write a full exposition of his work on acetylene chemistry. In compliance with this cable, the Chemical Officer of the European Theatre, Colonel Patrick F. Powers, directed his executive officer, Lt. Col. M. H. Bigelow, to assume responsibility for this problem and to effect an answer.

Dr. Reppe was contacted and he reluctantly agreed to do the work, provided he was released from detainment, given a suitable place to write, and allowed access to his numerous files, some of which were at the Anorgana Plant at Gendorf, about sixty miles southeast of Munich, and some at the I. G. Farben industrie factory at Ludwigshafen, on the Rhine River in the French Zone of Occupation.

On September 14th, the British authorities were asked to release Dr. Reppe to Lt. Col. Bigelow. One month later, the latter obtained the custody of Dr. Reppe, signing a formal receipt "for one live body named Reppe."

Many difficulties were encountered in finding lodging and food Military regulations forbade feeding Germans with U S Army rations The Frankfurt city government did not want to feed or house Reppe because he had not been a resident of that city. As he had joined the Nazi party, military regulations required that Dr. Reppe work on the road gang To circumvent this situation, Dr Reppe was held as a detainee, but this in turn caused him much chagrin

The task Dr Reppe undertook was almost impossible He had been the leader of a large number of experts, and at best he had only a general knowledge of the subject Consequently, he required the assistance of his former co-workers and needed access to his files Two of his valued assistants, Dr Hans Trieschmann and Dr Otto Hecht, were residing in the French Zone His files were scattered all over Germany Arrangements were made with Hecht and Trieschmann to visit Reppe every week or two Their entry into the American Zone was reminiscent of the days of rum running during the prohibition era When assembled, Reppe's files amounted to twenty-eight tons of documents, the greater portion of which were found to be valueless

Dr Reppe was far from cooperative The dismemberment of I G Farbenindustrie and Germany's defeat preyed upon his mind He had one ambition, namely to build a new chemical industry, and in so doing, to become the chemical leader of Germany Much of Reppe's time was devoted to directing the work at Ludwigshafen by remote control In the nine months that Reppe worked, he turned out a few hundred pages of generalities hardly worth translating (see Figure 1) At one time while he was working on the project, all twenty-eight tons of documents were secretly removed from Gendorf and transported by truck to Ludwigshafen, a distance of 230 miles The documents were recovered after three of his associates were arrested for participating in the deal

A request was received from Washington that Dr Reppe be offered a War Department contract to come to the United States This contract was very generous both financially and in other guarantees, but Reppe turned it down He contended that living in the United States would hamper his future plans

Finally, it became necessary to release Reppe from the task he had reluctantly accepted Lt Col Bigelow, together with Dr Karl Fischer, scanned the tons of documents, picking out those which appeared pertinent and used them as the basis of a manuscript This manuscript was then rewritten in its entirety by J W Copenhaver An earnest attempt has been made to correct all errors and to make the information presented as complete and reliable as possible by referring to the many reports of the Field Information Agency, Technical (*FIAT*), the British Intelligence Objectives

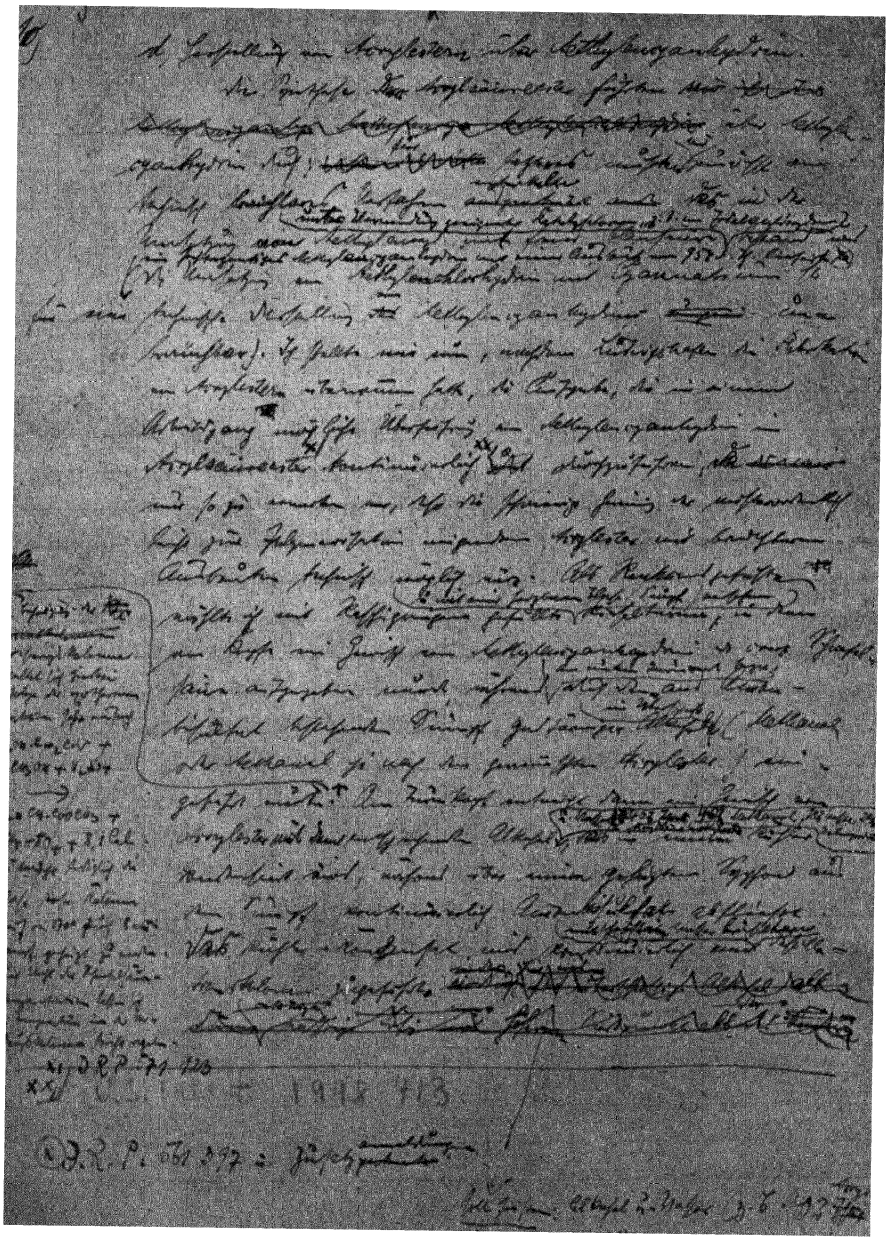


FIGURE 1. A facsimile of one of Reppe's manuscripts.

Sub-Committee (*BIOS*), as well as the reports of the Publications Board of the United States Department of Commerce (*PB* Reports); where used, or where known, the appropriate reference is indicated.

The authors have attempted only a factual presentation of the data available in the source material The theories outlined, except where otherwise indicated, are those of Reppe, undoubtedly many readers, even as some of the chemists associated with Reppe, will not be in accord

The primary objective of this book is to trace the development of the chemistry of acetylene reactions under pressure, and to indicate the techniques employed in the safe handling of acetylene in such reactions A secondary objective is to point out in lesser detail other important reactions and reaction products derived from acetylene in order to present a well-rounded picture of the German acetylene chemical industry However, it is obviously not possible within the confines of a single volume to follow all such reactions to their ultimate end products

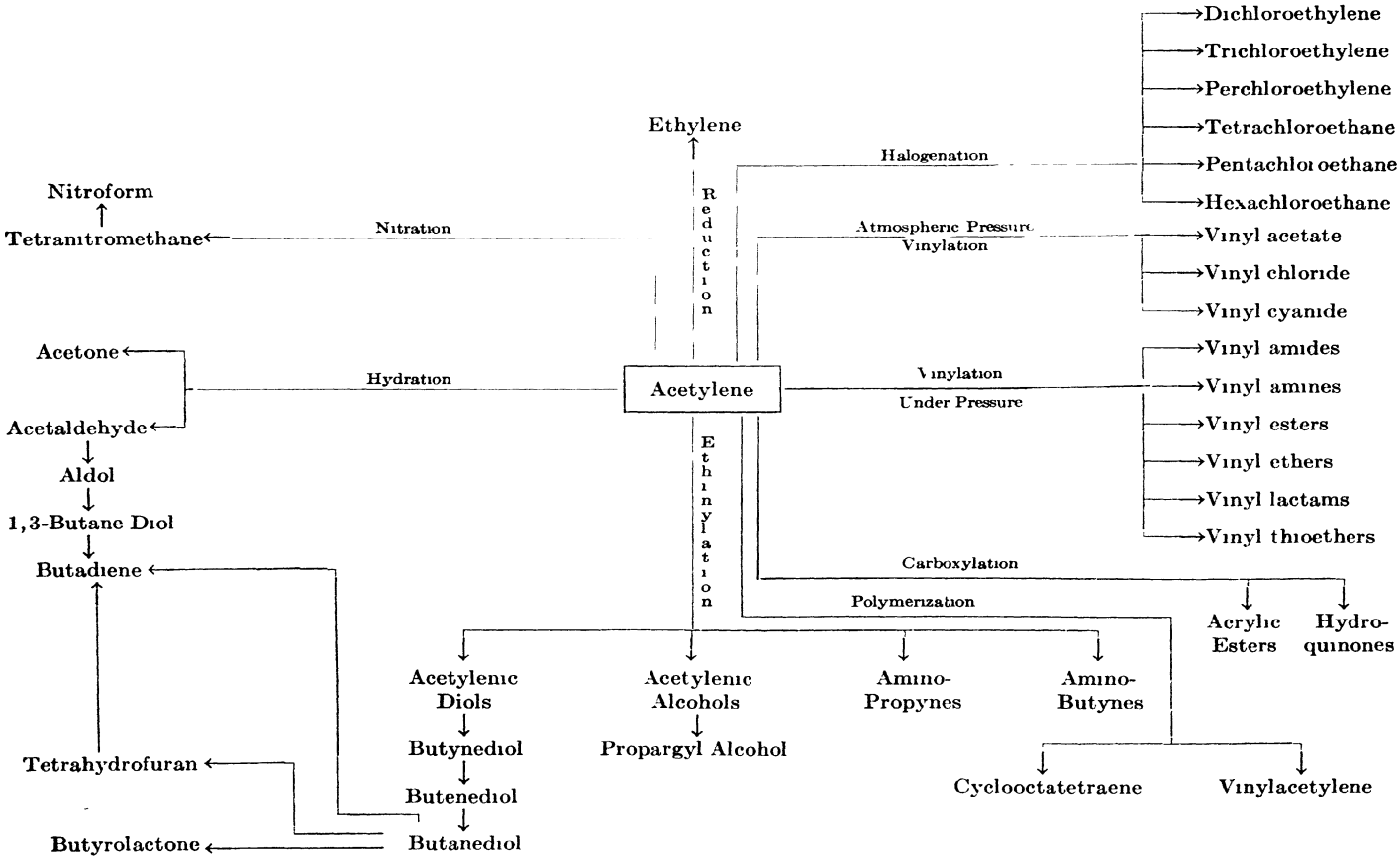
The attached chart may be of assistance to the reader in indicating the plan of organization and scope of this treatment. The reactions of acetylene without application of pressure, such as reduction, nitration and halogenation, are discussed briefly, but the resultant products are not further discussed, thus the chemistry of ethylene is not considered The chemistry of acetaldehyde is limited to its synthesis and conversion to butadiene On the other hand, the newer reactions of acetylene under pressure, now commonly referred to as vinylation, ethinylation, carboxylation and polymerization are discussed in detail, as are many of the unique reaction products derived therefrom. Finally, the results of tests on the explosive decomposition of acetylene under pressure, the methods employed to prevent such decompositions, and the experimental equipment developed for use in pressure reactions are described

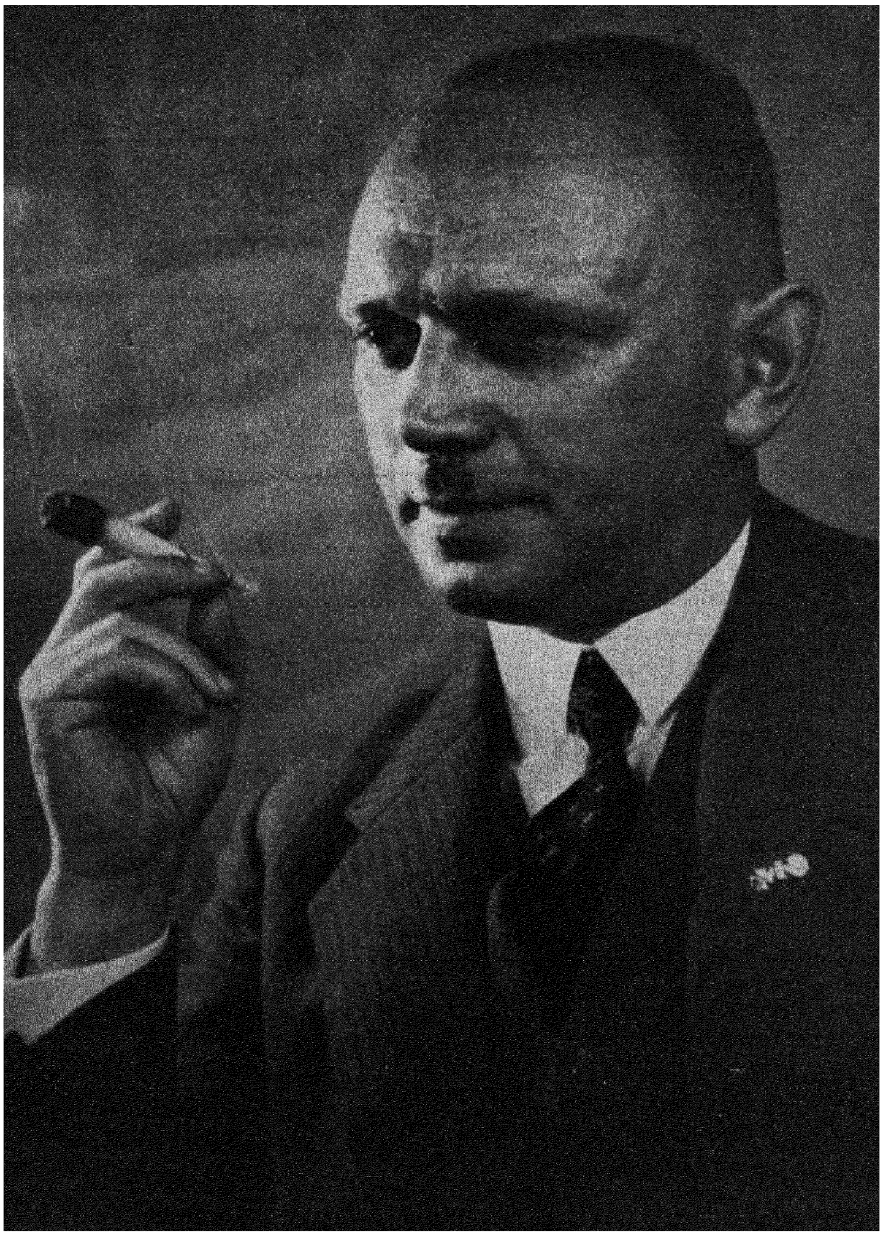
This book is offered with the hope that it contains some information of value to American chemists, but it is readily admitted that the work is far from complete. This much can be said, that the study of the reactions of acetylene and carbon monoxide has just started and that this new field of synthesis is in its infancy.

New York, N Y.
July, 1949

J. W. COPENHAVER
MAURICE BIGELOW

Reactions of Acetylene





Dr. Walter Reppe

Biographical Sketch of Dr. Julius Walter Reppe

Dr J. W. Reppe was born in Goringen, Germany on July 29, 1892 His father was Rudolph Reppe, a school teacher, and his mother was Marie Schrader

Dr. Reppe attended the public schools of Apolda in Thuringen from 1899 to 1908 He also spent two years in the high school at Weimar From 1911 to 1912 he studied at the University of Jena where he became—and still is—an active member of the Landsmannschaft "Hercynia " From 1912 to 1914 he studied at the University of Munich His studies at this point were interrupted by World War I, at which time he served as a First Lieutenant on both the Eastern and Western Fronts in the 248th and 504th German artillery regiments. At the conclusion of the war, he returned to the University of Munich and on December 10, 1920 received his Doctor of Philosophy degree in Chemistry The subject of his doctorate, taken under the direction of Professor K H. Meyer, was "The Reduction Stages of Aryl Derivatives of Nitric Acid "

On March 16, 1921 Dr. Reppe joined the main laboratory of the "Badische Anilin und Sodafabrik," Ludwigshafen/Rh as a chemist. There he was employed in the field of azo dyestuffs and was given the problem of preparing borneol from turpentine oil for the synthesis of camphor. He solved this problem, and on the first of January 1923, he was transferred to the indigo laboratory of this same company where his main efforts were focused on the production of hydrocyanic acid from formamide by catalytic dehydration After completing this problem, he was transferred from the indigo department and attached to the Carbide-Alcohol Plant.

During the next ten years of Reppe's chemical work he succeeded in developing a large-scale catalyst chamber for the hydrogenation of acetaldehyde and crotonaldehyde. He was also identified with the synthesis of butanol; the preparation of approximately one hundred new azo dyestuffs; the preparation of indigoid dyestuffs from low-temperature coal-tar distillates, and the catalytic hydrogenation of indigo to indigo white.

From 1925 on, Dr. Reppe was associated with the synthesis of butadiene and the manufacture of condensation products of acetylene. He developed a process for the preparation of vinyl ethers from acetylene and alcohols

under pressure with alkali or alcoholates as catalyst. This discovery was later recognized as a general method of introducing acetylene into organic compounds containing hydroxy groups.

On January 1, 1934 he was made director of the newly founded "Intermediate Plastics Laboratory" Within a period of four years, he developed this laboratory at Ludwigshafen from an insignificant status to the most modern laboratory in the I.G. Farbenindustrie In this undertaking, he was assisted by more than twenty chemists; here he developed large-scale continuous equipment for the reaction of acetylene under pressure

In 1938 he was made Director of Central Laboratory of the I.G Farbenindustrie in Ludwigshafen This was the largest research institute of the I.G., and its research activities extended into all branches of chemical science and technique. It was in this laboratory that the optimum methods for butadiene synthesis were developed. Based upon this development, a plant was built which produced 30,000 tons of Buna rubber per year. Some of the many products and processes of this laboratory were tetrahydrofuran, pyrrolidine, butyrolactone and pyrrolidone The new alkynol synthesis proved fruitful in the various fields of artificial resins and lacquers, textile intermediates, pharmaceuticals and photographic chemicals

On April 1, 1937, Dr. Reppe was appointed "prokurist" of the I G Farbenindustrie and on April 1, 1939, Director.

Dr Reppe was married in 1922 and has one son.

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Chapter I

Synthesis and Reactions of Acetylene at Atmospheric Pressure

Introduction

The unusual importance of acetylene as a basic chemical raw material was one of the noteworthy features of Germany's wartime chemical industry. This situation resulted from a lack of natural petroleum resources and a scarcity of carbohydrate material for ethyl alcohol production, thus necessitating reliance on acetylene from calcium carbide as the basic raw material for synthetic rubber and many other organic chemicals.

Hasche[1] has estimated that as of May, 1942, German carbide production was at a rate of 1,320,000 metric tons per year, of which some 53 per cent was used to produce acetylene for chemical processes requiring some 237,000 metric tons of acetylene per year. In addition, approximately 58,000 metric tons per year of arc acetylene and minor amounts of acetylene from other syntheses were available.

The minutes of an I G Farbenindustrie conference on September 22, 1943 indicate that the productive capacity of calcium carbide was expected to amount to approximately 145,000 metric tons per month by the end of 1943[2]. Moreover, after completion of construction under way and projected, the capacity was expected to rise to approximately 210,000 metric tons per month. The usage of acetylene for chemical derivatives was 27,000 metric tons per month and was expected to increase to approximately 41,500 metric tons per month. Of this 27,000 tons of acetylene, 24,000 tons came from carbide acetylene and about 3,000 tons per month from arc acetylene.

Hunter[3] estimates that in the chemical plants of the British, United States, and French zones of Germany the production of acetylene for chemical processing was approximately 300,000 tons per year during the war period. This figure would seem to indicate that the anticipated use of 41,500 tons of acetylene per month was probably never attained due to wartime difficulties.

It is of interest to note the statistics relating to the production of calcium carbide, and of acetylene for chemical processing, in the United States dur-

[1] *Chem Eng News*, **23**, 1840 (1945)
[2] *Chem. Eng News*, **23**, 1841 (1945)
[3] *PB* 91663 (*BIOS* 1053).

ing the same wartime years Data (converted from short tons to metric tons) for the production of calcium carbide are as follows:[4]

Year	1945	1944	1943	1942
Metric tons	610,155	716,134	597,845	454,326

During the same period, the use of acetylene for chemical processing (exclusive of industrial uses) was as follows (data converted from M cu ft. to metric tons to facilitate comparison):[5]

Year	1945	1944	1943	1942
Metric tons	119,900	127,800	91,870	106,470 (all uses)

Synthesis of Acetylene

Acetylene was synthesized in Germany by several methods. It is not the purpose of this book to describe these methods in detail, since this information is available in standard treatises, or in the more recent detailed reports of teams investigating the German chemical industry. However, the three most widely used processes of generating acetylene will be discussed briefly, and additional data may be found in the references cited

(1) **From Calcium Carbide.** The oldest and still most widely used method of generating acetylene is by the classical method from calcium carbide. The calcium carbide, which is generated in large electrical furnaces by the fusion of about 2 parts of lime or limestone with 1 part of coke by means of an electric arc, is reacted with water to produce acetylene and lime as shown in the following formulas:

$$CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$$

Although the starting materials are readily available, the process requires large amounts of electrical power (about 10 to 11 kwh per kilogram of acetylene) and considerable quantities of high-purity carbon electrodes (25 to 50 kg per metric ton of carbide). However, this process has the advantage that it produces no by-products other than lime, and the acetylene so generated is concentrated and of relatively high purity, the removal of traces of phosphine and other impurities involves relatively simple scrubbing operations requiring small chemical consumption.

Although German procedure for the most part followed conventional practice, several innovations had been developed. A novel process for continuously tapping calcium carbide from the furnace and feeding it directly to a rotary carbide chilling and cooling unit which discharged the products in lumps most of which did not exceed 80 mm in size was in prac-

[4] "Chemical Facts and Figures," 2nd Ed , p 22, Manufacturing Chemists' Assoc. of U. S., 1946

tice at Ludwigshafen[6] Improvements had also been made in the generation of acetylene from carbide. The so-called "dry procedure" using only about one-third the amount of water normally used in the conventional "wet process" was developed, so that it was possible to discharge lime which was free from unreacted carbide and from acetylene[7]. This lime, containing only 6 to 7 per cent moisture, could then be used directly for agricultural or chemical uses The design of various types of acetylene generators is discussed by King[8], as well as in the above-cited references

(2) **By the Arc Process.** Acetylene was synthesized at Huls by the cracking of hydrocarbon gases in an electric arc. Natural gas (primarily methane) from Bentheim, or by-product gases (primarily mixtures of methane and ethane) from coal hydrogenation, or mixtures thereof, were suitable feed stocks After purification in an Alkacid unit to reduce the sulfur content, the gas is compressed to 1 4 atmospheres absolute and passed to an electric arc reactor. The electric arc in each reactor transforms 7,000 kilowatts of electrical energy at 8,300 volts and 850 amperes d c into heat. The exact temperature at which acetylene is formed is not known, however, in its core the arc burns at about 3000°C, while at the end of the reactor tube the gas temperature is between 1600 and 2000°C At this point, the gas is quenched with a water spray to 150 to 200°C to prevent further cracking.

Each reactor produces about 4,200 cubic meters of product gas per hour from 2,800 cubic meters of feed gas Typical volumetric analyses for the arc inlet gas, which was made up of recycle and fresh gas, and for the outlet gas with both types of feed are as follows:

	Coal Hydrogenation Gas		Natural Gas	
	Inlet Gas	Outlet Gas	Inlet Gas	Outlet Gas
CO_2	0 2	0 0	0 3	0 0
C_2H_2	2 7	16 2	1 5	13 3
Olefins	3 2	3 6	1 4	0 9
O_2	0 2	0 2	0 3	0 2
CO	1 4	1 0	3 0	2 9
H_2	10 9	50 5	2 5	46 0
CH_4 and homologs	74 5	25 1	80 2	27 8
N_2	6 9	3 4	10 8	8 9
	100 0	100 0	100 0	100 0

The conversion to acetylene is about 50 per cent per pass; about 50 per cent of the energy is lost to the cooler and the quenching spray.

Two main reactions take place in the arc:

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

$$CH_4 \rightarrow C + 2H_2$$

---

[6] *PB* 44943 (*FIAT* 859)
[7] *PB* 63778 (*FIAT* 969).
[8] *PB* 3475 (*FIAT* 511).

However, these reactions do not explain all the reaction products; only about four moles of hydrogen per mole of acetylene instead of the expected five are produced, and about 10 to 12 per cent of the total acetylenes are diacetylene and higher homologs of acetylene

Originally, it was hoped that this dilute gas containing 13 to 16 per cent acetylene could be used for acetaldehyde production, but at the present time, the acetylene is concentrated and purified before hydration. It was stated that the dilute acetylene was not hydrated directly because this interfered with the recovery of the hydrogen, which was needed for other purposes. However, as will be shown later, the many impurities present, particularly diacetylene, also caused difficulty in the acetaldehyde synthesis due to catalyst poisoning, etc (see page 301)

The electrical requirements for the production of arc acetylene vary somewhat with the composition of the feed gas At full capacity with coal hydrogenation gas, the production of one kilogram of crude acetylene required 8.9 kwh; at 60 per cent of capacity with natural gas, the requirement for the arc itself was 10 7 kwh per kilogram of crude acetylene. However, including the electrical requirements involved in the purification process, the consumption of electrical power per kilogram of pure acetylene is increased to approximately 12 7 kwh for coal hydrogenation gas, and to 14 7 kwh for natural gas The overall electrical energy requirements are thus as high or higher than for the carbide process, however, if the four moles of hydrogen produced per mole of acetylene can be credited to the arc process, it then becomes more attractive than the carbide process Furthermore, the arc process is a potential source of other acetylenic homologs and by-products not available by other methods

Processes for the purification of the arc acetylene and for the isolation and utilization of some of the acetylenic homologs and diacetylene present in the crude gas will be discussed in Chapter VII.

The design and operation of the arcs, and purification of arc acetylene have been discussed by Fennebresque[9], Morrow[10], and Fuller, Weir, Zoss, Leaper and Direnga[11]

(3) **By Partial Combustion of Methane (Sachsse Process).** Acetylene may also be produced by the thermal cracking of methane.

$$2CH_4 \rightarrow HC{\equiv}CH + 3H_2 - 91{,}000 \text{ cal.}$$

The energy necessary for this endothermic reaction is supplied by combustion of a part of the methane with pure oxygen or with air. Under optimum operating conditions with preheated gases and essentially pure oxygen, the overall reaction may be approximated as:

$$45CH_4 + 30\ 25O_2 \rightarrow 8HC{\equiv}CH + 3\ 5CO_2 + 25\ 5CO + 54H_2 + 28H_2O$$

---

[9] *PB* 900

[10] *PB* 1852.

In actual operation, 800 m³/hr of methane and 400 to 500 m³/hr of oxygen are preheated separately to 500°C, thoroughly mixed and then burned in a burner of very critical design, shown in Figure I-1 The velocity of the mixed gases is considerably in excess of the rate of propagation of flame in the mixture The temperature of the gases reaches about 1400°C due to the partial combustion, and is rapidly lowered to about 80°C by means of

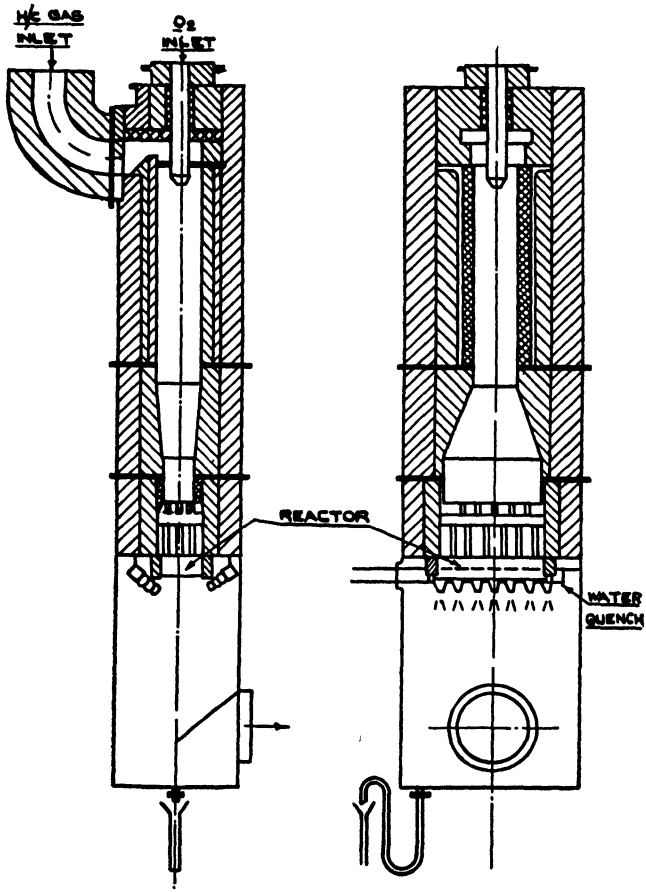


FIGURE I-1 Acetylene burner

a water quench. About 1500 m³/hr of product gases, having the following analysis on a dry basis, are produced:

	%
$HC{\equiv}CH$	8- 9
CO_2	3- 4
CO	24-26
H_2	54-56
CH_4	4- 6
O_2	0- 0 4

The yield of acetylene is about 31 per cent.

The Sachsse process produces a dilute acetylene which has been used principally for the synthesis of acetone (see page 8). Processes for concentration of this dilute acetylene had not been fully developed, although it is stated that a gas containing 70 per cent acetylene, less than 1 per cent hydrogen and 1 per cent carbon monoxide, and the remainder carbon dioxide, had been produced using a water wash under pressure

It is interesting to note that the Sachsse process, unlike the carbide and arc processes, does not require electric power as an energy source. Furthermore, it produces carbon monoxide and hydrogen in the ratio of 1:2, an ideal ratio for utilization in other syntheses

Further details of this process have been reported by Matthews[12] and by Carter and Cain[13].

Reactions of Acetylene at Atmospheric Pressure

The major chemical products into which acetylene was converted, together with their actual acetylene consumption per month in 1943 and the projected consumption, are:

Product		Acetylene Requirements (metric tons per month) 1943	Projected
Acetaldehyde		20,000	26,000
Acetone		485	485
Buna (Reppe process)		1,760	1,250
Ethylene by hydrogenation		2,890	8,555
Vinyl monomers	Vinyl chloride	1,080	1,720
	Vinyl acetate	480	720
	Vinyl ethers	150	200
	Acrylonitrile	—	615
Chlorinated products		850	850

The chemical process by which acetylene was converted into these products will now be considered.

Hydration of Acetylene

Production of Acetaldehyde. Acetaldehyde may be produced by continuous hydration of acetylene in the presence of a mercuric sulfate catalyst.*

$$HC{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3CHO + 33{,}880 \text{ cal}$$

However, as the reaction proceeds, the mercuric sulfate is reduced to mercurous sulfate, and finally to metallic mercury, which must be recovered and reconverted to the active catalyst. About ten years ago the I.G.

[12] *BIOS* 877

[13] *PB* 67790 (*FIAT* 988).

* For details of another method of synthesis from methyl vinyl ether, see page 46

developed a new process in which the active catalyst, mercuric sulfate, is generated continuously in the reactor by the action of ferric sulfate on metallic mercury:[14]

$$Hg + Fe_2(SO_4)_3 \xrightarrow{H_2SO_4} HgSO_4 + 2FeSO_4$$

The mercuric-ferric sulfate solution is continuously renewed by oxidation of the ferrous sulfate to ferric sulfate with nitric acid, and by addition of fresh mercury

Conversion of acetylene per pass is about 55 per cent and the yield of acetaldehyde 93 to 95 per cent of theoretical, the main losses occurring on distillation The product is recovered as a 7 per cent solution of acetaldehyde and the latter purified by distillation to 99.9 per cent purity. About 0 5 to 0 7 per cent of acetone (based on aldehyde) is recovered, but diacetyl, crotonaldehyde, and up to 2.0 per cent of acetic acid are discharged to the sewer Mercury consumption is about 0 1 per cent, based on acetaldehyde.

The production of acetaldehyde takes place in vertical metal towers (1 3 meters in diameter and about 15 meters high) lined with rubber. Acetylene from the acetylene generation system, containing 97 per cent of acetylene, 1 0 per cent of carbon dioxide, 2 per cent of nitrogen and hydrocarbons, is mixed with recycle acetylene of 75 per cent purity from the reactors at a pressure of about 1 2 atm gauge About 1,500 cubic meters of recycle gas per hour is used per reactor, making a total feed of 2,800 cubic meters per hour. This is fed into the bottom of the reactor after mixing with 1.5 tons of steam per hour and bubbles up through the liquid catalyst solution.

The temperature at the bottom of the reactor is 97°C and at the top 94°C The vapors from the reactor are scrubbed with water to give a dilute solution of acetaldehyde from which pure acetaldehyde is recovered by distillation Part of the undissolved gas (75 to 80 per cent acetylene) is then recycled, and part is taken to an acetylene purification system where the acetylene is purified by solution in water at 4 atm pressure, and finally recycled as about 96 per cent acetylene containing small percentages of hydrogen, nitrogen, and carbon dioxide

The catalyst solution, of which 2 5 m^3/hr are removed continuously for regeneration, contains 4 0 g of ferric iron, 36 g of ferrous iron, 0.6 g of mercuric sulfate and 180 g of total sulfates per liter (the high total sulfate figure is due to sulfuric acid). In addition, the catalyst solution contains a large amount of free mercury which is suspended in minute particles by the gas rising through the solution.

The spent catalyst, which is withdrawn continuously, is freed of metallic mercury and then degassed at 100°C with live steam to remove acetylene and acetaldehyde. After filtering, the solution is fed into the bottom of an oxidizer where it mixes with just enough 30 per cent nitric acid to convert

[14] *PB* 189, pp. 32–6; *PB* 44941 (*FIAT* 855).

all the ferrous iron to the ferric state The oxidation is carried out at 90°C. The liberated nitric oxide fumes pass to a recovery system, while the regenerated catalyst solution, after being freed of any dissolved nitric oxide, is pumped back into the reactor at the same rate as the spent catalyst is withdrawn.

Acetone. The major part of the acetone produced in Germany was synthesized by passing acetic acid over a cerium catalyst at 400 to 500°C[15]

$$2CH_3COOH \rightarrow CH_3\overset{\overset{O}{\parallel}}{C}—CH_3 + CO_2 + H_2O$$

However, about 540 tons per month of acetone were made directly from acetylene by hydration over a zinc oxide catalyst[16]

$$2HC{\equiv}CH + 3H_2O \rightarrow CH_3\overset{\overset{O}{\parallel}}{C}—CH_3 + CO_2 + 2H_2$$

The acetylene used was made by cracking methane by direct combustion with oxygen and quenching the gaseous products with water to 80°C (see page 4) The resultant gas contains only about 8 per cent of acetylene, 3 to 4 per cent of carbon dioxide, 24 to 26 per cent of carbon monoxide, 54 to 56 per cent of hydrogen and 4 to 6 per cent of methane (all on dry basis), and is saturated with water at 80°C After being preheated to 360°C, it was passed over a zinc oxide catalyst The reaction is exothermic and the exit temperature of the gas is 450°C Temperature control is apparently critical The acetone was recovered from the gas stream by water-washing and separated from the water and acetaldehyde by distillation

Conversion of the acetylene to acetone is high However, like the acetic acid process, only 75 per cent of the carbon content of the acetylene is utilized in the synthesis of acetone Catalyst life is only about one week due to carbon formation, but regeneration by burning off the carbon is possible

The off gas from the water washer went to a synthesis gas unit where the remaining methane was burned over a nickel nitrate catalyst to give synthesis gas for methanol

Butadiene from Acetylene via Acetaldol and 1,3-Butylene Glycol

In 1925 the I G. assigned Reppe the problem of developing on a suitable technical scale the synthesis of butadiene based on the classical four-stage process via acetaldehyde → aldol → 1,3-butyleneglycol → 1,3-butadiene. Within three years he succeeded in establishing the fundamental chemical knowledge of this process and in 1928 prepared 100 tons of butadiene in a pilot plant. The data obtained proved the feasibility of the process for the

[15] *PB* 91663 (*BIOS* 1053, pp 13–35)
[16] *PB* 91663 (*BIOS* 1053, pp 35–41)

large-scale synthesis of butadiene and, furthermore, its superiority to all procedures known at that time, *e.g.*, by cracking of cyclohexane, etc.

Aldol (acetaldol) was produced on a very large scale in Germany at various plants by slightly different procedures. Although some of this aldol was dehydrated to crotonaldehyde which was used in other syntheses, such as oxidation to crotonic acid, or maleic anhydride, reduction to *n*-butyraldehyde and *n*-butanol, etc., by far the largest amount was reduced to 1,3-butanediol which was then dehydrated to butadiene[17].

The details of the several different procedures used for aldol and crotonaldehyde manufacture are ably presented by Hunter[18]. The procedure used at Hüls, though not necessarily the best, did supply practically all the aldol which was used for butadiene, and will be briefly described here.

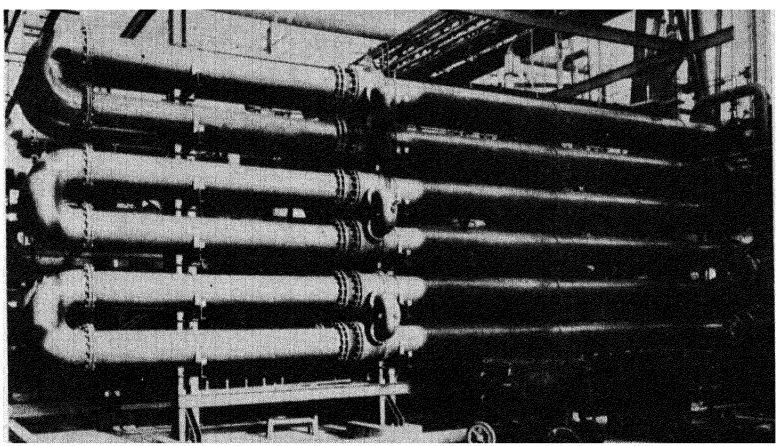


FIGURE I-2. Aldol reactors.

Aldol Production and Purification. Aldol is made by treatment of acetaldehyde with dilute potassium hydroxide solution at 20 to 30°C in a long heat exchanger cooled with water.

$$2CH_3CHO \rightarrow CH_3CHOHCH_2CHO + 26{,}400 \text{ cal.}$$

The conversion is 45 to 46 per cent per pass, and the ultimate yield 88 per cent of theoretical. The aldol solution is treated with dilute phosphoric acid to precipitate potassium phosphate, which is separated. The crude aldol is then separated from unconverted acetaldehyde by distillation.

Pure acetaldehyde is mixed with about an equal part of recycle aldehyde and pumped through the tubes in a reactor made up as a long horizontal tubular heat exchanger, cooled on the outside of the tubes with water for

[17] *BIOS* 1060

[18] *PB* 91663 (*BIOS* 1053, pp. 76-120).

about one-third of the surface Figure I-2 shows one view of the reactors

The temperature in the reactor is maintained at 20 to 30°C From 0 02 to 0 1 per cent of potassium hydroxide based on aldehyde is injected into the aldehyde just before the circulating pump

The aldehyde-aldol mixture is held at 45 to 46 per cent conversion to prevent formation of too much crotonaldehyde, higher aldehydes, and resins by controlling alkali concentration, withdrawal rate, etc Rapid recirculation through the heat exchangers is required, amounting to approximately 20 times the fresh input of aldehyde, or 180 to 250 m^3/hr The average time of contact is 2 to 3 hours

A typical analysis of the crude aldol shows 52 84 per cent of acetaldehyde, 0 32 per cent of crotonaldehyde, 44 80 per cent of aldol and residue, and 2 04 per cent of water This product is withdrawn from the circulating system and sent to a mixing vessel in which a dilute solution of phosphoric acid is added to reduce the pH to below 6 0 The liquid is then allowed to stand for one hour to permit the potassium phosphate to form large enough crystals for centrifuging The solution is centrifuged to remove phosphate, it is then sent to a leaf filter and finally to a mixer where the pH, which was too acid for distillation, was raised to from 6 3 to 6 4 (indicator, pH on glass electrode 8 0 to 8 3) by blending with alkaline aldol from the reactor

The crude aldol is pumped through a filter to three distillation towers in parallel (Figure I-3) Each tower contains 23 plates and the feed is on the eighth plate Here, at atmospheric pressure acetaldehyde is taken overhead at 21 to 25°C and at a reflux ratio of 1 to 5 The bottoms from the tower are sent to a series of three heat exchangers heated with 3 0 atm (gauge) steam to heat the aldol from 70 to 80 up to 100 to 110°C and flash off surplus water The aldol is then quenched to 65°C with an equal amount of finished cold aldol (to prevent side reactions) and cooled in cooling coils to 30 to 35°C It then goes to a mixer and storage The purified aldol has a pH of 5 7 with a typical analysis as follows:

	%	
Aldol	72 82	
Acetaldehyde	4 65	
Crotonaldehyde	1 59	
Residue	2 60	(higher aldehydes, resins)
Water	18 34	

Overall yields in the middle of 1944, at 46 per cent conversion per pass, were per 100 parts of aldehyde by weight:

	parts
Aldol	88 0
Acetaldehyde	5 61
Crotonaldehyde	2 42
Residue	3.14
Loss	0.83

The total capacity of the system using four reactors is about 10,000 tons a month.

Hydrogenation of Aldol to Butylene Glycol-1,3. Butylene glycol-1,3 was produced by the hydrogenation of aldol of the composition previously

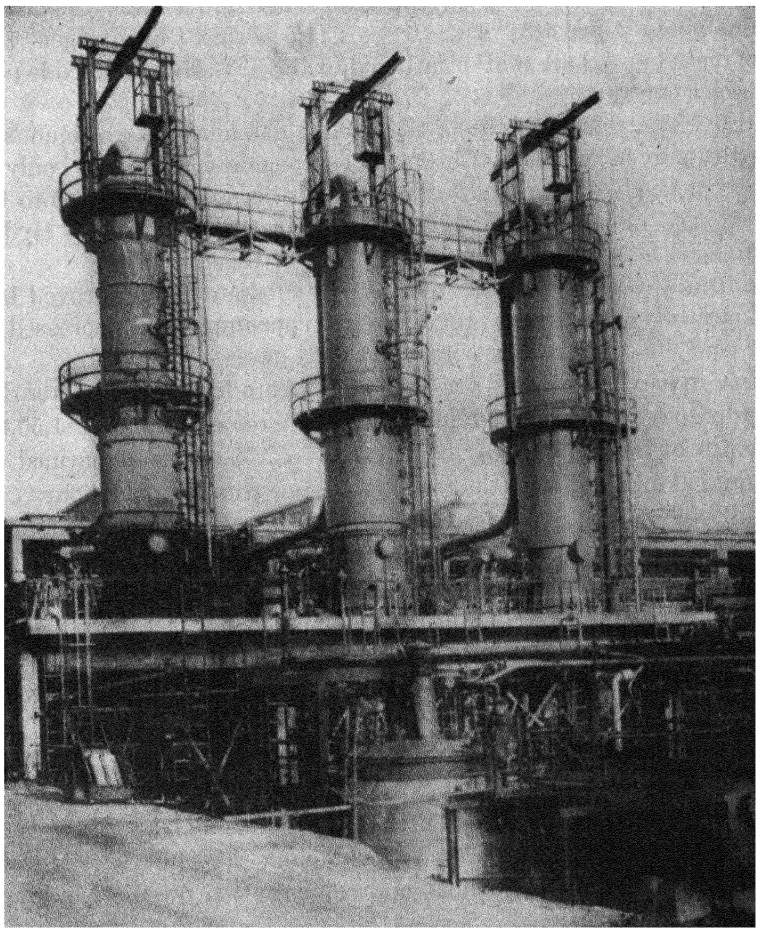


FIGURE I-3. Aldol distillation plant.

described in continuous vertical reactors at 300 atm hydrogen pressure and 50 to 150°C over a catalyst containing 17 to 20 per cent of copper and 0.7 to 1.0 per cent of chromium on calcined silica gel (B.B.E. catalyst)[19].

$$CH_3CHOHCH_2CHO + H_2 \rightarrow CH_3CHOHCH_2CH_2OH + 22{,}000 \text{ cal.}$$

[19] *PB* 189, pp. 39–43; *PB* 91663 (*BIOS* 1053, pp. 133–66).

Under these conditions 99.9 per cent of the aldol could be hydrogenated in a single pass. The butylene glycol was isolated by distillation.

The reaction is strongly exothermic and the temperature in the reactor is controlled by adjusting the amount and temperature of the gas feed.

The purity of the hydrogen used is of great importance, as in any catalytic hydrogenation. The hydrogen gas comes from a water gas plant and contains about 3 per cent of inert gases (1.5 per cent of nitrogen, 1.4 per cent of methane, 0.2 per cent of carbon dioxide). Carbon monoxide poisons the copper catalyst.

Approximately 20 per cent of the cycling gas must be continuously expanded to prevent increase of inert gas components. However, only 10 to 15 per cent need be expanded to the open air because the other 5 to 10 per cent expands automatically through leaks in the apparatus. Hydrogen consumption is approximately 125 per cent of theoretical.

The conditions of hydrogenation can be substantially improved by the use of electrolytic hydrogen, the hydrogen consumption is decreased 10 to 12 per cent due to the lower content of inert gases.

Thirty-five hundred liters per hour of aldol are fed to the reactor during the hydrogenation period. Each reactor, therefore, produces 1,500 tons per month of butylene glycol from 2,400 to 2,500 tons of purified aldol. The liquid aldol remains in the reactor for approximately one hour.

Distillation of the crude hydrogenation product is carried out in three identical continuously operating columns which have 30 plates, 3 meters in diameter and 500 mm apart. From the raw butylene glycol the following constituents are separated in the column number designated:

Col. 1. All low-boiling constituents (acetaldehyde, ethanol, butanol, esters, acetals, partly as azeotropic mixtures)
Col. 2. Water
Col. 3. Pure butylene glycol

Column 1 works under normal pressure, columns 2 and 3 under vacuum. The bottoms from column 3 are higher-boiling than butylene glycol and consist of higher acetals, alcohols, and condensation products of glycerin-like or resinous consistency.

Distillation of 169.2 kg of raw butylene glycol gives the following products:

100	kg pure butylene glycol
19.5	kg ethanol 100%
2.8	kg butanol 100%
3.8	kg residue (0.6 kg butylene glycol)
0.5–0.6	kg butylene glycol acetal (2,4-dimethyl-1,3-dioxane)
0.1	kg aldehyde first runnings
42.5	kg water

The pure butylene glycol has the following analysis:

Aldehyde (as acetaldehyde)	0.05%
Acetal (as diethyl)	0.3%
Esters (as ethyl acetate)	0.1%
Crotyl alcohol	0.2%
Water	0.2–0.6%
Butylene glycol	98.75–99.15%

Boiling range within 1.5° limits

The numerous impurities present in the crude hydrogenation product arise from the impurities originally present in the purified aldol. Thus

(1) $CH_3CHO + H_2 \rightarrow CH_3CH_2OH$
Ethanol

(2) $CH_3CH{=}CHCHO \xrightarrow{2H_2} CH_3CH_2CH_2CH_2OH$ *Butanol*; $CH_3CH{=}CHCHO \xrightarrow{H_2} CH_3CH{=}CHCH_2OH$ *Crotyl alcohol*

(3) $CH_3CHOHCH_2CH_2OH + CH_3CHO \rightarrow$ *2,4-Dimethyl-1,3-dioxane*; *2,4-Dimethyl-1,3-dioxane* $\xrightarrow{H_2}$ *Butanol* $+ C_2H_5OH$; *2,4-Dimethyl-1,3-dioxane* $\xrightarrow{H_2} C_2H_5OH +$ $CH_3CHOHCH_2CH_3$ *sec-Butanol*

(4) $CH_3CHO + CH_3CHOHCH_2CHO \xrightarrow{H_2}$ $CH_3CH_2CH(C_2H_5)CH_2OH$ *alpha-Ethyl-butanol*; $CH_3CHOHCH(H_3C{-}CHOH)CH_2OH$ *Hexanetriol*

Condensation of aldol with itself or with crotonaldehyde, etc., would give resinous materials.

Dehydration of Butylene Glycol-1,3 to Butadiene-1,3. Dehydration of butylene glycol at 280°C and 1 atm in the presence of steam over a catalyst containing sodium phosphates and free phosphoric acid on coke or graphite gives butadiene as shown in the equation[20]

$$CH_3CHOHCH_2CH_2OH \xrightarrow{-2H_2O} CH_2{=}CH{-}CH{=}CH_2 - 29{,}700 \text{ Cal}$$

[20] *PB* 189, pp. 44–8

The butadiene is purified by distillation The conversion per pass is essentially 100 per cent, but the ultimate yield of pure butadiene is only 81 per cent of theoretical

Five hundred to 700 kg/hr of butylene glycol of the composition just described is vaporized, preheated to 210°C, and mixed with an equal quantity of steam at 400°C and 1 atm gauge. The resulting gas mixture is then passed to a vertical dehydration tower containing the catalyst (12 m^3) which is maintained at 280°C by hot water under 65 atm pressure The product gas goes to a cooler to separate water and oils The average percentage composition of the gas is now about as follows: butadiene 80, propylene 2, butylenes 1, butyraldehyde 2, allyl carbinol 10, 2-ethylhexanol 1, and heavier oils 4

Purification and distillation of the butadiene coming from the catalytic reactors is performed in a three-part plant, consisting of butadiene purification, butadiene distillation, and oil distillation. A view of this plant is shown in Figure I-4 In the purification, the raw butadiene is separated by distillation from oily by-products (especially butyraldehyde) and caustic-washed in the gas phase to remove aldehydes It is then compressed and liquefied, whereby most of the moisture separates as water, which is insoluble in butadiene The raw butadiene is then dried with solid caustic potash, which also removes the last traces of aldehydes It is finally cooled to −30 to −40°C to remove the last traces of moisture This procedure is then followed by continuous distillation of the butadiene under normal pressure, which completely separates from the butadiene pure propylene boiling at −47°C A second column separates pure butadiene boiling at −4°C from the higher-boiling residue The composition of the pure butadiene is

99 4%	butadiene
0 5–0 6%	butylene + propylene
0 01–0 02%	water
0 001%	aldehyde (calculated as acetaldehyde)

The oil distillation yields valuable by-products, *e g* , butyraldehyde, allyl carbinol, and a small quantity of crotyl alcohol, which is separated from the higher-boiling non-volatile oils (products of condensation and polymerization, mostly of aliphatic nature) and from water The allyl carbinol may be recycled

The dehydration of butylene glycol-1,3 is highly endothermic, and apparently considerable difficulty was experienced in maintaining uniform temperatures throughout the reactor In addition, the catalyst itself is not chemically stable and fixed in composition but may undergo changes during reaction Consequently, the dehydration of the butylene glycol does not proceed cleanly by a single mechanism but instead gives rise to a variety

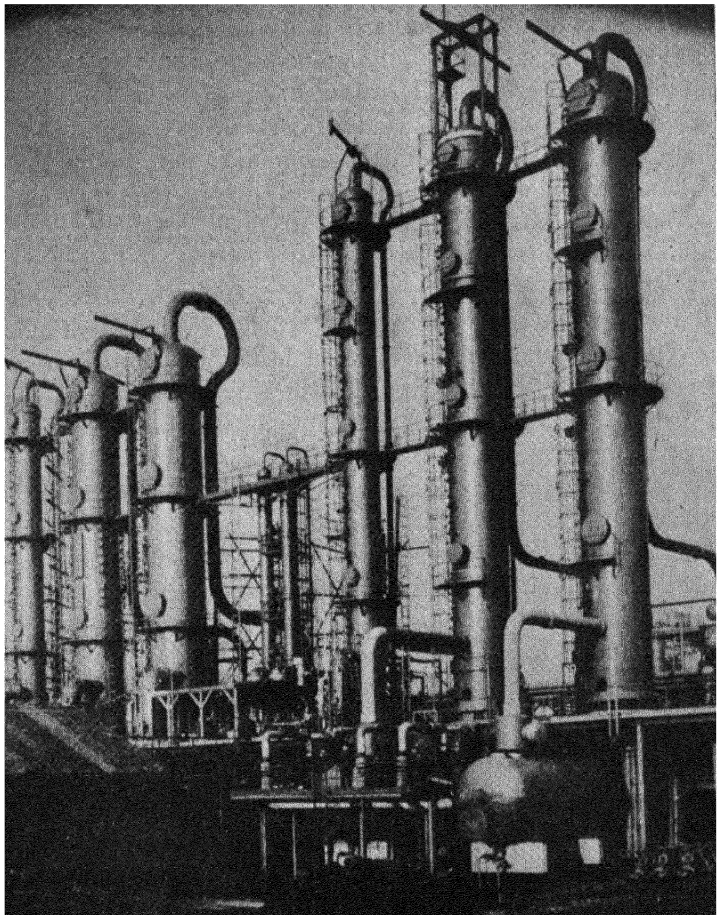
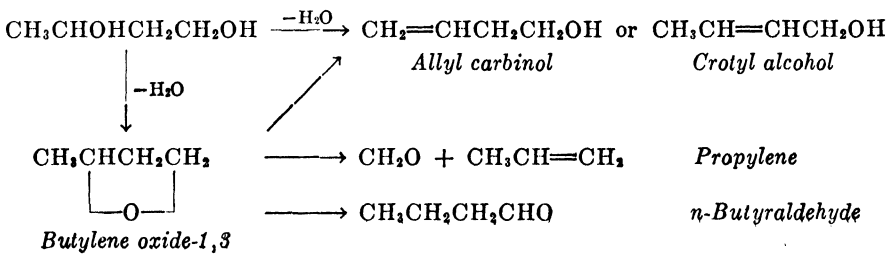


FIGURE I-4. Butadiene stills.

of partially dehydrated and isomerized compounds; a few of the many possible side reactions are as follows:



The dehydration catalyst is prepared by impregnating 100 parts of coke (5 to 8 mm granules) with 56 parts of disodium phosphate, 8.5 parts of phosphoric acid and sufficient butylamine so that only about 1 per cent of free phosphoric acid is left The catalyst is dried at 250°C, the phosphates are converted to a mixture of Madrell's salt $(NaPO_3)_2$ and sodium pyrophosphate ($Na_2P_2O_7$). This catalyst is similar to that used in the dehydration of butanediol-1,4 or tetrahydrofuran, except that its content of sodium pyrophosphate is lower (see page 103)

The life of this catalyst is short, usually only 4 to 6 weeks Catalyst regeneration is not possible, recovery is as follows The phosphate is extracted with water from the catalyst, which contains large quantities of resins The remaining support is then heated to glowing in a rotating furnace and freed from resin before it can be impregnated again Consumption of catalyst is 12 to 13 kilos per 100 kilos of butadiene production

The capacity of each dehydration unit was initially 130 to 140 tons per month of pure butadiene However, by improvements in design and operation, the capacity was doubled

Butadiene Peroxide In some cases, after long storage, the separation of a honey-like liquid peroxide from liquid butadiene has been observed This peroxide is insoluble in liquid butadiene and collects at the bottom of the storage tanks It explodes vigorously by slight friction or percussion, its shattering power is tremendous However, it has not been possible to produce this highly dangerous compound at will in the laboratory

German experience at Schkopau indicates that this peroxide forms only if the butadiene contains aldehydes (probably by way of aldehyde peroxides) This is another reason why complete removal of all aldehydes from butadiene is imperative It is possible to avoid the formation of peroxides completely if the removal of aldehydes is carefully watched, and if the bottom of the storage tank is covered with a 50 per cent aqueous solution of caustic potash In pumping off the butadiene, care must be taken that this caustic layer is not disturbed Separated peroxide can be destroyed by hot solutions of potassium hydroxide and ferrous sulfate, or by bisulfite Strong heating is to be avoided, however, because vigorous explosions have been observed even under water

Hydrogenation of Acetylene to Ethylene

Ethylene from cracking operations was not readily available, nor was it considered desirable to obtain ethylene from ethanol which in turn was made by fermentation of valuable food products Consequently, the Germans turned once more to their old stand-by, and prepared large amounts of ethylene by a vapor-phase catalytic hydrogenation of acetylene[21]

$$HC{\equiv}CH + H_2 \xrightarrow{Pd} H_2C{=}CH_2 + 42{,}000 \text{ cal}$$

[21] *PB* 354, *PB* 14954 (*BIOS* 171), *PB* 25051 (*BIOS* 1058)

The hydrogenation is carried out at atmospheric pressure. It is necessary to use as selective a catalyst as possible, and to remove the heat of reaction in order to prevent further hydrogenation of the ethylene to ethane. Control of the reaction is achieved by maintaining a low concentration of acetylene (10 to 12 per cent), by circulating large volumes of gas, and by injecting water before the second and third catalyst trays.

The plant built in 1941 at Gendorf had a design capacity of 70 tons per day and operated in the following manner. The 24 reactors, some of which are shown in Figure I-5, consisted of steel towers 2.8 m in diameter and 3.4 m high. During normal operation two such towers were connected in



FIGURE I-5. Ethylene reactors.

parallel. Acetylene (500 m^3/hr) was compressed to about 0.2 atm gauge in turbo-blowers and mixed with one to two volumes of hydrogen, likewise compressed to 0.2 atm. This fresh gas was mixed with about 35,000 m^3/hr of recycle gas at 250°C; the gas stream was split and fed to the top of the converters in which it passed downward through three wire-mesh catalyst trays covered with about 23-cm layers of palladium on silica catalyst. The reaction is exothermic and the temperature of the gases emerging from the first and second catalyst beds is lowered to 250 to 300°C with a manually controlled central water spray. The gas stream is forced into a circular path and directed into the water spray by spiral baffle plates.

The gas feed entering the converter and leaving the three trays had the following composition:

Component	Converter Inlet	Sample Point: After First Tray	After Second Tray	After Third Tray
C_2H_2	12 5	6 7	0 7	0 2
C_2H_4	39 0	48 5	56–57	63 0
C_2H_6	—	—	—	3 0
H_2	—	—	—	30 0
Inerts	—	—	—	2 7

The product gas also contains some higher hydrocarbons which could be condensed at room temperature.

The ratio of hydrogen to acetylene in the make-up gas increases with a decrease in the activity of the catalyst, as it is necessary to maintain the acetylene content of the withdrawn gas at 0 8 per cent or less When excess hydrogen is no longer effective in maintaining this limiting concentration, the product from the two converters in parallel may be passed through a third converter, or even two converters in series

Although about 35,000 m^3/hr of gas are circulated, only about 500 m^3/hr are withdrawn (steam-free basis) This is compressed to 28 atm and cooled to separate water Fractionation of this product in a Linde plant gave a product containing 96 per cent ethylene, 2 per cent ethane, 1 per cent nitrogen and 1 per cent hydrogen

The catalyst consists of palladium deposited on about 3 to 8-mm silica gel particles The quantity of palladium is approximately 0 175 g per liter of catalyst Catalyst life is 3 to 4 months, activity gradually decreases mainly due to the deposition of acetylene polymers on the catalyst However, after removal from the reactor, the catalyst may be reactivated with steam and air at 600°C

The yield of pure ethylene was 80 to 85 per cent of theoretical. Ethane produced was from 1 5 to 2 5 per cent, while 10 to 12 per cent of oils containing 85 per cent of heavy oil and 15 per cent of light oil (butenes, hexenes and octenes) were also formed

Chlorination of Acetylene[22]

The chlorination of acetylene followed by dehydrochlorinations and subsequent rechlorinations gives a valuable series of nonflammable solvents which are widely used in dry cleaning, metal degreasing, extractions of natural oils, and other specialized applications German manufacture of such chlorinated products apparently followed closely old and well established processes and will be discussed only very briefly.

[22] *PB* 79317 (*BIOS* 1056)

Chlorinated Products from Acetylene

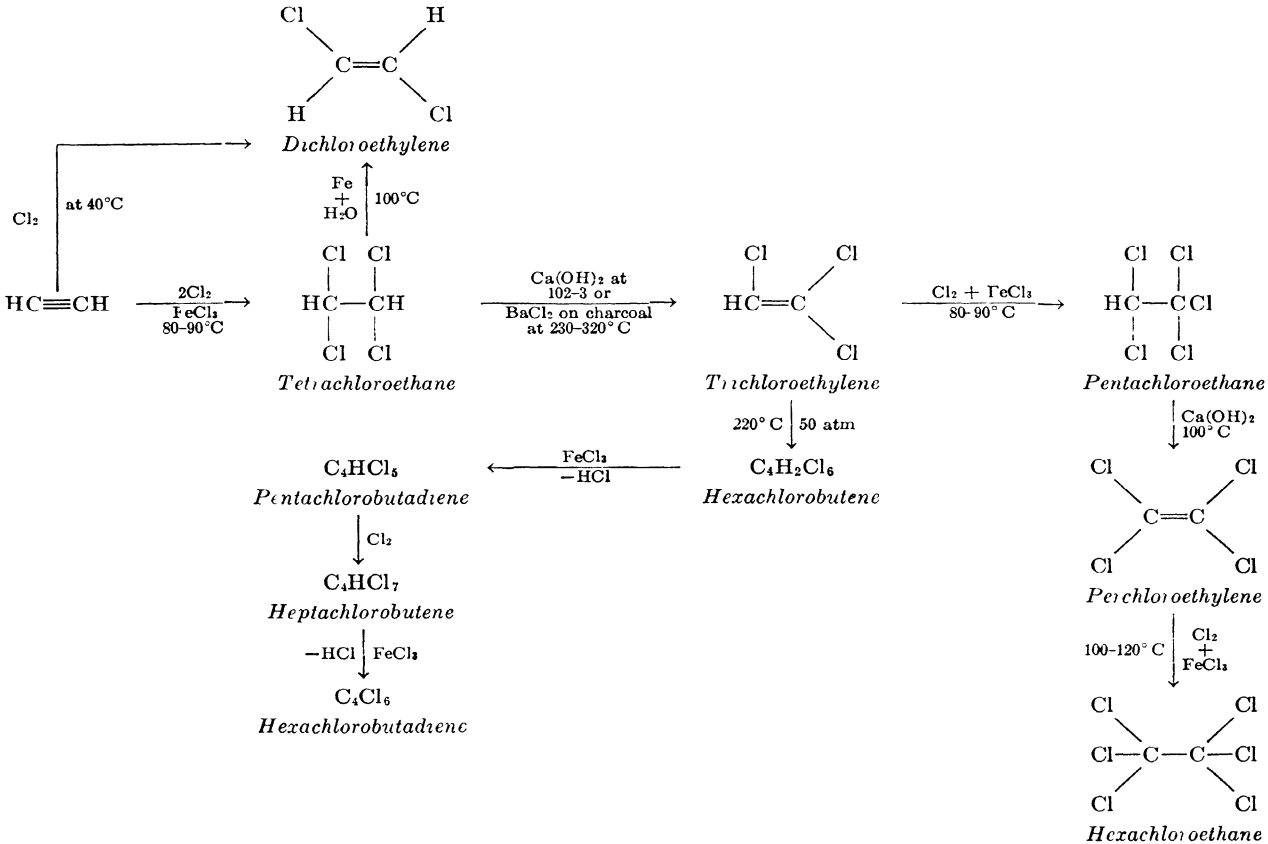
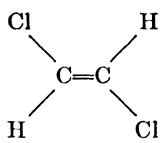
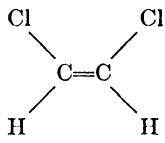
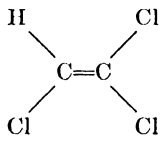
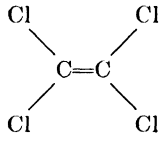
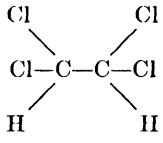
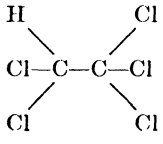
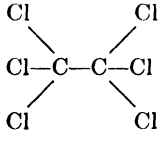


Table I-1 Physical Properties of Chlorination Products Derived from Acetylene

Name	Formula	Mol Wt	Boiling Point	Freezing Point	Sp Gr
Trans-dichloroethylene		96.9	48 4	−50	1 265
Cis-dichloroethylene		96 9	60 1	−80 5	1.291
Trichloroethylene		131 4	87 0	−73	1.4556
Perchloroethylene		165 8	121 2	−22 35	1 634
Tetrachloroethane		167 8	146 3	−43 8	1 600
Pentachloroethane		202 3	162 0	−29	1 6728
Hexachloroethane		236 76	185 5	186 9–187 4	2 091

The various chemical transformations involved in the syntheses are shown on page 19. The physical properties are listed in Table I-1.

Tetrachloroethane. Dry acetylene and chlorine in almost stoichiometric amounts are bubbled into a solution of tetrachloroethane containing

about 0.01 per cent of anhydrous ferric chloride as a chlorination catalyst in a packed tower 1.5 m in diameter by 11 m high. The operating temperature is 80 to 90°C, the tower is operated under reduced pressure (120 to 130 mm) so that the heat of reaction can be removed from the reaction zone by refluxing tetrachloroethane, which is removed at such a rate that the liquid level in the tower remains constant. During the reaction some dichloroethylene is formed as well as trichloroethylene, perchloroethylene and hydrogen chloride.

Due to its toxicity, tetrachloroethane was not widely used except as an intermediate in the synthesis of other chloro compounds. Hence, most of the output of the plant was taken to storage without purification.

Trichloroethylene. *Lime Dehydrochlorination.* Tetrachloroethane was mixed with a lime slurry (15 to 17 per cent of solids) and heated to 102 to 103°C in a vertical reactor. The trichloroethylene formed is separated by a ring-packed fractionation section in the top of the reactor. Calcium chloride and lime slurry are withdrawn from the base of the tower. The crude trichloroethylene is purified by continuous distillation.

Vapor-Phase Dehydrochlorination. Trichloroethylene may also be prepared by the vapor-phase dehydrochlorination of tetrachloroethane over a barium chloride on charcoal catalyst at 230 to 320°C. As shown later (see page 28), this process was also used to generate anhydrous hydrogen chloride, which was subsequently used in the synthesis of vinyl chloride. The trichloroethylene prepared by either process must be stabilized by the addition of triethylamine, naphthol, or phenol. Stabilization with phenol is claimed to reduce rust formation on the surface of degreased iron and steel articles. Trichloroethylene is probably the most important chlorinated solvent derived from acetylene and was widely used in metal degreasing and dry cleaning.

Dichloroethylene. *Dechlorination of Tetrachloroethane.* Tetrachloroethane is converted to symmetrical dichloroethylene by refluxing at 100°C in the presence of steam in a tower packed with iron turnings. The steam dissolves the film of ferrous chloride from the turnings and thus exposes a continuous clean surface. Crude dichloroethylene is taken overhead, ferrous chloride solution is withdrawn from the base of the tower. The crude dichloroethylene is purified by fractionation. The product is a mixture of about equal parts of the *cis* and *trans* isomers.

Direct Chlorination of Acetylene. Direct chlorination of acetylene in the gas phase at 40°C in the presence of an activated charcoal catalyst is claimed to yield practically pure *trans*-dichloroethylene with about 10 per cent of tetrachloroethane. Dichloroethylene is used in the formulation of rubber cements, for the extraction of oils from thermolabile natural products, and for the decaffeinization of coffee.

Pentachloroethane. Chlorination of trichloroethylene in liquid phase

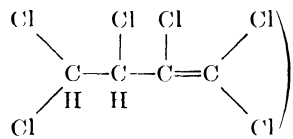
at 80 to 90°C in the presence of 0.2 to 0.3 per cent of anhydrous ferric chloride gives pentachloroethane. Pentachloroethane when inhaled, even in small quantities, over a considerable period of time causes severe and permanent liver damage, and hence is of little importance except as a chemical intermediate.

Perchloroethylene. Pentachloroethane is dehydrochlorinated with milk of lime at 110°C and 200 mm pressure by a process similar to that described for the conversion of tetrachloroethane to trichloroethylene. The crude overhead is purified by distillation at 180 mm pressure.

Hexachloroethane. Perchloroethylene is chlorinated at 100 to 120°C using 0.025 per cent of ferric chloride as the catalyst. When the conversion to hexachloroethane is about 60 per cent, the crude liquor is neutralized at 90°C with dilute caustic and pumped to shallow, jacketed pans for crystallization. The hexachloroethane is separated in a centrifuge and dried at 20 to 25°C. The mother liquor, a saturated solution of hexachloroethane in perchloroethylene, is recirculated to the chlorinator. Hexachloroethane was used in chemical smokes and as an insecticide.

Hexachlorobutadiene. Small quantities (4 tons/month) of hexachlorobutadiene were prepared by the following process. Trichloroethylene was polymerized to hexachlorobutene by heating at 220°C under 50 atm pressure.

The structure of the hexachlorobutene is probably



The conversion is about 30 per cent. After separation from the unreacted trichloroethylene, the hexachlorobutene is dehydrochlorinated by heating to 180°C for 15 to 20 hours in the presence of 0.05 to 0.05 per cent of anhydrous ferric chloride. The reaction mixture is cooled to 75°C and converted to heptachlorobutene by addition of chlorine. The crude heptachlorobutene is then dehydrochlorinated at 205 to 210° for 8 hours and the hexachlorobutadiene isolated by fractional distillation at 30 to 50 mm pressure. The main use was apparently as an additive for transformer oils.

Nitration of Acetylene

Tetranitromethane[23]. The use of nitric acid as an oxygen donor in the "V" weapons caused excessive corrosion. Tetranitromethane was investigated as a replacement, but it was unsatisfactory as such because of its high freezing point (14°C). However, a mixture with 30 per cent of nitrogen dioxide had a freezing point of −27°C. Ten tons of this mixture

[23] *PB* 47730 (*BIOS* 709).

were prepared and sent to Peenemunde for testing Apparently some corrosion problems, especially in the presence of water, were encountered with this mixture.

Initially, the tetranitromethane was prepared from acetic anhydride by the classical method,[24] but this process was not satisfactory because the

$$4(CH_3CO)_2O + 4HNO_3 \rightarrow C(NO_2)_4 + 7CH_3COOH + CO_2$$

product contained impurities which decreased its stability. Later, on the basis of the prior work of Orten and McKie[25], the reaction of acetylene with nitric acid was employed, using an all-glass reactor scaled to produce 10 kilos of tetranitromethane per day The steps involved in the reaction were believed to be:

$$HC{\equiv}CH + 2HNO_3 \longrightarrow (NO_2)_2CHCHO + H_2O$$

$$(NO_2)_2CHCHO \xrightarrow{HNO_3} (NO_2)_3CCHO + H_2O$$

$$(NO_2)_3CCHO + H_2O \xrightarrow{2HNO_3} (NO_2)_3CCOOH + 2NO_2$$

$$(NO_2)_3CCOOH + 2NO_2 \rightarrow CO_2 + (NO_2)_3CH$$

$$(NO_2)_3CH \xrightarrow{HNO_3} (NO_2)_4C + H_2O$$

or overall

$$HC{\equiv}CH + 6HNO_3 \rightarrow (NO_2)_4C + 4H_2O + 2NO_2 + CO_2$$

However, only 60 per cent of the acetylene reacted as above, while 40 per cent underwent complete oxidation

The first stages of the reaction were carried out in a tower 2 meters high and having a working capacity of 6 liters The liquid feed was 2 4 liters per hour of 98 per cent nitric acid containing 0 336 g of mercuric nitrate, which was the process catalyst Acetylene was introduced at the bottom of the tower at 93 5 liters per hour The reaction was maintained at 50°C The solution of nitroform in nitric acid overflowed to three steam-heated nitration vessels of 3-liter capacity, connected in series Sulfuric acid from the tetranitromethane purification tower was also fed to the first of these nitrators, which was heated to about 90°C. A total contact time in the nitrators of about 3 hours completed the nitration of the nitroform to tetranitromethane

The warm mixture leaving the final nitrator quickly separated, and the top layer of tetranitromethane was fed to a purification tower 2 meters high where it was contacted with 1 7 liters per hour of 95.5 per cent sulfuric acid Pure tetranitromethane (m p 13 8 to 14 0°C) left the top of the purification tower at a rate of 440 to 460 g per hour The sulfuric acid wash was fed back to the first nitrator

[24] "Organic Syntheses," Vol **21**, p 105, John Wiley & Sons, Inc , 1942
[25] *J Chem Soc* , **1920**, 283

Nitroform. Nitroform has been prepared by the reaction of tetranitromethane with potassium hydroxide and hydrazine, but the procedure was hazardous since hydrazoic acid, and not nitrogen, as believed by Orten and McKie, was formed simultaneously A second method was based on the reaction of tetranitromethane with potassium hydroxide and hydrogen peroxide·

$$C(NO_2)_4 + 2KOH + H_2O_2 \rightarrow KC(NO_2)_3 + KNO_2 + O_2 + 2H_2O$$

The nitroform was liberated from the potassium salt by distillation at reduced pressure in the presence of sulfuric acid

Later, it was discovered that nitroform could be extracted from the reaction product of acetylene and nitric acid using nitrogen dioxide at 0°C as the solvent It is believed that the idea of using nitrogen dioxide as a solvent for the recovery of nitro compounds had been applied to other systems as a means of reducing the sulfuric acid concentration load in German explosive plants Nitroform was an excellent rust inhibitor when incorporated in polyvinyl acetate emulsions and was superior to sodium nitrite as it did not break the emulsion

Some research was carried out on the addition of nitroform to unsaturated compounds, and reactions with carbonyl compounds Typical examples are

(1) *Addition to Methyl Acrylate*

$$CH_2{=}CHCOOCH_3 + CH(NO_2)_3 \rightarrow (NO_2)_3C{-}CH_2CH_2COOCH_3$$

Subsequent reactions of the methyl-gamma-trinitro butyrate led to dimethyl-gamma-keto pimelate

$$(NO_2)_3CCH_2CH_2COOCH_3 \xrightarrow[H_2O_2]{2KOH} KNO_2 + O_2 + 2H_2O + (NO_2)_2C(K){-}CH_2CH_2COOCH_3 \xrightarrow{HCl}$$

$$(NO_2)_3CCH_2CH_2COOCH_3 \xrightarrow[H_2O]{2KOH} (NO_2)_2CCH_2CH_2COOCH_3(K) + KNO_2 + O_2 + 2H_2O$$

$$(NO_2)_2CCH_2CH_2COOCH_3(K) + CH_2{=}CHCOOCH_3 \rightarrow CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2COOCH_3 \xrightarrow{H^+}$$

$$CH_3OOCCH_2CH_2C(=O)CH_2CH_2COOCH_3$$

(2) *Addition to Vinyl Methyl Ketone*

$$CH(NO_2)_3 + H_2C{=}CHCOCH_3 \rightarrow (NO_2)_3CCH_2CH_2COCH_3$$

The gamma-trinitropropyl methyl ketone was comparable to hexagen in explosive power

(3) *Addition to Acetylene*

$$HC{\equiv}CH + CH(NO_2)_3 \xrightarrow{Hg(NO_3)_2} CH_2{=}CHC(NO_2)_3 \xrightarrow{CH(NO_2)_3}$$

$$(NO_2)_3CCH_2CH_2C(NO_2)_3 + CH_3CH\begin{matrix}C(NO_2)_3\\ \\ C(NO_2)_3\end{matrix}$$

(4) *Reaction with Carbonyl Compounds*

$$HCHO + HC(NO_2)_3 \rightarrow HOCH_2C(NO_2)_3$$

The reaction, which apparently takes place spontaneously, is reversed by alkali

With unsaturated aldehydes such as crotonaldehyde, addition to both the unsaturated carbon-carbon bond and the carbonyl group may occur The carbonyl group may then be regenerated by the action of weak alkalies:

$$CH_3CH{=}CHCHO + 2CH(NO_2)_3 \rightarrow CH_3CHCH_2{-}\overset{H}{\underset{OH}{C}}{-}C(NO_2)_3$$

$$(O_2N)_3C$$

$$\xrightarrow{OH^-}$$

$$CH_3CHCH_2CHO + CH(NO_2)_3$$

$$C(NO_2)_3$$

Vinyl Monomers

Vinyl Acetate. Vinyl acetate monomer served as the basis for the production of polyvinyl acetate, polyvinyl alcohol and the polyvinyl acetals The vinyl acetate plant at Hoechst, with a production capacity of 1,000 tons per month, was the largest in Germany A new unit of 1,000 tons per month capacity was under construction, and a small portion of the equipment had already been installed

The old Wacker process employing a mercury catalyst in liquid phase was discarded in favor of the new catalytic vapor-phase process A description of the process follows[26]

Acetylene was generated from calcium carbide in "wet" type units The resulting gas was purified by scrubbing with a sulfuric acid-sodium dichromate solution, chilled to remove water, passed over a mixture of potassium bichromate and sulfuric acid on kieselguhr placed in 2-inch layers on a tray-type unit for further purification, and finally dried by

[26] *PB* 52878 (*BIOS* 745), *PB* 80576 (*BIOS* 1291)

passing over sodium hydroxide It was essential to remove all traces of hydrogen sulfide and phosphine from the acetylene

Fresh acetylene plus recycled gas was blown through acetic acid maintained at approximately 60°C to yield vapor containing 23 weight per cent of acetic acid The vapors passed through a heat exchanger and then through a preheater where they were superheated to a temperature of 170°C prior to entering the catalytic unit The temperature in the converter varied. Initially, with fresh catalyst, operation was begun at 170°C. This temperature was increased gradually to a maximum of 210°C at the completion of the catalyst life cycle The converter exit gases were interchanged, passed through a separator to remove carbon dust, cooled initially with water to 40°C, then to 10°C with cold water, and finally to 0°C with brine The resulting gases in part were bled to waste to remove the inert gases, the balance being reheated and recycled to the system by a blower

The liquid product collected contained approximately 60 per cent of vinyl acetate and 40 per cent of acetic acid This mixture was distilled continuously in a series of three columns to yield: (a) a low-boiling overhead consisting essentially of acetaldehyde and acetone, (b) vinyl acetate monomer; and (c) acetic acid for recycling In these distillation operations, thiodiphenylamine was added as a stabilizer to prevent resin formation The pure vinyl acetate monomer could be stored without the addition of stabilizers. The yield of vinyl acetate was 92 to 95 per cent on acetylene and 97 to 99 per cent on acetic acid

The converters (Figure I-6) consisted of steel units filled with a number of 2-inch diameter water-cooled tubes arranged horizontally. The converter was box-shaped, roughly 6 ft wide, 10 ft high and 20 ft long Gases entered through a top header, flowed downward through the catalyst bed and entered a lower bottom header The linear velocity of the gas flowing through the catalyst bed, based on the free space in the catalyst mass, was 2 0 ft per second The electrically heated reactor shown in Figure I-7 had recently been replaced by a high-pressure steam-heated unit

The catalyst was contained between a series of approximately $\frac{1}{8}$-inch steel plates set vertically 1 inch apart Each converter contained about 490 cubic feet of catalyst consisting of 3 to 5-mm granules of activated carbon impregnated with zinc acetate solution so as to contain 100 parts of carbon and 15 parts of metallic zinc equivalent. No promoters were used. Calcium, mentioned in the literature, showed no advantages; traces of copper were particularly harmful since copper tends to form cuprene.

The "on stream time" of a converter was about 2 months, during which time 700 to 900 tons of vinyl acetate were produced at a monthly rate of 400 to 500 tons. At the end of this period, the catalyst was removed by blowing it out with a current of air and discarded. In order to provide

continuous operation, three converters were piped so that two units in parallel could be "on stream" at any one time.

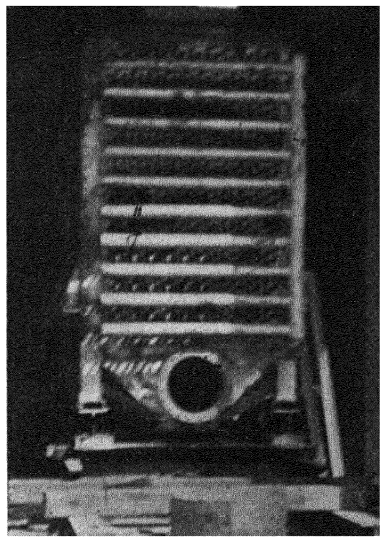


FIGURE I-6. Hochst vinyl acetate converter under construction.

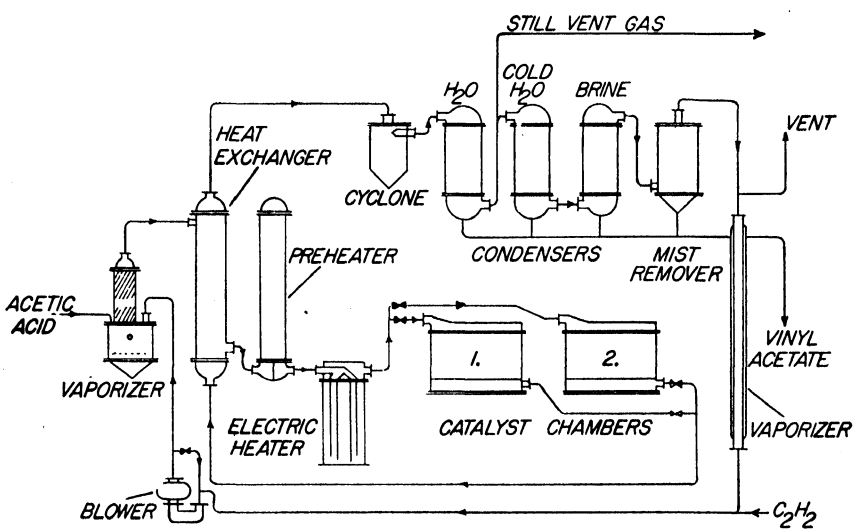


FIGURE I-7. Vinyl acetate flow scheme.

Vinyl Chloride. The Germans had several plants for producing vinyl chloride; except for minor differences in mechanical details, these were

based upon the same chemical reaction, namely, the addition of hydrogen chloride to acetylene:

$$HC{\equiv}CH + HCl \rightarrow H_2C{=}CHCl$$

The process employed in the Burghausen plant was the latest and will be described here

Preparation of Hydrogen Chloride Tetrachloroethane was catalytically decomposed at 250 to 300°C and atmospheric pressure using barium chloride as the catalyst:

$$CHCl_2{-}CHCl_2 \rightarrow CHCl{=}CCl_2 + HCl$$

Tetrachloroethane is vaporized and superheated to from 200 to 250°C The gas passes into a reactor consisting of vertical steel tubes 35 mm outside diameter and 6 meters long. The catalyst is embedded around the tubes, inside which flows high-pressure steam, so that at no point is it more than 2 cm from a tube. The total volume of catalyst is 4 cubic meters Hydrogen chloride coming from the reactor is scrubbed with trichloroethylene in a column 8 meters high and 1 meter in diameter filled with Raschig rings. The hydrogen chloride is cooled to −10°C in a brine cooler to remove traces of trichloroethylene

The catalyst is prepared by absorbing 30 to 40 per cent of barium chloride and 0 5 to 1 0 per cent of mercuric chloride on 3-mm active carbon particles Catalyst life is nearly 4,000 hours, but toward the end of this time the temperature must be raised to 300°C

Acetylene Purification. The acetylene must be pure and dry Impurities are removed by washing with chlorine water Absolute dryness is obtained by scrubbing with trichloroethylene containing 5 to 10 per cent of 2-methyl pentanediol-2,4 The scrubber is an iron tower 7 meters high with a volume of 8 cubic meters and is filled with porcelain Raschig rings. The gas passes upward through the tower at a rate of 600 cubic meters per hour against a downward flow of 6,000 liters of trichloroethylene per hour

Preparation of the Vinyl Chloride Monomer Acetylene and hydrochloric acid are combined by passing the mixture over activated carbon impregnated with barium chloride, and containing a trace of mercuric chloride. The final monomer is stored in steel tanks under pressure without added inhibitors.

The reactors (Figure I-8) are steel shells 4 5 meters long by 1.3 meters in diameter, containing a number of 6-meter iron tubes 3 cm in diameter The reactors hold 4 cubic meters of catalyst containing 30 to 40 per cent of barium chloride, 0.5 to 1 per cent of mercuric chloride and the balance activated carbon. The catalyst is packed around the tubes which carry cooling water.

Four hundred cubic meters of mixed gases, including not less than 40 per cent nor more than 50 per cent of nitrogen, is circulated per hour; 80 cubic meters of acetylene are added and 80 cubic meters of vinyl chloride are produced hourly. (Nitrogen is used to create a pressure of 10 to 15 cm of water throughout the equipment to prevent leakage of air into the

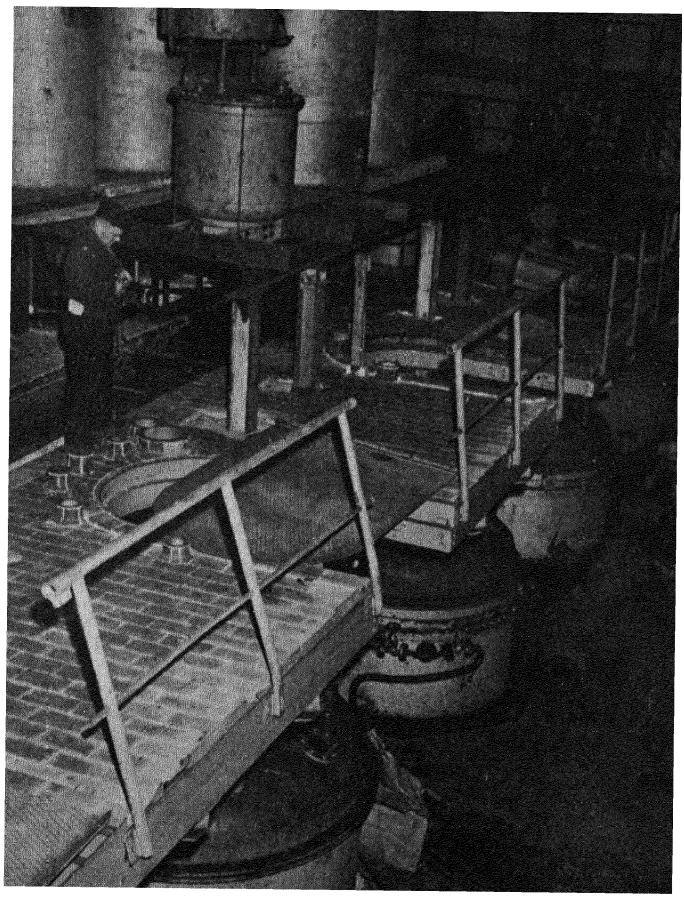


FIGURE I-8. Vinyl chloride monomer reactors in Burghausen plant.

system.) The gases enter the top and bottom of the reactors and leave at the middle. The quantity of each gas is accurately controlled by rotameters.

Water is required to cool the reactor and tubes, since the reaction is exothermic, yielding 36 to 40 kg cal per mole. With fresh catalyst the

operating temperature, controlled by water-cooling, is 120°C, with old catalyst the temperature is raised to 180°C

The gases leaving the reactors pass through a cooler, where their temperature is reduced to 10°C, and then through a scrubber filled with Raschig rings, where the vinyl chloride is washed out with trichloroethylene. A temperature of −10°C is maintained, and the resulting trichloroethylene solution contains 10 per cent of vinyl chloride This solution is pumped to a pressure column where the vinyl chloride is separated at 3 atm gauge pressure, 90 per cent pure vinyl chloride is removed The vinyl chloride is washed with a 15 per cent sodium hydroxide solution Final drying is accomplished by passing the monomer through towers containing calcium chloride. These towers are reloaded once a week

For each ton of vinyl chloride monomer, 418 cubic meters of acetylene, 600 cubic meters of hydrogen chloride, 4 kg of activated charcoal, 2 kg of barium chloride, 0 06 kg of mercuric chloride, 1.6 kg of calcium chloride, 30 kg of caustic soda as a 15 per cent solution, and 5 kg of trichloroethylene are required

Acrylonitrile[27]. In addition to the older process for preparing acrylonitrile by the dehydration of ethylene cyanohydrin, the direct addition of hydrogen cyanide to acetylene had been carried out in several small plants The largest plant employing the direct process was at Leverkusen, it had a capacity of approximately 120 kg per hour Although the equation.

$$HC{\equiv}CH + HCN \xrightarrow[HCl]{Cu_2Cl_2} H_2C{=}CHCN$$

would appear to represent a very simple synthesis, small percentages of impurities such as vinyl acetylene, divinyl acetylene, chlorobutadiene, cyanobutadiene, lactonitrile, and catalyst tars are formed, these introduce troublesome difficulties in operation and purification of the acrylonitrile produced Although acrylonitrile of better than 99 per cent purity can be obtained fairly readily, the material is not of sufficiently high purity for polymerization due to its divinylacetylene content, and the problem of further refining to polymer requirements is still under study

Process. The process is normally carried out by passing a 10/1 mixture of acetylene and hydrogen cyanide up through a vertical brick- or rubber-lined reactor 1 68 m in diameter and 7 5 m high, containing a solution of cuprous chloride, ammonium chloride and hydrogen chloride Acrylonitrile is removed from the product gas as a 1 5 to 2.0 per cent solution by extraction with water in an absorption column. The acetylene leaving the absorber carries with it appreciable percentages of vinyl acetylene, divinyl acetylene, etc. and presumably their presence in the recycle gas causes the formation of tar in the reactor with a subsequent decrease in catalyst life.

[27] *PB* 65681 (*FIAT* 1025)

The 1 5 to 2 0 per cent solution of acrylonitrile in water is distilled in a stripping column and subsequently redistilled in a second column at 140 mm pressure to give the so-called pure acrylonitrile of 99 per cent or better purity.

Catalyst The catalyst charge to the reactor is as follows

Cu_2Cl_2	7235 kg
H_2O	6225 kg
NH_4Cl	3911 kg
37% HCl	229 kg

Initially this catalyst solution produces 15 g of acrylonitrile per liter per hour, but after about 3 weeks' operation when it is discharged to recovery, this falls to about 9 g per liter per hour Hydrochloric acid continuously disappears from the catalyst and is replaced by the addition of 60 to 90 liters of 37 per cent hydrochloric acid per day to maintain a pH of 1 0

Chapter II

Vinylation

Vinyl Ethers

Shortly before 1930, at the close of his work on the development of the technical processes for the preparation of butadiene by the four-stage process via acetaldehyde, aldol, and 1,3-butylene glycol, Reppe and his group turned their efforts to new syntheses based on acetylene Syntheses for vinyl chloride, vinyl acetate, acrylonitrile, and acrylic esters from acetylene, or products derived therefrom, were known However, at the time, no suitable methods for preparing vinyl ethers were in existence, but it was believed that they should be included in the above list because polymers of this class of compounds should have unusual properties, and should not undergo hydrolysis The literature indicated only the following possibilities for the synthesis of vinyl ethers

(1) From chloroacetal and sodium at 130 to 140°C[1]

(2) From bromoacetal and magnesium powder at 100 to 110°C[2]

(3) From beta-iodoethyl ethyl ether and sodium methylate[3]

(4) By the reaction of acetylene with sulfuric acid under pressure at 0°C or lower, preferably in the presence of mercuric salts, followed by treating the vinyl sulfuric acid with alcohol[4]

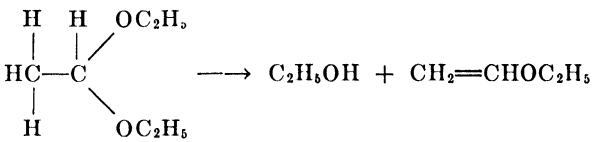
(5) From acetals by heating with phosphorus pentoxide in the presence of quinoline[5]

(6) By catalytic removal of alcohol from acetals[6]

Methods (1), (2), and (3) were not suitable for the preparation of large quantities of vinyl ethers because of low yields and the nature of the reactants Reaction (4) appeared questionable because the vinyl ethers are extremely sensitive to acids and undergo immediate resinification with sulfuric acid Attempts to check this patent yielded no trace of vinyl ether Reaction (5) did not appear promising. The yields from method (6), using nickel catalysts or fragments of clay, were small because primary and secondary by-products such as acetaldehyde, crotonaldehyde, carbon monoxide, methane, etc , were produced.

[1] *Ann* , **192,** 106 (1878)
[2] *Compt rend* , **140,** 795 (1905)
[3] *Bull soc chim* (2) **44,** 458 (1885).
[4] *D R Pat 338,281*
[5] *Ber.*, **31,** 1021 (1898).
[6] *Monatsh* , **51,** 234 (1929)

However, by the use of noble-metal catalysts, Reppe found that the preparation of vinyl ethers from the corresponding acetals can be made to go in about 90 per cent yields with a 60 to 65 per cent conversion per pass according to the reaction scheme[7]:



After many unsuccessful attempts to find a more feasible method than the above for preparing vinyl ethers, the surprising discovery was made, in contrast to all information in the literature, that vinyl halides react easily with alcoholates to produce the corresponding vinyl ethers in yields of 90 per cent[8]. The reaction may be carried out with excess alcohol as a solvent in the presence of alkali hydroxides at 80 to 100°C in an autoclave The usual procedure is to dissolve either the alkali metal or the alkali hydroxide in the alcohol, then to add the vinyl halide, and heat the reaction mixture to 80 to 100°C The reaction is complete when no further pressure drop occurs The salt is filtered off and the vinyl ether isolated by fractional distillation

The reaction of a vinyl halide with the alkali metal salt of a hydroxy compound is fairly general in scope, mono- and polyfunctional aliphatic alcohols, hydroaromatic and aromatic alcohols as well as mono- and polyfunctional phenols and napthols can be converted into the corresponding vinyl ethers. The reaction is somewhat more sluggish with aromatic compounds than with aliphatic, and the yields are usually poorer. Instead of vinyl halides, the more readily available alkylene dihalides or alkylidene dihalides may be used if sufficient alkali is present[9].

Reppe, as was apparently his habit, dramatized the events concerning the running of the first reaction of a vinyl halide with a sodium alcoholate in the following words:

"I charged a fairly large autoclave with several liters of absolute alcohol, dissolved in it a substantial amount of sodium metal and forced into the vessel under pressure vinyl chloride corresponding to the quantity of sodium The temperature in the autoclave rose quickly from 80 to 110°C without a remarkable increase in pressure. The final pressure of 5 atmospheres was due primarily to the partial pressure of the alcohol at the reaction temperature However, according to the ideas prevailing at this time, vinyl chloride and sodium alcoholate were supposed to form free acetylene, which in the sealed autoclave would be under pressure at ele-

[7] *D R Pat 525,836, U S Pat 1,931,858*
[8] *D R Pat 550,403, U S Pat 1,941,108*
[9] *D R Pat 513,679, 525,188, U S Pat 1,941,108*

vated temperatures In any case, an explosion was expected to occur and disastrous consequences were anticipated according to all that was known about acetylene explosions Nothing of that sort happened, however After cooling down, the autoclave was opened and found to contain only minor quantities of acetylene in addition to the alcoholic solution of vinyl ether and equivalent quantities of salt "

During this work on the reactions of vinyl halides with alcoholates, a very significant observation was made, namely, that the small quantity of acetylene which was formed as a by-product decreased when the reaction mixture was maintained at reaction temperature, or higher, for a long time after the primary reaction was presumably complete This observation naturally suggested the possibility that the alcohol, under the catalytic influence of sodium alcoholates, had added to the acetylene to produce a vinyl ether This concept, as will be seen later, was of fundamental importance in the development of a technically feasible method of synthesizing vinyl ethers, but more significantly, it led to an entirely new chemistry of acetylene, the outstanding feature of which is the use of acetylene under pressure

Experiments to prove the validity of the concept of the addition of alcohols to acetylene under pressure in the presence of alcoholates were immediately carried out. Reppe again dramatizes the conditions attending the first run as follows:

"I decided to carry out the reaction in a 5-liter autoclave fitted with a stirrer (at this time, I did not have the small, safe experimental devices which are in use today). The autoclave was charged with 2 liters of absolute alcohol containing 5 per cent of caustic potash in solution, and closed. The air was displaced by nitrogen, then 5 atmospheres of nitrogen were pressed into the vessel and then 10 atmospheres of acetylene from a steel cylinder, the total pressure amounting to 15 atmopsheres The stirrer was started and the temperature raised slowly. Nothing unusual happened—although a terrific explosion was likely to happen any second—and we continued heating. Nothing happened at 80°, nor at 100° except the normal pressure rise due to the higher vapor pressure of the alcohol at the higher temperature. The temperature was further increased to 120, 130, 140 and finally to 170°C, the pressure increasing to 30 atmospheres at the highest temperature. Our tension in the meantime had reached its peak. There was a likely chance that our experiments would miscarry, and on the basis of the existing knowledge of the behavior of acetylene under pressure at elevated temperatures, a violent explosion could be expected with certainty. But nothing of that sort happened. At 180°C, the pressure no longer rose but actually dropped, proving that the desired reaction had actually taken place. When the pressure at 180°C had dropped to 8–10 atmospheres, we pressed in more acetylene to bring the

pressure back to 20 atmospheres. Again, there was a rapid pressure drop to 10 atmospheres, and we continued the addition of acetylene until no more gas was absorbed. A rough calculation indicated that one mole of acetylene per mole of alcohol had been absorbed. After cooling, the autoclave was opened and the contents worked up to give a quantitative yield of ethyl vinyl ether."

Following this initial success, the addition of a wide variety of alcohols to acetylene was investigated. Later, it was shown that other hydroxy compounds such as phenols and carboxylic acids, and their sulfur analogs, and even amines, imines, and amides containing a hydrogen atom on the nitrogen atom would add to acetylene under pressure in the presence of an alkaline catalyst to yield the corresponding vinyl compounds The general process of adding such molecules to acetylene is now commonly referred to as "vinylation," which may be formulated as·

$$HC{\equiv}CH + -QH \rightarrow -QCH{=}CH_2$$

where Q may be oxygen, sulfur or nitrogen It should be noted that the "vinylation reaction" is an addition reaction involving the triple bond of acetylene, and that the resulting products are vinyl compounds containing a double bond instead of the triple bond originally present in the acetylene.

At the present time, the following generalizations concerning the "vinylation" of alcohols and phenols can be stated.

Temperatures. In general, a temperature of 150 to 160°C is favorable Methanol, however, will react readily at 120°C.

Pressures. With hydroxyl compounds boiling lower than the preferred vinylation temperature of 150 to 160°C, the vinylation reaction must be carried out under pressure. With low-boiling alcohols in liquid-phase vinylation, the total pressure in the system is largely dependent on the vapor pressure of the alcohol, and vinylations of methanol have been carried out at 30 atm pressure However, the vinylation of alcohols such as butanol may be performed without pressure if a quantity of alkali sufficient to raise the boiling point to the vinylation temperature is dissolved in the alcohol[10] This procedure is of no commercial significance, because the consumption of alkali is substantial due to side reactions between acetylene and alkali, and between alcohol and alkali. Another procedure by which the operating pressure can be reduced is to use high-boiling diluents[11]. Obviously, pressure is not required for the higher-boiling alcohols, such as glycols, octadecyl or montanic alcohol, etc

Catalysts. A solution of 0 5 to 1.0 per cent of sodium or potassium metal in the alcohol is sufficient. The same effect can be obtained more easily by the addition of 1 to 2 per cent of alkali hydroxide. Salts exhibiting a pronounced alkaline reaction, such as sodium or potassium cyanide, may be

[10] *U S Pat 2,021,869*

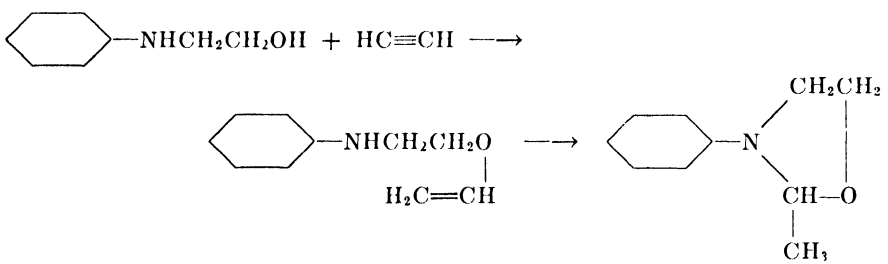
[11] *D R Pat , 726,547.*

used[12]. In special cases, such as in the vinylation of hydroxy carboxylic acid esters, esters of polyhydric alcohols (*e g*, mono and diacetin), chlorinated phenols, etc, it has been found advantageous to use zinc and cadmium salts of organic acids (zinc acetate, zinc naphthenate, etc)[13].

Alcohols. Addition of alcohols to acetylene takes place readily with primary and secondary alcohols of the aliphatic series up to montanic alcohol Tertiary alcohols react more slowly Polyfunctional alcohols such as glycol, glycerin, 1,3-and 1,4-butyleneglycol, sorbitol and partially etherified or acetalized carbohydrates having a free hydroxyl group, etc, may be vinylated to give partially or completely vinylated products In some cases, the polyfunctional alcohols may give the cyclic acetals rather than the vinyl ether Cyclohexanol, substituted cyclohexanols, decalols, terpene alcohols, hydroabietanol, etc, also yield vinyl ethers Heterocyclic hydroxyl-containing compounds, such as hydroxyfuran, etc, may be vinylated.

Vinylation of the hydroxyl group fails in certain cases where the hydroxyl group is of the allyl alcohol type Thus, allyl alcohol, crotoyl alcohol and 2-butene-1,4-diol cannot be successfully vinylated However, if the double bond is more remote, for example as in oleyl alcohol, vinylation takes place normally

Alkanolamines. Aliphatic and aromatic hydroxyalkylamines such as mono-, di- and triethanolamine, beta-hydroxyethylaniline, etc, can be readily vinylated using potassium hydroxide as the catalyst If the vinylation of a secondary alkanolamine such as beta-hydroxyethylaniline is carried out in the presence of zinc or cadmium acetate catalysts, the vinyl ether initially produced undergoes cyclization to the corresponding oxazolidine:



Phenols. Phenols in general react less readily than alcohols, however, the vinyl ethers of phenols, substituted phenols and naphthols can usually be prepared in satisfactory yields provided no group which is sensitive to alkali is present. The difference in reactivity between phenols and alcohols is attributed by Reppe to the greater acidity of the phenol, resulting

[12] *D.R Pat 584,840.*

[13] *U S Pat 2,157,348; Brit. Pat 481,389.*

in a stronger binding of the oxygen to the alkali metal, thus hindering the penetration of acetylene between oxygen and alkali metal As confirmation of this theory, he claims that a much smoother vinylation of phenols occurs if the more basic potassium is used instead of sodium. It is also claimed that hydroxyl groups of exceptionally pronounced acid character such as in alizarin cannot be successfully vinylated

Vapor Phase Vinylation. The vinylation of alcohols and phenols is usually done in liquid phase. However, in some instances it can be successfully carried out in the vapor phase by contacting the vapors of the alcohol and acetylene at 150 to 350°C with strongly basic compounds such as soda lime, sodium zincate, or an alkali hydroxide on carbon[14] The vinyl ethers are obtained in good yield, but apparently this process has never attained any technical importance, primarily because catalyst life is limited and difficulty is experienced in removing the heat of reaction

By-Products. The vinylation of an alcohol is generally a clean-cut reaction However, several side reactions may occur to a limited extent. Acetals corresponding to the alcohol used may be formed, particularly in the vinylation of polyfunctional alcohols containing hydroxyls situated 1,2 or 1,3 to each other so that cyclic dioxolanes, or 1,3-dioxanes can result A side reaction of greater importance is the gradual conversion of the alkali alcoholate to the alkali salt of the corresponding acid and hydrogen, for example, it is known that potassium butylate is converted to potassium butyrate and hydrogen at 185°C The control of this reaction is important in commercial manufacture of vinyl ethers because: (1) as the catalyst is consumed, the rate of reaction slows down, (2) the hydrogen concentration in the recycle gas gradually builds up and must be reduced or removed by venting it, together with some acetylene, from the system.

General Procedure for Production of Vinyl Ethers

Vinylation at Atmospheric Pressure. Alcohols boiling above the vinylation temperature of 160 to 180°C can be vinylated very simply in a reaction tower 1.2 meters in diameter and about 10 meters long, packed with Raschig rings The tower is filled with the appropriate alcohol containing 1 to 5 per cent of catalyst (preferably potassium hydroxide) and heated to reaction temperature. The air is displaced by nitrogen and the nitrogen in turn by acetylene, which is continuously recycled up through the liquid, the quantity of acetylene recycled by a circulating pump should be at least twice the quantity consumed in the reaction. Vinylation takes place rapidly The heat of reaction is approximately 30 kg cal per mole of vinyl ether and must be removed by cooling coils. The acetylene absorbed is replaced automatically from a gasometer A small amount of waste gas is continuously vented from the recycle gas to prevent build-up of inerts

[14] *D. R. Pat. 639,843, U. S. Pat. 2,066,076.*

and lowering of the acetylene concentration Measured quantities of alcohol containing about 1 per cent of dissolved catalyst are fed continuously to the top of the tower, an equivalent quantity of the vinylated mixture is withdrawn from the base of the tower by a siphon The vinyl ether is then isolated by distillation, preferably under reduced pressure The yield is practically quantitative

Vinylation under Pressure[15]. Vinylation of the lower alcohols from methyl through butyl must be carried out under pressure because of the low boiling point of the alcohols and the still lower boiling points of their vinyl ethers It may be carried out batchwise in an autoclave, but is preferably done by a continuous process The operating procedure in

Table II-1

Operating Data	Vinyl Methyl Ether	Vinyl Ethyl Ether	Vinyl Isobutyl Ether
Production of vinyl ether (kg/hr)	500	500	500
% KOH by weight in catalyst soln	20	15	12
Temperature of reaction (°C)	160–165	155–160	150–155
Pressure (atm)	20–22	18–20	4–5
% Acetylene by volume in gas cycle before tower inlet (remainder nitrogen)	55	60	90
Recycled gas (m^3/hr) (N T P)	870	640	220
Combined acetylene (m^3/hr) at 95% yield	215	173	124
% Acetylene in recycle gas	15	45	63
Alcohol feed (kg/hr)	700	800	900
KOH feed (kg/hr)	25	20	15
Acetylene feed (m^3/hr)	230	194	140

vinylating the lower alcohols is summarized in Table II-1, which gives the most important figures for continuous production of vinyl ethers in a tower 10 meters high and 1 2 meters in diameter, producing about 300 tons per month A schematic drawing of such a plant is shown in Figure II-1

In principle, vinylation under pressure is similar to atmospheric pressure vinylation. The empty tower which contains no packing is filled with nitrogen under pressure A catalyst solution somewhat more dilute than the desired concentration is introduced and heated to reaction temperature Circulation of nitrogen is started and the excess alcohol is distilled off This procedure removes water and favors the formation of the potassium alcoholate:

$$ROH + KOH \rightleftharpoons ROK + H_2O$$

[15] *PB* 79606 (*FIAT* 1080).

When the required catalyst concentration is reached, acetylene is introduced until the desired acetylene-nitrogen ratio is attained—acetylene, nitrogen and some hydrogen being vented Acetylene, alcohol and catalyst solution are now added at the rates shown in the table The vinylation takes place rapidly, the heat of reaction is removed by vaporization of the vinyl ether and some alcohol. The gas stream passes to a dephlegmator which condenses some of the alcohol and returns it to the tower. The gases are then condensed The condensate passes to a pressure degasser to remove the dissolved acetylene, which is appreciably soluble in the vinyl ether. The

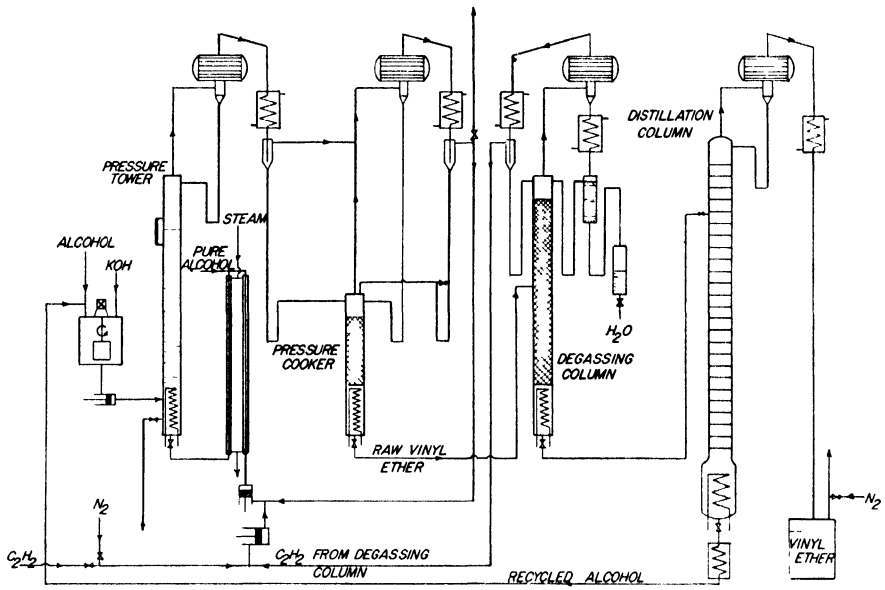


FIGURE II-1 Preparation of vinyl ether

ether is then distilled, usually 6 to 8 per cent of the alcohol is carried along as an azeotrope This crude ether is suitable for some purposes, such as in the preparation of acetaldehyde For polymerization, however, the ether must be further purified by washing with water to remove the alcohol, followed by drying and distillation, preferably over an alkali or alkali metal[16].

Some impurities, principally the alkali salt of the carboxylic acid derived from the alcohol, are formed during the reaction, so a purge amounting to perhaps 20 per cent of the volume of the ether/alcohol distilled is taken, from which the alcohol is recovered by distillation The recycle gas is also vented periodically to prevent build-up of impurities, particularly hydrogen.

About 30 to 60 per cent of the acetylene is consumed per pass, while 5

[16] *Ind Eng. Chem.*, **39**, 180 (1947)

to 10 per cent is lost in the off gas. The yield of vinyl ether is 90 to 95 per cent, based on the acetylene fed.

Reactions of Vinyl Ethers*

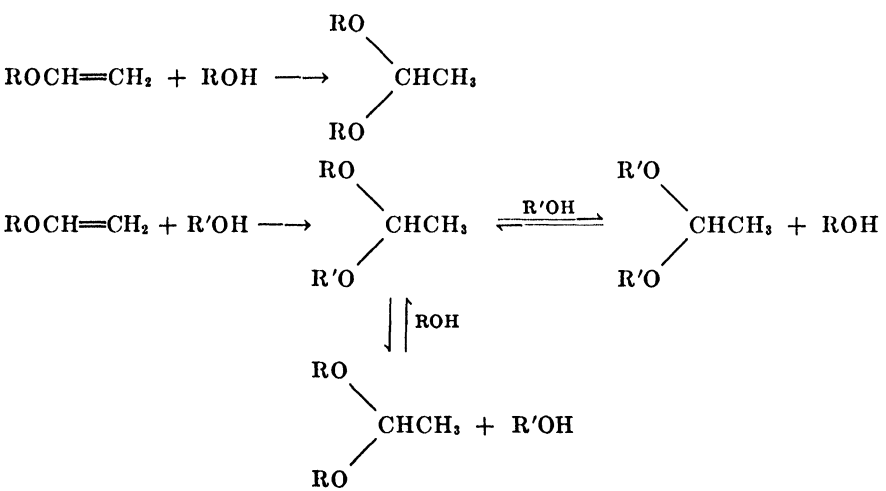
The vinyl ethers are unusually reactive vinyl compounds, as is shown by the ease with which they undergo: (a) numerous addition reactions involving the double bond; (b) hydrolysis with aqueous acids; and (c) polymerization with acidic catalysts.

Additions to the Double Bond. (1) *Addition of Hydrogen.* The vinyl ethers are easily reduced to the corresponding alkyl ethyl ether by hydrogen at room temperature in the presence of hydrogenation catalysts such as Raney's nickel.

$$ROCH{=}CH_2 + H_2 \rightarrow ROCH_2CH_3$$

Reppe claims that vinylation followed by reduction is a useful method of ethylating compounds which cannot be ethylated with ethyl halides or diethyl sulfate.

(2) *Addition of Alcohols.* Vinyl ethers react readily with alcohols and phenols, in many cases by simply heating, to yield acetals[17]. Anhydrous acidic catalysts such as hydrogen chloride, boron fluoride, etc., catalyze the addition. The acetals produced may be symmetrical or unsymmetrical depending on the alcohol used:



If an excess of an alcohol differing from the alcohol vinylated is used, the reaction mixture consists of a mixture of the unsymmetrical acetal and the

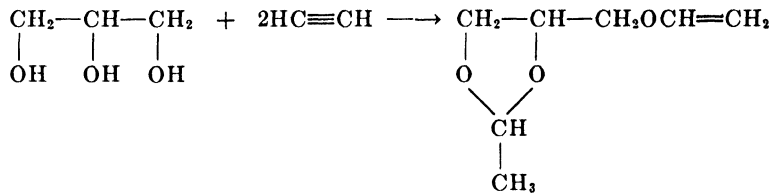
* Recently two American companies, Carbide and Carbon Chemicals Corp. and General Aniline and Film Corp., have announced the commercial availability of several of the lower aliphatic vinyl ethers.

[17] *D. R. Pat. 566,033; U. S. Pat. 2,000,252.*

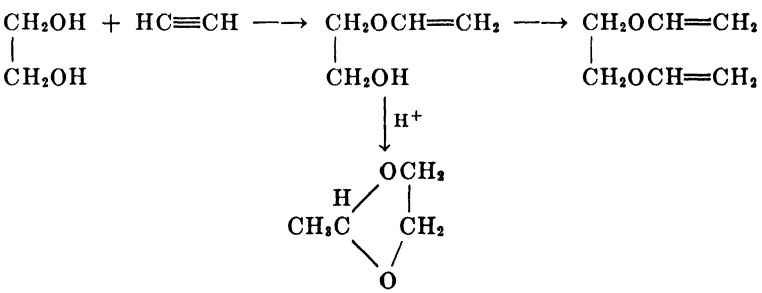
two symmetrical acetals. Where ROH is lower-boiling than R'OH, it is possible to shift the equilibrium by distilling out the more volatile alcohol, producing only the symmetrical acetal in which the alkyl group originally present in the vinyl ether has been displaced.

In general, the addition of an alcohol to a vinyl ether gives excellent yields of the desired acetal and is much superior to the classical methods involving acetaldehyde reactions.

The ease with which alcohols and phenols add to vinyl ethers is, of course, the reason why acetals are obtained as by-products in the synthesis of vinyl ethers. This is particularly true in the vinylation of 1,2 or 1,3-dihydroxy compounds where the formation of 5- and 6-membered rings is possible. Thus the vinylation of glycerin may take place as follows:



Likewise, while it is possible to prepare both the mono- and divinyl ethers of ethylene glycol, the main product of the vinylation if the temperature is too high, or if local acidity develops, may be almost exclusively methyl dioxolane. Furthermore, the monovinyl ether of ethylene glycol will rearrange with almost explosive violence in the presence of acidic catalysts to yield methyl dioxolane[18]:



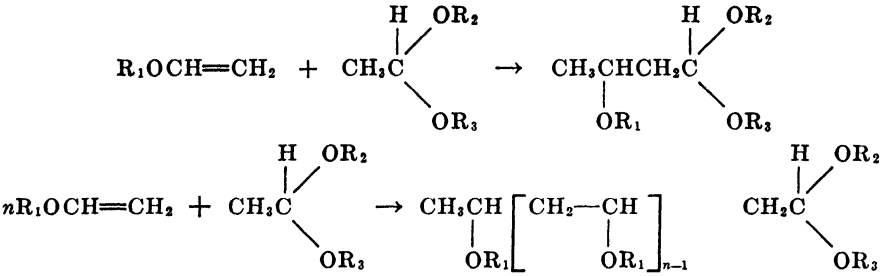
Hydroxypropylvinyl ether likewise rearranges to the 1,3-dioxane[19].

Polyvinyl alcohol, suspended in chloroform, reacts with the lower alkyl vinyl ethers in the presence of hydrogen chloride to form acetals which dissolve in chlorinated hydrocarbons[20].

(3) *Addition of Acetals.* Mueller-Cunradi claims that acetals in the

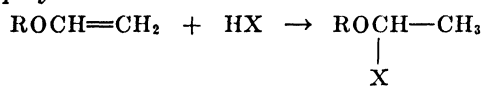
[18] *J. Am. Chem. Soc.*, **50**, 2716 (1928).
[19] *J. Am. Chem. Soc.*, **50**, 2725 (1928).
[20] *U. S. Pat. 2,061,946.*

presence of boron fluoride etherates react with one or more molecules of vinyl ether as follows[21]:



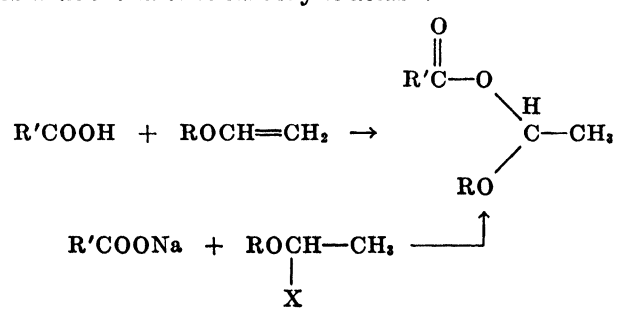
A similar reaction is reported to take place with acylals (ether esters).

(4) *Addition of Hydrogen Halides.* Hydrogen halides may be added to vinyl ethers at low temperatures, preferably in the presence of a diluent, without causing polymerization:



Alpha-halo ethers, particularly alpha-chloroethers, may be prepared in good yields by this reaction. Thus, *n*-butyl alpha-chloroethyl ether boiling at 38°C/14 mm results when vinyl *n*-butyl ether is saturated with dry hydrogen chloride at 0°C[22].

(5) *Addition of Carboxylic Acids.* Similarly, carboxylic acids may be added to vinyl ethers without causing polymerization[22]. The addition of low molecular-weight carboxylic acids may be carried out by mixing equivalent quantities of the acid and vinyl ether and heating. Traces of mineral acids may be used as catalysts and permit the addition without heating The higher carboxylic acids require higher temperatures and longer reaction times. This reaction of vinyl ethers is apparently of general scope and in general gives excellent yields. The products are ether esters or acylals, and are identical with those prepared by the reaction of alpha-chloroethers with the salts of carboxylic acids[23].



[21] *U. S. Pat. 2,165,962.*
[22] *D. R. Pat. 566,033.*
[23] *J. Am. Chem. Soc.*, **63**, 2201 (1941).

(6) *Addition of Hydrogen Cyanide.* More recently, Reppe has claimed the addition of hydrogen cyanide to vinyl ethers to produce alpha-alkoxypropionitriles[24].

$$ROCH{=}CH_2 + HCN \rightarrow CH_3CH(OR){-}CN$$

This reaction is considerably more difficult than the addition of a carboxylic acid and is usually carried out at 100–150°C under pressure. Alkaline compounds, particularly pyridine, are claimed to facilitate the reaction.

(7) *Addition of Halogens* The addition of halogens to vinyl ethers takes place with extreme ease, and in some cases may be explosive. Wislicenus prepared both alpha-beta-dibromo- and alpha-beta-dichloroethyl ether by halogenating vinyl ethyl ether at low temperatures in a diluent such as carbon disulfide or chloroform[25]. The alpha-beta dibromoethers from a number of alkyl vinyl ethers have been prepared and characterized by Shostakovskii and coworkers by bromination in carbon tetrachloride or chloroform at 0°C[26].

Wislicenus also observed that iodine not only added to the double bond of ethyl vinyl ether, but also caused polymerization, yielding a non-volatile product containing iodine. Chalmers reported a similar result with *n*-butyl vinyl ether[27].

Recently Cass has claimed that the halogenation of an alkyl vinyl ether in the presence of an alcohol at low temperatures (−78° to 0°C) yields about 50 per cent of the corresponding haloacetal[28]:

$$ROCH{=}CH_2 + ROH + X_2 \rightarrow \begin{matrix} RO \\ \diagdown \\ \quad CHCH_2X \\ \diagup \\ RO \end{matrix} + HX$$

(8) *Addition of Hydrogen Sulfide.* Reppe states that the addition of hydrogen sulfide to vinyl ethers produces ethers of thiodiglycol:

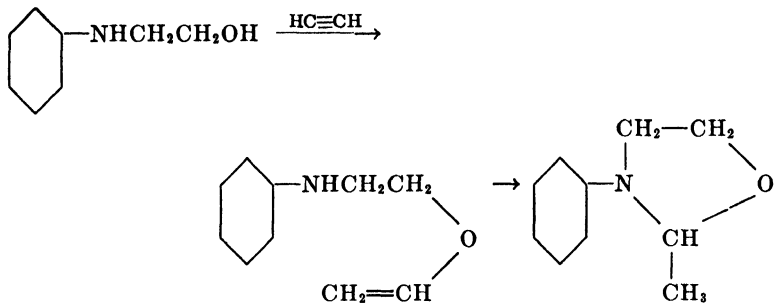
$$2ROCH{=}CH_2 + H_2S \rightarrow ROCH_2CH_2SCH_2CH_2OR$$

No details are available.

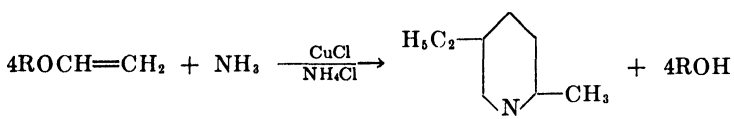
(9) *Reaction with Ammonia and Amines.* Reppe claims that in some cases the double bond of a vinyl ether may react with an amine. For example, in the vinylation of N-beta-hydroxyethyl aniline, 1-phenyl-2-methyl oxazolidine was obtained, as well as the expected vinyl ether.

[24] *Fr. Pat. 892,870; PB* 652.
[25] *Ann.*, **92**, 106 (1878).
[26] *J. Gen. Chem. (U. S. S. R.)*, **13**, 1-20 (1943); **14**, 102-112 (1944).
[27] *Can. J. Research*, **7**, 472-80 (1932).
[28] *U. S Pat. 2,433,890.*

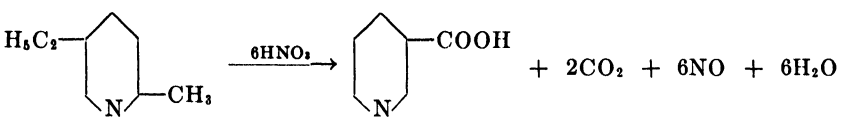
Presumably the vinyl ether is first formed and then reacts further with the secondary amino group to give the oxazolidine:



The reaction of ammonia with alkyl vinyl ethers in the presence of cuprous chloride-ammonium chloride catalysts gave excellent yields of 2-methyl-5-ethyl pyridine[29].



This reaction was apparently carried out at about 220°C and 200 to 225 atm pressure. It is claimed that the reaction product consists essentially of 2-methyl-5-ethyl pyridine and contains smaller percentages of other alkyl pyridines than are normally present in the so-called "aldehyde collidines" prepared from acetaldehyde and ammonia. The 2-methyl-5-ethyl pyridine was a starting material for the synthesis of nicotinic acid amide, since oxidation with 20 per cent nitric acid under pressure at 180°C gave nicotinic acid:

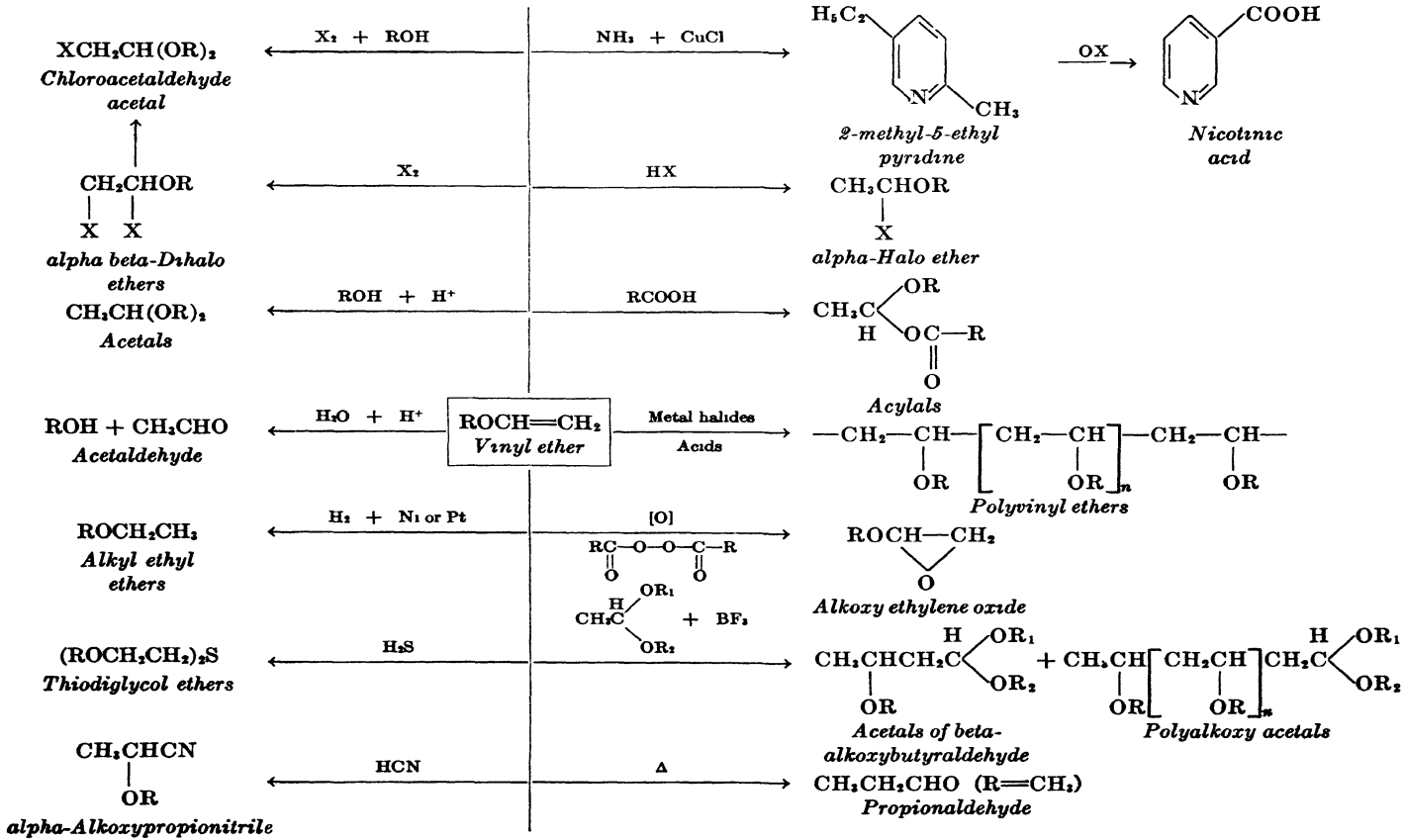


It is claimed that a 20 per cent solution of iron, aluminum, zinc or copper nitrate may be used instead of nitric acid.

(10) *Pyrolysis and Rearrangement.* The pyrolysis of ethyl vinyl ether at 377 to 448°C is reported to yield as primary products acetaldehyde and ethylene[30]. Butadiene has been obtained as one of the products of the pyrolysis of ethyl vinyl ether[31]. Methyl vinyl ether at 400°C undergoes rearrangement to propionaldehyde[32].

[29] *Fr. Pat. 893,375; PB* 602; *PB* 85173 (*FIAT* 1314).
[30] *Can. J. Research*, **21B**, 97–110 (1943)
[31] *Chem. Revs.*, **36**, 114 (1945); *J. Russ Phys. Chem. Soc.*, **47**, 1487 (1915).
[32] *U. S. Pat. 2,294,402*

Vinyl Ether Reactions



$$CH_3OCH{=}CH_2 \xrightarrow{\Delta} CH_3CH_2CHO$$

(11) *Reaction with Peracids.* The reaction of benzo-peracid with ethyl vinyl ether is reported to give the ether oxide[33]:

$$C_2H_5OCH{=}CH_2 + [O] \rightarrow C_2H_5OCH\text{—}CH_2 \quad (O \text{ bridges the two carbons})$$

Hydrolysis: Synthesis of Acetaldehyde. The vinyl ethers resemble acetals rather than ethers in their ease of hydrolysis in aqueous acids, and in their stability to aqueous alkali. They are rapidly hydrolyzed in the presence of aqueous acids at room temperature, yielding acetaldehyde and the corresponding alcohol. Presumably, the first step in the reaction is the addition of water, forming the hemi-acetal which then decomposes:

$$ROCH{=}CH_2 + H_2O \xrightarrow{H^+} RO\text{—}CHCH_3\text{—}HO \rightleftharpoons ROH + CH_3CHO$$

Under certain conditions the hydrolysis may be used as a method of determining the purity of vinyl ether samples[34].

The synthesis of acetaldehyde by the hydrolysis of vinyl ethers was apparently of some interest to the Germans, and by the end of 1937, a new process for producing acetaldehyde had been worked out by Reppe.[35] This process involved the reaction of acetylene with methanol in the presence of sodium alkoxides to form methyl vinyl ether, which was then hydrolyzed to acetaldehyde and methanol. The overall steps involved are:

$$CH_3OH + HC{\equiv}CH \xrightarrow{OH^-} CH_3OCH{=}CH_2$$

$$CH_3OH + CH_3CHO \xleftarrow{H_2O,\ H^+} \text{(from above)}$$

This reaction scheme is a way of hydrating acetylene without the use of mercuric sulfate catalysts.

Reppe claimed great advantages for this new process as compared to the usual hydration procedures using mercury catalysts,* both as regards operating efficiency and purity of product. The vinylation reaction can be carried out with relatively impure acetylene since the potassium hydroxide, unlike mercuric sulfate, is not poisoned by phosphine, hydrogen sulfide,

[33] *Ber.*, **54**, 2153.
[34] *Anal. Chem.*, **19**, 1025 (1947).
[35] *PB* 40121 (*BIOS* 370); *PB* 79606 (*FIAT* 1080).
* See page 6 for a description of this process.

etc. Danger of mercury poisoning as well as the loss of approximately one kilogram of mercury per ton of acetaldehyde produced is avoided. In addition, it is claimed that the acetaldehyde so produced is purer; blemishes and decomposition spots in sheets or films of cellulose acetate due to traces of mercury in the acetic acid used are eliminated.

A plant having a capacity of 170 tons per day of acetaldehyde was projected but never built. However, the process had been run on a semi-works scale (800 kg/day) at Ludwigshafen.

Description of Process. Crude methyl vinyl ether (85 per cent ether plus 15 per cent methanol) is fed continuously to the base of a hydrolysis tower 10 m high and 2.5 in diameter, which contains a 0.25 per cent solution of sulfuric acid. The hydrolysis takes place at 80 to 100°C under a pressure of 2.5 atm. Acetaldehyde, methanol and water are continuously vaporized and led to a distillation column 15 m high and 2.6 m in diameter. This column may be either a bell-and-plate type or Raschig ring-packed. Acetaldehyde is distilled overhead. Aqueous methanol is run off from the base of the column to a stirred vessel where any traces of acetaldehyde remaining are resinified by treatment with weak alkaline. It is then distilled and recycled to the vinylation tower.

The yield of vinyl ether from acetylene was 97 per cent and of acetaldehyde from vinyl ether 99 per cent, or an overall yield of acetaldehyde of 96 per cent. Estimates indicated a slightly higher installation cost but a slightly lower production cost for the vinyl ether process.

However, due to a shortage of alloy steel, the apparatus could not be made from V4A steel but had to be constructed from V2A and Remanit. Corrosion took place in various parts of the apparatus. It was found that this serious corrosion problem could be eliminated if the hydrolysis of the vinyl methyl ether was carried out in the vapor phase over a solid, acid-containing catalyst. Necessary alterations on the apparatus which had been used for liquid-phase hydrolysis were made, and large-scale experiments were carried out in the following way.

Vinyl methyl ether is pumped from a tank-car into two storage vessels under 2.5 atm nitrogen pressure. The ether is then pumped into the reaction tower by 6 atm nitrogen pressure, where it contacts the catalyst at 210°C in the presence of the required quantity of steam.

The reaction tower, made from V2A steel, is 8m high and 120 mm in diameter. Heating (210°C) is effected by high-pressure steam (21 atm). The catalyst (80 liters) consists of siliceous extrudings (4 mm) impregnated with 6 per cent phosphoric acid. Siliceous extrudings without added phosphoric acid have some catalytic activity. Throughput of vinyl methyl ether (88 per cent pure with 12 per cent methanol) is 40 liters per hour. The water required for the hydrolysis is supplied by 11.5 cubic meters of 5-atm steam per hour (15 per cent surplus).

The vapors from the catalytic tower are advantageously cooled to 90°C. (The heated cooling water can be used to heat column 2.) They enter column 1 (11 m high, 200 mm diameter) which is packed with Raschig rings (15 mm). This column is fed with 40 liters of water (room temperature) per hour, and 95 per cent acetaldehyde is continuously distilled off. The raw acetaldehyde is contaminated with dimethylacetal, methanol and water. The still pot of this column is heated to 115°C, and the bottoms leave it with a content of 25 to 30 per cent methanol and 0.5 per cent crotonaldehyde. This aqueous methanol can be worked up and again subjected to vinylation.

The raw acetaldehyde from column 1 is now distilled in column 2 (8 m high, 200 mm diameter, packed with 15-mm Raschig rings). The dephlegmator operates at 1:1 reflux and take off is 25 liters of 99.7 to 100 per cent acetaldehyde per hour. It is cooled and runs into the receivers.

The bottoms contain a mixture of 29 per cent methanol, 22 per cent acetaldehyde, 39 per cent acetal and 6 per cent water which is recycled to the catalytic tower by a small pump (1 kilo per hour). Dimethylacetal is there decomposed to methanol and acetaldehyde.

No data are available on yields, catalyst life, etc. However, it is apparent that the vapor-phase process was considered satisfactory, and it is indicated that the process was easier to operate than the original liquid-phase process.

Polymerization: Polyvinyl Ethers

The vinyl ethers in general polymerize only very slowly under the influence of heat, light, or peroxide-type catalysts to give very low molecular-weight polymers. On the other hand, vinyl ethers polymerize very readily, sometimes even violently, in the presence of acid-type catalysts[36]. Active catalysts include iodine, concentrated mineral acids, metallic halides such as those of zinc, tin, iron and aluminum, boron fluoride and its complexes with alkyl ethers, tetrahydrofuran, dioxane and gamma-butyrolactone, boron fluoride hydrates, sulfur dioxide[37], etc. In general, the preferred catalysts are boron fluoride[38], or one of its hydrates or complexes. The required quantity of catalyst is very small. All the aliphatic vinyl ethers can be polymerized easily with approximately 15 mg of $BF_3 \cdot 2H_2O \cdot C_4H_8O$ or $SnCl_4 \cdot 2(C_4H_9)_2O$ per kg of vinyl ether.

Polymers of widely different properties are formed depending upon the type and amount of catalyst, the temperature, the diluent, the vinyl ether and its purity, and the polymerization technique[39]. The polymeric vinyl

[36] *D. R. Pat. 662,936; 663,779, 679,607; 684,820; 706,018; 751,603, 762,871, Fr Pat. Pat. 814,349; 848,577.*

[37] *D. R. Pat. 625,017.*

[38] *D. R. Pat. 591,845.*

[39] *U. S. Pat. 2,061,934; 2,098,108; 2,104,000,*

ethers may be sticky balsam-like sirups, tacky rubbery solids, or non-tacky wax-like materials. The higher molecular-weight polymers are formed only at relatively low temperatures under very favorable conditions of polymerization in a diluent such as liquid propane, using a very dilute catalyst solution.

The vinyl ethers may be interpolymerized with other polymerizable monomers such as vinyl chloride, vinyl acetate, acrylic esters, etc.[40] to give polymers of modified properties. The interpolymerization may be carried out by bulk, solution, or emulsion methods using peroxide-type catalysts. In the case of interpolymerization systems where water is present, it is necessary to maintain the system at pH 7.0 or higher, to prevent hydrolysis of the vinyl ether.

Bulk Polymerization of Vinyl Ethers. Polymerization of the lower aliphatic vinyl ethers may be carried out in bulk at the boiling point of the ether. Stainless steel kettles fitted with agitators, cooling coils and reflux condensers, and able to withstand only very low pressures of the order of 5 atm may be used The heat of polymerization is removed mainly by vaporization and condensation of the vinyl ether, the condensate is returned to the reaction. Initially, only a small fraction of the total batch charge is polymerized, but after this is started, the remainder of the vinyl ether and catalyst solution are fed continuously. Precautions must be taken to insure that the added vinyl ether is polymerized continuously and does not accumulate and later polymerize in an uncontrolled manner.

When spontaneous polymerization is completed, the product is heated slowly to remove the last traces of unreacted monomer, either by polymerization or by distillation. The product is then forced out of the kettle under nitrogen pressure and is either sold in this form, or dissolved in water or organic solvents depending upon its end use

The higher molecular weight vinyl ethers, such as octadecyl vinyl ether, may be polymerized even more simply because they are less reactive, and their heat of polymerization (per unit weight) is considerably lower. Much larger quantities can be polymerized in large batches without danger of sudden temperature increases

The bulk polymerization of vinyl methyl ether is carried out as follows[41]. Seventy liters of vinyl methyl ether are run into a kettle of one cubic meter capacity at 3 to 5°C and then over a period of 30 minutes, 100 to 150 cc of a catalyst solution (3 per cent boron fluoride dihydrate in dioxane) are added. The temperature rises to 12°C and is kept under control by brine cooling and by adding more vinyl methyl ether at 3 to 4°C. During 3 to 4 hours, 1130 liters of monomer and 800 to 1000 cc of catalyst solution are added by manual operation of the feed valves at 10-minute intervals. The kettle is then closed and the reaction carried on under the vapor pressure

[40] *U. S. Pat. 2,066,330, 2,016,490; 2,054,019; 2,047,398, PB* 87913 (*BIOS* 1602)
[41] *PB* 52876 (*BIOS* 742).

of the ether. The temperature and viscosity gradually increase. Sixteen to 18 hours from the start, when the current drawn by the stirring motor has increased from 15 to 40 amperes, stirring is stopped and the temperature allowed to rise to 100°C. When the temperature is constant and the pressure has fallen, the reaction is finished by distilling off any unpolymerized vinyl methyl ether monomer.

The yield of polymeric vinyl methyl ether is 92 to 93 per cent of theoretical. The k value is usually 45 to 50 (max. 60).*

Solution Polymerization. Polymerization at low temperatures in a low-boiling solvent such as propane was used to prepare polyvinyl ethers of high molecular weight (high k value). The polymerization was effected at about −50°C, the heat of polymerization being removed by evaporation of the propane. A continuous process in which such a polymerization was carried out on a revolving endless belt completely enclosed in a vapor-tight housing was used to prepare rubbery polyvinyl ethers such as "Oppanol C" (polyvinyl isobutyl ether) and "Oppanol A" (polyvinyl isopropyl ether)[42].

Properties of Polyvinyl Ethers

The properties exhibited by the polyvinyl ethers naturally depend upon the nature of the vinyl ether used, the conditions of polymerization and the k value of the polymer. However, all polyvinyl ethers, in contrast to the monomeric vinyl ethers, are remarkably stable toward hydrolysis by either acids or alkalies.

The solubility of the polyvinyl ethers may be varied over wide limits. The lowest member of the series, polyvinyl methyl, is not only soluble in organic solvents but is miscible with water below 35°C Above 35°C, the solubility is reversed and the polyvinyl methyl ether separates from its solution, but upon cooling to 35°C or lower, it redissolves The polyvinyl ether of 3-hydroxytetrahydrofuran behaves similarly In both of these cases, the monomeric vinyl ether has a very limited solubility in water.

All other polyvinyl ethers are water-insoluble, but dissolve in most organic solvents unless cross-linked to three-dimensional polymers by the addition of appropriate agents such as divinyl ether, etc. The solubility of some polyvinyl ethers in various solvents is shown in Table II-2.

The specific gravity of some polyvinyl ethers may be found in Table II-3.

Physically, the polyvinyl ethers may be oils, soft resinous sirups, wax-like or rubbery. Generally speaking, the polyvinyl ethers from the branched-chain alcohols are harder and more rubbery than those from straight-chain alcohols. Molecular weights as determined by light scattering apparently

* For definition of the term "k value," see footnote page 671.

[42] *PB* 67694 (*FIAT* 944).

range from 100,000 for the viscous sirups to 600,000 to 800,000 for the rubbery solids.

The high molecular weight polyvinyl isobutyl ("Oppanol C") and polyvinyl isopropyl ("Oppanol A") ethers are rubber-like thermoplastics.

Table II-2 Solubility of Polyvinyl Ethers

Solvent	Polyvinyl-methyl	Polyvinyl-ethyl	Polyvinyl-isobutyl	Mixed Polymer (60% isobutyl, 40% decalylvinyl)
Methanol	+	−	−	−
Ethanol	+	+	−	−
Butanol	+	+	+	−
Acetone	+	+	−	−
Ether	+	+	+	+
Methyl acetate	+	+	−	−
Ethyl acetate	+	+	+	−
Butyl acetate	+	+	+	+
Benzene	+	+	+	+
Toluene	+	+	+	+
Xylene	+	+	+	+
Gasoline	−	+	+	+
Methylene chloride	+	+	+	+
Chloroform	+	+	+	+
Carbon tetrachloride	+	+	+	+
Trichloroethylene	+	+	+	+
Water	+	−	−	−
Transformer oil	−	+	+	+
Spindle oil	−	+	+	+
"Vaseline"	−	+	+	+

Table II-3 Specific Gravity of Polyvinyl Ethers

Ether	Sp Gr
Polyvinylmethyl (*k* 40)	1 045–1.05
Polyvinylethyl (*k* 50)	0 95 –0 97
Polyvinylisobutyl (*k* 60)	0 90 –0.92
Polyvinylisobutyl (high *k*)	1.037
Polyvinyl-beta-decalyl	1.067
Mixed polymer (40% isobutyl, 60% beta-decalylvinyl)	0.95

They are soluble in gasoline, benzene, chlorinated hydrocarbons, esters and ethers and can be blended in any proportion with rubber, Buna, gutta percha and balata. They are practically odorless, colorless and non-toxic. They resist the action of dilute acids and of dilute and concentrated alkalies; their aging properties are superior to those of natural rubber and they are more stable toward ozone.

Recent investigations in the United States, however, have shown that the high polymers of the lower alkyl vinyl ethers are not completely stable to heat, light or aging, even at room temperature[43]. The incorporation of 0.5 to 1.0 per cent of a stabilizer of the antioxidant type was found effective in preventing such changes[44].

Applications of Polyvinyl Ethers

The main fields of application of polyvinyl ethers are:

(1) Lacquer raw materials and plasticizers
(2) Adhesives
(3) Artifical resins
(4) Leather
(5) Textiles
(6) Oil additives
(7) Miscellaneous uses

Lacquers. Blends of polyvinyl methyl ether ("Igevin M") with nitrocellulose are used, particularly for lacquer foils The polyvinyl methyl ether acts as a plasticizer and, despite its water solubility, perfectly waterproof films are obtained even if the ratio of ether to nitrocellulose is 1:1.

Solutions of polyvinyl methyl ether ("Igevin 40") in nitrocellulose are insoluble in motor fuels and are used in gasoline-resistant packings.

Polyvinyl methyl ("Igevin M40") and polyvinyl ethyl ("Igevin A25 and A50") are plasticizers for lacquers. A mixed polymerizate ("Igevin AD28") consisting of 80 per cent beta-decalyl vinyl ether and 20 per cent ethyl vinyl ether is self-hardening in lacquers.

The polyvinyl ethers derived from the vinyl ethers of the acetalized alcohols from sugars, such as diacetone-glucose, diacetone-fructose, or diacetals with aldehydes such as formaldehyde, butyraldehyde, etc., are promising new lacquer resins. They have remarkably high softening points (160 to 170°C), are miscible with most lacquer raw materials and with cellulose acetate, and are fast to light. The copolymerization of 25 per cent vinyl isobutyl ether with 75 per cent vinyl chloride gives a polyvinyl chloride (m.p. 400°C) mixed polymer whose solubility has been improved to the point where it can be used in the preparation of corrosion-resistant paints for interior and exterior use. The polyvinyl ethers derived from camphenyl carbinol and dipentenylcarbinol are clear, colorless, lacquer resins which have turpentine-like odors.

Adhesives. Solutions of the polyvinyl ethers in organic solvents are primarily used as adhesives; for example, polyvinyl isobutyl ethers ("Igevin I60") dissolved in organic solvents with or without fillers are the "Cosal U" brand adhesives. These, together with other soft vinyl ether resins

[43] *Ind. Eng. Chem.*, **39**, 180 (1947).
[44] *U. S. Pat. 2,395,684.*

such as polyvinyl methyl and polyvinyl ethyl ether in organic solvents, are used in impregnating and coating cellulose ethers or esters in the manufacture of artificial leather Polyvinyl ethyl, isobutyl, beta-decalyl and mixed beta-decalyl isobutyl ethers blend readily with mineral oils, paraffin and bitumen, yielding mixtures useful for impregnating paper.

The soft resins, *e.g.*, polyvinyl methyl and polyvinyl ethyl ethers, may be used to improve the adhesiveness to metal of other film-forming agents such as Celluloid Similar blends with higher polyvinyl ether contents are useful in the shoe industry.

Polyvinyl isobutyl ether ("Igevin I60") mixed with "Oppanol C" and artificial or natural resins gives adhesives which are useful in the shoe industry, and in insulating and adhesive tapes. Mixtures of polyvinyl ethyl ("Igevin A50 and A25") and of polyvinyl isobutyl ("Igevin I60 and I30") ethers with resins have been used in making flypaper. Polyvinyl isobutyl ether ("Igevin I60") was used in adhesive plasters and in devices to protect trees against caterpillars

High molecular-weight polyvinyl isobutyl ether ("Oppanol C") does not show cold flow and may be used as an adhesive between $-20°$ and $+70°C$, or if mixed with inorganic fillers between 0 and $+70°C$. Mixed with other polyvinyl ethers and artificial resins, adhesives useful in the shoe industry and in the fabrication of auto bodies are produced

The water-insoluble polyvinyl ethers may be dissolved in hydrocarbons and dispersed in water to give emulsions having exceptionally good adhesive properties; these have been used with success for interior or exterior wall paints, particularly if blended with various pigments Casein, sodium polyacrylate or a partially saponified acrylonitrile-methyl acrylate copolymer have been used as emulsifying agents in such paints.

In addition to the above-described dispersions of polyvinyl ethers, emulsions resulting from the emulsion polymerization of vinyl ethers with other vinyl monomers are of importance in the artificial fiber industry and in resins and paints, it is claimed that the vinyl ether molecules in the polymer chain act as non-volatile internal plasticizers as contrasted to mechanically admixed plasticizers such as tricresyl phosphate and phthalates. Polyvinyl alcohols, sodium polyacrylate, octadecyl alcohol-ethylene oxide products or "Amphosoap" were used as emulsifying agents.

The so-called "Acronal" dispersions had the following compositions:

Name	% Solids	% Vinyl Isobutyl Ether	% Methyl Acrylate	% Ethyl Acrylate	% Acrylic Acid	% Acrylonitrile	% Styrene
"Acronal 400D"	40	22	66	—	—	—	12
"Acronal 450D"	40	20	—	66	2	—	12
"Acronal 550D"	50	50	50	—	—	—	—
"Acronal 600D"	40	20	—	80	—	—	—
L.R. ..	30	50	20	—	—	30	—

The "Acronal" dispersions are used where softness, pliability, and high elasticity of the film are desired. Consequently, their usage is in adhesives, particularly when mixed with water-soluble colloids, for the impregnation of fabrics, and for the production of artifical leather and leather substitutes.

Artificial Resins. Polyvinyl dihydroabietyl ether is an excellent hard resin (artificial resin "PVH"), especially useful when mixed with nitrocellulose, drying oils and alkyd resins.

Polyvinyl-beta-decalyl ether ("Igevin Z") is an excellent substitute for natural hard resins.

Leather. The mixed polymer of 60 per cent isobutyl and 40 per cent beta-decalylvinyl ethers ("Igevin IZ") was used as a dressing for leather belts. Polyvinyl isobutyl ether or the mixed isobutyl-beta-decalyl polymers were useful leather auxiliaries and could replace train oil, degras and castor oil.

The polyvinyl ethers of the higher alcohols were called "Densodrins"; some representative members of this series are:

"Densodrin NH": polyvinyl beta-decalyl ether
"Densodrin V": polyvinyl cetyl ether (C_{16} alcohols) or polyvinyl wax alcohol ether (C_{18} and a little C_{16} alcohols)
"Densodrin W": mixed polymer from 3 parts wax alcohol vinyl ether and 1 part cocoalcohol vinyl ether (C_{12-16} alcohols)
"Densodrin NW": polyvinyl isobutylether ("K20-30")
"Densodrin H": 2 parts "Densodrin V" plus 1 part rosin

The H brands serve for the waterproofing of shoe soles, while the V and W brands are used for the impregnation of shoe upper leather. The NW brand is a substitute for train oil or degras.

Polyvinyl octadecylether ("I.G. Wax V") is a colorless, unsaponifiable wax melting at 45 to 50°C which can be used in the formulation of shoe polishes, wax polishes, and as a dental wax.

The "Acronal" emulsions resulting from the copolymerization of vinyl isobutyl ether and acrylic derivatives are used instead of nitrocellulose or linseed oil for the production of leather substitutes. Fabrics such as wool, cotton, mixed fibers or even paper are coated and "leatherized" with a pliable film-forming agent by a printing procedure, or fibrous material such as tanned leather waste, or cellulose or textile wastes may be milled with the "Acronal" binder, shaped, pressed and dried to give fiber leather. "Acronal 400D and 550D" are suitable for the preparation of fiber leather.

Textile Aids. Polyvinyl methyl ether ("Appretan WL"), combined with other colloids which are water-soluble, is used in the textile industry as a finishing agent where it gives body to fabrics of artificial silk, staple fibers, cotton/rayon, wool, and wool blends. It increases the strength of lining fabrics, improves durability, and increases the absorbent properties of wool. Polyvinyl methyl ether also finds use as a thickener and sensitizer for emulsions of artificial resins, rubber latex and adhesives.

Oil Additives. Polyvinyl oleylether and its mixed polymerizates with isobutyl vinyl ether are excellent pour-point depressants for mineral oils (Pour-point depressant "PVO"). Polyvinyl isobutyl ("Igevin I60") and the mixed vinyl isobutyl-beta-decalylvinyl ether served as thickening agents for cable oils.

Miscellaneous Uses. Synthetic drying oils have been prepared from the condensation of vinyl ethers with crotonaldehyde[45]; isohexyl and isoheptyl vinyl ethers were condensed in emulsion with crotonaldehyde or other unsaturated aldehydes and ketones by an alkaline catalyst at low temperatures. The synthetic oils blend readily with alkyd resins and dry quickly in the presence of siccatives.

The copolymer of vinyl ethyl or vinyl methyl ether (60 per cent), vinyl isobutyl ether (30 per cent) and butanediol divinyl ether (10 per cent) was reputedly better than linseed oil in the manufacture of linoleum. It was not, however, resistant to hydrocarbon solvents.

Polymers of 2-ethylhexyl, nonyl, or fatty alcohol (from reduction of oxidized C_5-C_9 paraffins) vinyl ethers were of interest as plasticizers in the rubber industry.

Vinyl ethers of the hydroxyethylated phenols and cresols were interpolymerized with butadiene to give interesting soft, rubber-like materials. Polymerized cresylhydroxyethyl vinyl ether is a soft plastic resin useful as a binder for paints, or for blending with vinyl chloride. The polyvinyl ether from beta-napthoxy ethyl vinyl ether is a rosin-like, hard resin, soluble in chlorinated hydrocarbons.

The polymeric vinyl ethers derived from the hydroxyethylated amines (alkanolamines) are interesting and unique in that they are soluble in acid. Interpolymers, particularly of dimethylaminoethyl vinyl ether, with other vinyl compounds are of interest in the textile field.

The vinyl ethers of hydroxyethylaniline and its homologs can be coupled in pyridine with suitable diazo compounds to give azo dyes having free vinyl groups

Ethyl, isobutyl and *n*-butyl vinyl ethers and butanediol divinyl ether, alone or in mixture, were tested as rocket fuels[46]. Ethyl vinyl and butanediol divinyl ethers apparently gave the best results.

Among the vinyl ethers of heterocyclic alcohols, the most interesting are those heterocyclic compounds containing oxygen in the ring. In general their polymers are easily soluble in all organic solvents and blend readily with many elastomers and plasticizers. The polymeric 3-hydroxy tetrahydrofurfuryl vinyl ether is noteworthy because it is water-soluble and is compatible with all plasticizers and film-forming agents including the cellulose derivatives.

[45] *D. R. Pat. 699,432.*

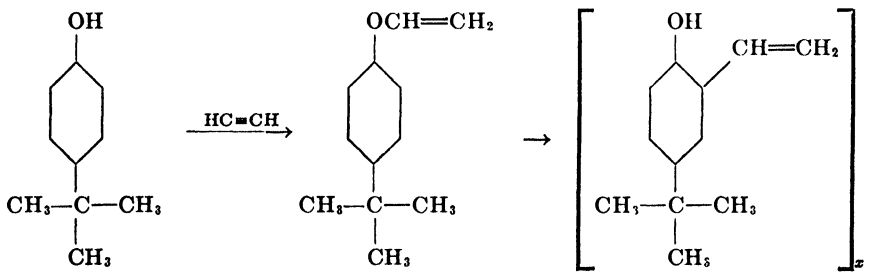
[46] Technical Oil Mission Microfilms, Reel 112.

Koresin

Acetylene reacts with phenols and naphthols in the presence of alkaline catalysts to yield vinyl ethers[47]. However, in the presence of zinc or cadmium salts as catalysts, the vinyl group does not remain on the phenolic oxygen but enters the ring, forming resinous materials The reaction may possibly involve the rearrangement of the initially formed vinyl ether to a hydroxystyrene, which then polymerizes to a resinous product[48]. The softening point and solubility of the resulting resins can be varied by the choice of phenol and the amount of acetylene introduced. The most soluble resins are obtained from the alkyl phenols, such as isobutyl and octyl phenol, in which the molecular ratio of phenol to actylene can be as high as 1:2. Although insoluble in alcohol and alkali, they are very soluble in aliphatic hydrocarbons and drying oils, in combination with the latter, they are suitable raw materials for varnishes. The resins from alkyl phenols and acetylene have a remarkable compatibility with natural rubber and with Buna, where a coating with a solution of the resin imparts the tack necessary for the fabrication of tires The resin made from *t*-butyl phenol and acetylene was called "Koresin"* in Germany

"Koresin" may be prepared by heating a mixture of *p-t*-butylphenol with about 10 per cent by weight of zinc naphthenate to 160°C and introducing a mixture of 2 parts of nitrogen and 1 part of acetylene to 200 psi total pressure The reactants are maintained under these conditions until a resinous material having the requisite predetermined physical constants is obtained. The degree of polymerization is not large, probably of the order of 7, and the product contains some unreacted *p-tert.*-butyl phenol

Reppe believed the reaction first led to the substituted phenyl vinyl ether which, under the conditions of the reaction, rearranged to give a hydroxy styrene which then polymerized:



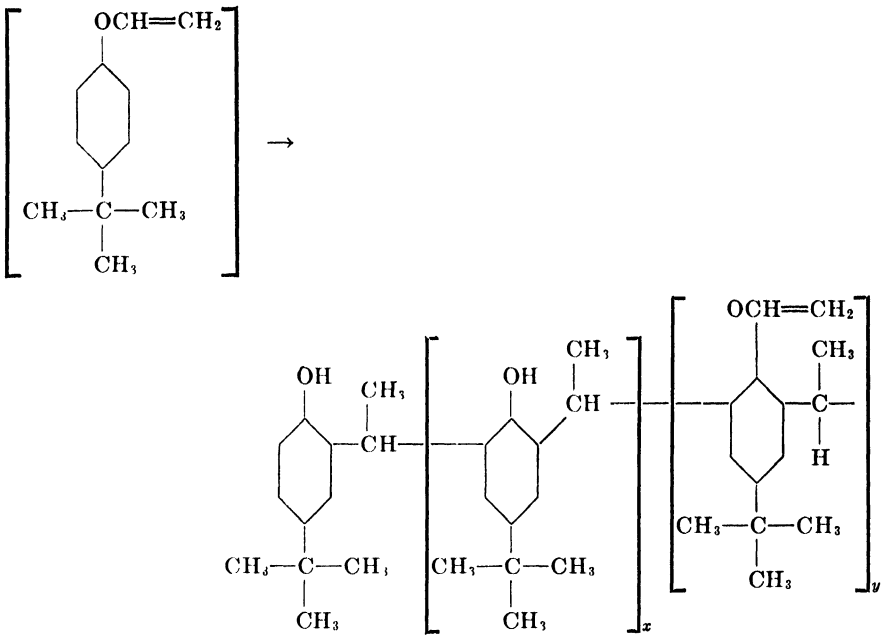
However, other investigators have noted that very similar products can be prepared from vinyl ethers and *p-tert.*-butyl phenol, or from acet-

[47] *D. R. Pat. 643,220.*

[48] *D. R Pat. 642,686; 645,112*

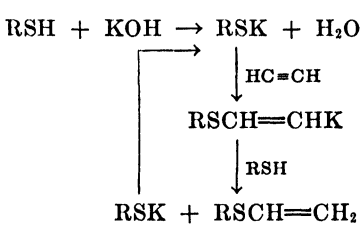
* More recently this product was offered as a rubber tackifier under the same name in this country by General Aniline and Film Corp.

aldehyde and the phenol; furthermore, infrared absorption shows the presence of methyl groups as well as hydroxy groups[49] Hence an alternative ethylidene structure has been proposed:



VINYL THIOETHERS

Aliphatic, aromatic, hydroaromatic and heterocyclic mercaptans undergo vinylation under the same general conditions as do alcohols and phenols; vinyl thioethers are formed in practically quantitative yield[50]

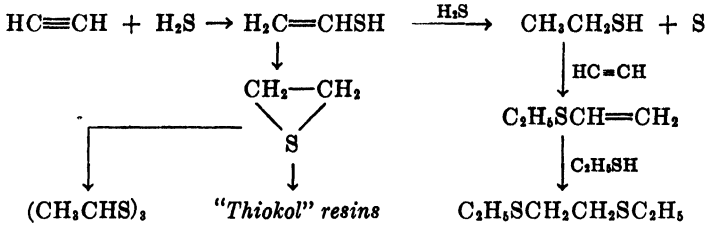


The vinylation of hydrogen sulfide to yield either vinyl mercaptan or divinyl sulfide has not been realized. When the reaction is carried out at 120°C in glycol as a solvent and using potassium hydrosulfide as a catalyst, the vinyl mercaptan apparently reacts further by two routes: (1) polymerization, possibly through ethylene sulfide as an intermediate, to resins of the "Thiokol" type, or to trithioacetaldehyde; (2) by reduction with

[49] *Ind. Eng. Chem.*, **40**, 1171 (1948).

[50] *D. R. Pat. 617,543; PB* 17658, frames 1955-7.

excess hydrogen sulfide to ethyl mercaptan and sulfur, followed by vinylation of the mercaptan to vinyl ethyl sulfide and subsequent reaction of the vinyl sulfide with mercaptan to yield ethylene bis-ethyl sulfide[51]:



This reaction may be used as a simple method for the preparation of ethyl mercaptan on a small scale.

Reactions of Vinyl Thioethers

The vinyl thioethers are in general much more sluggish in their chemical behavior than the corresponding vinyl ethers; hydrogenation, hydrolysis and polymerization are considerably more difficult. No data are available on the polymerization except the statement that best results are obtained with acid catalysts in liquid sulfur dioxide solution[52].

(1) *Addition of Hydrogen.*

$$RSCH{=}CH_2 \xrightarrow{H_2} RSCH_2CH_3$$

Reported to go quantitatively but no data available on reaction conditions.

(2) *Addition of Hydrogen Sulfide and Mercaptans*[52].

$$RSCH{=}CH_2 + H_2S \rightarrow RSCH_2CH_2SCH_2CH_2SR$$
$$RSCH{=}CH_2 + R'SH \rightarrow RSCH_2CH_2SR'$$

This reaction is of general scope and is apparently catalyzed by either inorganic, or organic bases, or acids.

(3) *Addition of Alkali Bisulfites.* Alkali bisulfites add readily in good yields to the aliphatic vinyl sulfides, but less readily and in poorer yields to the aromatic vinyl sulfides:

$$RSCH{=}CH_2 + NaHSO_3 \rightarrow RSCH_2CH_2SO_3Na$$

The resulting products are readily oxidized to the sulfoxide with sodium hypochlorite, and to the sulfone with hydrogen peroxide.

(4) *Oxidation.* The vinyl sulfides may be oxidized to the corresponding vinyl sulfoxide or vinyl sulfone without any appreciable attack on the

[51] *D. R. Pat. 625,660.*
[52] *PB* 76315.
[53] *D. R. Pat. Anmeldung J-50, 286.*

vinyl group[54]. With the theoretical amount of hydrogen peroxide or with sodium hypochlorite, at mild temperatures, vinyl sulfoxides result. At higher temperatures (80 to 100°C) with excess hydrogen peroxide, the vinyl sulfones are obtained in good yields:

$$RSCH{=}CH_2 \xrightarrow[\text{or } H_2O_2]{NaOCl} RSOCH{=}CH_2 \xrightarrow[80\text{-}100^\circ C]{H_2O_2} RSO_2CH{=}CH_2$$

The oxidation of the sulfur atom to either the sulfoxide or sulfone level results in an extraordinary increase in the reactivity of the vinyl group. The vinyl sulfoxides and sulfones add hydrogen sulfide[55], mercaptans[55], sulfinic acids[56], alkali bisulfites[57], ammonia and amines[58]. In general, the vinyl sulfoxides are less reactive than the vinyl sulfones, but the above-mentioned additions often take place spontaneously with either type without the use of catalysts.

(5) *Miscellaneous Reactions of Vinyl Thioethers.* Ammonia and amines could not be added to vinyl sulfides. Organic hydroxy acids such as salicyclic, beta-hydroxynaphthoic, etc., likewise could not be added. Halogens, phosgene, thionyl chloride, sulfuryl chloride, and hypochlorous acid gave no definite reaction products. In most cases, the vinyl group was split off and the liberated mercaptan added to the vinyl sulfide to yield the corresponding ethylene bis-sulfide; however, benzoyl chloride with vinyl *p*-tolyl sulfide gave mainly the *p*-tolyl thioester of benzoic acid. Attempts to effect cyclization of vinyl *p*-tolyl sulfide with oleum, aluminum chloride, alkali fusion, or dehydrogenation catalysts were unsuccessful.

Work on the evaluation of the vinyl thioethers was apparently not completed, so final judgment as to the potential applications and utility of this class of vinyl compounds cannot yet be passed.

Vinyl Esters

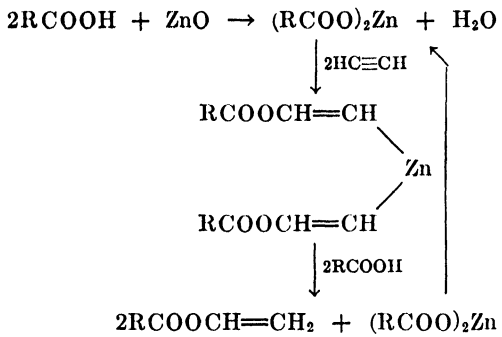
Although vinyl acetate has been produced technically for many years, the preparation of the vinyl esters of the higher fatty acids such as butyric, etc., by the known methods gave only very poor yields and failed completely with acids containing more than four carbon atoms. However, as a result of the work on the pressure vinylation of alcohols, etc., it was found possible to prepare the vinyl esters of the higher fatty acids up to montanic.

The vinylation of acids may be carried out in liquid phase in an autoclave or in a tower using the same general procedure as used for vinyl ethers. Zinc or cadmium salts of organic acids (acetate, benzoate, naphthenate, etc.) are generally the preferred catalysts, although the potassium salt of

[54] *D. R. Pat. Anmeldung J-49, 736.*
[55] *D. R. Pat. Anmeldung I-50, 314* (IVc/12o).
[56] *D. R. Pat. Anmeldung I-51, 251* (IVc/12o).
[57] *D. R. Pat. Anmeldung I-51, 249* (IVc/12o) and *I-51, 252* (IVc/12o).
[58] *D. R. Pat. Anmeldung J-49, 928.*

the higher fatty acids may be used; for example, potassium stearate may be used in the vinylation of stearic acid. Undoubtedly, solubility of the salt in the acid to be vinylated is of major importance. As the reaction temperature is about 160 to 180°C, the vinylation of acids boiling above 180°C can be accomplished without pressure in a tower. Generally, however, the vinylation is carried out with acetylene under about 200 psi pressure. Yields of 90 per cent are claimed.

The reaction was represented as involving the following steps:



The vinylation is truly catalytic, and 1 to 3 per cent of metal salt on the weight of carboxylic acid vinylated is sufficient.

The vinyl esters of the higher fatty acids may be polymerized alone, or interpolymerized with other polymerizable materials, by the same general techniques useful for vinyl acetate. The applications of the polymers and interpolymers have apparently not been fully developed as yet. The polyvinyl esters of the high molecular weight unsaturated acids are reported to have interesting drying characteristics. Noteworthy is the tall oil vinyl ester, which was very interesting in Germany as a possible solution to the critical shortage of drying oils[59]. Tall oil, consisting of a mixture of about 65 per cent linoleic and linolenic acids and 35 per cent of resin acids, principally abietic acid, is a by-product from the preparation of cellulose by the sulfate process. The tall oil vinyl ester can replace linseed oil in color printing and has given good results as a size.

Vinyl Amines

According to the prior literature, ammonia and acetylene react in the presence of various catalysts, usually at relatively high temperatures, to give heterocyclic nitrogen compounds containing certain pyridine bases[60]. Under different conditions acetonitrile is the main reaction product[61].

[59] *Swed. Pat. 98,482; Ital. Pat. 376,011.*
[60] *D. R. Pat. 685,566; 516,765; 504,238.*
[61] *D. R. Pat. 477,049.*

The experience obtained in the vinylation of alcohols, phenols and mercaptans was applied to the vinylation of ammonia and amines.

Attempts to vinylate ammonia to yield vinyl amine or ethylene imine were unsuccessful, despite the numerous experimental conditions studied:

$$HC{\equiv}CH + NH_3 \longrightarrow H_2C{=}CHNH_2 \quad \text{or} \quad H_2C\!\!<\!\!\begin{matrix}\diagup\\ \\ \diagdown\end{matrix}\!\!\begin{matrix}N\\ |\\ H\end{matrix}\!\!>\!\!CH_2$$

However, in the presence of special catalysts, such as complex cobalt and nickel salts (*e.g.*, hexaminocobaltochloride), acetylene and ammonia condensed in liquid phase at approximately 100°C and 225 lb pressure to yield 2-methyl-5-ethylpyridine. Small percentages of high molecular-weight basic resins are formed as by-products.

According to Reppe, vinyl amine is the intermediate in this reaction. By condensation, splitting off ammonia, 2-methyl-5-ethylpyridine results:

$$4HC{\equiv}CH + 4NH_3 \longrightarrow 4CH_2{=}CH{-}NH_2 \longrightarrow \text{(2-methyl-5-ethylpyridine)} + 3NH_3$$

(Compare the reaction of vinyl ether with ammonia, page 44.)

Vinylation of primary and secondary aliphatic amines using alkaline catalysts does not proceed smoothly or uniformly. Acetylene is absorbed readily, but no uniform products are obtained.* The vinyl amines, if actually formed, are apparently very unstable and either decompose or polymerize very readily. Actually the vinyl amines were successfully prepared from diethylamine and dicyclohexylamine in the presence of zinc and cadmium salts. However, they were very unstable, and although they could be distilled at low pressures, attempts to distill them at atmospheric pressure resulted in decomposition to acetylene and the amine.

The aromatic amines, such as aniline, ethylaniline, toluidine, etc., also react with acetylene under pressure in the presence of alkaline catalysts with the production of resins

However, the vinylation of certain aromatic secondary amines of low basicity, such as diphenylamine, or phenyl alpha- and phenyl beta-naphthylamine, leads to the corresponding N-vinyl compounds which, though easily polymerized by oxygen in the air, can be isolated[62]. Vinyl amines

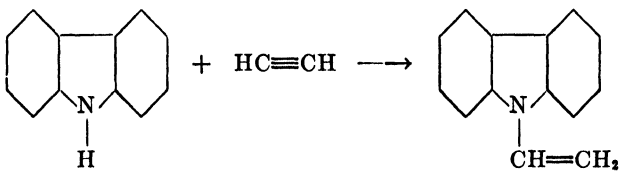
* However, as will be shown in Chapter III, definite homogeneous products (aminobutynes, etc.) result from the reaction of acetylene and amines in the presence of heavy-metal acetylide catalysts.

[62] *D. R. Pat. 636,213.*

of greater stability result from the vinylation of cyclic imino compounds containing the pyrrole nucleus, as in pyrrole itself, indole, or carbazole[63], or from certain other heterocyclics such as the imidazoles[64].

The vinylation of amines of the type just described is conveniently done by batch procedures with acetylene under pressure using alkalies, zinc or cadmium oxides, or their salts with organic acids, or mixtures thereof as catalysts. The reaction temperature is between 150 and 200°C. The vinylation is preferably carried out in solution or in suspension, particularly with high-melting amines. The reaction takes place readily and smoothly; in fact, the vinylation of carbazole is usually cited as the standard of vinylation.

Vinyl Carbazole[65]



A 40 to 50 per cent by weight suspension of carbazole in hexahydrotoluene or hexahydroxylene was vinylated in a stirred autoclave at 180°C under 15 atm pressure (10 acetylene, 5 nitrogen), using 3 per cent by weight of a mixed catalyst consisting of 3 parts of potassium hydroxide and 1 part of zinc oxide Vinylation is quite rapid, requiring only 4 to 5 hours, the N-vinyl carbazole dissolving in the solvent. When no more acetylene is absorbed, the solution is filtered, washed with alkali and distilled. The vinyl carbazole distills at about 180°C/15 mm. Polymerization during distillation can be retarded by adding 0.5 per cent of phenyl beta-naphthylamine, or 1 to 3 per cent of potassium hydroxide. The vinyl carbazole was further purified by recrystallization from methanol, the pure product melting at 67°C. The yield of crude product is above 85 per cent, but losses during purification lower this figure to about 75 per cent.

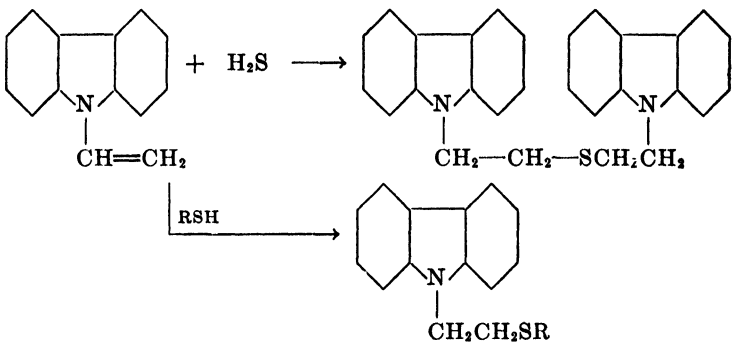
Monomeric vinyl carbazole is somewhat toxic and must be handled with care. It is irritating to the skin and may cause swelling at any part of the body as well as discoloration of the skin. Traces of the fine powder in the air are sufficient in some cases to cause irritation. It is worthy of note that the sensitivity varies with the individual; peculiarly, red-haired persons are not sensitive to the skin irritation.

The vinyl amines exhibit some typical properties of vinyl compounds. They absorb hydrogen readily, giving N-ethyl amines in high yields. In

[63] *D. R. Pat. 618,120; 642,939; 651,734.*
[64] *D. R. Pat. 708,262.*
[65] *PB* 52879 (*BIOS* 746).

the presence of acids they undergo hydrolysis to acetaldehyde and the amine; in this respect they resemble the vinyl ethers, although their hydrolysis is not quite as facile. However, hydrolysis can be used as an analytical method.

Hydrogen sulfide and mercaptans may be added to the double bond[66]:



As mentioned previously, the vinyl amines, with the exception of vinyl carbazole, are sensitive to oxygen. They polymerize on heating, either alone or in the presence of acids or oxidizing agents, as contrasted to the vinyl ethers, which polymerize only with acid catalysts[67].

Polyvinyl Carbazole[68]

Apparently polyvinyl carbazole is the only N-vinyl amine to have attained any commercial importance. Although vinyl carbazole may be polymerized in bulk, in solution, or in emulsion, as well as copolymerized by more or less standard procedures, Reppe claims that it was necessary for him to develop a fundamentally new process of polymerization—the polymerization of suspensions with alkaline oxidants—before polyvinyl carbazole could be used technically. Like many other discoveries, this new process resulted accidently while he was trying to oxidize vinyl carbazole to the N-carboxylic acid, according to the Bozel-Moletra procedure for the oxidation of toluene to benzoic acid. No oxidation whatever resulted, but the vinyl carbazole polymerized quantitatively. During the course of further investigation the following process was worked out for the polymerization:

Vinyl carbazole (20% moisture)	750 kg (dry basis)
Sodium chloride	112 kg
Sodium hydroxide (50% solution)	75 kg
Sodium dichromate	13.5 kg
Water	1500 kg
Sodium butylnaphthalene sulfonate	5–6 kg

[66] *D. R. Pat. 624,622.*
[67] *D. R. Pat. 664,231.*
[68] *PB* 33272.

The above suspension was stirred (50 to 60 rpm) and heated to 80°C. Over about 36 hours or longer the temperature was raised to 180°C. The main reaction probably takes place at 135 to 140°C after about 10 hours. The alkali prevents any hydrolysis, while the naphthalene sulfonate prevents agglomeration of the polymer particles

Upon cooling, the polymeric polyvinyl carbazole which separated as small lumps, 1 to 20 mm in size, was filtered off, milled to 0.5 to 1.0 mm and washed with water to remove the mother liquor. If unreacted monomer was present in large proportions, it was removed by multiple extraction with hot methanol. The yield of polymer was 70 to 75 per cent, based on the carbazole originally vinylated.

Properties and Uses of Polyvinyl Carbazole. Polyvinyl carbazole with a *k* value of about 40 to 75 was sold in Germany under the trade mark "Luvican". More recently a similar product known as "Polectron" has been manufactured in this country by General Aniline and Film Corporation.

Polyvinyl carbazole is soluble in aromatic hydrocarbons, chlorinated aromatics, methylene chloride, and tetrahydrofuran. It has several unusual properties. It is outstanding in its high softening point, its ability to resist heat, and in its electrical properties. The softening point varies with the chain length. High-viscosity polyvinyl carbazole prepared by polymerization at −15°C in trichloroethylene with a boron fluoride-di-*n*-butyl etherate catalyst has a Martens point of 210. Softening points of 150 Martens are reported for other samples, as compared to Martens 75 for polystyrene. Like styrene, polyvinyl carbazole has a minute dielectric loss angle which is practically independent of frequency and temperature. It is an excellent high-frequency insulator because of its high electrical resistance and low power factor and has been used for this purpose. "Polectron" was used in the United States in making condensers for proximity fuses.

Although its electrical properties are as good as those of styrene and its softening point much higher, its impact strength and other mechanical properties are inferior. It can be injection-molded at about 200 to 230°C, which is of course possible only because of its extreme stability to heat. Injection-molded polyvinyl carbazole has a pronounced fibrous structure, the fibers running parallel to the direction of injection or flow. At right angles to this direction, the mechanical strength is generally impaired. Fibrous oriented polyvinyl carbazole exhibits an x-ray fiber pattern.

Compression molding may be carried out on material preoriented in an extruding press at 230°C. The resulting fibers are arranged in completely random fashion before compression molding, which is carried out at 200 to 230°C so that there is no coalescing of the heterogeneously arranged fibers. The compression-molded parts are uniform in strength in all directions and

show substantially better impact strength than injection moldings. Reppe claims that large parts, weighing several kilos, have been produced by this technique.

It is possible to cast thin foils from a solution of the polymer in tetrahydrofuran Such foils may be used as substitutes for mica in condensers.

Polyvinyl carbazole is usually silver-brown in color and it is difficult to obtain attractive shades. It has good resistance to chemical agents, and is stable toward boiling water, dilute and concentrated alkalies and dilute acids, including hydrogen fluoride. Nitric acid and sulfuric acid, however, destroy it.

Several types of polyvinyl carbazole were manufactured in Germany. "Luvican M-150" was pure polyvinyl carbazole, while "Luvican M-125" was a mixed polymer with styrene, which had a lower softening point and was more easily molded than M-150. "Luvican M-100" was a similar product of even lower molecular weight and softening point.

Vinylation of Tertiary Bases

During the course of certain experiments in which organic tertiary amines were used as catalysts in aqueous solutions, it was unexpectedly found that these tertiary bases could be vinylated with acetylene to give quaternary vinyl ammonium hydroxides, which were detected and identified as their picrates[69]. Salts of the tertiary bases with any inorganic or organic acid also reacted readily with acetylene or its derivatives containing a terminal triple bond Presumably the reaction involves the following steps:

$$R_3N + H_2O \rightarrow [R_3NH]^+OH^- \xrightarrow{HC\equiv CR} [R_3N{-}CH{=}CHR]^+OH^-$$

$$R_3N + HA \longrightarrow [R_3NH]^+A^- \xrightarrow{HC\equiv CR} [R_3N{-}CH{=}CHR]^+A^-$$

The conditions of reaction are generally surprisingly mild. The reaction is usually carried out in aqueous solution, or if the solubility of the tertiary amine is limited, in suspension, or with added auxiliary solvents such as alcohols. With acetylene itself, the process is usually carried out under pressure between 30 and 180°C, preferably between 60 and 70°C More reactive acetylene derivatives may be used without pressure.

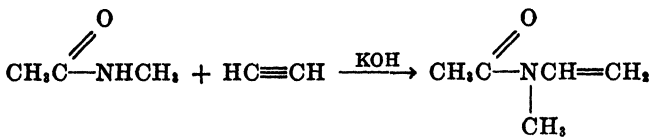
Usually the reaction goes smoothly without the use of added catalysts, the tertiary amine itself normally acting as the catalyst. In the case of amine salts, a small amount of the free amine is sufficient to start the reaction. Catalysts useful in normal vinylations may be used in addition, if necessary. Not more than the stoichiometric amount of acetylene should be added in order to avoid resin formation. Yields may be as high as 80 to 90 per cent.

[69] *D. R. Pat. Anmeldung I-37, 024* (IVe/12o).

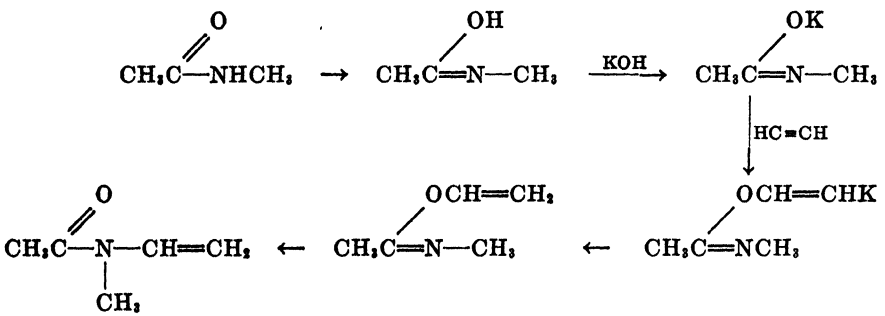
The vinylation of tertiary amines is apparently of very general applicability. The substituent groups on the nitrogen can apparently be similar or different, and of the most varied nature. Heterocyclic tertiary amines such as pyridine, quinoline and isoquinoline also react. Furthermore, the reaction is apparently general for almost all acetylenic derivaties; acetylene, alkyl acetylenes, phenyl acetylene, diacetylene, propargyl alcohol, aminopropynes and aminobutynes all undergo vinylation.

Vinylation of Aliphatic and Cyclic Amides

In the previous section on the vinylation of amines, it was shown that the less basic nitrogen compounds in the amine series vinylate quite readily. It was a natural assumption then that certain amides having a hydrogen atom on the nitrogen atom should also undergo vinylation. Investigation showed that this was indeed the case, carboxylic acid amides in the presence of their potassium salts as catalysts readily undergoing vinylation under the usual reaction conditions[70].



Reppe considered that this reaction might well occur through the vinylation of the intermediate tautomeric compound according to the following formulation:



Of greatest interest in this field are the cyclic amides such as alpha-pyrrolidone, alpha-piperidone, etc. This class of amide can generally be vinylated by first forming the potassium salt by mixing the cyclic amide with about 2 per cent by weight of powdered potassium hydroxide and distilling off about one-third of the amide, which carried with it the water produced in the salt formation. Vinylation is then carried out at about 15 atm pressure with a 2/1 mixture of acetylene and nitrogen at 140 to 160°C until no more acetylene is absorbed. The vinyl amide is then iso-

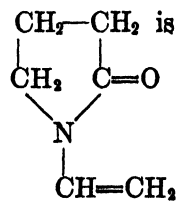
[70] *D. R. Pat. Anmeldung I-63,373* (IVd/12o).

lated by fractional distillation, usually at reduced pressure. The yields are good and may reach 90 per cent. In place of acetylene, substituted acetylenes or diacetylene may be used.

The vinyl lactams exhibit a few typical reactions of the double bond, such as hydrogenation, etc. However, the only reaction of any real interest is their polymerization, which has produced a new class of polymeric materials which are soluble in water and organic solvents and possess other unusual properties. The polymerization of N-vinyl pyrrolidone and the properties and uses of its polymers will be discussed in detail.

Polyvinyl Pyrrolidone ("Periston" or "Kollidon")[71]

For commercial production, polymerization of the pure monomer in block and in solution has been developed first; these processes give "Periston" and "Kollidons" with k values* of 20 to 100. The copolymerization is being further investigated.

Block Polymerization. Vinyl pyrrolidone (VP)  is easily block-polymerized in a simple manner with hydrogen peroxide[72]. Thirty-five kg of vinyl pyrrolidone are added to 150 cm³ of hydrogen peroxide (30 per cent) and heated to 110°C. The polymerization is exothermic and the temperature rises to 180 to 190°C. The molten polymer is poured from the kettle, cooled on plates and milled in a ball mill to a fine, white, somewhat hygroscopic powder.

This process gives a more or less strongly discolored product due to the high temperature; the product also has an unpleasant odor attributable to decomposition products caused by the rapid initiation of polymerization. Furthermore, the polymers contain up to 10 per cent of monomeric vinyl pyrrolidone, which is probably responsible for the hygroscopicity of the material.

If the polymerization kettle is used repeatedly without being cleaned,

[71] This is apparently the same paper which Callomon and Kline translated as *PB* 1340 and published in *Modern Plastics*, **23**, 157 (1945). *PB* 25652 (*BIOS* 354) contains the same data.

* *Translators' Note:* Fikentscher's viscosity coefficient, k, is calculated as follows:

$$\frac{\log n_{rel}}{c} = \frac{75\,k^2}{1 + 1.5\,k.c.} + k$$

where c is the concentration in g/100 cm³ of solution and n_{rel} is the ratio of the viscosity of the solution to that of the pure solvent. The k values are reported as 1,000 times the calculated viscosity coefficient in order to avoid the use of decimals.

[72] *D. R. Pat. Anmeldung OZ-11,697.*

the polymer sticking to the kettle walls becomes insoluble as a consequence of overheating, thus strongly impairing the filterability of the aqueous solutions. Finally, the *k* values attainable in block polymerization are low.

In spite of all this, "Periston" is still being manufactured by this process because its low viscosity is desirable for this application as a blood substitute.

In order to remove the toxic monomeric vinyl pyrrolidone, the powdered polymer is extracted with ether before being dissolved in water and filtered.

Addition of 3 per cent of water tempers the initial reaction and yields polymers of lighter color and better filterability.

Solution Polymerization[73]. In the long run, block polymerization would not be satisfactory for commercial production, and polymerization in aqueous solution was therefore developed.

It was observed that polyvinylpyrrolidone, like pyrrolidone itself, has the tendency to form hydrates. Physical investigations (heat of reaction, infrared absorption) indicate that one mole of vinyl pyrrolidone combines with one mole of water. When the polymerization is conducted in an aqueous solution with hydrogen peroxide catalysts, the reaction mixture becomes more acid as the amount of hydrogen peroxide is increased. The acidic medium causes splitting off of acetaldehyde, which has an unfavorable influence on the polymerization and the polymer. It is therefore necessary to add alkaline buffers.

At this point it was observed that the addition of ammonia, or amines, or their salts have—apart from their buffering action—a strong activating effect on the polymerization. With the help of ammonia, or of amines and their salts, it became possible to shorten the latent period and to increase the polymerization speed to such an extent that polymerization could be carried out at lower temperatures and with smaller amounts of catalyst, thus giving polymers of high *k* values.

Definition of Polymerization Velocity. Polymerization velocity (PG) is defined as the number of kilograms of polymer formed per hour per cubic meter of solution. In the case of emulsion polymerization, the volume of solution is taken as that of the aqueous phase and not the volume of the whole emulsion.

The polymerization velocity is determined by plotting the amount of polymer formed in kilograms per cubic meter of solution as the ordinate against the time of polymerization as the abscissa, and drawing the tangent at the point where the straight-line portion ends and the curve bends toward the abscissa. The tangent of the angle formed by the intersection of this straight line with the abscissa gives the PG (see Figure II-2).

Definition of Induction Period. Induction period (LZ) is defined as

[73] *D. R. Pat. Anmeldung OZ-14,473.*

the time elapsed in minutes from the origin to the point of intersection of the tangent to the curve with the abscissa (see Figure II-2).

The percentages of the accelerator (hydrogen peroxide) and of the activator (ammonia) are based in the case of solution polymerization on the amount of monomer.

Unless otherwise stated, an initial pH of 8, was used and this was not allowed to fall below pH 7.

Effect of Ammonia and Amines. Table II-4 shows the effect of ammonia and a few amines in the presence of a small amount of hydrogen peroxide on the induction period (LZ), polymerization velocity (PG), and the k value.

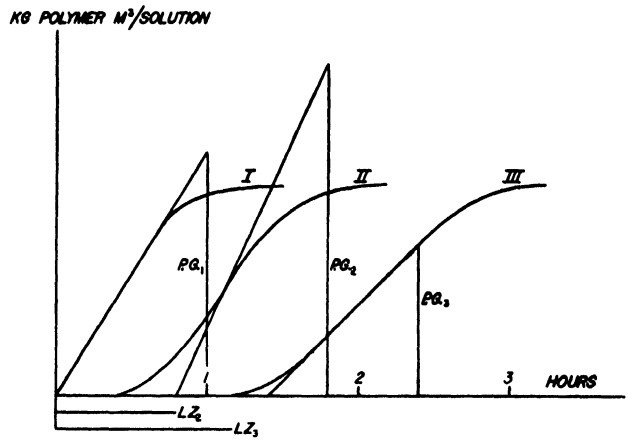


FIGURE II-2 Determination of induction period and polymerization velocity of vinyl pyrrolidone from concentration-time curves

The added amounts of amines are proportional to their molecular weights Consequently, ammonia is more active than the amines in its effect on both induction period (LZ) and polymerization velocity (PG) The type of amine added seems to have no essential influence on the k value. That the action of ammonia and the amines is a specific one becomes evident from the fact that polymerization had not started even after 4 hours when equivalent amounts of sodium hydroxide and sodium bicarbonate were added.

Effect of Percentage of Ammonia. The percentage of ammonia added has a great influence on the polymerization velocity (PG), but less on the induction period (LZ), as shown in Figure II-3 and Table II-5.

With the small amount of 100 per cent ammonia (0.04 per cent based on VP), 0.5 per cent of sodium bicarbonate had to be added later to maintain the neutrality.

Effect of pH. The pH also has an effect on the induction period and the polymerization velocity but none on the k value, as shown in Table II-6.

Effect of Temperature. The polymerization velocity (PG) is most critically dependent upon the polymerization temperature (see Figure II-4 and Table II-7).

The influence of the temperature on the k value is surprisingly small, namely, about 2 units per 10°C.

Table II-4. Dependence of LZ, PG, and k Value on the Type of Amine
(30% VP in water; 0.5% of 30% hydrogen peroxide; temperature 50°C)

Material Added	% Added	pH		LZ (min.)	PG	k Value
		Initial	Final			
None	—	7	Had not started even after 4 hours			
Ammonia (100%)	0 1	9	8	5	250	52
Monoethylamine	0.27	11	8	12	175	58
Triethylamine	0.6	11	7.5	30	175	43
Tetramethyl ammonium hydroxide	0.58	12	12	120	ca 100	58
Sodium hydroxide	0.23	12	Had not started even after 4 hours			
Sodium bicarbonate	0.5	7	Had not started even after 4 hours			

Table II-5. Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on the Percentage of Ammonia Added
(30% VP in water; 0.5% of 30% hydrogen peroxide; temperature 50°C)

Ammonia (100%) %	LZ (min)	PG	k Value
None	Does not start		—
0.04	180	200	63
0.1	5	250	53
0.4	0	500	56
1.6	0	850	62

Effect of Percentage of Hydrogen Peroxide. On the other hand, one can fix the k value by the percentage of hydrogen peroxide added, as shown in Figure II-5 and Table II-8.

By further reducing the hydrogen peroxide below 0.25 per cent, the k value can be increased to 90 or more. In this case, it is necessary to add the small percentage of hydrogen peroxide in portions; otherwise it is consumed before polymerization is complete (see Table II-9).

The curve for dependence of the k value on the percentage of hydrogen peroxide is so easily reproducible that the figure necessary for a certain k value can be taken directly from Figure II-6 or computed from the equation:

$$k = \frac{40}{c^{0.3}}$$

If the hydrogen peroxide is increased to more than 2 percent, the k value is even lower than calculated while the polymerization velocity

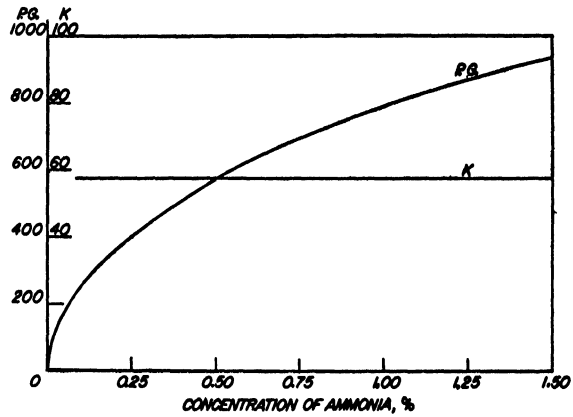


FIGURE II-3 The relation of polymerization velocity and k value to ammonia concentration during polymerization of vinyl pyrrolidone.

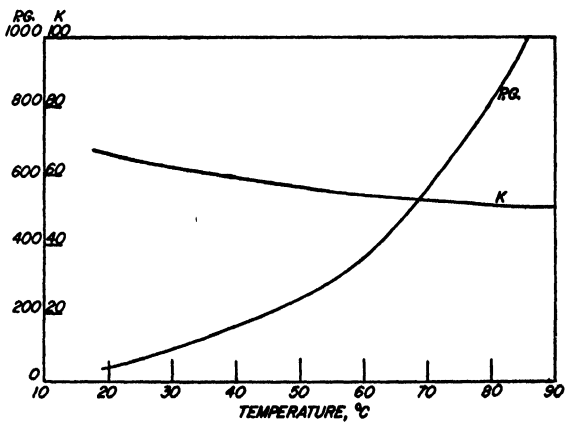


FIGURE II-4 The relation of polymerization velocity and k value to temperature during polymerization of vinyl pyrrolidone.

again decreases. With 5 per cent of hydrogen peroxide a k value of about 20 is obtained.

Effect of Concentration of Vinyl Pyrrolidone. The concentration of vinyl pyrrolidone in the original mixture also has an influence on the induction period, polymerization velocity, and k value. As Figure II-6 and Table II-10 show, at first the polymerization velocity increases strongly

with increasing concentration up to about 30 per cent vinyl pyrrolidone, as is customary for solution polymerization. It then remains constant to about 60 per cent vinyl pyrrolidone, but decreases sharply thereafter

Table II-6 Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on the pH of the Solution

(30% VP in water, 0.5% of 30% hydrogen peroxide; 0.1% of 100% ammonia, temperature 50°C)

Initial pH	LZ (min)	PG	k Value
6	60	45	56
9	5	250	55
10	0	210	55

Table II-7 Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on the Temperature

(30% VP in water, 0.5% of 30% hydrogen peroxide; 0.1% of 100% ammonia)

Temperature (°C)	LZ (min)	PG	k Value
30	40	100	63
50	5	250	56
70	2	530	54
90	0	1200	52

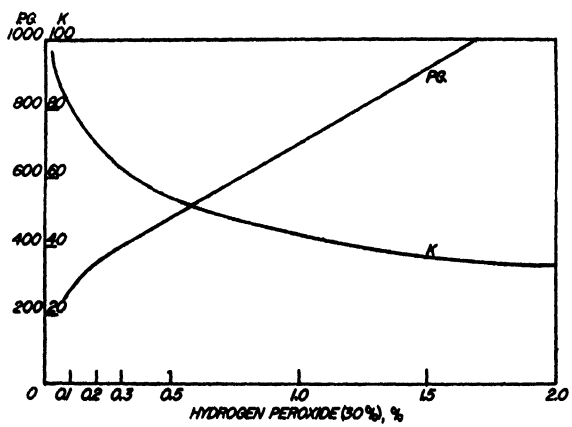


FIGURE II-5. The relation of polymerization velocity and k value to hydrogen peroxide concentration during polymerization of vinyl pyrrolidone.

The decrease in polymerization velocity with increase in concentration is attributed to a decreased tendency toward hydrate formation. With 100 per cent vinyl pyrrolidone, polymerization does not start at all, indi-

cating that water is very important for this process. The extent to which the k value is independent of the concentration is surprising; this is not ordinarily observed in solution polymerization.

Table II-8 Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on the Percentage of Hydrogen Peroxide
(30% VP in water, 0 3% of 100% ammonia; temperature 50°C)

Hydrogen Peroxide (30%) Based on VP	LZ (min)	PG	k Value
2 0	0	1100	33
1 5	0	800	38
1 0	0	700	45
0 5	0	400	56
0 25	10	350	65

Table II-9 Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on Very Small Percentages of Hydrogen Peroxide

Hydrogen Peroxide (30%) Based on VP	LZ (min)	PG	k Value
2 × 0 1	20	290	80
3 × 0 05	23	225	90
3 × 0 01	Does not start		—

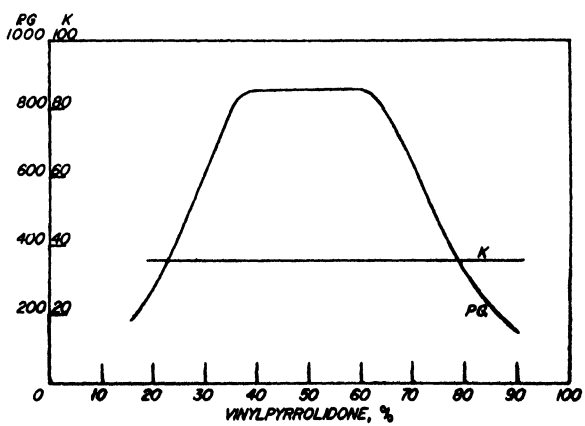


FIGURE II-6 The effect of vinyl pyrrolidone concentration during polymerization on the polymerization velocity and the k value

Effect of Rate of Addition of Monomer. It is possible to carry out the polymerization by progressively adding the monomer solution without changing the k value very much. This is technically of great advantage because the dissipation of heat of polymerization is difficult in highly

concentrated batches. The experimental data in Table II-11 show this relation.

The small increase of the k value from 30 to 38, for addition times from 0 to 120 minutes, is probably caused by the gradual decomposition of the hydrogen peroxide and the decrease of its concentration with prolonged addition time.

Table II-10 Dependence of Induction Period (LZ), Polymerization Velocity (PG), and k Value on the Concentration of Vinyl Pyrrolidone

(VP in water; 2% of 30% hydrogen peroxide; 0.4% of 100% ammonia; temperature 50°C)

VP %	LZ	PG	k Value
10	Does not start		—
20	0	250	34
40	0	850	39
50	0	850	35
60	0	850	35
80	10	350	35
90	10	150	—
100	Does not start		—

Table II-11. Dependence of k Value on the Rate of Addition of a 50% Solution of Vinyl Pyrrolidone in Water

(2.0% of 30% hydrogen peroxide; 0.4% of 100% ammonia; temperature 50°C)

Time of Addition (min.)	k Value
0 (everything added at start)	30
12	33
120	38

Effect of Oxygen. By excluding the molecular oxygen from the air—*i.e.*, by displacing it with nitrogen—a further shortening of the induction period and an increase in polymerization velocity, especially at lower temperatures, can be obtained. For example, 30 parts of vinyl pyrrolidone in 70 parts of water together with 0.5 per cent of 30 per cent hydrogen peroxide and 0.1 per cent of 100 per cent ammonia at 20°C does not polymerize in the presence of atmospheric oxygen. In a stream of nitrogen, on the other hand, polymerization starts at once and is practically finished within two hours. Without the addition of ammonia, no reaction takes place even when using the nitrogen. The k value of the product was determined as 56.

Commercial Production of Polyvinyl Pyrrolidones ("Kollidons")

Commercial N-vinyl pyrrolidone may contain up to 2 per cent of oily impurities which are insoluble in water; in small quantities these impurities often cause turbidity when diluted with water during the subsequent polymerization. In accordance with the preceding investigation, the commercial production of the "Kollidons" is carried out at present in 400-liter batches; the 30 to 60 per cent monomer solution is either added at the start or gradually during the polymerization.

The product is dried by spraying in a Nubilosa dryer. The drying of solutions of higher viscosity is difficult. "Kollidon F33" ($k = 33$) is polymerized in a 30 per cent solution because the product can still be dried in this concentration. In order to dry the high viscosity solutions of the higher polymeric "Kollidons" (up to k values of 100), or the more concentrated solutions, drum drying is contemplated.

Properties of Polyvinyl Pyrrolidones

Pure polyvinyl pyrrolidones, polymerized by light as a catalyst, are glass-clear masses. Exposed to air, they gradually absorb water and form highly viscous solutions in water. The E.P. (softening point) is over 100°C. In contrast to the high polymer produced by light polymerization, the block polymer is more or less discolored yellow to brown and of low viscosity. By solution polymerization, colorless products from $k = 20$ to $k = 100$ can be made.

Solubility. The polyvinyl pyrrolidones give clear solutions in water; viscosity depends on their k value Highly concentrated warm solutions of alkalies and sodium chloride will salt them out, but they cannot be precipitated by strong acids. The aqueous solutions are completely neutral and very resistant to saponifying agents. However, when boiled with concentrated alkali, they form an insoluble product.

The "Kollidons" are soluble and compatible with water and organic solvents. They dissolve easily in alcohols, ketones, tetrahydrofurane, chlorinated hydrocarbons, pyridine and lactones. They swell in esters and aromatic hydrocarbons and are insoluble in ether and aliphatic hydrocarbons. The addition of ligroin to monomeric vinyl pyrrolidone gives a turbidity or precipitate if the monomer has started to polymerize in storage. The monomeric vinyl pyrrolidone is miscible with all organic solvents.

Non-miscibility of Vinyl Pyrrolidone in Ternary Systems. In order to extract the remaining monomeric vinyl pyrrolidone from aqueous solutions of the solution polymer, its non-miscibility in some ternary systems was investigated. Figures II-7, 8, 9 show the systems:

vinyl pyrrolidone/ethyl ether/water
vinyl pyrrolidone/ethyl acetate/water
vinyl pyrrolidone/methylene chloride/water

The positions of the tie lines and the distribution curves (see Figure II-10) indicate that methylene chloride is the best solvent for removing monomer from polymer solutions.

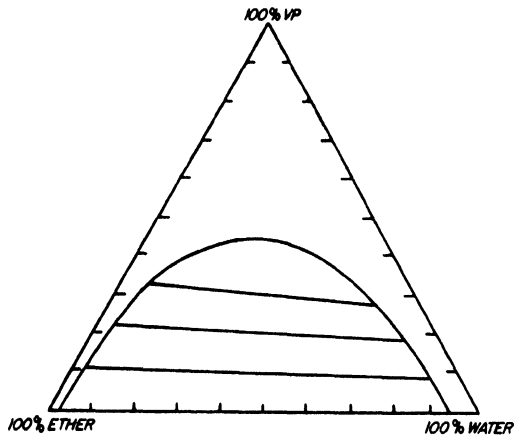


FIGURE II-7 Ternary diagram for the system vinyl pyrrolidone-ethyl ether-water at 25° C

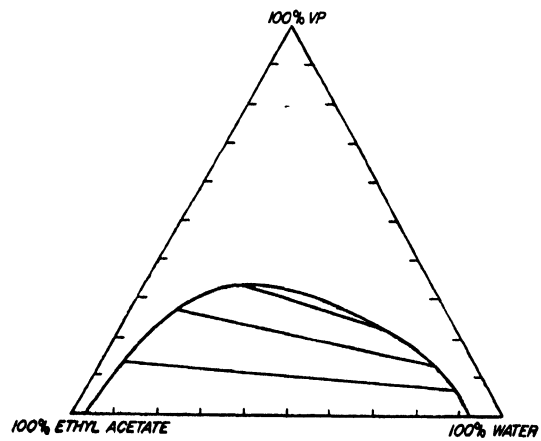


FIGURE II-8 Ternary diagram for the system vinyl pyrrolidone-ethyl acetate-water at 25° C

With low concentrations of vinyl pyrrolidone, the solubility of vinyl pyrrolidone in methylene chloride is ten times that in water.

While in the system methylene chloride/water, the monomeric vinyl pyrrolidone for the most part passes over into the methylene chloride, it is

surprising that the circumstances in the polymer solution are reversed In the presence of water, polyvinyl pyrrolidone is sparingly soluble in

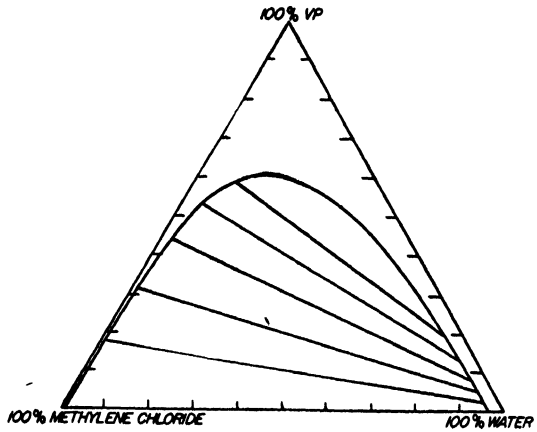


FIGURE II-9. Ternary diagram for the system vinyl pyrrolidone-methylene chloride-water at 25° C

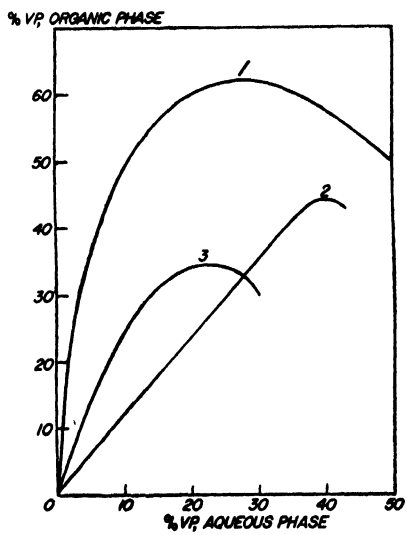


FIGURE II-10. The distribution of vinyl pyrrolidone between water and organic solvents at 25°C.

Curve 1—Methylene chloride
Curve 2—Ether
Curve 3—Ethyl acetate

methylene chloride or, in general, in organic solvents not miscible with water, whereas it dissolves easily in these solvents in the absence of water. Therefore, it is possible even in production to extract monomeric vinyl

pyrrolidone from aqueous solutions of polyvinyl pyrrolidone with methylene chloride.

If water and solvents miscible with water are used at the same time, non-miscibility occurs at certain concentrations, *i.e*, the solutions separate into two liquid phases.

Non-miscibility of Polyvinyl Pyrrolidones in Acetone/Water. This non-miscibility has been studied thoroughly for the system polyvinyl pyrrolidone/acetone/water (see Figure II-11).

Non-miscibility was determined by adding to several concentrated solutions of "Kollidon" in acetone (left side of the isosceles triangle) and in water (right side of the triangle) increasing amounts of water and acetone, respectively, until turbidity occurred.

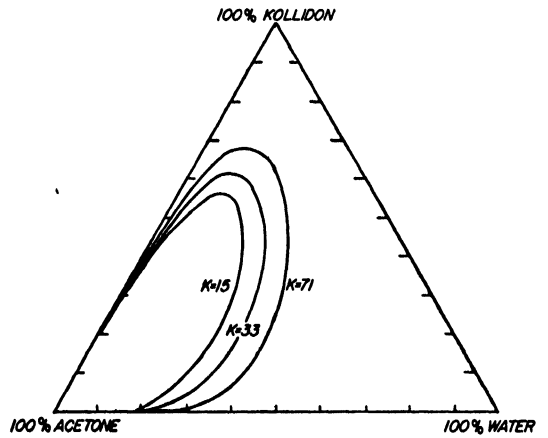


FIGURE II-11. Ternary diagram for the system "Kollidon"-acetone-water at 25°C for "Kollidons" of various k values

In Figure II-11 it is evident that very small additions of water to a solution of "Kollidon" in acetone quickly causes the separation into two phases, probably because a hydrate is formed which is insoluble in acetone.

Abnormal Position of the Conjugated Points of Polymerically Non-homogenous "Kollidons". If one tries, through direct mixing of the three components in a proportion that corresponds, for example, to points A, B, or C within the non-miscible area, to determine the conjugation line (Fig. II-12) by analyzing the composition of the two phases, the conjugated points A_1, A_2, B_1, B_2 or C_1, C_2 are not—as first expected—on the boundary line of non-miscibility, but outside or inside this line.

Also the corresponding points A_1-A-A_2, B_1-B-B_2, or C_1-C-C_2 are not situated on a straight line, as is usually the case in non-miscibility. For "Kollidons" of different k values, the non-miscibility becomes greater with increasing k value (Figure II-12). In this case, the extent of non-mis-

cibility seems to be independent of the degree of molecular homogeneity of the polymer. Even two products with a k value of 15, one of which was obtained by direct polymerization, and the second by mixing 5 parts of "Kollidon" of k value 33 with 21 parts of monomeric vinyl pyrrolidone, give duplicate non-miscibility regions within the limits of error.

Dependence of Non-miscibility on the *k* Value. The abnormal positions of the conjugated points can be explained from the three-dimensional representation of non-miscibility as related to the k value (Figure II-12). Polymerization always produces to a greater or lesser degree mixtures of polymers with varying k values, and the two phases therefore contain "Kollidons" of different mean k values. Therefore, the conjugated points,

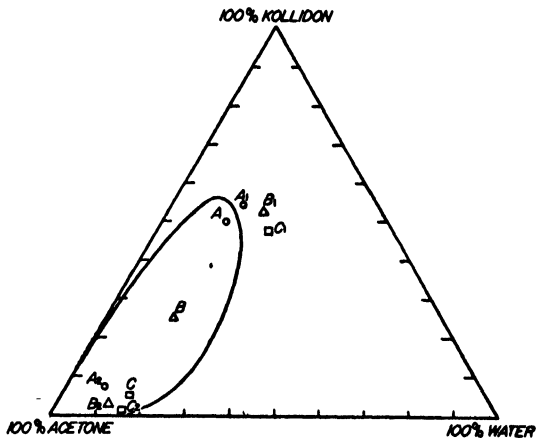


FIGURE II-12 Ternary diagram for the system "Kollidon" (k value 15)-acetone-water at 25°C, showing conjugated points.

according to the degree of non-homogeneity, are situated more or less above or below the surface representing non-miscibility. The connecting lines of the three points, which in normal non-miscibility in ternary systems would be situated on straight lines, are in this case probably three-dimensional irregular curves.

Fractionation of the "Kollidons." This is an explanation for the possibility of precipitating the "Kollidons" from aqueous solutions with acetone into fractions of varying k values, which was first pointed out by Dr. Hecht of Elberfeld. With an exact knowledge of the non-miscibility, one can fix the optimum conditions for fractionation. In order to separate by fractionation, for example, the low-viscosity component from "Kollidon F33," it is necessary to start with a relatively concentrated, aqueous "Kollidon" solution (about 30 per cent) and mix this solution with an equally concentrated solution of "Kollidon" in acetone in the proportion of 1:3.

Because the position of non-miscibility varies with the k value (Figure

II-13), it is possible, especially in the range of low k values, to determine the k values by titration of aqueous solutions with acetone.

Summary. The polyvinyl pyrrolidones represent a completely new type of polymerization product, soluble in both water and organic solvents.

They can be commercially produced without any difficulty in aqueous solutions in viscosity grades ranging in k value from 5 to 100. The addition of ammonia strongly activates the polymerization reaction.

The exact investigation of the reaction conditions in the polymerization process (induction period and polymerization velocity) and the properties

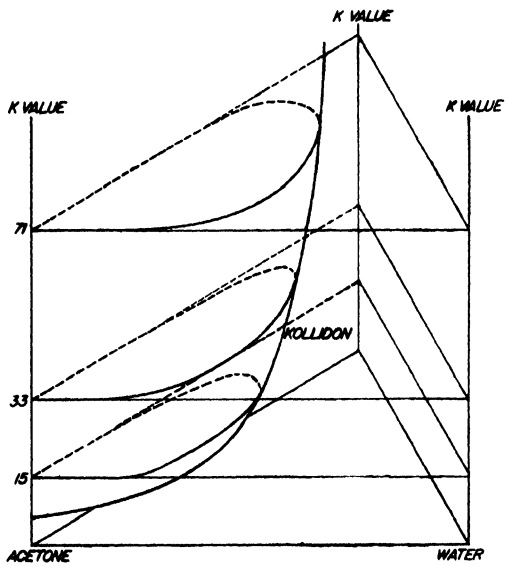


FIGURE II–13. The system "Kollidon"-acetone-water at 25° C in relation to the k value

of the polymers (k value) resulted in many surprises which can probably be explained on the basis of hydrate formation by the monomeric as well as the polymeric vinyl pyrrolidone. In this category belong the rapidly increasing and equally rapid decreasing polymerization velocity with increasing vinyl pyrrolidone concentration in the original mixture, having little influence on the k value; the strong acceleration of the polymerization velocity through increased amounts of ammonia; the decisive influence of the added amount of hydrogen peroxide on the k value; and the relatively minor influence of temperature on the k value.

The investigation of non-miscibility in ternary systems revealed for the first time the correlation between the extent of non-miscibility and the k value. This presents a possible means for the separation of non-homogeneous polymers into fractions with high and low k values and the deter-

mination of their absolute values. The conjugated points of such polymers are not situated, as might be expected, on the non-miscibility curve but above or below this curve on the surface of the non-miscibility space which corresponds to the whole k value range.

Applications of Polyvinyl Pyrrolidone

The polyvinyl pyrrolidones may be used for various purposes which depend in large part on their degree of polymerization as indicated by their k value. They are of interest as gums and glues, raw materials for adhesives, substitutes for animal glues, bonding agents in the film, reproduction, and coating industries, and as thickeners for emulsions, solutions, and for soaps and cosmetic preparations. They may be used as sizing agents for paper, fibers and fabrics, and are reported to bring out a deeper color tone, particularly in combination with basic dyes. Polyvinyl pyrrolidone films can be rendered water-insoluble by reaction with diisocyanates

A unique and important application for the low-viscosity polyvinyl pyrrolidone (k value 30, mol. wt. approx. 40,000) was as a blood plasma substitute, where it was called "Periston."[74] To prepare the "Periston" solution, polyvinyl pyrrolidone was dissolved in water to give a 20 per cent solution, filtered and sterilized at 120°C. The manufacturing formula is as follows:

NaCl	800 g	N/1 HCL (1710 cc)	1728 8 g
KCl	42 g	$NaHCO_3$	168.0 g
$CaCl_2 \cdot 6H_2O$	50 g	Kollidon (20 per cent soln.)	12,500 cc
$MgCl_2$ $6H_2O$	0 5 g	Water (distilled)	101.3 kg

The solution prepared from the above recipe is filtered and sterilized in 100, 250 and 500-cc ampoules at 105°C for one hour. The ampoules are stored at 30 to 35°C for three weeks to permit detection of any separation of material from solution.

Reppe states that "Periston" has proved of value in all cases in which transfusion of blood was not possible, particularly in actual combat where the lives of many thousands of soldiers of "all" nations have been saved by the use of this chemical. "Periston" is superior to preserved blood by virtue of its independence of blood groups and because its stability permits indefinite storage without refrigeration.

"Periston" is used as a blood plasma substitute to replace loss of blood in the following cases:

(1) Acute loss of blood (lesions, operations, childbirth, etc.)

(2) Shock due to trauma, operations or narcosis.

[74] *PB* 67620.

(3) Thickening of the blood resulting from increased loss of liquid due to diarrhea, vomiting or protoplasmic collapse.

"Periston," which can only be used intravenously, has no toxic effects, and may be used simultaneously with other water-soluble pharmaceuticals. In the 100,000 to 200,000 cases where "Periston" was used by the military, only one case of "drug fever" was reported; this of course could have been due to some other cause. When it is administered in cases of shock caused by hemorrhage, capillary permeability is reduced, the pressure and viscosity of the blood increased, the water content raised and the erythrocyte and hemoglobin content lowered by dilution as is the fibrin, albumen and globulin content. The preparation remains in the circulation in significant quantity for 2 or 3 days, but thereafter cannot be found in the urine. However, not more than 50 per cent can be accounted for by urinary excretion. It is believed that in the body "Periston" is broken down into amino acids.

To combat shock in adults 500 to 1000 cc is used, although as much as 2000 cc has been used. Infants do not tolerate "Periston" as well as older patients; recommended dosages are 25 cc/kg of body weight. Two or three cases of hematuria have been observed in the thousands of babies treated; however, the urine cleared promptly and there were no signs of permanent injury. Although Reppe claims that "Periston" has no deleterious effects on humans, German Army pathologists have called attention to certain cases of liver and kidney damage.

Kleiderer, Rice and Conquest[75], members of an American team investigating German pharmaceutical activities comment as follows on "Periston":

"(1) The claim that 'Periston' is equal or superior to blood plasma is probably unfounded. However, it does appear to be superior to gum acacia and simple saline.

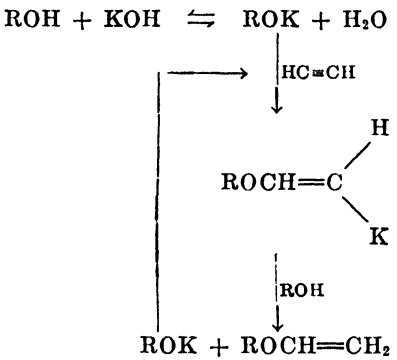
"(2) No comparisons have been made with degraded gelatin. This should be done and if 'Periston' is superior to gelatin, there is probably a place for it in therapeutics."

Reppe in his manuscript states that unfortunately the work on possible applications of polyvinyl pyrrolidone was interrupted in the early stages by the war developments. However, he expressed interest in attempting to trace the decomposition of polyvinyl pyrrolidone in the body using the heavy nitrogen isotope as the tracer element. Also, he mentions the possible use of polyvinyl pyrrolidone in combination with insulin and the use of very high polymers (k values of 100) in the treatment of lung diseases. It is not clear whether these statements are conjectures, or whether they have some basis in fact.

[75] *PB* 248.

Mechanism of the Vinylation Reaction

Reppe postulates that in vinylation the first reaction is formation of a metal alcoholate from the alcohol and the alkali hydroxide. Acetylene then acts on the alcoholate, placing itself between the oxygen and the metal to form the metal salt of the vinyl ether; upon reaction with alcohol this gives the vinyl ether and the alcoholate, which may then undergo a similar reaction with acetylene.



Such a mechanism explains the catalytic effect of the alkali.

Reppe considers that this reaction is analogous to that of carbon monoxide with methanol in the presence of catalytic proportions of alcoholate:

$$CH_3OH + CO \xrightarrow{NaOCH_3} HCOOCH_3$$

the carbon monoxide entering between the hydrogen and the oxygen of the hydroxyl group just as acetylene does in the vinylation reaction.

Hanford has suggested the following mechanism, which is based on the observed reaction of aqueous trimethylamine or trimethylamine acetate with acetylene to give trimethyl vinyl ammonium hydroxide or acetate respectively:[76]

$$(CH_3)_3N + H_2O \rightarrow [(CH_3)_3NH]^+OH^- \xrightarrow{HC\equiv CH} [(CH_3)_3N{-}CH{=}CH_2]^+OH^-$$

Since no catalyst is employed in the reaction and since secondary and tertiary amines are known catalysts for the vinylation of alkylated phenols, Hanford believes that Reppe has isolated an intermediate product in the vinylation of a tertiary amine. If this is so, then the mechanism for the vinylation of an alcohol is as follows:

$$KOH + ROH \rightleftharpoons ROK + H_2O$$
$$ROK \rightleftharpoons RO^- + K^+$$
$$RO^- + HC{\equiv}CH \rightleftharpoons ROCH{=}CH^-$$
$$ROCH{=}CH^- + ROH \rightarrow ROCH{=}CH_2 + RO^-$$

The same mechanism would hold for other vinylations.

[76] W. E. Hanford, Paper presented at 110th Meeting of American Chemical

General Summary of Vinylation Reactions

Consideration of the various reactions discussed in this chapter on vinylation shows that in all cases the vinylation involves:

(1) The addition of an active hydrogen attached to a hetero-atom such as oxygen, sulfur, or nitrogen to the triple bond of acetylene or a derivative thereof.

(2) The formation of a vinyl compound in which the vinyl group results from the triple bond of the acetylenic derivative and is joined in the adduct through a hetero-atom; in other words, no new carbon–carbon bonds are formed. For example:

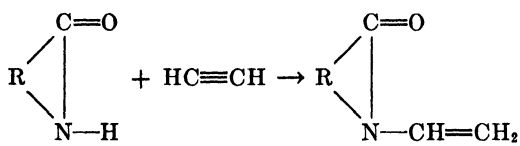
$$ROH + HC{\equiv}CH \rightarrow ROCH{=}CH_2$$

$$RSH + HC{\equiv}CH \rightarrow RSCH{=}CH_2$$

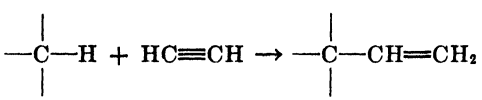
$$RCOOH + HC{\equiv}CH \rightarrow RC(=O)OCH{=}CH_2$$

$$R_2NH + HC{\equiv}CH \rightarrow R_2N{-}CH{=}CH_2$$

$$R_3N + H_2O + HC{\equiv}CH \rightarrow [R_3N{-}CH{=}CH_2]^+ OH^-$$



The question naturally arises: is it possible to vinylate a carbon atom carrying an active hydrogen with the formation of new carbon–carbon linkages, *viz.*



Examples of such a reaction immediately come to mind; the addition of acetylene to itself according to Nieuwland's technique to form vinyl acetylene, the polymerization of acetylene to cyclopolyolefins (see page 177) and the addition of hydrogen cyanide to acetylene to form acrylonitrile. The reaction catalysts in these reactions are, however, not typical vinylation catalysts and at present, "carbon vinylation" is not a general reaction like the vinylations discussed above. Apparently attempts had been made to vinylate unsaturated compounds containing acidic hydrogen atoms such as indene, fluorene and cyclopentadiene, in the presence of their potassium

compounds. Acetylene was actually absorbed at high temperatures. It is not clear whether small quantities of monomeric vinyl compounds were actually isolated and characterized; in any event, it is evident that polymerization under the reaction conditions necessarily imposed was a serious obstacle in the study of the reaction.

Similarly, experiments with phenyl sodium and similar metalloorganic compounds did not yield the expected result, the reaction with acetylene apparently forming sodium acetylide and regenerating the hydrocarbon. Likewise, alkali metal-hydrocarbon adducts such as disodium naphthalene did not react to give carbon vinylation.

Compounds having active methylene character such as acetoacetic ester, benzoylacetic acid ester, malonic ester, etc., readily take up acetylene. However, this does not necessarily represent carbon vinylation as it is possible in such known keto-enol tautomeric compounds that the vinylation first takes place on the oxygen of the enol form.

The vinylation of organic compounds containing an active hydrogen jointed to a hetero-atom such as oxygen, nitrogen or sulfur by addition to acetylene, with or without pressure, in the presence of basic catalysts is of broad general scope. Allylic type alcohols cannot, however, be successfully vinylated. The vinylation technique is standardized, only minor variations in experimental conditions such as temperature, pressure, kind and amount of catalyst, solvent or diluent, etc., being necessary.

The outstanding feature of the vinylation technique is the use of acetylene under pressure. This new method of handling acetylene under pressure makes available for the first time an unlimited number of vinyl compounds which are rich in energy, easily polymerizable and highly reactive.

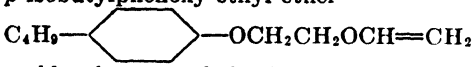
The great variety of reactive vinyl compounds which have been prepared by Reppe and his associates is evident from the following tabulation.

Appendix to Chapter II

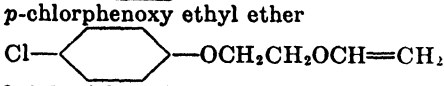
Vinylation Products of:

(1) *Alcohols* (a) *Aliphatic*	(°C)
Vinyl methyl ether	b.p. 66°
Vinyl ethyl ether	" 37°
Vinyl propyl ether	" 64°
Vinyl isopropyl ether	" 54°
Vinyl butyl ether	" 92°
Vinyl isobutyl ether	" 81°
Vinyl isoamyl ether	" 111°
Vinyl isohexyl ether	" 40–42°/14 mm
Vinyl isoheptyl ether	" 50–55°/14 mm
Vinyl octyl ether	" 67–70°/3 mm
Vinyl ethyl hexyl ether	" 74–76°/12 mm
Vinyl decyl ether	" 120–125°/12 mm

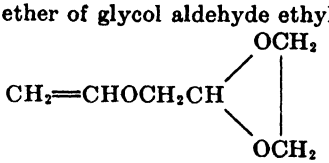
Vinyl dodecyl ether	"	130–135°/4 mm
Vinyl tetradecyl ether	"	140–145°/2 mm
Vinyl cetyl ether	"	160°/2 mm
Vinyl octodecyl ether	"	175°/2 mm
Vinyl ether of Montan alcohols	"	200–300°/2 mm
Vinyl oleyl ether	"	170–180°/6 mm
Vinyl ether of octadecandiol	"	203–205°/2 mm
Mono vinyl ether of ethylene glycol	"	135–140°
Divinyl ether of ethylene glycol	"	124°
Monovinyl ether of diethylene glycol	"	108°/12 mm
Divinyl ether of diethylene glycol	"	85°/12 mm
Vinyl ether of 1,3-butylene glycol	"	160–165°
Vinyl ether of ethylene glycol ethyl ether	"	127°
Vinyl ether of diethylene glycol ethyl ether	"	90–92°/16 mm
Divinyl ether of triethylene glycol	"	90–96°/1, 2 mm
Vinyl ether of triethylene glycol ethyl ether	"	100–125°/10
Vinyl ether of methyl glycol	"	108–109°
Vinyl ether of methyl diglycol	"	78–80°/18 mm
Divinyl ether of butandiol-1,4	"	52–69°/0, 6–1, 5 mm
Vinyl ether from butol ether	"	130–138°
Vinyl phenoxy ethyl ether $CH_2{=}CHOCH_2CH_2OC_6H_5$	"	122°/16 mm
Vinyl-*p*-cresoxy ethyl ether	"	133°/16 mm
Vinylxylenoxy ethyl ether	"	126–127°/10 mm
Vinyl ether of methoxybutanol	"	137–142°
Vinyl *p*-isobutylphenoxy ethyl ether	"	126–127°/10 mm



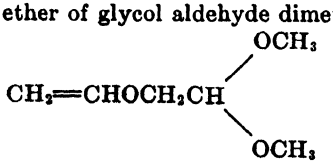
Vinyl *p*-chlorphenoxy ethyl ether



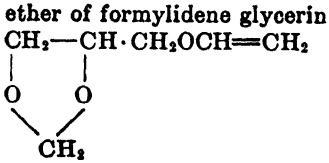
Vinyl-2,4,6-trichlorphenoxy ethyl ether
Vinyl-2,4-dichlorphenoxy ethyl ether
Vinyl 2-chlorphenoxy ethyl ether
Vinyl ether of glycol aldehyde ethylidene acetal



Vinyl ether of glycol aldehyde dimethyl acetal



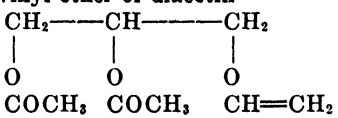
Vinyl ether of formylidene glycerin " 53°/10 mm



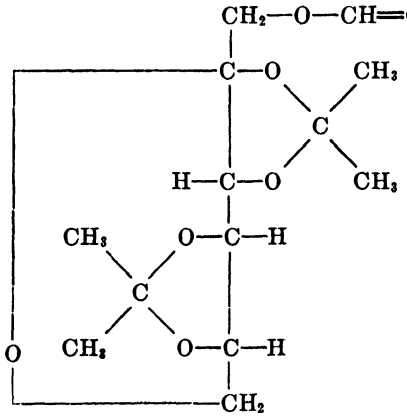
Vinyl ether of glycerin ethylidenacetal — " 56°/9 mm
Vinyl ether of benzylidene glycerin — " 120°/2 mm
Vinyl ether of isopropilidene glycerin — " 57°/10 mm
Vinyl ether of cyclohexylidene glycerin
Trivinyl ether of trihydroxyethyl glycerin — " 100–120°/0.6 mm
Trivinyl ether of tetrahydroxyethyl pentaerythritol — " 100–120°/0.6 mm
Trivinyl ether of trihydroxy ethyl trimethylol propane
Trivinyl ether of trihydroxy ethyl hexantriol-2,4,6
Vinyl ether of glycol acetate — " 39.5–41.5°/0.2 mm

$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}O{-}OC{-}CH_3$

Monovinyl ether of diacetin — " 72–80°/0.15 mm



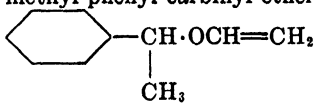
1-Vinyl-2,3,4,5-diacetonfructose — " 112–115°/1.5 mm, m p. 43–45°



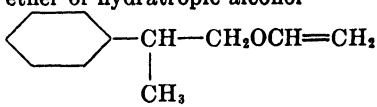
Mixture of 1-vinyl-2,3,4,5-diacetonfructose and 3-vinyldiacetonglucose — b p. 134–135°/1 mm

(b) *Cycloaliphatic*

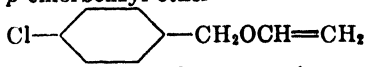
Vinyl benzyl ether — " 147°
Vinyl abietinol — " 178–184°/2 mm
Vinyl methyl phenyl carbinyl ether — " 65–66°/9 mm



Vinyl ether of hydratropic alcohol

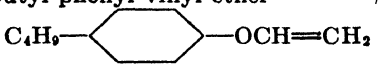
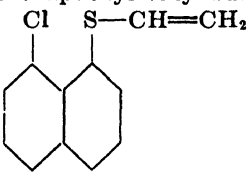
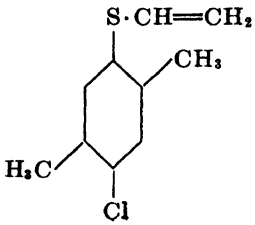


Vinyl-*p*-chlorbenzyl ether — " 99–102°/10 mm

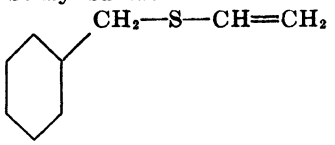


Vinyl ether of 1-phenyl-3-propanol — m.p. 224°

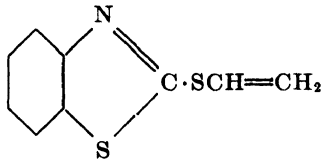
(2) *Phenols, Naphthols, etc.*

Vinyl phenyl ether $C_6H_5OCH{=}CH_2$	b.p. 54–55°/17 mm
Vinyl-*m*-cresyl ether	" 72°/16 mm
Vinyl-*p*-cresyl ether	" 74–76°/17 mm
p-Isobutyl phenyl vinyl ether 	
p-Isohexyl phenyl vinyl ether	" 91–93°/1 mm
Vinyl ether of tetralol	" 143°/18 mm
Vinyl-alpha-naphthyl ether	" 152°/16 mm
Vinyl ether of borneol	" 100–103°/12 mm
Vinyl ether of isoborneol	" 75–78°/2 mm
Vinyl ether of terpineol	" 78–80°/2 mm
Vinyl ether of amyl salicylate	" 150–160°/12 mm
Vinyl ether of methyl salicylate	" 105–112°/4 mm
Octyl phenyl vinyl ether	" 107–110°/2 mm
Dodecyl phenyl vinyl ether	
Octodecyl phenyl vinyl ether	" 70°/2 mm
2,4,6-Trichlorophenyl vinyl ether	
(3) *Mercaptans*	
Vinyl ethyl sulfide $C_2H_5{\cdot}S{\cdot}CH{=}CH_2$	" 91°/760 mm
Thiodiglycol vinyl ether	" 110–150°/12 mm
Dodecyl vinyl sulfide $C_{12}H_{25}{\cdot}S{\cdot}CH{=}CH_2$	" 128–130°/3 mm
Octodecyl vinyl sulfide $C_{18}H_{37}{\cdot}S{\cdot}CH{=}CH_2$	" 183–185°/2 mm
Palmcern vinyl sulfide	" 120–173°/2 mm
Vinyl phenyl sulfide $C_6H_5{\cdot}S{\cdot}CH{=}CH_2$	" 76–78°/4 mm
p-Tolyl vinyl sulfide $CH_3C_6H_4{-}S{-}CH{-}CH_2$	" 98–110°/14 mm
o-Tolyl vinyl sulfide	
8-Chloronaphthyl vinyl sulfide 	" 148–150°/0.6 mm
Vinyl-alpha-naphthyl sulfide	" 124-126°/0 6 mm
Vinyl-2,5-dimethyl-4-chlorophenyl sulfide 	" 110-112°/4 mm

Vinyl benzyl sulfide " 73°/3 mm



Vinyl-2-mercaptobenzothiazyl sulfide " 135–140°/2 mm



Vinyl butyl glycollate sulfide " 93–96°/1.5 mm

(4) *Alkanol Amines*

Monoethanol amine " 42% 50°
35% 50–115°/14 mm
23% 115–130°

Diethanol amine " 50% 100°
50% 110–135°/5 mm

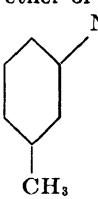
Triethanol amine " 75–155°/12 mm

Butanol-1-amine-4 " 50–60°/3 mm

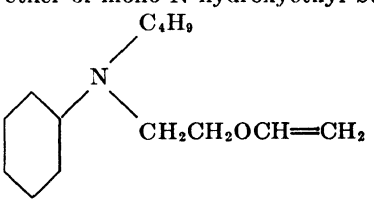
Vinyl ether of mono-N-hydroxyethylaniline " 128–132°/9–10 mm

$C_6H_5NH\ CH_2CH_2OCH{=}CH_2$

Vinyl ether of mono-N-hydroxyethyl-*m*-toluidine " 142–146°/11–12 mm



Vinyl ether of mono-N-hydroxyethyl-butylaniline " 146–153°/9–10 mm

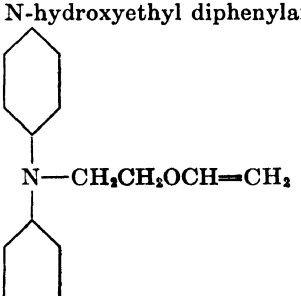


Divinyl ether of di-N-hydroxyethyl-*m*-chloraniline " 198–201°/12 mm

Vinyl ether of N-hydroxyethyl butylcresidine " 164–169°/10 mm

Vinyl ether of N-hydroxyethyl-*p*-cresidine " 160–163°/11 mm

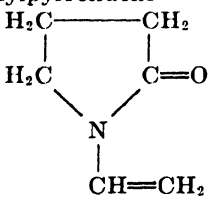
Vinyl N-hydroxyethyl diphenylamine " 150–160°/3 mm



Vinyl dimethylaminoethyl ether	" 50°/16 mm
Vinyl diethylaminoethyl ether	" 51–55°/15 mm
Vinyl ether of N-hydroxyethylpyrrolidine	" 70–90°/16 mm
Vinyl 5-diethylamino isopentyl ether	" 106–115°/24 mm
Divinyl ether of N,N-dihydroxyethyl aniline	" 104–150°/2 mm

(5) *Amines*

Vinyl carbazole	m p 64°
	b.p. 170–180°/15 mm
Isopropyl vinyl carbazole	" 145–155°/0 2 mm
Vinyl diphenylamine	m p 52°
Vinyl *p*-acetoxydiphenylamine	b p. 115–158°/8 mm
Vinyl phenyl-alpha-naphthylamine	m p. 80–83°
Vinyl-*p*-tolyl-alpha-naphthylamine	" 72–78°
Vinyl methyl-alpha-naphthylamine	b p. 116–120°/1 mm
Vinyl phenyl-beta-naphthylamine	m.p 79–82°
Vinylindole	b.p. 70–72°/1–2 mm
Vinyl-2-methylindole	" 105°/2 mm
N-Vinylpyrrolidone	" 100–102°/16–17 mm



(6) *Carboxylic Acids*

Vinyl valerate	b.p. 130–140°
Vinyl capronate	" 50–60°/10 mm
Vinyl caprylate	" 90–100°/12 mm
Vinyl laurate	" 110–125°/5 mm
Vinyl myristate	" 140–150°/3 mm
Vinyl palmitate	" 165°/2 mm
Vinyl stearate	" 178°/2 mm
Vinyl oleate	" 175°/2 mm
Vinyl linoleate	" 160–170°/3 mm
Vinyl phenylacetate	" 88–90°/4 mm
Vinyl-2-ethyl caprylate	" 128–130°/20 mm
Vinyl-alpha-naphthoate	" 145–155°/5 mm
Vinyl-beta-naphthoate	" 153°/4 mm
Vinyl cinnamate	" 153°/4 mm
Vinyl benzoate	" 72–74°/3 mm
Vinyl ethyl phthalate	" 173°/3 mm
Vinyl acetyl salicylate	" 145–150°/3 mm
Vinyl abietate	" 194–200°/2 mm
Vinyl naphthionate	" 176–183°/2 mm
Vinyl ester of paraffin fatty acids (C_6–C_7)	" 50–85°/12 mm
Vinyl ester of paraffin fatty acids (C_{11}–C_{18})	" 80–150°/1.5 mm

Chapter III

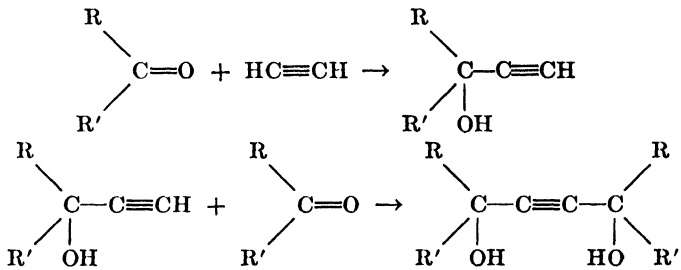
Ethinylation

Introduction

In 1937 Reppe extended his work on acetlene reactions to a fundamentally new type of reaction In contrast to vinylation, it is not an addition reaction involving the triple bond, but rather a reaction of the methine hydrogens of the acetylene. Reppe designated this type of reaction as "ethinylation," which he defined as a process in which acetylene or its derivatives, containing a free methine hydrogen in the presence of certain catalysts, reacts directly with the carbon atom of the reactant without loss of the triple bond. This may be done (1) by adding a methine hydrogen to the carbonyl group of an aldehyde or ketone, or to the double bond of a vinyl amine, (2) by eliminating water between the methine hydrogen and labile hydroxy groups of the other reactant.

Three types of ethinylation reactions were studied by Reppe:

(1) Reactions of aldehydes and ketones to give alkynols and alkyndiols:

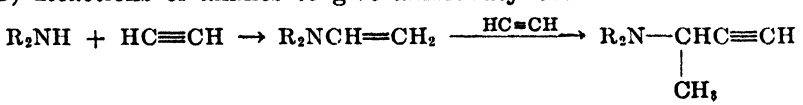


(2) Reactions of methylol amines to give propargyl amines (aminopropynes):

$$R_2NCH_2OH + HC{\equiv}CH \rightarrow R_2NCH_2C{\equiv}CH + H_2O$$
$$R_2NCH_2C{\equiv}CH + R_2NCH_2OH \rightarrow R_2NCH_2{-}C{\equiv}C{-}CH_2NR_2 + H_2O$$

If the acetylenic compound contains two or more methine hydrogens, ethinylation may take place so that one or more of the methine hydrogens are involved. Furthermore, if the other component is multi-functional, ethinylation may occur on a single or multiple basis.

(3) Reactions of amines to give aminobutynes:



As catalysts for these reactions, it was found that the metallic acetylides derived from the metals appearing in Group I of the periodic table, namely copper, silver, gold and mercury, were essential except in the ethinylation of ketones where hydroxyl ions were the only effective catalysts. For practical reasons, copper acetylide was usually the preferred catalyst. With acetylene itself high pressures were required for high yields, whereas little or no pressure was required with acetylene homologs, derivatives or substitution products

The reader at this point may well wonder how the ethinylation process using metallic acetylides as catalysts and acetylene under pressure was ever conceived and worked out. In Reppe's own words the development was as follows:

"Originally, it was my intention to synthesize propargyl alcohol and 1,4-butynediol by combining two cheap substances, formaldehyde and acetylene. Using copper compounds as catalysts, I worked under such conditions (addition of strong acids, etc.) that the formation of the highly dangerous copper acetylide was avoided. As happens with any chemist, university lecture demonstrations had left a strong impression on my memory, and I was continually aware of how highly explosive copper acetylide could be. The results of all my experiments were negative throughout. Acetylene was indeed absorbed, but only oily products smelling strongly of caramel were obtained from formaldehyde and acetylene.

"However, as it later turned out, the basic premise was erroneous, and consequently all experimental variations tested over three-quarters of a year of continuous daily work failed to yield either propargyl alcohol or butynediol. During this time, however, I began to realize the importance of copper acetylide as a catalyst. By the addition of supposed accelerators such as aldehydes and amines, I discovered the reaction of acetylene with methylol amines. Investigation of the catalytic agent indicated that copper acetylide had been formed from the original copper salt present. This observation led to the deliberate addition of copper acetylide as a catalyst, and to a thorough study of its properties and behavior. I very soon learned that only by observing certain precautions which permitted the copper acetylide to form and remain stable did the reaction of acetylene with aldehydes and amines take place and proceed smoothly. The result of this work was the discovery of the generally applicable 'ethinylation reaction'."

The use of copper acetylide as a catalyst and acetylene under pressure must appear very surprising and extremely dangerous, particularly to an acetylene specialist. Acetylene under pressure was considered by every chemist as a dangerous chemical; it seemed absurd that anyone should use copper acetylide as a catalyst, since the work of Stethbacker had shown that copper acetylide could be used as a primer for explosives. Naturally,

everyone assumed that the combination of the two must inevitably explode. Reppe admits that he was, of course, aware of this possibility in his early work. However, by the use of the most modern techniques available, including study of the catalyst structure by x-ray, oscillographic determination of the limits of explosion of acetylene under pressure in the presence of copper acetylide, and under the reaction conditions, and kinetic studies, it was found practical to carry out such reactions on the largest technical scale.

ETHINYLATION OF ALDEHYDES

Synthesis of Alkynols and Alkynediols

Propargyl alcohol, the simplest acetylenic alcohol (alkynol) was first prepared by Henry in 1872 by the dehydrohalogenation of 2-bromoallyl alcohol:[1]

$$CH_2{=}C(Br){-}CH_2OH \xrightarrow{\text{aq KOH}} HC{\equiv}C{-}CH_2OH$$

Some thirty years later Iotsitch discovered the first acetylenic glycol (alkynediol) when he reacted acetylenedimagnesium bromide with aldehydes and ketones:[2]

$$2\left(\begin{matrix} R^1 \\ \diagdown \\ C{=}O \\ \diagup \\ R^2 \end{matrix}\right) + BrMgC{\equiv}C{-}MgBr \rightarrow \begin{matrix} R^1 & & & & R^1 \\ \diagdown & & & & \diagup \\ & C{-}C{\equiv}C{-}C & & & \\ \diagup & | & & | & \diagdown \\ R^2 & OH & & HO & R^2 \end{matrix}$$

Since that time numerous papers have appeared describing other methods of synthesis, and investigations of the reactions of the acetylenic alcohols and glycols. (For a comprehensive review consult the excellent treatise of Johnson[3]) However, most of the available synthetic methods did not give too satisfactory yields, and the processes involved were generally not suited to large-scale production.

The work of Reppe on the reaction of acetylene with aldehydes in the presence of copper acetylide catalysts offered the first feasible method of synthesizing acetylenic alcohols and glycols on a commercial scale. For example, when acetylene under 5 to 15 atm pressure reacts with aqueous formaldehyde at about 90 to 100°C in the presence of a copper acetylide catalyst, butyne-2-diol-1,4 is formed in 92 per cent yield. At the same time, 5 to 6 per cent of propargyl alcohol is formed, and if desired, this can be recycled and converted ultimately to 1,4-butyne diol:[4]

[1] *Ber.*, **5**, 453, 569 (1872).

[2] *Bull. soc. chim.*, **30**, 210 (1903).

[3] Johnson, A. W., "The Chemistry of the Acetylenic Compounds," Vol. I, "The Acetylenic Alcohols", Edward Arnold & Co., 1946.

[4] *D. R. Pat. 725,326; 726,714; Fr. Pat. 841,501.*

$$HC{\equiv}CH + H_2C{=}O \rightarrow HC{\equiv}C{-}CH_2OH \xrightarrow{H_2C=O} HOCH_2C{\equiv}CCH_2OH$$

Other aldehydes, particularly of the aliphatic series, react readily under similar conditions. As the molecular weight increases, the tendency to form acetylenic glycol decreases. With acetaldehyde the final product consists of approximately 50 per cent butyne-3-ol-2 and 50 per cent hexyne-3-diol-2,5; with butyraldehyde, of approximately 80 per cent hexyne-5-ol-4 and 20 per cent decyne-5-diol-4,7.

The catalytic effect of heavy-metal acetylides on the methine hydrogen is not limited to acetylene alone, but is apparently general for many types of substituted acetylenes so long as there is an available acetylenic hydrogen. By starting with vinyl acetylene it is possible to obtain alcohols containing both a double and a triple bond:[5]

$$RCHO + H_2C{=}CHC{\equiv}CH \rightarrow H_2C{=}CHC{\equiv}C\underset{\displaystyle OH}{\underset{|}{C}}HR$$

Acetylenic alcohols containing a methine hydrogen may be reacted with an aldehyde differing from that used in the first step of the reaction so that the resultant glycol is unsymmetrical:[6]

$$RCHO + HC{\equiv}CH \rightarrow \underset{\displaystyle OH}{\underset{|}{R}}CHC{\equiv}CH \xrightarrow{R'CHO} \underset{\displaystyle OH}{\underset{|}{R}}CHC{\equiv}C\underset{\displaystyle OH}{\underset{|}{C}}HR'$$

In the second step, the heavy-metal acetylide derived from the acetylenic alcohol may serve as the catalyst [7]

Other derivatives of acetylene, such as the aminopropynes or aminobutynes, may also react with aldehydes. Simply refluxing an aqueous solution of formaldehyde with 3-dimethylaminopropyne-1 in the presence of cuprous hydroxide gave good yields of 4-dimethylaminobutyne-2-ol-1:

$$(CH_3)_2NCH_2C{\equiv}CH + H_2C{=}O \rightarrow (CH_3)_2NCH_2C{\equiv}CCH_2OH$$

The copper acetylide catalyst necessary for these ethinylations may be prepared from inorganic or organic copper salts. Cupric salts serve as well as cuprous salts, for in the presence of the added aldehyde they are reduced to the cuprous stage. Difficultly soluble salts, such as cupric sulfide, cupric phosphate, cuprous iodide, cuprous cyanide, and even metallic copper, slowly form copper acetylides under the conditions of the reaction. The catalyst may be prepared in a separate step and added to the reaction mixture, or it may be generated during the reaction.

The active catalyst is apparently not the hydrated cuprous acetylide, $Cu_2C_2 \cdot H_2O$, normally obtained by passing acetylene into aqueous solutions

[5] *D. R. Pat. 740,988.*
[6] *D. R. Pat. 728,466.*
[7] *D. R. Pat. 728,466.*

of curpous salts, but is rather the addition compound of the cuprous acetylide with one or several molecules of acetylene. Analytical investigations indicated that the cuprous acetylide hydrate, $Cu_2C_2 \cdot H_2O$, was rapidly changed to $Cu_2C_2 \cdot H_2O \cdot C_2H_2$; during the course of the reaction its formula varied from $Cu_2C_2 \cdot H_2O \cdot C_2H_2$ to $Cu_2C_2 \cdot H_2O \cdot C_5H_6$, $Cu_2C_2 \cdot H_2O \cdot C_{16}H_{19}$ up to $Cu_2C_2 \cdot H_2O \cdot C_{30}H_{40}$. The hydrogen content is therefore higher than would be expected on the basis of complex formation with acetylene molecules. This is, of course, in contrast to cuprene formation, where less hydrogen is present than is required for a polymer of acetylene ($C_{10}H_8$ instead of $C_{10}H_{10}$). However, it is known that cuprene is always formed to some extent in any acetylene reaction, and the interpretation of the above figures is not clear. It was claimed that in the continuous tower experiments at a later date, analysis of the catalyst indicated the formula to be $Cu_2C_2 \cdot H_2O \cdot C_6H_6$

It was demonstrated that copper acetylide and acetylene combine readily to give fairly stable addition compounds with the release of considerable heat These addition compounds decompose *in vacuo*, or when swept with nitrogen at 60 to 70°C, regenerating acetylene and copper acetylide. Furthermore, it was found that in the formation *in situ* of the copper acetylide catalyst by the reduction of copper salts on a catalyst support with formaldehyde followed by reaction with acetylene, three times the stoichiometric quantity of acetylene required to form $Cu_2C_2 \cdot H_2O$ was actually necessary.

On the basis of these observations, Reppe believed that the ethinylation with formaldehyde involved the following steps: the copper acetylide and acetylene first form an unstable addition compound which transfers the activated acetylene molecule to the formaldehyde, generating propargyl alcohol and copper acetylide. Acetylene again reacts with the copper acetylide, forming a new active catalyst which repeats the process. The propargyl alcohol, however, is activated by copper acetylide and adds an extra molecule of formaldehyde, thus producing butynediol.

After successfully developing the synthesis of alkynediols by a batch process, Reppe initiated work on the development of a continuous process, which was obviously necessary if the contemplated large-scale production was to be realized. Such a continuous process might be based on either a sump-phase process or on a trickling tower process. The sprinkling or trickling tower process was preferable if the following requirements could be met:

(1) Avoid formation of cuprene which would choke the towers after a short time.

(2) Fix the catalyst in such a way that it could not be rinsed off by the liquid stream.

(3) Activate the catalyst to such an extent that

(a) acetylene pressure could be substantially decreased, thus de-

(b) a high yield in a single pass could be obtained.

These conditions were eventually met and the trickling process was adopted for the large-scale production of alkynols and alkynediols.

However, it required systematic and tedious work, and consideration of the entire periodic system to find chemicals which were able to suppress the formation of cuprene when using copper acetylide catalysts. Iodine iodine compounds, and mercury proved to be most efficient. Other chemicals, such as bismuth, cerium, selenium and its oxides or salts, were considerably less efficient, but a certain activity was observed. The conclusion was reached—and proved analytically—that formation of cuprene is caused mainly by the presence of small quantities of metallic copper in the copper acetylide catalyst resulting from the reducing action of formaldehyde. The activity of metallic copper in forming cuprene from acetylene is well known from the literature.

The use of mercury was not desirable because of its unpleasant physiological properties. However, there were not enough iodine and iodine compounds in Germany; hence they were restricted to the use of bismuth compounds. The effect of chemicals like mercury and iodine or their compounds supposedly was due to amalgamation or reaction with the metallic copper However, the role of bismuth in decreasing cuprene formation is apparently a controversial issue among the chemists who actually worked on the problem; many believe that it has no real effect except perhaps to give a catalyst of superior mechanical properties. Variation of the reaction conditions (dilution of formaldehyde, lowering of reaction temperature) also decreased the formation of cuprene substantially, although at the expense of throughput and conversion per pass.

Experiments furthermore demonstrated that some metals, such as nickel cobalt, chromium, and especially iron, favored the formation of cuprene and were therefore not suitable for construction materials. It was for this reason, in addition to corrosion resistance, that in production all parts carrying liquids are lined or plated with superior alloy steel (V_2A, V_4A V_8A, $V_{17}A$ and others). The reactors or towers subjected to pressure are made of iron.

The other two desired qualities, namely a highly reactive and wear-resistant catalyst, were successfully developed. However, even the most active catalysts developed appear to be relatively inactive when compared to catalysts used in other chemical processes and require long contact times (0.33 to 3.5 hours) depending on the recycling system and the percentage of unchanged formaldehyde that can be tolerated in the reaction product.[8]

The Reppe Butadiene Process

Most of the butadiene produced in Germany was made by the aldol process, which involved the following four steps (see page 8):

[8] *Ind. Eng. Chem.*, **40**, 1176 (1948).

(1) Hydration of acetylene to acetaldehyde.
(2) Aldol condensation of acetaldehyde to aldol.
(3) Reduction of aldol to butylene glycol-1,3.
(4) Dehydration of butylene glycol-1,3 to butadiene.

$$2HC{\equiv}CH \rightarrow 2CH_3CHO \rightarrow CH_3CHOHCH_2CHO \xrightarrow{H_2}$$

$$CH_3CHOHCH_2CH_2OH$$
$$\downarrow$$
$$H_2C{=}CH{-}CH{=}CH_2 + 2H_2O$$

However, when Allied investigators first entered Germany they soon heard of another synthesis of this essential diene. This new synthesis, usually called the Reppe Process, involved the following steps:

(1) Formation of butynediol-1,4 by the reaction of acetylene and dilute formaldehyde solution in the presence of copper acetylide at 4 to 5 atm pressure and 100 to 120°C.

(2) Hydrogenation of butynediol-1,4 at 300 atm and 120°C over a nickel-copper catalyst, giving butanediol-1,4.

(3) Dehydration of butanediol-1,4 to butadiene, either directly or via tetrahydrofuran.

$$HC{\equiv}CH + 2CH_2O \rightarrow HOCH_2C{\equiv}C{-}CH_2OH \xrightarrow{2H_2} HOCH_2CH_2CH_2CH_2OH$$

$$H_2O + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \xrightarrow{-H_2O} H_2C{=}CHCH{=}CH_2 + 2H_2O$$

All stages of this synthesis gave good yields, and development of this method was apparently encouraged for several reasons:

(1) Butadiene via butynediol should be as cheap and possibly cheaper than by the old four-stage process, if laboratory results could be achieved in plant-scale operations.

(2) Only one-half as much acetylene is required as in the four-stage process, the other half of the carbon coming from formaldehyde which, of course, was readily available from water gas. Thus, it is claimed that the power requirements for producing carbide were halved.

(3) Butynediol was a versatile raw material from which many other valuable chemical intermediates such as tetrahydrofuran, adipic acid, adiponitrile, hexamethylene diamine, butyrolactone, etc. could be prepared.

The chemistry of each of these intermediate products was investigated in detail. Even today, after several hundred investigators have searched the files of the I. G. Farbenindustrie and interrogated all personnel available who had a part in this development, it is doubtful if all the ramifications of the chemical industry based on the ethinylation reaction have come to light. The many products developed run the gamut of usefulness from

such as sulfadiazine, "Atabrin" and "Plasmochin," and finally to a synthetic blood plasma substitute.

The industrial exploitation of the ethinylation reaction took place rapidly under the pressure of German economic needs, the translation of the first pilot plant data from a 300-ton per month pilot plant at Schkopau to a 2,500-ton per month plant at Ludwigshafen requiring only two years

During wartime difficulties caused by untrained personnel, war alerts and bomb damage, the yields obtained in the large-scale operations apparently never quite came up to expectations, and it is problematical whether the process ever produced butadiene at a price economically favorable in comparison with the old four-stage process. Regardless of the economic merits of the process for the synthesis of butadiene, it cannot be denied that the development of these novel processes, together with the tremendously fertile fields opened up by the readily available intermediates, was a most interesting and impressive achievement.

The whole story of the butynediol-butanediol-butadiene process has been covered in minutest detail by several investigators. To anyone interested in the technical and engineering details, the excellent reports of Monrad[9], Copeland and Youker[10], Appleyard and Gartshore[11], and Fuller, Weir and Zoss[12] are recommended.

The synthesis of these key intermediates as developed for the production of butadiene will be discussed in some detail in the following pages. Later the chemical reactions of the various intermediate products will be discussed in a separate chapter.

Manufacture of Butynediol. *Process.* Acetylene and aqueous formaldehyde diluted with recycle liquid to a maximum formaldehyde content of about 12 per cent are passed co-currently downward over a copper bismuth acetylide catalyst on granular silica gel at about 5 atm pressure and 90 to 110°C. The excess acetylene is separated and recycled, as is a part of the product stream, so that the butynediol concentration in the aqueous reaction product is about 30 to 33 per cent. The liquid product withdrawn from the product stream is distilled to remove methanol (present in formaldehyde feed), unreacted formaldehyde, and propargyl alcohol (as azeotrope with water). The formaldehyde and propargyl alcohol are recirculated to the reactor. The major reaction product is butynediol as shown by the following formulation:

$$HC{\equiv}CH + 2HCHO \rightarrow HOCH_2C{\equiv}CCH_2OH$$

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[9] *PB* 4604.
[10] *PB* 20078 (*FIAT* 720).
[11] *PB* 28556 (*BIOS* 367).
[12] *PB* 80334.

The reaction,

$$HC{\equiv}CH + CH_2O \rightarrow HC{\equiv}C{-}CH_2OH$$

leading to the formation of propargyl alcohol, is largely suppressed by the presence of excess formaldehyde and by recycling the aqueous propargyl alcohol distillate.

Converters. The reaction is carried out in a series of vertical steel towers of 1.5 m internal diameter and 18 m in height. These towers are built to withstand a maximum pressure of 100 atm. .The catalyst packing has a depth of 16.7 m and a volume of 24 m^3. Normally six such converters were used in sets of three pairs, but the plant had never been operated as designed and was still considered to be in the experimental stage.

Catalyst. Silica gel (3 to 8 mesh granules, irregularly shaped) in wire baskets was immersed in the impregnating solution containing copper nitrate and bismuth nitrate or citrate in the ratio of 4 parts copper to one part bismuth. After immersion for 20 minutes at room temperature, the basket is removed, the particles drained and then roasted for 15 to 20 minutes at 500°C. The nitrates are converted to the oxides; the roasting is controlled by observing the disappearance of the nitrate ion. The catalyst is now screened to remove fines. It contains approximately 3.2 to 5.5 per cent of bismuth and 11.5 to 12.7 per cent of copper. The dry catalyst is charged to the converters by a telescoping chute, so arranged that the fall of the catalyst is arrested at the lower end of the chute, which is always held at one meter above the upper surface of the catalyst bed as it rises. This procedure is regarded as essential to give a loose, even filling with minimum tendency to channel and minimum resistance to flow.

The catalyst is developed, *i.e.*, converted, to the active copper acetylide on silica gel by flooding the converter with dilute formaldehyde solution (4 to 8 per cent) at 60°C, which reduces the cupric oxide to cuprous oxide. Acetylene is then gradually introduced, starting with dilute acetylene-nitrogen mixtures (10 per cent acetylene). The temperature is held at 70°C. The cuprous oxide is converted to the copper acetylide, and then to the copper acetylide-acetylene addition complex. The acetylene concentration is then increased to 85 per cent, followed by the start of formaldehyde circulation. Over a 3 to 4-day period the whole plant is gradually adjusted and brought up to operating conditions.

A catalyst made in this manner has such high efficiency that it permits a substantial decrease in the required pressures when compared with the batch process in autoclaves. For example, butynediol-1,4 can be obtained from acetylene and formaldehyde with a satisfactory rate of reaction using only 5 atm pressure instead of 15 to 20. The copper acetylide adheres firmly to the siliceous carrier and cannot be rinsed off in practical use.

The useful life of the catalyst is extremely variable; at best it appears to be limited to 2 to 4 months. Cuprene is gradually deposited on the surface

of the catalyst; as it builds up the pressure drop gradually increases, then rises rapidly, and the reaction must be stopped and the catalyst discharged.

Feeds. The liquid feed per hour to the first reactor is made up as follows:

3.8 m^3 fresh formaldehyde (40 per cent solution containing 1 per cent methanol)

0.3 m^3 recycled formaldehyde-propargyl alcohol from distillation column

2.2 m^3 water

5.7 m^3 recycled butynediol solution from separator

The total feed is 12 m^3 containing 10 to 12 per cent of formaldehyde. Its pH is adjusted to 4.0 to 5.0 by neutralization of the formic acid with sodium bicarbonate. It is preheated to 60 to 70°C, distributed through a sparger ring, and then through ring packing over the cross section of the converter. As the liquid passes over the catalyst, it reacts exothermally (55 kcal/kg mole in vapor phase, 22 kcal/kg mole in liquid phase) with the acetylene; the temperature in the reactor is 90 to 110°C. The liquid containing about 30 per cent of butynediol and the gas pass to a separator at 90°C, then to a cold separator at 30°C. The two liquid streams from these separators are combined, pumped through a preheater and pass to the second converter operating at 100 to 120°C, which reduces the formaldehyde content from about 5 to 0 5 per cent. After passing to separators as before, about half of the liquid product is recycled, as is the disengaged gas from the various separators. The remainder of the product goes to the distillation system. The feed gas per hour to the first converter is made up of 800 m^3 of recycle gas and 420 m^3 of fresh acetylene This gives a gas containing 85 per cent of acetylene and 15 per cent of nitrogen and inerts. About 60 per cent is fed to the top of the converter, the remainder through side ports at various positions and in varying amounts to assist in the regulation of the temperature. Pressure in the system is from 5 to 5.5 atm

The second converter requires only 270 m^3/hr of fresh acetylene for make-up.

Workup of Product. The 30 to 33 per cent solution of butynediol from the hot separator (6 m^3/hr from 2 converters) contains about 0.1 to 1.0 per cent each of methanol, formaldehyde, propargyl alcohol and a small amount of non-volatile resinous material. It is fed to a bubble-plate column and the above volatile impurities stripped off as an aqueous solution and reworked in a separate column. The bottoms contain about 35 per cent of butynediol which contains a small amount of dissolved silica from the catalyst support and formic acid. They are neutralized to a pH of from 7.0 to 7.5 with sodium hydroxide or magnesium oxide, settled and filtered in Scheibler filters to give pure butynediol solution.

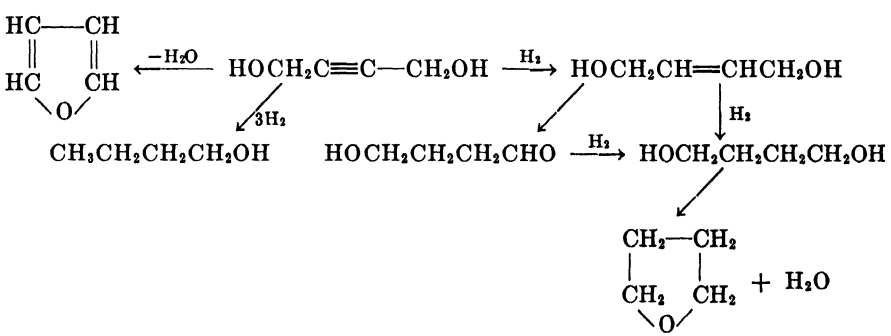
Yields, Throughputs, etc. The yields of butynediol have been variable and apparently not up to expectation based on laboratory results. How-

ever, it would appear that yields of at least 90 per cent based on formaldehyde, or 80 per cent on acetylene have been achieved. The space-time yield, calculated for two converters in series, is about 1.0 kg of 100 per cent butynediol per liter of catalyst per 24-hour day.

Reduction of Butynediol to Butanediol-1,4. The raw 35 per cent aqueous butynediol solution, after being freed of formaldehyde, methanol and propargyl alcohol, is hydrogenated in a tower at 70 to 140°C and 300 atm pressure over a nickel-copper-manganese catalyst on a siliceous carrier. This catalyst is prepared by impregnating the carrier with a solution of the metal nitrates, followed by ignition to the oxides at 600°C and by reduction at 270°C under 300 atm pressure. The finished catalyst contains 15 per cent of nickel, 5 per cent of copper and 0.7 per cent of manganese.

The hydrogenation of the butynediol solution is carried out at 70°C with fresh catalyst, but the temperature must gradually be increased to 140°C as the catalyst becomes older and less active. The pressure was maintained at 300 atm, not because this pressure was required but because higher throughput and longer catalyst life were thus attained. The yield of product was 95 per cent of theoretical. The throughput per day was approximately four times the catalyst volume.

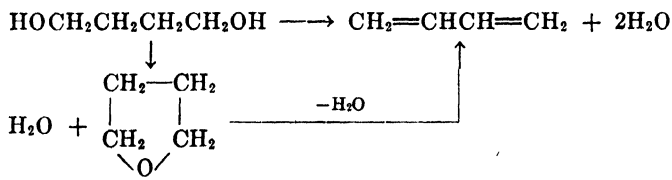
The reactions involved in the hydrogenation of butynediol to butanediol are:



For best results it is essential that the reaction temperature remain constant and that the butenediol stage be passed rapidly. If the catalyst or solution is slightly acid, the butenediol rearranges to gamma-hydroxybutyraldehyde, which is reduced to butanediol only at a considerably higher temperature. A small amount of *n*-butanol, possibly rising from hydrogenolysis of the butenediol, as well as lesser amounts of furan and tetrahydrofuran are always formed.

Conversion of Butanediol and Tetrahydrofuran to Butadiene. Butanediol-1,4 may be converted to butadiene by the removal of 2 molecules of

water[13] or by conversion to tetrahydrofuran from which another molecule of water is eliminated in a subsequent stage:



Investigation proved that the direct dehydration could be carried out only on purified butanediol and not on the aqueous 30 to 35 per cent solution available from the hydrogenation stage Furthermore, even using 100 per cent butanediol, the catalyst must remove two moles of water per mole of butadiene. On the other hand, the conversion to tetrahydrofuran is very easy and can be carried out on the aqueous butanediol solution. Ultimately, the tetrahydrofuran is isolated without evaporation of the water carried into the process from the aqueous formaldehyde The isolation of the tetrahydrofuran also serves as a purification step and eliminates the various impurities carried along in the process. In the final dehydration to butadiene, removal of only one molecule of water per molecule of butadiene is necessary, thus decreasing the load on the catalyst. Furthermore, tetrahydrofuran is an extremely valuable solvent and intermediate, and its availability for these purposes was an added advantage for the two-step procedure.

In connection with the synthesis of butadiene from tetrahydrofuran, it is interesting that Ostromislensky in his extensive publications stated that the easiest method of preparing butadiene was by the dehydration of tetrahydrofuran[14]. However, Reppe claims that at this time tetrahydrofuran was not properly described in the literature and that incorrect physical properties were listed. Ostromislensky did not indicate how he had prepared his supposed tetrahydrofuran, furthermore, according to Reppe, hydrocarbons made by his process in 80 per cent yield using aluminum oxide consisted mainly of propylene with only very little butadiene present.

The removal of 2 moles of water from butanediol to give butadiene caused great difficulty in the beginning, and for some time, it was feared that poor results in this stage would kill the whole process. Under the optimum conditions previously developed for the dehydration of butylene glycol-1,3 using a phosphate catalyst, butanediol-1,4 gave mainly formaldehyde and propylene with only a small yield of butadiene. Experiments with tetrahydrofuran gave similar results.

[13] *D R Pat. 578,994; 610,871*

[14] *J. Russ. Phys Chem. Ges.*, **47**, 1472-94, 1969 (1915); *Centr.*, I, 780, 1133 (1916).

$$HO(CH_2)_4 \rightarrow CH_2O + H_2O + CH_3CH{=}CH_2$$



$$\rightarrow CH_2O + CH_2CH{=}CH_2$$

Many hundreds of catalysts were made and evaluated, but the results were not satisfactory. Work was then resumed on the use of the original phosphate catalyst. Variations in the reaction conditions soon established that the dehydration was in fact easily carried out in good yields, if, in contrast to the dehydration of butylene glycol-1,3, it was carried out in two steps. However, complete conversion of the butanediol to butadiene was not possible, a major part of the reaction product being tetrahydrofuran, which was separated and recycled together with fresh butanediol. Apparently, about 20 per cent of the butanediol feed was converted to butadiene, the remainder to tetrahydrofuran.

It is claimed that this procedure had the advantage of insuring a constant reaction temperature in the reactors and also of permitting preheating the feed to 330°C Yields of 95 per cent were claimed. Catalyst life was four weeks; throughput was 0.4 kg of butadiene per liter of catalyst per day. Formation of butylene was not observed; propylene was formed to the extent of 0.15 per cent.

Catalyst. The catalyst finally selected is very similar to the phosphate catalyst used for the dehydration of butylene glycol-1,3. It contains the same amount of primary sodium phosphate (45 to 50 per cent) and *n*-butylamine phosphate on a granular graphite carrier. However, the amount of free phosphoric acid is doubled (13 per cent calculated as sodium phosphate). The catalyst is dried at a slightly different temperature so as to preserve the microcrystalline structure. Coarse crystals are less efficient and have a much shorter life. The finished catalyst contains 40 to 50 per cent total phosphate, of which 60 to 80 per cent was Madrells salt ($NaPO_3$), besides sodium pyrophosphate ($Na_2H_2P_2O_7$) and free phosphoric acid. (For analytical methods see Wurzschmitt and Schuhknecht[15].)

Graphite as a carrier was not available in Germany in the quantities required for the butadiene synthesis Other catalyst supports such as siliceous extrudings were not nearly so effective, and much poorer yields of butadiene resulted. However, high-temperature coke, which on the basis of x-ray analysis contains preformed graphite nuclei, was a satisfactory substitute. Yields were approximately 1 to 2 per cent lower, purity 1 to 1.5 per cent inferior and life one week less than with the graphite catalysts.

The catalyst was made by spraying the granular coke with a solution of monosodium phosphate-phosphoric acid solution in a heated rotating drum

[15] *Angew. Chem.*, **52**, 711 (1939).

at 100 to 120°C. A part (30 to 50 per cent) of the phosphoric acid was neutralized with an organic amine, such as *n*-butylamine or triethanolamine. Drying was then carried out as follows:

24 hours at 80–100°C
16 hours at 130–150°C
16 hours at 190–200°C
16 hours at 240–250°C

Preparation of Tetrahydrofuran

Crude tetrahydrofuran saturated with water was prepared from technical butanediol in a 550-ton per month plant at Schkopau by the following process. The raw 35 per cent aqueous butanediol solution was topped to remove the *n*-butanol formed as a by-product and then passed through a series of Wofatit K-ion exchangers to remove cations, particularly sodium ions present from the alkali used to adjust the pH of the formaldehyde solution. The treated solution containing some free formic acid was then blended with approximately 0.05 to 0.10 per cent of phosphoric acid so that the pH was 2.0, and pumped through preheaters to the base of three pressure towers in series. These towers were 800 mm in diameter and 18 m tall, and were equipped with electric heating jackets. Impurities such as butynediol, butenediol, and hydroxybutyraldehyde in the butanediol solution apparently produce resins melting above 80°C, most of which separate in the towers and can be drawn off through small heated separators. The reaction products are cooled to about 130°C in heat exchangers which supply heat to the preheaters and are finally expanded into a column. The heat content is still ample to flash off practically all the tetrahydrofuran. Still bottoms containing approximately 5 to 6 per cent of unreacted butanediol are filtered through sawdust to remove resinous material and pass to a fourth pressure column for further treatment.

The raw tetrahydrofuran is purified by refractionation in two addition columns. The overhead is an azeotrope containing 94 per cent of tetrahydrofuran and 6 per cent of water, (b.p. 64°C) and is pumped to the butadiene plant, or stored for further processing if it is to be used as a solvent or intermediate.

The dehydration of butanediol to tetrahydrofuran:

$$HOCH_2CH_2CH_2CH_2OH \rightarrow \begin{array}{l} CH_2{-}CH_2 \\ | \quad\quad | \\ CH_2 \quad CH_2 \\ \diagdown O \diagup \end{array} + H_2O$$

takes place under the above conditions at 260 to 280°C and a pressure of 90 to 100 atm. The reaction is homogeneous in the liquid phase and only 3.2 kcal per g mole are released. The throughput is 4 tons of tetrahydrofuran per day per m^3 of reactor volume. Yields of 99 per cent are claimed.

Preparation of Propargyl Alcohol

As previously indicated, it is believed that in the reaction of acetylene with formaldehyde, propargyl alcohol is the initial reaction product:

$$HC{\equiv}CH + CH_2O \rightarrow HC{\equiv}CCH_2OH$$

However, propargyl alcohol still contains a methine hydrogen and can undergo reaction with a second molecule of formaldehyde to give butynediol.

The relative yields of propargyl alcohol and butynediol are governed in large measure by the time of reaction, the temperature, the pressure, and concentration of acetylene. Usually the butynediol is formed in approximately 92 per cent yields with only 5 to 6 per cent of propargyl alcohol. Although propargyl alcohol can be isolated as its azeotrope with water from the forerun when butynediol solutions from the butynediol reactors are distilled, this forerun—which also contains some methanol and formaldehyde—was normally recycled.

A pilot plant study of a process for the production of propargyl alcohol had been started, but the invasion of Germany by the Allies forced the dismantling of the equipment, which was shipped to Gendorf but never reassembled.

Batch Experiments. Obviously, to favor propargyl alcohol formation at the expense of butynediol, the acetylene concentration should be increased. Batch experiments directed toward increasing acetylene concentration by the use of a solvent for the acetylene were successful. For example, 5 grams of cuprous acetylide (prepared in the usual manner from cuprous chloride and acetylene) were added to 100 cc of a 15 per cent formaldehyde solution in tetrahydrofuran. Acetylene under 15 atm pressure was passed in at 100°C. About 90 per cent of the formaldehyde reacted, yielding up to 80 per cent of propargyl alcohol and 20 per cent of butynediol.

Other solvents for acetylene, such as methanol and acetone, have been used also, but tetrahydrofuran was preferred.

Continuous Reaction in a Tower. The usual butynediol-copper acetylide on silica catalyst has been used for the production of propargyl alcohol in a tube of 35 mm inner diameter and 3 m length at 100°C and 15 atm pressure. A 10 per cent formaldehyde solution in tetrahydrofuran (prepared by diluting the usual 30 per cent formaldehyde) was fed at a rate of 100 to 500 cc/hr/liter of catalyst concurrently with pure acetylene at such a rate that the pressure was maintained at 15 atm. Reaction of the formaldehyde was essentially complete. About 75 to 90 per cent of the reacting formaldehyde was ethinylated to a mixture containing approximately 80 per cent of propargyl alcohol and 20 per cent of butynediol.

The rate of the reaction and the distribution of the products depends largely on the pH—the lower the pH, the slower the reaction; but the rate

of butynediol formation is reduced to a greater extent than is propargyl alcohol formation. The pH is adjusted to about 3.0 by the addition of sulfuric acid. Measurements of pH were made using a glass electrode which, of course, in this system gave relative rather than absolute values.

The crude product is purified by distillation. At first the tetrahydrofuran-water azeotrope is removed with traces of acetals and formaldehyde. Then at 60 to 100 mm the water-propargyl alcohol azeotrope can be removed. From the azeotrope, pure propargyl alcohol can be isolated by the following scheme.

Isolation of Anhydrous Propargyl Alcohol. The propargyl alcohol-water azeotrope boils at 96°C and has an approximate composition of 65 per cent of water and 35 per cent of propargyl alcohol. Initially, attempts to dehydrate this azeotrope by azeotropic distillation of the water with benzene, decalin, dioxane, and similar liquids were not successful. However, 2,5-dimethyltetrahydrofuran, boiling at 90 to 92°/760 mm, forms with water a heterogeneous azeotrope, boiling at 78°/760 mm This azeotrope has a composition of approximately 13 per cent of water and 87 per cent of 2,5-dimethyltetrahydrofuran. The upper phase, the dimethyltetrahydrofuran layer, contains about 1.5 per cent of water, while the lower aqueous phase contains approximately 5 per cent of dimethyltetrahydrofuran.

During the heating period required to remove the water with the entrainer, the propargyl alcohol should be protected against decomposition induced by the alkali present in glass by the addition of 1 to 2 per cent of succinic acid, or other non-volatile carboxylic acid After removing the dimethyltetrahydrofuran, distillation of the residue at 80 to 100 mm pressure gave a forerun containing small percentages of water, and finally 99 to 99.8 per cent propargyl alcohol.

The use of dimethyltetrahydrofuran for the dehydration of the 3-butyn-2-ol-water azeotrope (b p. 92/760 mm) was also effective.

Analytical Determination of Propargyl Alcohol. An analytical method for determining propargyl alcohol may be based upon the reactivity of the triple bond, or upon the reaction of the methine hydrogen with metallic ions to give insoluble precipitates. Determination of the triple bond by an addition reaction, for instance with bromine, is not satisfactory because the addition of the halogen takes place too slowly. Therefore, it was decided to base the determination on the precipitation of heavy-metal salts. Titration of the propargyl alcohol with an ammoniacal solution of cuprous salt gave unreliable results, especially with dilute solutions.

Preliminary tests showed that propargyl alcohol gives a white crystalline precipitate with silver nitrate in the presence of sodium acetate Two moles of silver nitrate are required for each mole of propargyl alcohol. It is assumed that the precipitate has the composition $Ag—C{\equiv}C—CH_2OHAgNO_3$, since acetylene gives a precipitate with silver

nitrate which has the composition $Ag_2 \cdot C_2 \cdot AgNO_3$. Based upon this observation, a volumetric method was tried which, in principle, is very much like the Volhard determination of chlorine. The results checked very well, so full attention was given to this reaction. It is naturally assumed that no other compound which is capable of reacting with silver ions must be present.

Procedure. The determination can be carried out by weighing a 1-gram sample of propargyl alcohol and diluting it with water to a 500 cc volume; 25 cc of this solution are now placed in a 100-cc measuring flask and mixed with 1 cc of sodium acetate solution, prepared by dissolving one part of sodium acetate in two parts of water. To this, 25 cc of 0.1 *N* $AgNO_3$ solution are added and the flask shaken well. (The $AgNO_3$ solution should be added cautiously by running slowly down the walls of the flask and not directly into the liquid, to avoid formation of foam.) The measuring flask is filled to the 100-cc mark with water, shaken well and filtered into a dry flask. The first 10 cc are discarded, just as it is done in the Volhard chlorine determination; 50 cc of the filtrate are now mixed with 3 cc of ferrous ammonium sulfate, acidified with HNO_3, and the surplus of $AgNO_3$ is back-titrated with 0.1 *N* ammonium thiocyanate solution. The percentage of propargyl alcohol is then calculated from the formula

$$\frac{28 \times V\text{AgNO}_3 \times \text{Vol}}{100 \times E \times a} = \%$$

28 = half the molecular weight of propargyl alcohol
$V\text{AgNo}_3$ = consumption of 0.1*N*$AgNO_3$
Vol = volume to which the weighed sample has been diluted (in this case 500 cc)
E = weight of the sample
a = quantity of solution to be titrated

A blank should be run on the sodium acetate solution. Usually, the amount of silver nitrate solution consumed is so small that it may be neglected.

Results. Solutions of different concentration were prepared by diluting 99 per cent propargyl alcohol.

1.98% Solution: 12 270 g diluted to 200 cc; 25 cc used for titration and consumed 10.80 cc of 0.1*N* $AgNO_3$. Found 1.97%.

28.9% Solution: (1) 3.472 g diluted to 500 cc; 25 cc used for titration, which consumed 17.88 and 17.96 cc of 0.1*N* $AgNO_3$. Found 28.84% and 28.97%. (2) 4.612 g diluted to 500 cc; 25 cc used for titration, which consumed 23.20 cc of 0.1*N* $AgNO_3$. Found 28.18%.

53.41% Solution: 1.775 g diluted to 500 cc; 25 cc used for titration and consumed 16.92 cc of 0.1*N* $AgNO_3$. Found 53.38%.

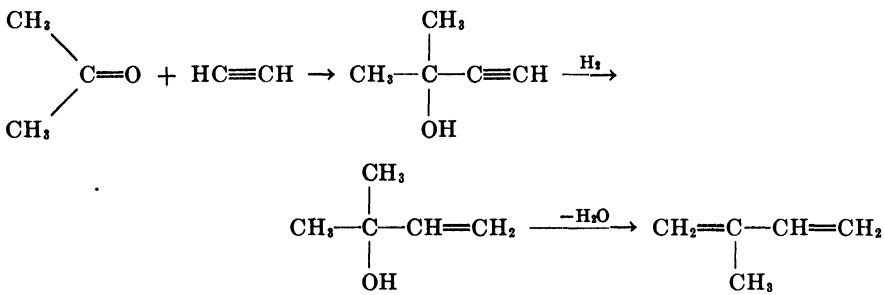
0.99% Propargyl Alcohol: 1.917 g diluted to 1000 cc; 25 cc used for titration, which consumed 16.86, 16.78, 16 80 cc of 0.1*N* $AgNO_3$. Found 98.51%, 98.04% and 98.16%.

These results show that the new analytical method gives perfectly reliable results for concentrated and diluted solutions of propargyl alcohol. Technical solutions of propargyl alcohol, such as from butynediol plants, can also be analyzed successfully.

Ethinylation of Ketones

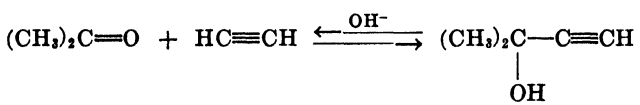
2-Methyl Butyne-3-ol-2

Since Merling's synthesis, 2-methyl butyne-3-ol-2, has been the focal point of many efforts to synthesize isoprene by the reaction scheme:



However, the use of sodium, or of sodium amide, required in Merling's synthesis, limited the possible application of this procedure on a large technical scale.

A successful technical synthesis appeared to be at hand in 1937 when Reppe first showed that aldehydes condensed with acetylene in aqueous solution under pressure in the presence of heavy-metal acetylides as catalysts Although this reaction gave good yields with nearly all aldehydes, it soon proved of little value for the addition of acetylene to the carbonyl group of ketones. However, during a study of the reaction of ketones with acetylene under pressure, the catalytic influence of hydroxyl ions was found to be very pronounced, and it was shown that under their influence ketones such as acetone combine reversibly with acetylene:



The equilibrium depends upon the concentration of the reacting components. With acetylene at atmospheric pressure, the equilibrium is almost completely in favor of dissociation, but at 20 atm acetylene pressure, approximately 15 per cent of methyl butynol is formed. The rate of the reaction increases with higher hydroxyl ion concentrations and with increasing temperatures, but the yield is reduced because of condensaton reactions of the acetone leading to mesityl oxide, phorone, etc. With a 5 per cent aqueous sodium hydroxide solution at 95 to 100°C, equilibrium

is obtained in 8 to 10 hours without appreciable loss of acetone by side reactions. The reaction product may be separated outside the reaction chamber and the reactants recycled with fresh acetylene.

On the basis of these observations, a pilot plant was built which supplied large quantities of methyl butynol in a continuous run for many months.

Approximately 5 liters of acetone and 2.25 liters of 5 per cent caustic potash solution per hour are introduced into a stirred reactor containing 80 liters of the liquid reaction mixture. The bottom of the reactor is equipped with a Hoesch stirrer running at 1400 rpm, which effects thorough mixing of the liquid with an acetylene-nitrogen mixture. The acetylene content of the entering gas is about 80 per cent, and the total pressure should be 20 to 24 atm. Four to 5 atm of acetylene must be added per hour and 0 5 to 1.0 atm of nitrogen every 14 to 15 hours. The temperature of the reactor is held at 95 to 98°C with steam.

The liquid reaction product is continuously expanded to a cooler, and the caustic neutralized with carbon dioxide to prevent dissociation of the methyl butynol during the separation from unreacted acetone, which is continuously flashed off. The methyl butynol is then distilled from the aqueous solution as an azeotrope consisting of 74 per cent of methyl butynol and 26 per cent of water, boiling at 90°C. The aqueous residue contains mesityl oxide, phorone and 2,5-dimethyl-2,5-dihydroxyhexyne-3. The ratio of the acetylenic alcohol to the diol is about 7 to 10/1.

Approximately 18 kg of the constant-boiling solution, or only about one-seventh of the reactor volume, were obtained per day. The space-time yield is therefore very poor. Attempts to improve this space-time yield by the use of other catalysts were unsuccessful. It was believed that improved mixing of the liquid and gas could be secured by changes in designs of the reactor. Preliminary experiments were satisfactory, and it was claimed that the space-time yield was improved several times so that the reactor would produce its own volume of product per day.

In this connection, it should be noted that Zeltner and Genas[16] and later Weizmann[17] have claimed that the reaction of acetylene with acetone takes place rapidly at −10 to −15°C with almost quantitative yields if the reaction is carried out in an acetal as a solvent, and in the presence of a catalyst consisting of the complex formed from potassium hydroxide and the acetal. This method would appear to be superior to Reppe's procedure for the ethinylation of ketones.

Methyl butynol can be separated from its constant-boiling mixture with water by the addition of potassium carbonate. The anhydrous chemical boils at 103 to 104°C.

It is claimed that methyl butynol is the best solvent known for poly-

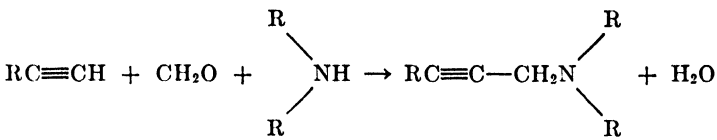
[16] *Brit. Pat. 544,221; U. S. Pat. 2,345,170.*
[17] *Brit. Pat. 573,527; 580,921.*

amides. A 10 per cent solution of Lupamid No. 6040 in 74 per cent aqueous methyl butynol remains clear for 7 days at room temperature, in contrast to a 10 per cent solution in the usual solvent, 90 per cent aqueous methanol, which solidifies after 2 hours.

Ethinylation of Amines

Propargyl Amines

Mannich and Chang[18] showed that substituted propargyl amines could be obtained in good yields by heating a phenyl or phenyl-substituted acetylene with formaldehyde and a secondary aliphatic amine in dioxane solution at 100°C:

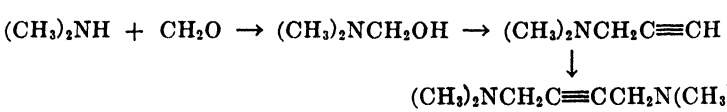


Later Coffman[19] prepared alpha-dialkylaminomethyl-beta-vinyl acetylene by heating a dioxane solution of vinyl acetylene, paraformaldehyde, and a secondary amine at 100°C for 14 to 17 hours:

$$CH_2{=}CHC{\equiv}CH + CH_2O + R_2NH \rightarrow CH_2{=}CH{-}C{\equiv}C{-}CH_2N_2R + H_2O$$

This process, however, cannot be used with acetylene itself because the methine hydrogens are not sufficiently reactive, even under pressure, to react with the labile hydroxyl group of the initially formed methylolamine. Presumably, phenyl acetylene and vinyl acetylene are more reactive than acetylene because of the activating influence of the phenyl and vinyl groups

In the presence of copper acetylide as a catalyst, the methine hydrogens of acetylene become activated and react readily, even at room temperature.[20] For instance, dimethyl methylolamine (from dimethylamine and formaldehyde) reacts with acetylene to give a 70 per cent yield of 3-dimethylamino propyne-1, together with about 10 per cent of 1,4-tetramethyldiamino-butyne-2:



822 parts of glacial acetic acid are added to 450 parts of 50 per cent aqueous dimethylamine while stirring and cooling between 10 and 20°C. The resulting solution is charged with a solution of 40 parts of copper acetate in 972 parts of 40 per cent formaldehyde into an autoclave. Five atm of

[18] *Ber.*, **66**, 418-20 (1933).
[19] *J. Am. Chem. Soc.*, **57**, 1978 (1935).
[20] *Fr. Pat. 839,875; D R Pat. 724,759; U. S. Pat. 2,273,141.*

nitrogen and 10 atm of acetylene are pressed in and the reaction mixture stirred at 40°C until no further decrease in pressure takes place. The acetylene used is replenished from time to time. After from 10 to 20 hours, the absorption of acetylene is completed. The copper salts are filtered off and the filtrate neutralized with sodium hydroxide solution while cooling. The organic layer is separated and the aqueous layer extracted exhaustively with ether. After distilling off the ether, the residue is combined with the separated organic layer, dried and distilled. The dimethylaminopropyne-1 boils at 79 to 80°C and the tetramethyldiaminobutyne-2 at 180°C.

Methylolamines derived from saturated aliphatic, alicyclic, saturated monocyclic, heterocyclic, alkyl aryl amines, and aldehydes or ketones are stated to be suitable compounds.

Ethinylation of methylolamines takes place not only with acetylene but with its derivatives and substitution products, provided at least one methine hydrogen atom is present. The reactions ordinarily take place in liquid phase at room temperature, although in some cases moderate heating to 50 to 60°C is required. Pressure also increases the reactivity.

An interesting application of two distinct types of ethinylation is the synthesis of 1-diethylaminopentanol-4, an intermediate required in the synthesis of the highly important and necessary antimalarials "Plasmochin" and "Atabrin":

$$CH_3CHO + HC{\equiv}CH \rightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HC{\equiv}CH \xrightarrow{(C_2H_5)_2NCH_2OH}$$

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}H{-}C{\equiv}CCH_2N(C_2H_5)_2 \xrightarrow{H_2}$$

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_2N(C_2H_5)_2$$

Using copper acetylide or copper butynolide catalysts in the presence of acetic acid, yields approaching theoretical are claimed.

Of special interest was the reaction of methylolamides, *e.g.*, dimethylol urea with acetylene under pressure in methanol in the presence of copper acetylide. Water is eliminated and a labile hydroxyl group of the dimethylol urea is replaced by an ethine group. The subsequent reactions are not as yet elucidated, but apparently polymerization takes place, with a significant increase in the hardening point of the resin. Such products have found application in the resin field as hardening agents for the "Luphen" plastics (plasticized phenolformaldehyde resin).[21] Dimethylol

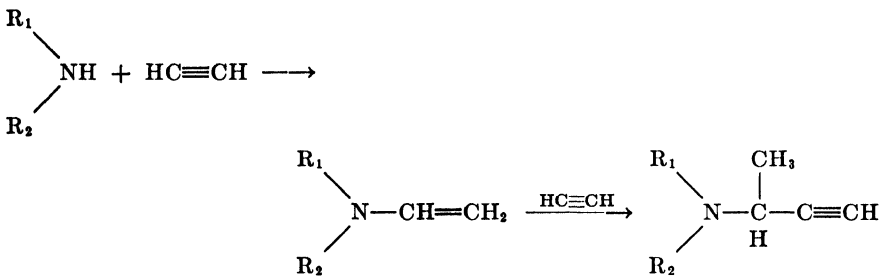
[21] *D. R. Pat. 730,648; U. S. Pat. 2,316,653.*

urea, 302 parts, 1280 parts of methanol and 7 parts of cuprous chloride are treated in an autoclave at 20 to 30°C with a mixture of equal parts of nitrogen and acetylene under a pressure of 20 atm. After 20 to 24 hours, one molecular proportion of acetylene has been absorbed and the reaction is completed. The reaction mixture is filtered and the methanol distilled off under reduced pressure (25 to 50 mm) and 30 to 50°C pot temperature. There is obtained 270 to 300 parts of a highly elastic resin, which may be dissolved in ethylene glycol monomethyl or monoethyl ether. After evaporation of the solvent, a hard insoluble product is obtained after about 1½ days.

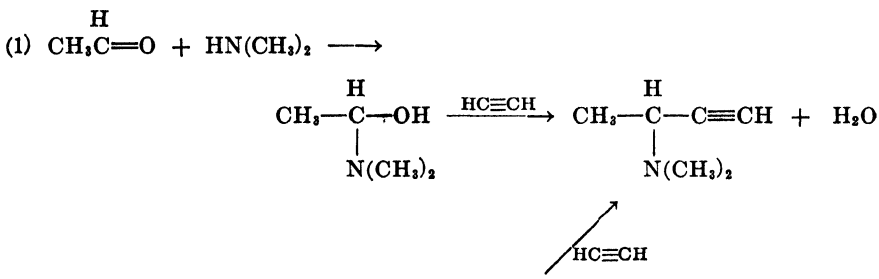
Aminobutynes from Acetylene and Amines

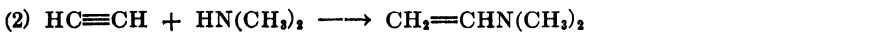
Amines are known to react with acetylene under the catalytic effect of alkalies, alkaline earths, zinc and cadmium salts to yield complex products which have not been well characterized for the most part.

However, under the influence of heavy-metal acetylides, particularly copper acetylide, acetylene reacts with amines under pressure to give aminobutynes:[22]



The structure of the reaction product was established by the two independent syntheses of 3-dimethylaminobutyne-1[23]:





The syntheses of 3-aminobutyne derivatives by the ethinylation of amines appears to be general for primary and secondary aliphatic, aralkyl and

[22] *D. R. Pat. 734,241; U. S. Pat. 2,378,129; Fr. Pat. 846,475.*
[23] *D. R. Pat. 734,759.*

heterocyclic amines. Polyfunctional amines may react at more than one amino group. Thus, hexamethylene diamine gives N,N′-bis-3-butynyl-1,6-diaminohexane:

$$NH_2(CH_2)_6NH_2 + 4HC{\equiv}CH \longrightarrow HC{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}NH(CH_2)_6NH\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C{\equiv}CH$$

Improvements in the ethinylation process which overcame initial difficulties are claimed when the amines used are partially converted to their salts with mineral acids. The ethinylation of a primary aromatic amine may be carried out as follows:

Production of 3-Phenyl-aminobutyne-1. The reaction of aniline with acetylene is advantageously done in benzene solutions. If tetrahydrofuran is used as the solvent, better yields are obtained, but some phenyl-pyrrolidine is generated, which is hard to separate from the phenyl-aminobutyne.

The reaction mixture charged to a 100-liter autoclave is as follows:

40 liters benzene
9300 g. aniline
copper acetylide paste made from 274 g. $CuSO_4 \cdot 5H_2O$

The autoclave is partially evacuated and the copper acetylide paste, mixed with benzene, is drawn in. Aniline and benzene are charged in the same way. The intake pipe is shut off and air is removed by pressing 30 to 50 atm of nitrogen three times into the vessel and expanding it. Finally, 8 atm of nitrogen pressure are charged into the autoclave, and acetylene is added until the total pressure mounts to 20 atm. The autoclave is now stirred and acetylene is rapidly absorbed, the pressure decreasing Acetylene is replaced periodically until no further pressure drop occurs. The autoclave is then heated with steam at 1 8 to 1.9 atm, the temperature inside rising to 125 to 130°C within 2 to 3 hours. If during the heating period the pressure rises above 25 atm, it is cautiously lowered to 20 atm *without stirring*. The pressure decreases during heating; usually no further pressure drop is observed after 10 to 20 hours. Heating is stopped and the autoclave is cooled with water while stirring. When a temperature of 30 to 25°C has been reached, fresh copper acetylide is fed to the autoclave (made from 274 g of $CuSO_4 \cdot 5H_2O$). The intake pipe is washed clean with benzene, and the reaction between aniline and acetylene is carried out again just as described above.

The autoclave is again cooled after no further pressure decrease occurs at 125 to 130°C. The stirrer is stopped and the product is discharged from the autoclave under 3 to 4 atm of nitrogen pressure. The catalyst is removed by filtration and destroyed with hydrochloric acid. The reaction product is further processed as follows:

The filtered yellow solution is charged to a still and 35 to 38 liters of

benzene distilled off on a steam bath; the residue is fed to an enamel-lined kettle in which it is distilled *in vacuo*. First runnings consist of a little benzene, then between 80–110°/20 mm unreacted aniline, and finally at 110 to 130°/2 mm; the phenylaminobutyne distills and frequently crystallizes. The pure chemical is obtained by redistillation in glass flasks.

Appendix to Chapter III

The various ethinylation products with such physical data as are known are collected in this appendix.

Ethinylation Products

(1) *Reaction Products from Aldehydes and Ketones with Acetylene and Substituted Acetylenes*

(a) *With Acetylene* (°C)

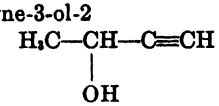
Propargyl alcohol — b.p. 113°/755 mm



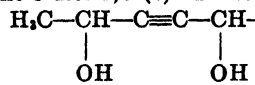
Butyne-2-diol-1,4 — " 105–108°/1 mm



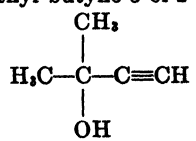
Butyne-3-ol-2 — " 109°/755 mm



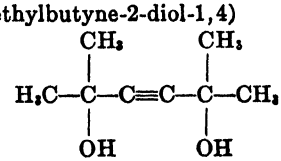
Hexyne-3-diol-2,5 (1,4-dimethyl-butyne-2-diol-1,4) — " 95–97°/1–2 mm



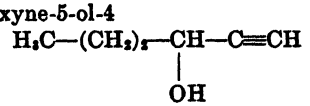
2-Methyl-butyne-3-ol-2 — " 103–104°/760 mm



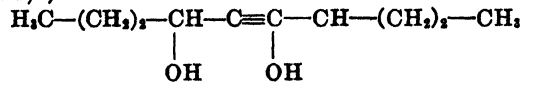
2,5-Dimethylhexyne-3-diol-2,5 (1,1,4,4-tetramethylbutyne-2-diol-1,4) — m.p. 95°, b.p. 95–100°/1–2 mm



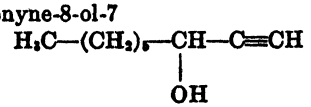
n-Hexyne-5-ol-4 — " 145–146°/755 mm



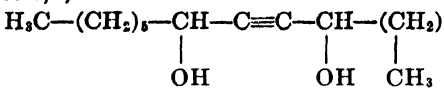
n-Decyne-5-diol-4,7 (1,4-Di-*n*-propyl-butyne-2-diol-1,4) — " 107–110°/2 mm



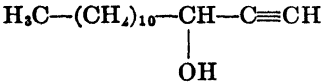
n-Nonyne-8-ol-7 — " 63–64°/2 mm



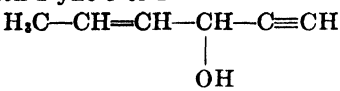
n-Hexadecyne-8-diol-7,10 (1,4-Di-*n*-hexyl-butyne-2-diol-1,4) " 170–172°/1 mm



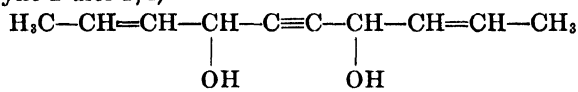
n-Tetradecyne-13-ol-12 " 182–188°/1 mm



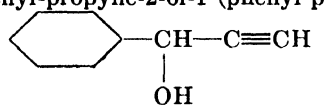
n-Hexen-2-yne-5-ol-4 " 153–154°/760 mm



n-Decadien-2,8-yne-5-diol-4,7 (1,4-Di-*n*-propenyl-butyne-2-diol-1,4) " 103–105°/1 mm



1-Phenyl-propyne-2-ol-1 (phenyl propargyl alcohol) " 92–93°/2 mm

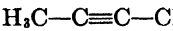


(b) *With Substituted Acetylenes*

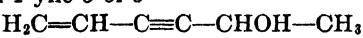
Penten-1-yne-3-ol-5 " 35–36°/1 mm



Butyn-2-ol-4 " 117–120°/755 mm

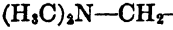


Hexen-1-yne-3-ol-5 " 57–60°/10 mm

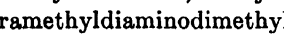


(2) *Reaction Products of Alkanol Amines and Acetylene*

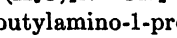
Dimethylamino-1-propyne-2 b.p. 79–81°/760 mm



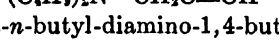
Tetramethyldiamino-1,4-butyne-2 " 178–180°/760 mm
(tetramethyldiaminodimethyl acetylene)



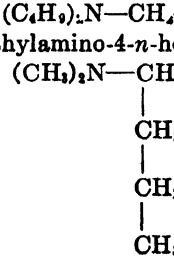
Di-*n*-butylamino-1-propyne-2 " 87–89°/19 mm



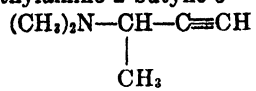
Tetra-*n*-butyl-diamino-1,4-butyne-2 " 133–135°/1 mm



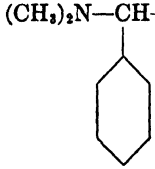
Dimethylamino-4-*n*-hexyne-5 " 135–136°/755



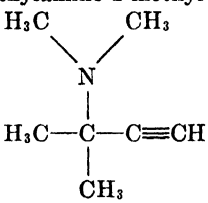
Dimethylamino-2-butyne-3 " 95–96°/755 mm



Dimethylamino-1-phenyl-1-propyne-2 " 59–60°/1 mm



Dimethylamino-2-methyl-2-butyne-3 m.p. 95–97°

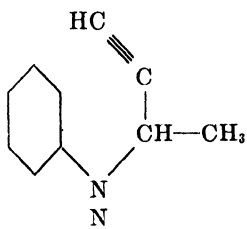
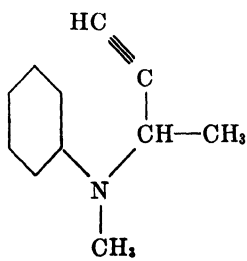


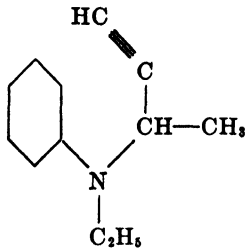
(3) *Reaction Product of Aliphatic, Cycloaliphatic and Aralkyl Amines and Acetylene*

Dimethylamino-2-butyne-3	b.p 95–96°/755 mm
Diethylamino-2-butyne-3	" 127–128°
	m p + 10°
n-Butylamino-2-butyne-3	b p 147–149°/755 mm
Benzylamino-2-butyne-3	" 60–62°/1 mm
Piperidino-2-butyne-3	" 58–59°/12.5 mm
Cyclohexylamino-2-butyne-3	" 58–60°/4.5 mm

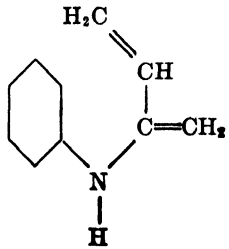
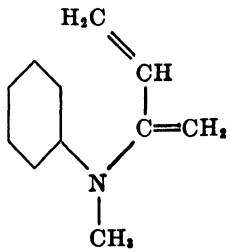
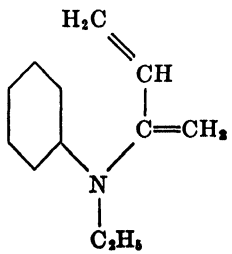
(4) *Reaction Products of Aromatic Amines and Acetylene*

(a) *Direct Reaction Products*

Name	Formula	(°C)	n_D^{20}	d_4^x
2-Phenylamino-butyne-3		m.p. +74° b.p. 110–112°/15 mm	—	—
2-(N-Methyl)-phenylamino-butyne-3		b p. 110–113/10 mm " 116°/15 mm	1,5496	0,9970

2-(N-Ethyl)-phenylamino-butyne-3		" 120–122°/ 15 mm	—	—

(b) *Isomerization Products*

2-Phenylamino-butadiene-1,3		b.p. 112–115°/ 10 mm.	(1,6039)	(0,9958)
2-(N-Methyl)-phenylamino-butadiene-1,3		b.p. 120–123°/ 10 mm	1,5917	1,0028
2-(N-Ethyl)-phenylamino-butadiene-1,3		b.p. 120–125°/ 10 mm	1,5952	1,024

Chapter IV

Reactions of Products Derived from the Ethinylation Reaction

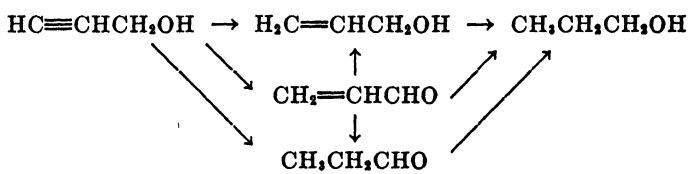
Introduction

The development of the ethinylation reaction made available for the first time commercial quantities of acetylenic alcohols, acetylenic glycols, aminopropynes and aminobutynes. The reactions of these classes of organic compounds were investigated on a very broad basis by German chemists, with the result that many new and interesting routes to the synthesis of both old and new compounds were developed. Possibly many of these methods never again will attain any commercial significance; some undoubtedly will in time find a place in the chemical industry of countries other than Germany. In any event, these studies represent valuable additions to our knowledge of the chemistry of the above-mentioned classes of organic compounds and will be discussed in some detail. Several charts at the close of this chapter depict a number of the more important types of reactions for the various acetylenic derivatives.

Reactions of Acetylenic Alcohols

Hydrogenation

Hydrogenation of Propargyl Alcohol. The hydrogenation of propargyl alcohol is an interesting example of selective catalysis. Depending on the catalyst used and the reaction conditions (mainly pH), it is possible to produce practically without by-products either allyl alcohol, propionaldehyde, *n*-propyl alcohol, or acrolein.



Reduction to Allyl Alcohol. The reduction of propargyl alcohol at low pressure, at 120 to 130°C over a metallic palladium catalyst mixed with iron and precipitated on a siliceous carrier having an alkaline reaction gave allyl alcohol.

Reduction to Propionaldehyde[1]. The hydrogenation of propargyl alcohol at low pressures using the same catalyst as above, except that the carrier had an acid reaction, at a slightly lower reaction temperature (100 to 105°C) gave practically pure propionaldehyde. Presumably, the allyl alcohol initially formed rearranges to propionaldehyde before it is hydrogenated to *n*-propanol, while the propionaldehyde is not further reduced under the reaction conditions

The following catalyst proved satisfactory: 5 g of palladium chloride are dissolved in 200 g of water and mixed with 500 g of diatomaceous earth (containing 3 per cent iron, 1.7 per cent SO_4) The putty is dried and the powder shaped to tablets which are treated with hydrogen at 200°C

Then, 100 cc of this catalyst are contacted at 105°C, with 40 liters of hydrogen per hour and 50 g of a mixture of 70 per cent of propargyl alcohol with 30 per cent of water in the presence of traces of acid. The vapors are condensed and the propionaldehyde is isolated by distillation. More than 90 per cent of the propargyl alcohol could be converted and 95 per cent yields of propionaldehyde were obtained

Reduction to n-Propanol. Perhydrogenation of propargyl alcohol to *n*-propanol can be effected with all efficient hydrogenation catalysts such as precious metals, nickel, chromium, and copper, or their mixtures

Isomerization to Acrolein. Propargyl alcohol over copper catalysts rearranges to acrolein according to statements in Reppe's manuscript; no details are available on the reaction conditions used to effect this isomerization. On the other hand, it is reported that propargyl alcohol when passed over a copper silica gel catalyst, decomposed quantitatively to acetylene and formaldehyde.[2]

Hydrogenation of Butynol. The hydrogenation of butynol (butyne-3-ol-2) is very similar to that of propargyl alcohol. Reduction with all the usual metallic catalysts gives secondary butanol, partial hydrogenation with iron catalysts gives methyl vinyl carbinol in poor yields (No reaction takes place at low pressure.) Partial hydrogenation can be carried out however just as in the reduction of propargyl alcohol to allyl alcohol, using the same palladium-iron catalyst on an alkaline diatomaceous earth [3] In addition, it is advisable to carry out the reduction in dilute solution to avoid side reactions or rearrangements such as:

$$CH_3C(H)(OH)-C\equiv CH \rightarrow CH_3C(=O)CH=CH_2 \rightarrow CH_3C(=O)CH_2CH_3$$

An aqueous solution of 250 to 300 g of butyne-3-ol-2 per hour and the

[1] *D.R.Pat. 717,062*

[2] *PB* L73715, Frames 6270–3.

[3] I. G. Farbenindustrie patent proposal *O.Z.-12,697.*

required quantity of preheated hydrogen is passed through a preheater which is kept at 200°C and fed to the reactor which is held at 200 to 250°C. The products of the reaction are continuously distilled and the hydrogen is recycled. Spent hydrogen is continuously replaced; a cycle of 4 to 5 times theoretically required quantity of hydrogen is necessary in the small reactors for the conversion of the butyne-3-ol-2 In the 9-liter reactor a cycle of 8 to 12 times the theoretical quantity was needed to carry off the 33 calories of heat of reaction. The course of the reaction is to a large extent independent of temperature; formation of secondary butanol between 150 and 300°C was not observed in any case. A mixture of 98 per cent methyl vinyl carbinol and 2 per cent butynol which was obtained in one cycle was recharged to the reactor under the same conditions. Methyl vinyl carbinol remained unchanged and only the butynol was partly hydrogenated.

The concentration of the butynol solution should not exceed 25 per cent to avoid formation of substantial quantities of high-boiling unsaturated ketone oils (boiling point 100 to 340°C, molecular weight 100 to 240) and to check dehydration to vinyl acetylene and butadiene.

If the temperature of the reaction is kept below 200°C, slightly more than 1 per cent of unreacted butynol will remain. The life of the catalyst was ten weeks. After this time, more than 3 per cent of butynol remained unconverted in a single cycle.

The distillate from the top of the column contains approximately 60 per cent of methyl vinyl carbinol, 5 per cent of aldehydes and ketones, 1 per cent of butynol and 34 per cent of water. The ketone oils and water are continuously removed, and the raw methyl vinyl carbinol is purified by a wash with 10 per cent of a saturated solution of sodium bisulfite (5 hours, 60°C) and finally distilled. The distillate is methyl vinyl carbinol containing 26 to 30 per cent of water but free from aldehydes and ketones. The last fraction may still contain some butynol. The ketone and aldehyde bisulfite compounds are discharged from the still bottoms.

Methyl vinyl carbinol boils constantly at 85 to 86°C with 26 per cent of water. The product is dried with potash and distilled over potash, and then boils at 97.4°C. Methyl vinyl carbinol adds 2 atoms of bromine; this reaction may be used for analytical determination.

The dehydrogenation of the alcohols produced by the perhydrogenation of the acetylenic alcohols was used to prepare ketones. For example, butyne-3-ol-2 was reduced to secondary butyl alcohol which was dehydrogenated to methyl ethyl ketone.

Oxidative Coupling

Primary acetylenic alcohols may be converted to diacetylenic glycols by Zalkind's method using air and a cuprous salt catalyst[4]. By this procedure

[4] *Ber.*, **69**, 128 (1936).

propargyl alcohol gave hexadiynediol-1,6 in 50 to 60 per cent yield. However, the product was highly contaminated and the consumption of cuprous chloride was high.

Work on the mechanism of the reaction showed that with a molecular ratio of propargyl alcohol to cuprous chloride of from 2:1 to 5:1, there was little oxidation of the cuprous chloride to cupric chloride; instead, the cuprous chloride acted as a catalyst and gave yields of hexadiynediol of the order of 95 per cent of theoretical.

The equation for the production of hexadiynediol from propargyl alcohol is

$$2\ HC{\equiv}C{-}CH_2OH + 1/2\ O_2 \rightarrow HOCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2OH + H_2O + 83\ \text{k cal.}$$

Obviously, pressure should favor the reaction. Experiments using air compressed to 10 to 20 atm showed that the rate was increased from 3 to 8 times over rates obtained with the same reactants with air, or even oxygen, at atmospheric pressure. The rate is substantially constant during the early stages, but as the ratio of propargyl alcohol to cuprous chloride decreases and the quantity of precipitated hexadiyne diol increases, the catalytic solution changes slowly into a paste of lowered catalytic activity and the rate falls off. In the larger pilot plant, this was avoided by adding propargyl alcohol at intervals to maintain the propargyl alcohol/cuprous chloride ratio at the most favorable ratio of 2:1 to 4:1, and by continuously removing hexadiynediol by centrifuging a portion of the reaction slurry, the liquors being recycled.

The following description of an experiment will explain the reaction under pressure:[5] A rotating stainless steel (V_4A) autoclave of 92.8-liter capacity was filled with 26.1 liters (= 30.25 kg) of a mixture of 18,440 g H_2O, 5,760 g NH_4Cl, 1,800 g Cu_2Cl_2 and 4,260 g 95 per cent propargyl alcohol (= 4,040 g pure propargyl alcohol). Air was pressed in to 20 atm and the autoclave was started rotating at 10 to 12°C. The temperature in the autoclave rose to 26°C after 20 minutes, and the pressure fell to 18.5 atm. It was not desirable that the pressure fall to 16 atm, indicating complete consumption of the 4 atm of oxygen which were contained in the 20 atm of air, because the rate of hexadiynediol formation would decrease. The pressure was released and the treatment continued with 20 atm of fresh air, causing a temperature rise to 27°C, and a new drop in pressure to 18.5 atm. This procedure was repeated and lasted 20 minutes for each operation. The total absorption of oxygen during three treating periods was 4.5 atm equivalent to 300 liters of oxygen calculated for the autoclave volume of 66.75 liters (92.8 − 26.1 = 66.75 liters) and took 60 minutes. Assuming that the oxygen was used only for the oxidation of the propargyl alcohol, this absorption would be equivalent to the conversion of 3070 g

[5] *PB* 27124.

of propargyl alcohol to hexadiynediol: 970 g of propargyl alcohol should have remained unchanged, and the initial mole proportion of cuprous chloride to propargyl alcohol should have decreased from 1:4 to 1:1.

A further 2,055 g of propargyl alcohol was added and the process repeated. This cycle was repeated until 18.045 kg of propargyl alcohol had been converted. The contents of the autoclave were filtered, and the solid dissolved in a minimum of water at 60°C. Higher temperatures during recrystallization caused decomposition of the hexadiynediol, even in an atmosphere of nitrogen. The solution was cooled to 0°C and the hexadiynediol removed by filtration. The aqueous filtrate on extraction with ether gave more of the diol. The total yield of crude hexadiynediol was 15.45 kg from 18.045 kg of 100 per cent propargyl alcohol, or 89 per cent. Including recovered propargyl alcohol, the yield was 93 per cent.

Purification of the crude diol by recrystallization from water was attended by high losses, and only 60 per cent of the white crystalline diol, melting point 112°C, was obtained. However, it was believed that these losses could be greatly reduced by reworking the aqueous filtrates in a continuous process.

Butynol-3 under the same conditions was reported to give octadiyne-3,5-diol-2,7 in good yield. Unfortunately, a description of this work is unavailable because all files pertaining to this subject were destroyed by fire.

Catalytic hydrogenation in the presence of metals of the iron group, especially nickel, reduces the diyne diols to alkane diols. These diols are of great interest in the chemistry of polyurethanes and polyamides.

Oxidation of hexanediol-1,6 leads to adipic acid, a process which makes this important acid available independently of the usual methods based on benzene derivatives. Conversion to the 1,6-dinitrile followed by hydrolysis affords a new synthesis of suberic acid.

Partial hydrogenation of hexadiynediol gives hexadienediol.

Oxidation of Propargyl Alcohol to Propargyl Aldehyde[6]

Attempts to dehydrogenate propargyl alcohol to propargyl aldehyde by catalytic processes similar to those successfully used for the synthesis of formaldehyde from methanol were unsuccessful; apparently, isomerization to acrolein occurred in the vapor phase over both copper and silver catalysts. However, chemical oxidation using mild oxidizing agents such as manganese dioxide in acid solution was successful on a laboratory scale in yields of 50 to 60 per cent of theoretical.

$$HC{\equiv}CCH_2OH \xrightarrow{[O]} HC{\equiv}C{-}CHO + H_2O$$

Propargyl aldehyde was of interest because on condensation with guanidine it yielded 2-aminopyrimidine, which could be converted to 2-*p*-amino-

[6] *PB* 80380 (*FIAT* 915); *D. R. Pat. Anmeldung I-76,416* (Jan. 12, 1943).

phenylsulfoamidopyrimidine, a very useful and effective sulfa drug ("devenal", sulfadiazine).

Procedure. A mixture of 800 g of manganese dioxide, 2,000 cc of water, 100 cc of concentrated sulfuric acid and 250 g of sodium sulfate was stirred in a reaction vessel. Then 480 g of propargyl alcohol was added, and the reaction mixture warmed to 40°C under a vacuum of 100 mm. During two hours, a mixture of 1800 cc of water and 500 cc of concentrated sulfuric acid was added at a temperature of 46 to 50°C. A mixture of water, propargyl alcohol, and propargyl aldehyde distilled over. The first 500 cc of distillate contains the major part, 135 g, of the produced propargyl aldehyde, while the next 500 cc contains an additional 15 g. The reaction is completed when 1,000 cc of distillate have been obtained. The total distillate is fractionated at 100 mm pressure A 90 per cent solution of propargyl aldehyde distills at 27 to 32°. Including the forerun and tails, about 200 to 230 cc of an 80 per cent distillate, or 160 to 184 g of 100 per cent propargyl aldehyde is obtained; yield 50 to 60 per cent From the distillation residue, 166 g of propargyl alcohol can be recovered by salting out with potassium carbonate.

Condensation of Propargyl Aldehyde with Guanidine Carbonate.[7] A mixture of 400 g of 80 per cent sulfuric acid and 90 g of guanidine carbonate was cooled and stirred in a reaction vessel fitted with a stirrer, reflux condenser, dropping funnel and thermometer. Later 54 g of propargyl aldehyde was added during 0.5 hour with cooling to maintain a reaction temperature of 30 to 40°C. After about 2 hours, when the odor of the aldehyde had disappeared, the dark red solution was diluted with 200 cc of ice water and neutralized with milk of lime at 35 to 40°C. The calcium sulfate was filtered off and washed with water to a filtrate volume of about 2 liters, 50 cc of 30 per cent sodium hydroxide solution was added to the filtrate which was let stand 3 days; a small amount of a reddish brown precipitate separated on the vessel walls. The solution was decolorized with 5 g of carbon, cooled and extracted with ether. The ether was distilled, leaving 45 g (47.5 per cent) of slightly yellow 2-amino-pyrimidine (m. p. 123 to 125°C).

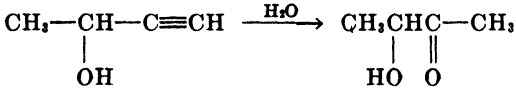
Addition of Water

Hydration of the triple bond of propargyl alcohol to yield acetol (hydroxyacetone) may be carried out using acid mercury catalysts.

$$CH{\equiv}CCH_2OH \xrightarrow{H_2O} CH_3C(=O)CH_2OH$$

[7] *D.R.Pat. Anmeldung I-73,052* (Aug. 25, 1942).

In the same way, butynol gives butane-3-one-2-ol in very good yields.

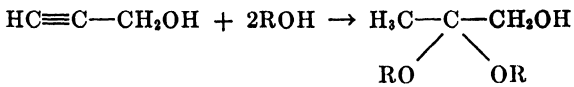


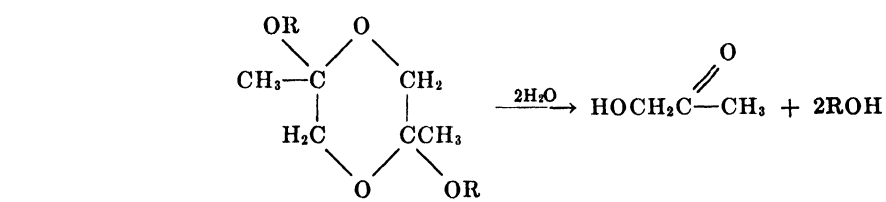
By reduction, these hydroxy ketones are converted to the vicinal glycols, 1,2-propylene glycol and 2,3-butylene glycol. The addition of water and hydrogenation of the keto alcohols is easier and gives better yields than does the same reaction with butynediol.

Dehydration of the butane-3-one-2-ol leads to vinyl methyl ketone. Dehydrogenation of the 2,3-butylene glycol gave diacetyl.

Addition of Alcohols

Alcohols may be added to the triple bond of propargyl alcohol under the influence of an acid mercury catalyst. The reaction, however, differs from that with acetylene where acetal is formed. Instead of the expected hydroxy ketal, cyclic acetals, derivatives of 1,4-dioxane are obtained.





Crystalline 2,5-dimethoxy-2,5-dimethyl-1,4-dioxane is formed[8] when 56 parts of anhydrous propargyl alcohol are heated to 60 to 70°C with 64 parts of methanol containing 2 parts of boron trifluoride etherate and 5 parts of mercuric chloride. On hydrolysis with acids, acetol (hydroxyacetone) results in excellent yields

Addition of Hydrogen Halides

Although propargyl alcohol readily adds hydrogen bromide to the triple bond, hydrogen chloride will not add except in the presence of mercuric salts. Addition is limited to one molecule of hydrogen chloride, and no attack of the hydroxyl group occurs. The reaction may be carried out with pure propargyl alcohol or a 30 per cent aqueous solution, and in either liquid or gaseous phase, with the catalyst free, or on a carrier such as char-

[8] Technical Oil Mission Microfilms, Reppe Patent Applications, Reel 159, Frame 2056.

coal: 500 g of a 30 per cent aqueous solution of propargyl alcohol containing 6 to 8 g of mercuric chloride is warmed to 60°C and hydrogen chloride gas is then passed in very rapidly for two hours to avoid addition of water to the triple bond, the rate being about 400 liters per hour. The temperature is held at 80°C. When no more hydrogen chloride is absorbed and tests show that no propargyl alcohol remains unreacted, the solution is distilled *in vacuo*, yielding 225 g of beta-chloroallyl alcohol (b.p. 135 to 140°C at 750 mm)[9].

A continuous process in gaseous phase using aqueous propargyl alcohol and excess hydrogen chloride at 30 to 40 mm pressure and 80 to 90°C gave a 65 per cent yield per pass. Higher temperatures gave higher conversions but also more by-products such as chloroallyl ether and polymerized propargyl alcohol.

Replacement of Hydroxyl with Thionyl Chloride

Thionyl chloride with propargyl alcohol gives propargyl chloride.

$$HC{\equiv}CCH_2OH + SOCl_2 \rightarrow HC{\equiv}C{-}CH_2Cl + SO_2$$

Replacement of Methine Hydrogen

Chlorine in alkaline solution gives chloropropargyl alcohol.

$$HC{\equiv}C{-}CH_2OH + Cl_2 + NaOH \rightarrow ClC{\equiv}C{-}CH_2OH$$

Dehydration of Acetylenic Alcohols

The dehydration of 2-methyl-butyne-3-ol-2 in the vapor phase over aluminum oxide or other dehydrating catalysts gives 2-methyl butene-1 yne-3 (isopropenyl acetylene).

$$(CH_3)_2C(OH){-}C{\equiv}CH \xrightarrow{-H_2O} CH_2{=}C(CH_3){-}C{\equiv}CH + H_2O$$

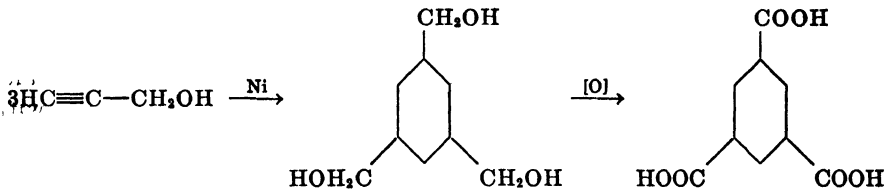
The dehydration of butyne-3-ol-2 to vinyl acetylene is not so easily accomplished because the rate of decomposition into acetaldehyde and acetylene is too great. However, the problem appeared to be of interest as a means of synthesizing vinyl acetylene free from divinyl acetylene.

Trimerization of Propargyl Alcohol

The trimerization of acetylene and its derivatives to benzene or its derivatives by thermal methods is well known. Diels has described the trimerization of esters of acetylene dicarboxylic acid in the presence of tertiary organic bases. Ebel and Spanig, in studying reactions of propargyl alcohol, found that it too could be trimerized by heating an aqueous

[9] Technical Oil Mission Microfilms, Reppe Patent Applications, Reel 158, Frame 1967 ff. (*D. R. Pat. 769,595*).

solution with Raney nickel for 30 hours. Although the conversion was only about 10 per cent, the unreacted propargyl alcohol could be recovered and reused. The major product of trimerization in this case was proved to be 1,3,5-trimethylol benzene by oxidation to the known trimesic acid.



Following Reppe's observation that complexes of triphenylphosphine with nickel halides or nickel carbonyl polymerized acetylene smoothly under mild conditions to yield 88 per cent benzene and 12 per cent styrene, Klager tested these complexes as catalysts for the trimerization of propargyl alcohol.

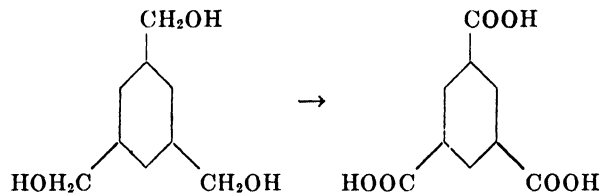
It was established that an aqueous 30 per cent or 70 per cent propargyl alcohol solution can neither be polymerized by the complex triphenyl phosphine-nickel halides, nor by the triphenyl phosphine-nickel carbonyl compounds. If anhydrous propargyl alcohol is used, no reaction occurs with $NiBr_2 \cdot (C_6H_5)_3P$. On the other hand, when anhydrous propargyl alcohol is treated with triphenyl phosphine-nickel carbonyl and heated to about 70°C, a reaction occurs accompanied by a gradual temperature rise to the boiling point of propargyl alcohol; ultimately the viscous mass turns dark brown with continued rise of temperature to about 200°C and decomposes with the evolution of white fumes. The intensity of this reaction can be diminished by the use of diluents such as the lower aliphatic alcohols, tetrahydrofuran and benzene.

By dissolving the catalyst in the solvent and adding the propargyl alcohol dropwise at reflux temperature, the reaction could be controlled by the rate of addition without further heating. Finally, it was refluxed further after the addition of the propargyl alcohol until the conversion was complete, or until the end of the polymerization was indicated by titration of the propargyl alcohol content of the reaction. The weight of solvent in a batch process amounted to 2 or 3 times the propargyl alcohol used for the reaction. The amount of catalyst used was roughly 7 per cent of the weight of propargyl alcohol, corresponding to 0.65 per cent of nickel by weight.

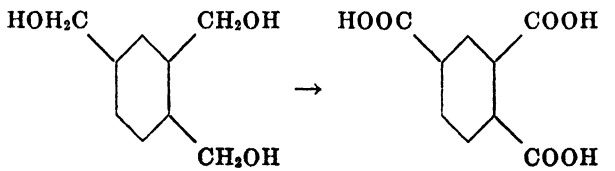
The course (yield, rate, products, etc.) of the reaction depended upon the type of solvent used. With alcohols only about 40 per cent of the propargyl alcohol was polymerized despite an increase in the amount of the catalyst, while the conversion was practically quantitative after a few hours in benzene. Tetrahydrofuran gave a yield of 50 to 60 per cent and was inferior to benzene not only as far as the yield was concerned but also with regard to rate of reaction.

The yield of the trimerization products was more than 90 per cent of theoretical; however, due to the losses on purification, only about 75 per cent was obtained as pure product. In most cases, such as for oxidation, the crude product of trimerization was suitable.

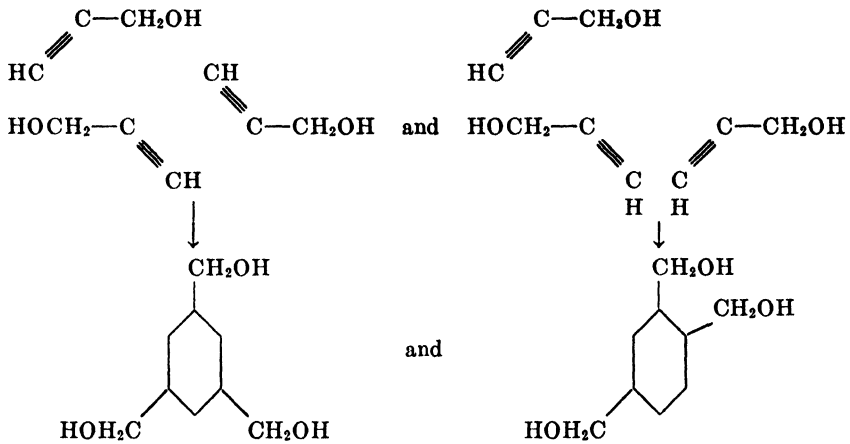
The trimerization product was not a homogeneous compound, although the boiling point of the product and of the triacetate indicated a homogeneous compound. The oxidation of the trimerization products with concentrated nitric acid, however, gave a mixture of two acids, one of which was very insoluble in concentrated nitric acid and in water even when heated, while the second acid was very easily soluble in both. An equivalent weight of 73 was found for the difficultly soluble acid; the trimethyl ester prepared by esterification with methanol melted at 143 to 144°C and gave no melting-point depression when mixed with trimesic acid trimethyl ester. The yield of this acid amounted to about 40 per cent of theoretical. Therefore, about half of the trimerization products consist of 1,3,5-trimethylolbenzene, which is converted into trimesic acid by oxidation with nitric acid



The more easily soluble acid can be freed from the rest of the trimesic acid and purified by recrystallization from about five times the concentration of nitric acid. It melted between 210° and 220°, dependent upon how the melting point was taken. The equivalent weight was found to be 72 Esterification with methanol and sulfuric acid did not give a crystalline ester. These properties correspond to the reported properties of trimellitic acid, but a direct comparison was not made at Gendorf owing to unforeseen events. This acid was obtained in somewhat more than 40 per cent yield, while the rest was obviously a difficultly separable mixture of both acids, besides small amounts of other degraded acids such as oxalic acid. The very probable presence of trimellitic acid as a second oxidation product indicated that besides 1,3,5-trimethylolbenzene, 1,2,4-trimethylolbenzene is also formed in the trimerization.



The oxidation of the triacetates with nitric acid gave similar results. Both acids were isolated from the oxidation of the crude trimerization products with potassium permanganate in alkaline solution. From these results, it follows that the trimerization product represents a mixture of essentially equal parts of 1,3,5-trimethylolbenzene and 1,2,4-trimethylolbenzene.



In a similar way butynol, $HC{\equiv}C{-}CHOHCH_3$, could be trimerized, although in poorer yields. The trimerization product was a honey-yellow sirup and was not further investigated.

The mode of action of the catalyst which influences this reaction in such an extraordinary simple manner is unknown. It was noted that after the end of the trimerization the benzene solution was inactive in new reactions. From the benzene solutions none of the originally used complex could be isolated; a white substance, crystallizable from ligroin in long needles, was found and identified as triphenyl phosphine. The nickel was not found in the benzene portion after the reaction but appeared in the trimer and was separated by working up as an insoluble nickel compound. A quantitative determination of the nickel in the crude trimer was not made.

Since only triphenylphosphine was recovered, the catalyst was destroyed either by the reaction, or by contact with air. Probably the poor yields using alcohols as solvents can be traced to a rapid decomposition of the catalyst in alcoholic solution. Although the experiments of Ebel and Spanig with Raney nickel suggest such a conception, the catalysis does not appear to be due only to specific action of the nickel, since the nickel halide-triphenyl phosphine complex does not cause trimerization. On the other hand, the experiments of Ebel and Spanig show that the grouping $-Ni(CO)_2$ alone cannot be responsible. By analogy with the addition of butyl bromide to triphenylphosphine-$NiBr_2$ to form a phosphonium salt, propargyl alcohol may add in a similar manner, producing a complex

which can be polymerized. Perhaps the acidic hydrogen atom plays a role in such complex formation since butynediol under the same conditions did not trimerize.

Experimental Part. Two grams $[(C_6H_5)_3P]_2$-Ni$(CO)_2$* was dissolved in 75 cc of benzene and under reflux was slowly treated with 28 g of anhydrous propargyl alcohol (97 per cent). Following the addition, it was heated for 2 hours more, until no more propargyl alcohol could be detected. After cooling, the benzene solution was decanted from the precipitated thick brown oil. The trimer was dissolved in water, decolorized with carbon, filtered, and the clear water solution was evaporated. The residue of 25 g corresponded to 92 per cent of theory. The yellow sirup showed no tendency toward crystallization.

The trimer can be purified by distillation in a high vacuum, but yields are not good.

Reactions of Acetylenic Glycols

The acetylenic glycols are multifunctional compounds containing a reactive triple bond and reactive hydroxyl groups, and as such undergo a wide variety of chemical reactions.

Hydrogenation

On reduction, butynediol-1,4 behaves much like propargyl alcohol which, as previously shown, gave a wide variety of reaction products depending on the activity of the catalyst, the pH of the catalyst carrier, and the temperature. The reduction of butynediol-1,4 to butanediol-1,4 was of great importance in the Reppe synthesis of butadiene from acetylene and formaldehyde (see page 101). At high temperatures over copper catalysts, *n*-butanol is the chief product of reduction[10]. Partial hydrogenation gives butenediol[11].

$$\begin{array}{ccc} HOCH_2C{\equiv}CCH_2OH & \xrightarrow{H_2} & HOCH_2CH{=}CHCH_2OH \\ \Big\downarrow{\scriptstyle 3H_2} & & \Big\downarrow{\scriptstyle H_2} \\ CH_3CH_2CH_2CH_2OH + H_2O & & HOCH_2CH_2CH_2CH_2OH \end{array}$$

Hydrogenation of Butynediol-1,4 to n-Butanol. In the hydrogenation of butynediol-1,4 to butanediol in the presence of copper or nickel catalysts, the formation of a small quantity of *n*-butanol has always been observed. The quantity of butanol increases with increasing temperature of the reaction. The hydrogenation (butynediol + 3 H_2 → butanol + H_2O + 91 cal) produces water, and it is therefore advantageous to use

* See page 260 for the preparation of this catalyst.

[10] *Fr.Pat. 853,148* (Example 4).

[11] *Brit.Pat. 508,543; D.R.Pat. 727,476; 753,951; Fr.Pat. 45,600.*

dehydrating hydrogenation catalysts in order to obtain a high yield of butanol.

Continuous hydrogenation of aqueous solutions of butynediol with copper on silica gel at 200°C with 200 atm of hydrogen pressure yielded 40 per cent butanol, with butanediol as the chief product. Experiments with Raney copper, which has no dehydrating action, gave only 10 per cent of butanol. Hydrogenation in the presence of copper chromite catalysts, which easily converts the less stable butanediol-1,3 to a mixture of secondary and primary butanol, did not give any butanol from butane-, butene-, or butynediols at 300°C and 300 atm.

Catalysts with too strongly pronounced dehydrating action are unsuitable for the reaction because they promote resinification. Copper catalysts on extrudings of bolus alba or silica gel have a useful lifetime of only 3 to 7 days, at a throughput of 0.5 kg of butynediol per day per liter of catalyst.

The best results were obtained with copper catalysts on activated alumina which had been conditioned at 800°C. The yield of butanol was 70 to 80 per cent at a reaction temperature of 150 to 200°C. At lower conditioning temperatures the catalyst formed more resins during hydrogenation, whereas the yield of butanol decreased at higher conditioning temperature with increased useful life of the catalyst. This is probably due to partial conversion of γ-Al_2O_3 to α-Al_2O_3, the dehydrating efficiency of which is considerably less. Useful life of the catalyst baked at 800°C did not exceed 18 days at a throughput of 1 kg of butynediol per day per liter of catalyst; the catalyst becomes inefficient because of resin formation. Useful life of the catalyst can be increased approximately three times, if the reaction is carried out in such a way that 45 per cent of butanol and 55 per cent of butanediol are produced.

The butanol is freed from water by azeotropic distillation but contains traces of unsaturated by-products which cause a more-or-less pronounced discoloration. (Color, compared with an iodine scale: 200 to 400.) Those by-products can be removed almost entirely by chlorination followed by distillation with alkali, or by after-hydrogenation with nickel catalysts under pressure. This brings the color of the butanol down to 10 to 30.

Butene-2-diol-1,4 from butyne-2-diol-1,4. *Catalytic Hydrogenation.* The earlier processes for the partial hydrogenation of butynediol used catalysts containing cobalt, copper, or nickel, which were readily poisoned by carbon monoxide or sulfur-containing compounds. The life of these catalysts was usually short due to the resins formed. Reppe found that carbonyl iron and electrolytic iron were very suitable catalysts for partial hydrogenation, if the reaction took place under pressure.

At first, it was found that exhaustive hydrogenation of butynediol to butanediol took place with Raney iron (obtained by the decomposition of

iron aluminum alloy with caustic soda), carbonyl iron, and electrolytic iron at a pressure of approximately 25 atm of hydrogen and at 40°C in small autoclave tests. Under less drastic conditions no hydrogenation took place. It was not possible to confirm observations previously reported with other derivatives of acetylene, namely that hydrogenation stopped automatically at the ethylene stage for the reduction of butynediol → butenediol → butanediol. If the hydrogenation is stopped as soon as the butynediol disappears, it is possible, however, to isolate some butenediol, due to the slowness with which it absorbs hydrogen. In any case, a considerable quantity of butanediol (10–20 per cent) will be found because of the long reaction time (30 hours), even though the conditions of hydrogenation may have been mild (50°C, 50 to 100 atm of hydrogen pressure).

Much more favorable results are obtained with continuous runs because of the shorter time of contact with the catalysts[12]. The apparatus required consists of a high-pressure trickling tower with a jacket which is filled with a heating agent (preheated in a storage vessel to an exact temperature and circulated with a gear pump). The hydrogen pressure is kept constant, and the gas is recycled. Starting material is fed to the tower by a reciprocating pump. The reaction product is discharged continuously from the separator.

Eight liters of the 25 per cent aqueous solution of butynediol (pH 5 to 7) per liter of catalyst are pumped through the tower at 50 to 100°C and 150 to 200 atm of hydrogen pressure. Heat of the reaction is 37,000 calories per mole, which is removed by the hydrogen cycle. Hydrogenation does not stop automatically at the ethylene stage[13]; hence hydrogen pressure, temperature and throughput must be carefully kept constant. In this way, it is possible to retard the formation of butanediol which occurs at higher temperature, higher pressure and lower throughput, and to avoid a residue of unchanged butynediol which does not react at lower temperatures, lower pressures and higher throughputs.

A 25 per cent solution of aqueous butenediol leaves the separator. Water is distilled off at first, carrying over traces of C_4 alcohols (less than 0.5 per cent of crotyl alcohol and *n*-butanol), then the unchanged formaldehyde from the starting solution, some allyl alcohol and *n*-propanol (from propargyl alcohol in starting solution). The raw butenediol is distilled under vacuum. Besides butenediol, it contains 5 per cent of butanediol and 2 per cent of unchanged butynediol. Perfect separation of the three components was not possible because the boiling points of the three products are so close (butanediol 229°C, butenediol 234°C, butynediol 238°C). The sensitivity of the butenediol to heat further limits the separation. Dis-

[12] I. G. Farbenindustrie patent proposal *O.Z.-12,670*.

[13] *Compt. rend.*, **206**, 608 (1938); *Bull. soc. chim.* (5), **6**, 218 (1939); *J. Am. Chem. Soc.*, **62**, 2555 (1940).

tillation of the raw butenediol under vacuum must be done with great care because the distillation residue will vigorously decompose if contacted with air at elevated temperature. By proper adjustment of the conditions of the process, it is possible to make products which contain less than 0.1 per cent of butynediol and 10 per cent of butanediol, or less than 0.1 per cent of butanediol and 10 per cent of butynediol.

The product is analyzed by bromination with nascent bromine, or with an excess of a 2*N* solution of bromine in a saturated solution of sodium bromide in methanol. Unabsorbed bromide is back-titrated with arsenite solution. Butenediol absorbs two atoms of bromine, butynediol adds 2.5 atoms of bromine* and butanediol does not react with bromine at all. In conjunction with the mercuric chloride method (report of Dr. Kerckow, October 30, 1941) for determining butynediol, it is possible to calculate the percentage of all three components in the reaction product.

The hydrogenation catalyst is produced from purest carbonyl iron powder, or from electrolytic iron. A thick paste, made from the iron powder and *n*-butanol, is fed to an extruding press and the extrudings are reduced in hydrogen. Butanol is evaporated at first, and the temperature is finally raised to 500°C (carbonyl iron) and 600°C (electrolytic iron) The soft extrudings are baked within 10 hours, the shape is conserved, and the final catalyst is solid and stable. The particles of electrolytic iron are larger than those of carbonyl iron and hence require a higher temperature in order to be sufficiently mechanically stable. This catalyst is ready for use in the reactor, but may also be after-treated with hydrogen at 400°C to reduce traces of oxide.

The activity of the catalysts is not constant, activity increasing in the beginning, remaining constant for some time and finally decreasing. These fluctuations in activity can be compensated to a large extent by varying the working conditions of the tower. Life of the catalyst depends upon throughput and is approximately 6 weeks at a feed rate of 2 kilos of 100 per cent butynediol per day per liter of catalyst. Hydrogenation activity decreases considerably after this time, although no formation of resins could be observed

Chemical Reduction. In the course of 2 hours, while stirring at 20°C, 304 g of 35 per cent caustic soda solution are added to a mixture of 344 g of butynediol-1,4, 180 g of water and 352 g of 78 per cent electrolytic zinc dust, ice water is used to make sure that the temperature does not rise appreciably above 20°C. After the mixture has been stirred for 20 hours at 20°C, the zinc oxide formed is filtered off and the filter residue washed with water to a weakly alkaline reaction. The filtrates are combined and hydrochloric

* No additional information on these methods has been located. It would appear that the statement that butynediol adds 2.5 atoms of bromine is erroneous since it should add either 2 or 4 atoms.

acid added thereto until the solution is acid to litmus. The water is then evaporated therefrom under reduced pressure, and the oily residue is filtered by suction from the salts precipitated by the evaporation of the water. The filter residue is washed several times with alcohol, the alcoholic filtrates combined with the oily fraction and the alcohol expelled by distillation under reduced pressure. The residue is purified by vacuum distillation, whereby 315.5 g (90 per cent yield) of *cis*-butenediol-1,4 are obtained, which boils between 91 and 100°C at a pressure of from 0.3 to 0.4 mm (of Hg). By repeated distillation, a pure butenediol having a boiling point of from 104 to 107°C at a pressure of 0.7 to 0 8 mm (of Hg) is formed. The compound cannot be solidified by cooling with a mixture of ice and common salt.

Partial Hydrogenation of Other Acetylenic Alcohols with Iron Catalysts. Following the experience with the partial hydrogenation of butynediol, the applicability of the method to other acetylenic alcohols was tested.

Unilaterally-Substituted Acetylenes. In general, unilaterally-substituted acetylene derivatives and acetylene itself, can be reduced to ethylenic compounds in very poor yields with iron catalysts. The final product always contains starting material as well as a considerable quantity of the saturated compound. Acetylene, propargyl alcohol, butyne-3-ol-2, and 2-methyl butyne-3-ol-2 yielded between 50 to 70 per cent of the ethylenic compounds.

Bilaterally-Substituted Acetylenes. Pentyne-3-diol-2,5 can be converted to the ethylenic compound under conditions similar to those used for the preparation of butynediol. Results are even more favorable with hexyne-3-diol-2,5 which was hydrogenated discontinuously to hexene-3-diol-2,5 (b. p. 124°C, 13 mm) with an iron catalyst in an autoclave at 100°C under 100 atm of hydrogen pressure in 95 per cent yield. Only 5 per cent was exhaustively hydrogenated to hexanediol. In strong contrast to the hydrogenation of butynediol, the reaction stops at the ethylenic stage, in this case probably due to the decreased activity of the double bond caused by the large substitutent groups. Still better yields are obtained in continuous runs in a trickling tower with iron catalysts. The reaction does not require high constancy of pressure, temperature, or throughput, and 98 to 99 per cent yields of hexenediol, besides 0.2 to 0.5 per cent unreacted hexynediol, are obtained at 100°C and 100 atm of pressure.

The above experiments have demonstrated that hydrogenation of butynediol with iron catalysts under pressure leads to formation of butenediol only if the pressure, temperature and throughput are carefully adjusted in the reactor. Pressureless partial hydrogenation of propargyl alcohol to allyl alcohol also requires close control of the reaction conditions. The homologous methyl-substituted compounds, on the other hand, give partly hydrogenated products, independently of reaction conditions. This was

exhibited in the hydrogenation under pressure of hexynediol with iron catalysts, and pressureless hydrogenation of butynol with palladium catalysts. It can be concluded that the double bond becomes less reactive towards hydrogen with increasing molecular size of the ethylenic alcohol and therefore partial hydrogenation of substituted acetylenic alcohols can be carried out in almost quantitative yields.

Addition of Sodium Bisulfite

Refluxing an aqueous solution of sodium bisulfite with butynediol-1,4 is reported to give good yields of the sodium butanediol-1,4 disulfonate-2,3.[14]

$$HOCH_2C{\equiv}CCH_2OH + 2NaHSO_3 \longrightarrow HOCH_2\underset{\displaystyle NaO_3S}{\underset{|}{C}}H\underset{\displaystyle SO_3Na}{\underset{|}{C}}H{-}CH_2OH$$

Replacement of Hydroxyl Groups with Halogen

The reaction of butynediol-1,4 with thionyl chloride gives 1,4-dichlorobutyne-2. The reaction may be carried out by mixing the diol with the stoichiometric quantity of thionyl chloride and heating cautiously until no more gas is evolved.

$$HOH_2CC{\equiv}C{-}CH_2OH + 2\,SOCl_2 \rightarrow ClCH_2C{\equiv}C{-}CH_2Cl + 2\,HCl + 2\,SO_2$$

Alternatively, the reaction may be carried out in the presence of pyridine[15]. A 90 per cent yield of 1,4-dichlorobutyne-2 (boiling at 68 to 69°C/17 mm, 165 to 166°C/760 mm, N_D^{20} 1.5072, d_4^{20} 1.258) is claimed. Johnson also prepared the dibromo- and diiodobutynes and has studied a number of reactions of these acetylenic dihalides.

Although the Germans[16] claim that the treatment of 1,4-dichlorobutyne-2 with alkaline agents furnishes an excellent method for the preparation of diacetylene, Johnson successfully carried out numerous metathetical reactions with sodium alkoxides, phenoxides, ammonia and amines; however, dichlorobutyne is inert to both potassium or cuprous cyanide.

The action of thionyl chloride on 2,5-dimethyl hexyne-3-diol-2,5 gave 2,5-dichloro-2,5-dimethyl hexyne-3, boiling at 60 to 70°C/11 mm.

Isomerization of Butynediol to Hydroxymethyl Vinyl Ketone[17]

Butynediol readily undergoes a Meyer-Schuster rearrangement to hydroxymethyl vinyl ketone[18]

$$HOCH_2C{\equiv}CCH_2OH \longrightarrow HOCH_2\overset{\displaystyle O}{\overset{\|}{C}}{-}CH{=}CH_2 \quad (20\ cal)$$

[14] *Fr.Pat. 858,185; Chem. Centr.*, **1941**, I, 1738.
[15] Johnson, *J. Chem. Soc*, **1946**, 1009.
[16] *D. R. Pat. 740,637.*
[17] *PB* 75631; I. G. Farbenindustrie patent proposal *O.Z.-13,357.*
[18] *Ber.*, **55**, 819–23 (1922).

Mercuric, silver and cupric salts of strong acids are effective catalysts, as is mercuric oxide-boron fluoride etherate. The action of these compounds is catalytic.

The isomerization is strongly exothermic, particularly with mercuric salts as catalysts, and should be carried out in the presence of a diluent, or in solution. Inert solvents such as ethers and esters, in which neither the butynediol nor the catalyst is completely soluble, may be used, provided agitation is sufficient for adequate contact. Solvents such as water and alcohols, which permit carrying out the reaction homogeneously, can be used, but since hydroxyl compounds react readily with both the butynediol and its isomerization product, care must be taken to avoid side reactions. This may be accomplished by running the reaction at moderate temperatures and interrupting the reaction as soon as the isomerization is complete, either by cooling or by neutralizing the catalyst. Another method is to distill out under reduced pressure an aqueous solution of hydroxymethyl vinyl ketone as rapidly as it is formed. The hydroxymethyl vinyl ketone is then separated from the water by refractionation, or subjected to further reactions in aqueous solution. With alcohols, it is claimed that the rate of reaction with butynediol or hydroxymethyl ketone is directly dependent on the number of carbon atoms in the alcohol; methanol reacts so rapidly that it is not recommended, but ethanol and higher homologs are satisfactory solvents.

The progress of the isomerization may be conveniently followed by determination of the carbonyl number of the reaction mixture. When this value corresponds to the theoretical value for hydroxymethyl vinyl ketone, the catalyst is neutralized and the hydroxymethyl vinyl ketone isolated by distillation or extraction, or subjected to further reactions in solution.

Hydroxymethyl vinyl ketone is a colorless liquid of extremely pungent odor. It is soluble in water and has a boiling point of 45 to 46°C/10 mm. In pure form, it is stable only a short time at room temperature. In the presence of air, it is rapidly transformed into a jelled mass which slowly changes to a hard glass-like odorless polymer.

Details of the evaluation of this readily polymerized monomer, or polymers thereof have not been located. Apparently, some work has been carried out on catalytic reduction to 1,2-butanediol.

The following examples describe the isomerization procedure:

Example 1. A solution of 100 parts of butynediol in 400 parts of ethyl acetate was vigorously agitated with a catalyst prepared by mixing 5 parts of mercuric oxide, 5 parts of boron fluoride etherate, 5 parts of ethyl acetate and 1.5 parts of trichloroacetic acid at 50 to 60°C. The reaction mixture was warmed to 40°C and maintained at approximately 45°C during the isomerization (about 1 hour) by reducing the pressure so that the reflux temperature corresponded to the desired temperature. When the reaction

was over, as shown by a decrease in the temperature, the acid catalyst was neutralized with sodium carbonate. Vacuum distillation yielded approximately 20 g of hydroxymethyl vinyl ketone, b.p. 45 to 46°C/10 mm.

Example 2. A mixture of 4,000 parts of a 10 per cent aqueous solution of butynediol and 28 parts of concentrated sulfuric acid was warmed to 40°C, and 24 parts of mercuric sulfate added. As the mercuric sulfate dissolved, the reaction temperature began to rise but was maintained at 50 to 52°C by applying a vacuum of 95 to 100 mm; the reaction heat was removed by evaporation and condensation of water in the condenser. The course of the reaction is followed by sampling and determination of the carbonyl number; the catalyst is neutralized as soon as a carbonyl number of 65 (theoretical) is obtained. This usually requires about one hour.

By distillation at 40 mm, 3,820 parts of a 6.4 per cent aqueous solution of hydroxymethyl vinyl ketone are obtained. Separation of pure ketone from this aqueous solution by distillation is difficult since it is highly volatile in steam.

Example 3 A mixture of 100 parts of a 10 per cent aqueous solution of butynediol and 6 parts of mercuric sulfate is stirred at 50°C. Distillation at 100 to 120 mm is started and 900 parts of a 10 per cent aqueous solution of butynediol is added continuously over one hour. The reaction vessel is heated sufficiently to distill out during the same time 900 parts of a 4.4 per cent aqueous hydroxymethyl vinyl ketone solution, while maintaining a reaction temperature of 50 to 55°C

Hydration of Butynediol-1,4

Butynediol in aqueous solution adds one molecule of water in the presence of mercuric catalysts to form 1,4-dihydroxybutanone-2[19]

$$HOCH_2C{\equiv}C{-}CH_2OH + H_2O \xrightarrow{HgSO_4} HOCH_2\overset{\overset{O}{\|}}{C}CH_2CH_2OH$$

Although the above equation indicates that the 1,4-dihydroxybutanone-2 is formed by the direct addition of water to the triple bond of butynediol, it is probable that the major part, if not all, of the dihydroxybutanone arises from the isomerization of butynediol to hydroxymethyl vinyl ketone (discussed on page 135), followed by addition of water to hydroxymethyl vinyl ketone:

$$HOCH_2C{\equiv}CCH_2OH \xrightarrow[H^+]{HgSO_4} HOCH_2\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2 \xrightarrow[H^+]{H_2O} HOCH_2\overset{\overset{O}{\|}}{C}{-}CH_2CH_2OH$$

[19] *D.R.Pat. 750,057, PB* 92206.

The isolation of the dihydroxybutanone is very difficult as this compound has a tendency to condense with itself and also to dehydrate to hydroxymethyl vinyl ketone which, of course, polymerizes easily (*vide supra*).

For this reason, the aqueous solution resulting from the hydration of butynediol is usually immediately processed by reduction to butane-1,2,4-triol, which has properties similar to, and can be used as a substitute for glycerin. The trinitric acid ester of butane-1,2,4-triol is an excellent explosive. Its energy content is almost that of nitroglycerin. It gelatinizes well with nitrocellulose, is only slightly volatile, and is very stable at low and elevated temperatures.

Synthesis of Butane-1,2,4-Triol. *Hydration of Butynediol to 1,4-Dihydroxybutanone-2.* A solution of mercuric sulfate (5 to 6 per cent of the weight of diol) dissolved in sulfuric acid (1 to 2 per cent of the total reaction weight) was added to a stirred 10 per cent aqueous solution of butynediol-1,4. The reaction was mildly exothermic (27 kg cals), and the temperature was maintained at 15 to 20°C for six hours, then at 20 to 30°C for another six hours by cooling as needed. The reaction mixture was allowed to settle for one hour and the separated sludge (spend catalyst, mainly free mercury) removed. The aqueous solution was then heated to 40°C for 60 hours to complete the addition of water to the hydroxymethyl vinyl ketone, and carefully neutralized to pH 4.5 with calcium carbonate. The neutralized batch was treated with charcoal, filtered, and the filtrate concentrated at 40 to 50°C and 60 to 70 mm of mercury pressure until the concentration of dihydroxybutanone was approximately 50 per cent. Prior to hydrogenation, the solution passed through a Wofatite ion exchanger to replace calcium ions with sodium ions.

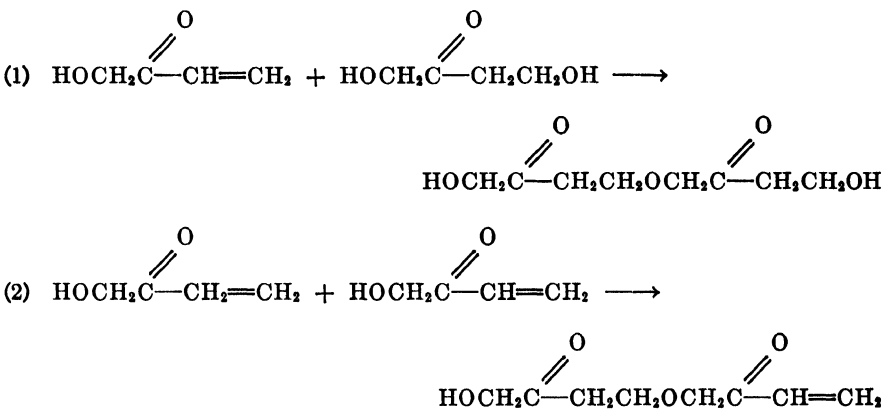
Hydrogenation of 1,4-Dihydroxybutanone-2 to Butanetriol-1,2,4. The 50 per cent aqueous solution of the dihydroxybutanone was preheated and fed at the rate of 20 liters per hour to the top of a hydrogenator, together with hydrogen. The gas and liquid streams flowed down over a catalyst consisting of 20 per cent copper and 0.5 per cent chromium on silica gel particles (B B E catalyst). The temperature was 80°C with fresh catalyst, and was gradually increased to 100°C on continued use; the pressure was 200 atm. The product passed to a separator; the uncondensed gas was continuously recycled. The hydrogenation product was neutralized to pH 7.0 with sodium hydroxide. The water was removed at 60 to 70 mm of pressure, and the residue topped at 5 to 10 mm to remove volatile impurities up to 140°C. The triol was then distilled at 140°C at 1 to 2 mm pressure. The space-time yield was 2 kg of triol per day per liter of catalyst.

The main fraction of butane triol was usually yellow in color and was not sufficiently pure for conversion to the trinitrate ester. In order to obtain a nitration grade triol, it was necessary to rehydrogenate over a catalyst

consisting of 16 per cent nickel, 5 per cent copper and 0.7 per cent manganese on silica rods. The hydrogenation was carried out at 100 to 140°C under 100 to 200 atm pressure. The rehydrogenated product was practically colorless and was further purified by redistillation. The pure butanetriol-1,2,4 had the following properties: b.p. 140/1–2 mm, n_D^{20} 1.4535, D_4^{20} 1.860–1.867, hydroxyl number 1517–1529.

The yield of crude butane-1,2,4-triol was 70 to 80 per cent; the loss upon rehydrogenation varied between 10 and 20 per cent.

By-Products. A considerable number of by-products may form during the hydration of the hydroxymethyl vinyl ketone; other hydroxyl-containing compounds may add to the very reactive vinyl ketone, for example:



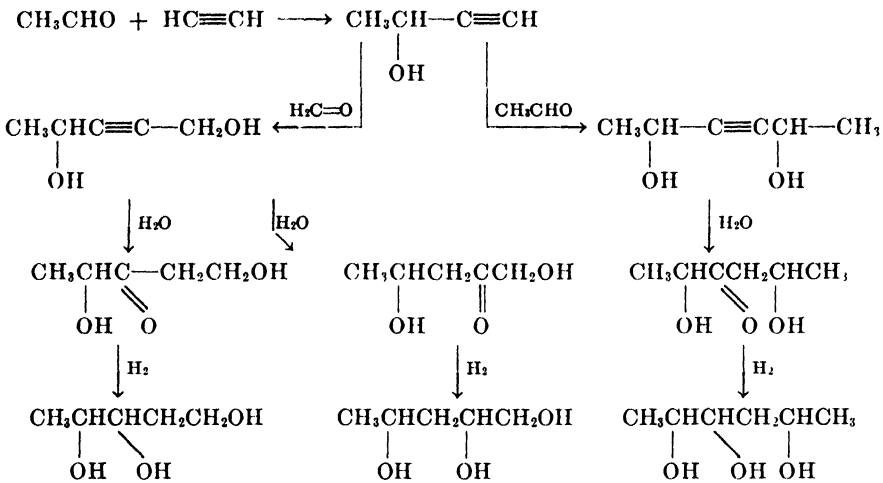
The formation of these high molecular-weight ethers, which are subsequently reduced to polyhydroxy compounds, can be minimized by carrying out the hydration in as dilute a solution as is feasible and by controlling the temperature. Further reaction of the vinyl ketoether formed by self condensation of hydroxymethyl vinyl ketone, as in (2), leads to a non-distillable tars.

If the hydration of the hydroxymethyl vinyl ketone is not complete or if the temperature during reduction is too high, butane-1,2-diol is formed; in fact, at hydrogenation temperatures above 100°C the yield of butane-1,2-diol can be increased to 70 per cent.

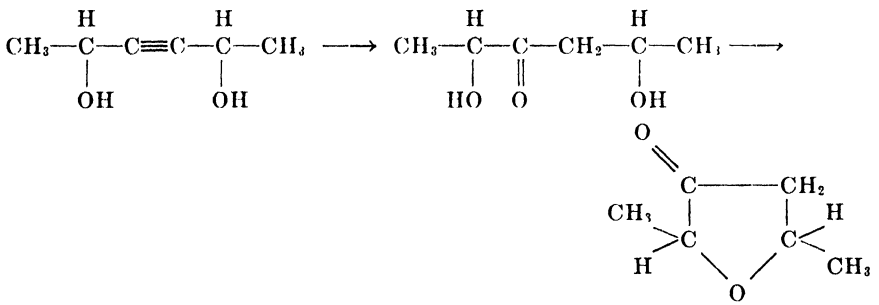
Propane-1,2-diol is formed by the reduction of acetol which arises from the hydration of any propargyl alcohol originally present in the technical butynediol solution. Any unreacted butynediol would, of course, yield butane-1,4-diol. Another by-product is 3-hydroxytetrahydrofuran which results from cyclic dehydration of the triol, or from cyclic dehydration of the dihydroxybutanone followed by reduction.

Synthesis of Other Triols. By starting from acetaldehyde and acety-

lene, the two isomeric pentanetriols, the 1,2,4- and the 1,3,4, as well as the 2,3,5-hexanetriol can be prepared:



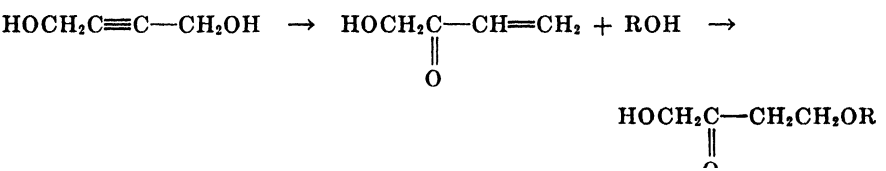
The disubstituted dihydroxybutanones, such as 2,5-dihydroxyhexanone-3, tend to cyclize to the 3-ketotetrahydrofuran by splitting out water



If the addition of water to the alkynediol is carried out at 70 to 80°C, the 3-ketotetrahydrofuran results directly

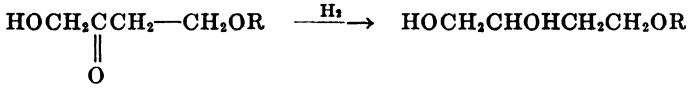
Addition of Alcohols

The addition of alcohols to alkynediols in the presence of mercuric salts does not lead to the expected ketal of the dihydroxyalkanone. Instead, the alkynediol first rearranges to the hydroxymethyl vinyl ketone which adds one molecule of alcohol to the double bond and forms the monoalkyl ether of 1,4-dihydroxybutanone-2



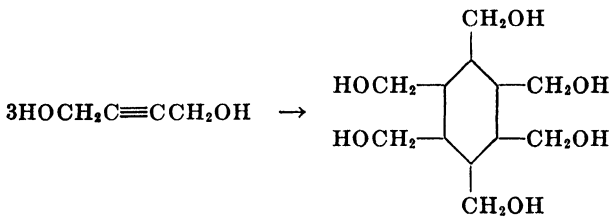
With methanol the rate of addition is so rapid that the intermediate vinyl ketone cannot be isolated; with higher alkyl alcohols, the rate is slower and the hydroxymethyl vinyl ketone can be isolated.

It is also possible that the reaction may take place through the formation of a 1,4-dioxane which by saponification yields the 4-alkoxybutanol-1-one-2. Reduction of these alkoxy ketones gave the monoethers of butane triol-1,2,4.



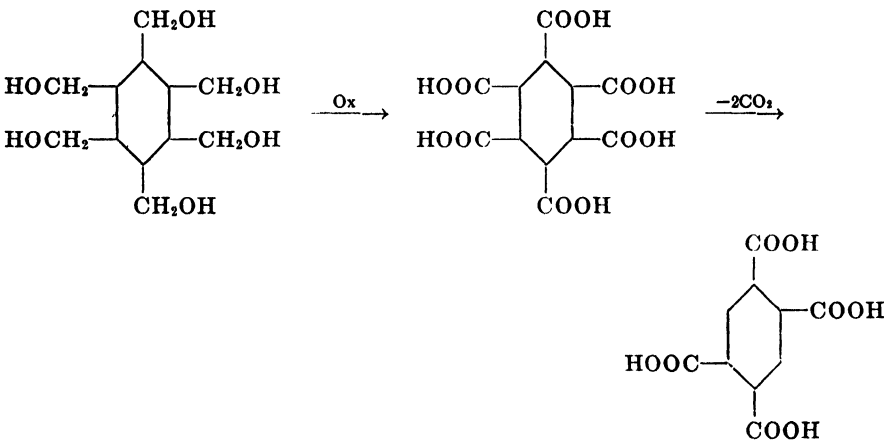
Trimerization of Butynediol

Butynediol undergoes trimerization to hexamethylol benzene when its aqueous solutions are refluxed with Raney nickel.



Yields after 30 hours of heating are only about 30 per cent. However, it is claimed that the unreacted starting material can be recovered.

The structure of the reaction product was determined by oxidation to mellitic acid and by degradation of the mellitic acid to pyromellitic acid.



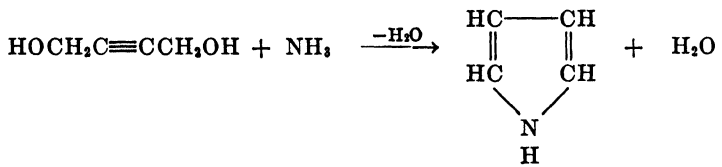
Smith reports that the trimerization is effected in 30 per cent yield by heating butynediol with 5 per cent nickel acetate or cyanide at 120°C[20].

[20] "German Synthetic Fiber Developments," p. 539, Textile Research Institute, 1946.

In contrast to the trimerization of propargyl alcohol under the influence of triphenyl phosphine-nickel carbonyl complexes (see page 126), both butynediol and butynediol diacetate were not effected by this catalyst. Complexes of triphenyl phosphine with mercuric and zinc halides also were without catalytic activity.

Reaction with Ammonia and Amines

Passage of a current of ammonia and butynediol vapors over an aluminum oxide (95 per cent)-thorium oxide (5 per cent) catalyst at 300°C is reported to give a good yield of pyrrole[21].



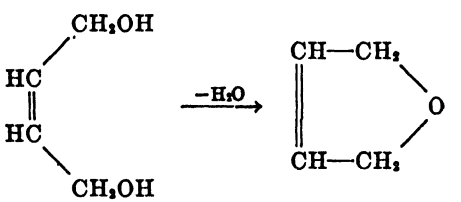
The ammonia may be replaced by primary amines, thus producing N-substituted pyrroles. For example, aniline gives N-phenylpyrrrole.

Reactions of 2-Butene-1,4-diol

Dehydration of Butenediol[22]

Butenediol as produced by the partial hydrogenation of butynediol is readily dehydrated in good yields to dihydrofuran by catalysts such as aluminum oxide, bauxite, silica gel, etc. However, if acid catalysts are utilized, the yield of dihydrofuran is reduced by the formation of hydroxybutyraldehyde and crotonaldehyde, and in extreme cases, crotonaldehyde may in fact be the major product. Condensation and resinification of these aldehydes soon inactivates the catalyst.

Butenediol, of course, can exist in both a *cis* and *trans* form; normally, the butenediol from hydrogenation is believed to be mainly the *cis* form. The *cis* form should dehydrate readily to the cyclic dihydrofuran.



However, it is much more difficult to dehydrate the *trans* form, and rearrangement to the hydroxyaldehyde takes place instead. Dehydration of

[21] *U.S.Pat. 2,421,650.*
[22] *D.R.Pat. 695,218; 695,219.*

the hydroxyaldehyde and migration of the double bond would yield crotonaldehyde.

$$HOCH_2—CH \rightarrow HOCH_2CH_2CH_2CHO \rightarrow CH_2{=}CHCH_2CHO + H_2O$$
$$\quad\;\; \| \qquad\qquad\qquad\qquad\qquad\quad \downarrow$$
$$\quad CH—CH_2OH \qquad\qquad\qquad\qquad CH_3CH{=}CHCHO$$

Since more aldehyde, particularly crotonaldehyde, is formed when using acid catalysts, it was assumed that the butenediol reacts principally in the *trans* configuration.

The process for the preparation of 2,5-dihydrofuran from butenediol was carried out in an electrically heated Huerden furnace over 25 liters of activated aluminum oxide. At 160°C and 70 to 90 per cent conversion, the crude dihydrofuran contained 84 per cent of dihydrofuran, 11 per cent of water, 1.5 to 2 0 per cent of crotonaldehyde and about 2.5 per cent of diols. Dihydrofuran was of interest as an intermediate for the preparation of a number of tetrahydrofuran derivatives and for oxidation to maleic anhydride.

Reaction with Hydrogen Cyanide[23]

Butenediol reacts with hydrogen cyanide to give 1,4-dicyanobutene-2, the dinitrile of dihydromuconic acid.

$$HOCH_2CH{=}CHCH_2OH + 2\ HCN \rightarrow CNCH_2CH{=}CHCH_2CN + 2\ H_2O$$

This reaction is carried out in liquid phase at 60 to 80°C in the presence of a cuprous chloride-ammonium chloride catalyst. Yields of 70 per cent are claimed. Other active alcohols such as allyl and benzyl alcohols are reported to undergo this novel reaction. An alternative synthesis from butenediol via the reaction of sodium cyanide with 1,4-dichlorobutene-2 is also possible. Thus, another route from acetylene to polyamide chemistry is opened up by reduction of the dihydromuconic nitrile to hexamethylenediamine-1,6.

Reactions with Aldehydes

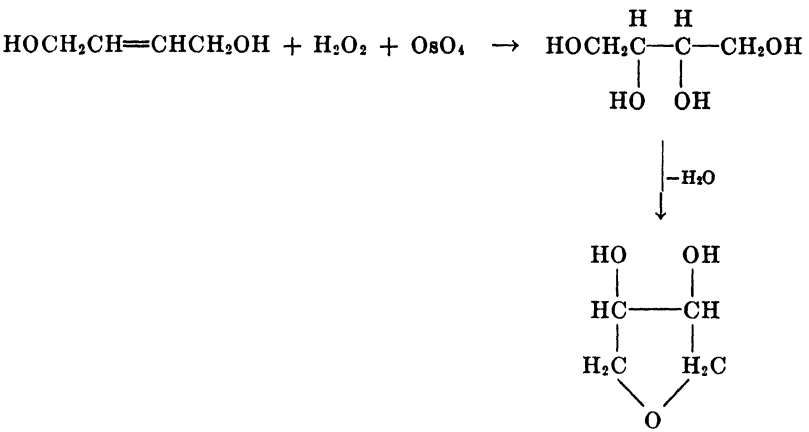
Butenediol reacts with aldehydes by the usual methods to give acetals which will polymerize.

Perhydroxylation

Oxidation of butenediol with hypochlorous acid, hydrogen peroxide or sodium persulfate gives racemic erythritol. Potassium permanganate or potassium perchlorate, in the presence of osmium tetroxide catalysis, leads to *meso*-erythritol (m.p. 124°C).[24]

[23] *D.R.Pat. 512, 182.*
[24] *PB* 7416.

The perhydroxylation may be carried out by reacting butenediol with aqueous hydrogen peroxide in the presence of osmium tetroxide at 30 to 60°C. The yield of *meso*-erythritol is between 45 and 70 per cent. With arsenic or mercury catalysts at 90°C, a viscous oil which apparently consisted chiefly of *trans*-dihydroxytetrahydrofuran was obtained, as shown by the fact that its benzoate gave a melting-point depression when mixed with the benzoate of dihydroxytetrahydrofuran prepared from *meso*-erythritol.



Although it was believed that the dihydroxytetrahydrofuran was obtained from the erythritol by dehydration, it is possible that the reaction may involve dehydration to the dihydrofuran, followed by perhydroxylation and ring opening to erythritol

Efficient catalysts for the addition of hydrogen peroxide are, in addition to osmium tetroxide, various compounds of chromium, vanadium, molybdenum, tungsten, arsenic, selenium, mercury, tin and bismuth. Reaction generally takes place at 30 to 60°C

The addition of hydrogen peroxide to hexene-3-diol-2,5 gave 1,4-dimethyl erythritol for the first time in crystalline form (m.p. 161°C).

These polyfunctional alcohols were of interest as substitutes for glycerin, and for the synthesis of plasticizers, textile waxes, alkyd resins, etc. The tetranitrate ester of *meso*-erythritol was used as a spasmolytic agent for heart diseases, and as an explosive.

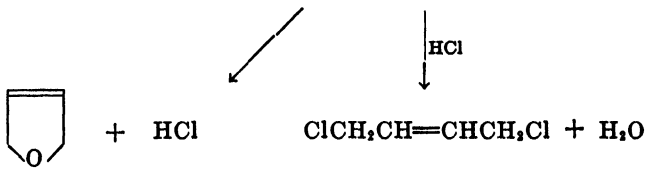
Dehydrogenation

Dehydrogenation of butenediol is reported to give succinic dialdehyde in 30 per cent yield. Furan is a by-product. No details are available.

Reaction with Halogen Acids

Hydrogen chloride reacts readily with butenediol at 50 to 60°C, forming 1,4-dichlorobutene-2 in 90 to 95 per cent yields. The reaction apparently involved the following steps:

$$HOCH_2CH{=}CHCH_2OH + HCl \rightarrow ClCH_2CH{=}CH{-}CH_2OH + H_2O$$



At 0 to 10°C the chlorobutenol is formed, but during distillation, even at reduced pressure, is converted to dihydrofuran. Likewise, if the reaction temperature is higher than 60°C, dihydrofuran is formed in 80 to 85 per cent yields.

The 1,4-dichlorobutene-2 is a very reactive difunctional allyl chloride-type halide[25]. It is lacrymatory and has some irritant and vesicant properties. Chlorination of the 1,4-dichlorobutene-2 gives a mixture of tetrachloro compounds. Addition of hypochlorous acid followed by treatment with lime yields 1,4-dichlorobutane oxide. Sodium sulfite gives the sodium salt of butenedisulfonic acid. When heated with alcohols in the presence of alkalis, diethers result. Reaction with sodium cyanide gives the dihydromuconic nitrile, but the yields are not good since the reaction mixture tends to resinify: this may be due to the formation of 1-cyano-1,3-butadiene by dehydrohalogenation of the intermediate chloronitrile:

$$ClCH_2CH{=}CHCH_2Cl \rightarrow ClCH_2CH{=}CH{-}CH_2CN \rightarrow CH_2{=}CH{-}CH{=}CHCN$$

If the reaction is carried out in the absence of air and in a solvent such as acetonitrile, increased yields are obtained.

Reaction with Halogens

Butenediol adds chlorine to the double bond to give 2,3-dichlorobutanediol-1,4:

$$HOCH_2CH{=}CHCH_2OH + Cl_2 \rightarrow HOCH_2\underset{Cl}{CH}\underset{Cl}{CH}CH_2OH$$

$$HOCH_2\underset{Cl}{CH}\underset{Cl}{CH}CH_2OH \xrightarrow{-HCl} CH_2{-}\underset{O}{CH}\underset{O}{CH}{-}CH_2$$

which on treatment with alkalis gave butadiene dioxide.

[25] *PB* 636.

Catalytic Oxidation of Butenediol to Maleic Anhydride

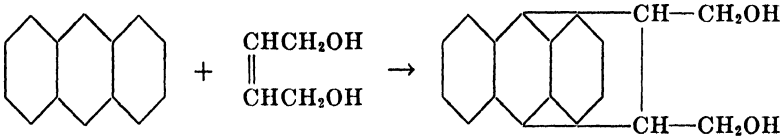
Dihydrofuran obtained from butenediol by cyclic dehydration can be catalytically oxidized to maleic acid in 72 to 78 per cent yields[26].

Attempts to oxidize the butenediol directly, using oxidation catalysts such as vanadium, molybdenum and titanium oxides on dehydration catalysts such as aluminum oxide, in an effort to combine the two reactions, were only partially successful, since the dehydration takes place at about 200°C, the oxidation at 350°C.

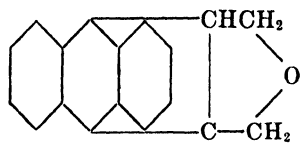
However, by separating the two phases into two different reaction zones, each operating at the optimum temperature, yields were increased from 50 per cent to 60 per cent of theoretical. The 25 to 30 per cent aqueous crude butenediol could be used as feedstock.

Diels-Alder Reactions of Butenediol

Butenediol can be added to anthracene in the diene synthesis and water eliminated to give the anthracenyl tetrahydrofuran derivative.



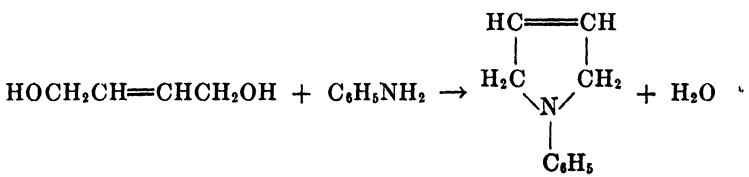
m.p. 121° C



m.p. 181° C

Reaction with Ammonia and Amines

Butenediol reacts with ammonia and primary amines in the vapor phase at 300° over an aluminum oxide-thorium oxide catalyst to yield pyrroline or N-substituted pyrrolines[27].



[26] *D.R.Pat. 709,370; 713,965.*
[27] *U S.Pat. 2,421,650*

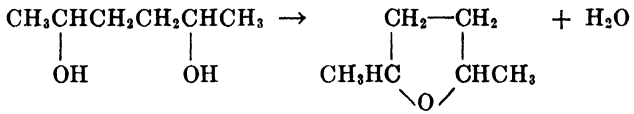
Reactions of 1,4-Butanediol

Dehydration

Dehydration to Butadiene. Butanediol can be dehydrated to butadiene over a sodium phosphate-phosphoric acid catalyst at 280°C, as previously discussed in the Reppe butadiene process (page 101).

Dehydration to Tetrahydrofuran. Butanediol-1,4 is readily dehydrated to tetrahydrofuran as described in detail on page 104.

Hexanediol-2,5 likewise is readily dehydrated to 2,5-dimethyl tetrahydrofuran which was used in the preparation of anhydrous propargyl alcohol.

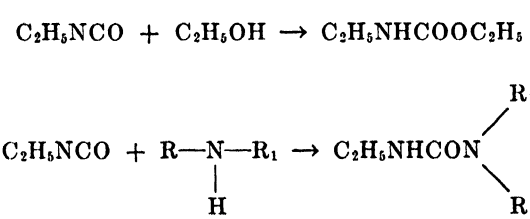


Oxidation

Oxidation with nitric acid gave succinic acid This same reaction may also be carried out on tetrahydrofuran.

Reaction with Isocyanates

Recognizing the value of nylon-type plastics, the I.G. Farben-industrie sought to develop a similar plastic based on acetylene. Abstracts of reports dated 1941 to 1943 indicate that Dr. Bayer of the Leverkusen plant investigated reactions between isocyanates, or diisocyanates, and diamines, secondary amines, alcohols and glycols[28]. Characteristic reactions were as follows:

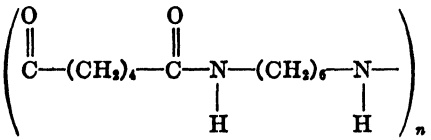


Longer-chain aliphatic diamines and diisocyanates were investigated, but the resins produced were not hydrophobic and consequently were abandoned. Emphasis was then placed upon the reaction of straight-chain diisocyanates and glycols. The similarity between the polyamide structure

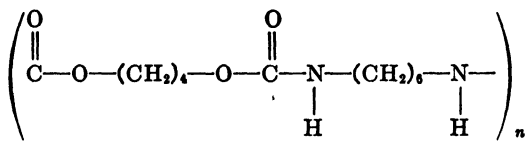
[28] *PB* 1812.

and the polyurethane structure produced from the latter is evident in the following formulas:

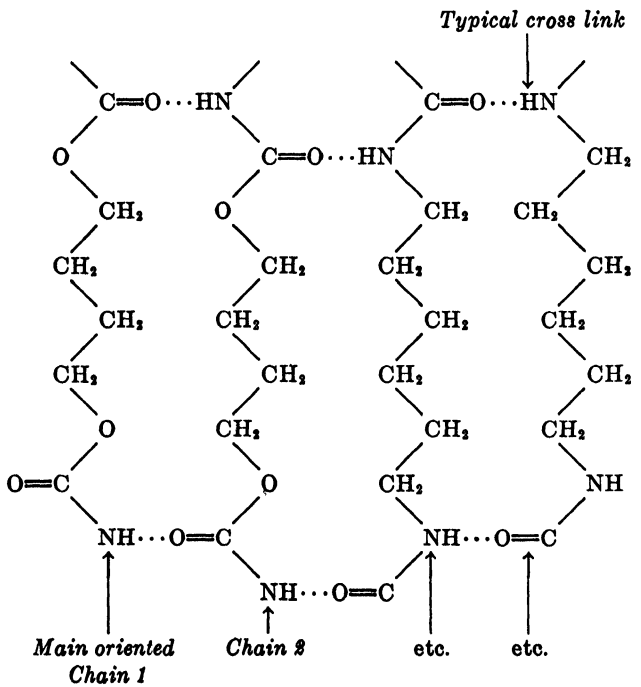
Polyamide



Polyurethane



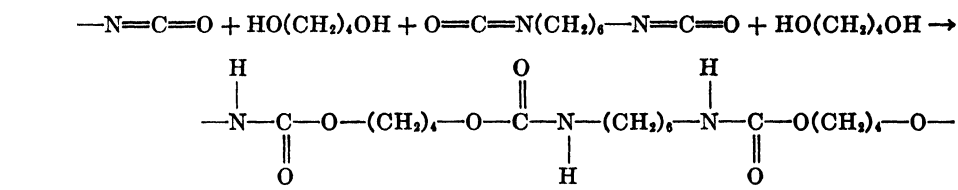
A diagrammatic formula for the complex polymer has been worked out and as given below shows the principal oriented chains with weak cross linkages. The unoriented material consisted of twisted chains with irregular, or no cross linkages.



German reports indicate that the urethane-type polymer was easily prepared by reacting 1,6-hexanediisocyanate with 1,4-butanediol, the isocyanate and hydroxyl groups reacting to form long-chain polymeric urethanes.

The process of preparation is much simpler than for the polyamide type

because the polymerization reaction is an addition polymerization rather than a condensation polymerization.



One mole of 1,6-hexane diisocyanate was added to one mole of 1,4-butanediol in a solvent such as monochlorobenzene at 60 to 70°C. The heat of polymerization was 52 calories per mole. After one hour of polymerization, almost quantitative yields were obtained. The chain length could be altered by using other non-reactive solvents such as dichlorobenzene.

Table IV-1

	"Igamid U"	"Igamid A"	"Igamid B"
Specific gravity	1.21	1.14	1.15
Melting point	183°	255°	210°
Injection molded material			
Brinnell hardness	750	1,000	600
Impact	100	100+	—
Compression molded material—non-oriented			
Tensile strength (kg/cm²)	620	—	380
Cold test (no details)	+8	—	+13
Oriented material			
Tensile, as above	1,874	—	1,050
Cold test	−30	—	−30

Table IV-1 lists the physical properties of the polyurethane ("Igamid U") from hexamethylene diisocyanate and 1,4-butanediol, and of 6-6 nylon ("Igamid A"), and of polyepsilonamino caprolactam ("Igamid B").

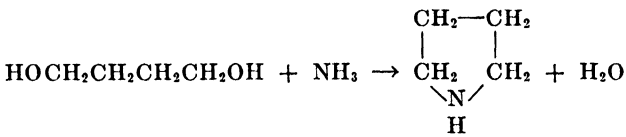
The tensile strength of the drawn polyurethane fibers was very good, 7.5 g per denier compared with the normal value of 3.5 for natural silk. The water absorption of "Igamid U" was 0.5 per cent after being immersed for ten days at 20°; and after immersion for ten days at 80° was only 2.4 per cent. "Igamid U" was fairly resistant to acids. The "Igamids" dyed as well as acetates and in this respect were said to be superior to the American product. The polyurethane from 1,4-butanediol and 1,6-hexanediisocyanate was especially suitable as a replacement for silk, for yarns, and for bristles.

A complete discussion of the polyurethane plastics can be found in the following books: "German Synthetic Fiber Developments" by Leroy H.

Smith (Textile Research Institute, Inc., 10 East 40th St., New York, N. Y.) and "German Plastics Practice" by DeBell, Goggin and Gloor (Debell and Richardson, Springfield, Mass)

Reaction with Ammonia and Amines[29]

Butanediol reacts with ammonia in the vapor phase at 300°C over an aluminum oxide (95 per cent)-thorium oxide (5 per cent) catalyst to give good yields of pyrrolidine.

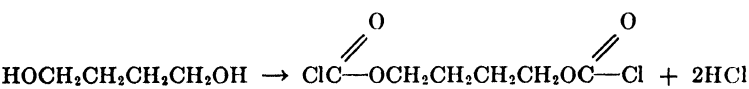


Primary amines react analogously to yield N-substituted pyrrolidines.

Esterification

Butanediol-1,4 readily undergoes esterification with either mono- or polycarboxylic acids. Such esters are claimed to be of great promise for plasticizers, textile acids, and alkyl resins

The reaction with phosgene has been studied and a process worked out for the continuous production of 1,4-butanediol dichloroformate[30]

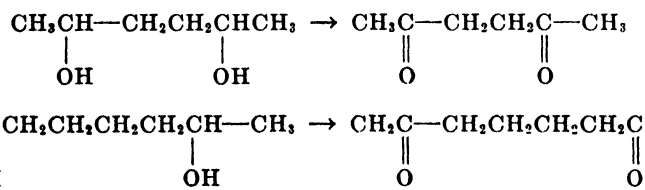


The reaction takes place at 6 to 8° and yields directly the ester of about 96 per cent purity. The pure, colorless ester can be obtained by molecular distillation, but ordinary vacuum distillation, even at 1 mm , causes spontaneous decomposition

No information is available as to the intended use of this dichloroformate. However, it is stated that valuable waxes of the polycarbonate type have been prepared from the reaction of phosgene and butanediol

Dehydrogenation

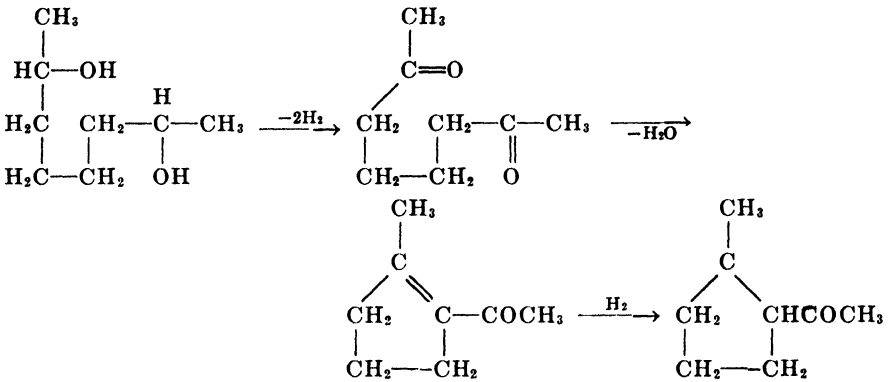
(1) **To Diketones.** Dehydrogenation of hexanediol-2,5 gave acetonyl acetone and of octane diol-2,7, octane dione-2,7.



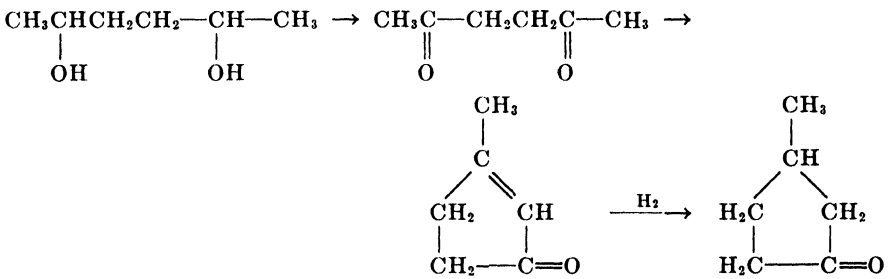
[29] *U.S.Pat. 2,421,650.*

[30] *PB* 58619.

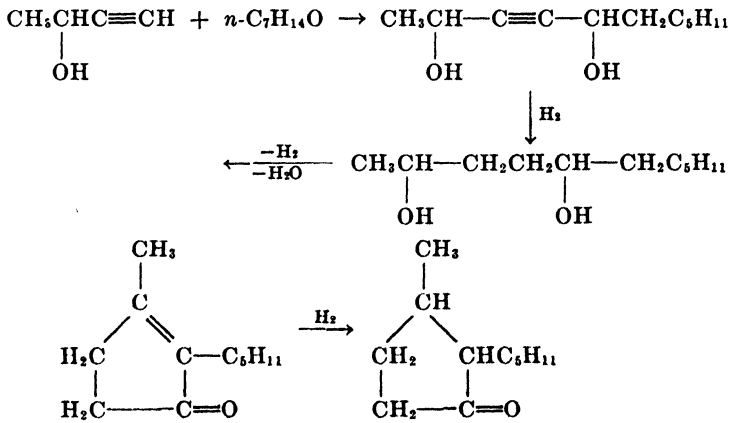
(2) **To Cyclic Ketones.** However, in the presence of suitable catalysts, the dehydrogenation of diols does not give the diketone but leads to cyclization with the formation of cyclopentenyl ketones which are reduced to the cyclopentyl ketone by the hydrogen split off in the first stage of the reaction.



If the two hydroxyls are 1–4 with relation to each other, the reaction gives a cyclopentanone

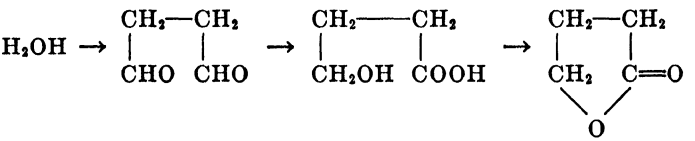


This synthesis opens up a new route to long-chain alkyl cyclopentanones, such as tetrahydrojasmone, which are valuable perfumes; for example the

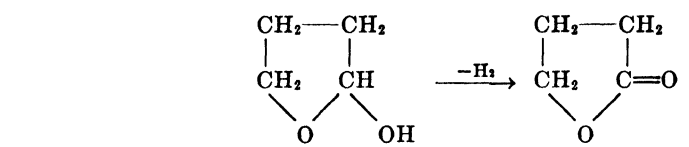


ethinylation of *n*-heptaldehyde with butyne-3-ol-2 and reduction gives undecane diol-2,5 which by dehydrogenation gives dihydro- and finally tetrahydrojasmone.

(3) **To Lactones.** Dehydrogenation of butane-1,4-diol over a copper catalyst at 200–250°C gave gamma-butyrolactone instead of the expected succinic dialdehyde[31]. Reppe considered that this reaction took place by a dehydrogenation followed by an internal Cannizzaro type reaction leading to butyrolactone.



However, an alternative mechanism seems likely in view of the nature of the catalyst.



Butyrolactone was of considerable importance as a chemical intermediate for the synthesis of various plasticizers, substitutes for citric acid, etc., but even more important was its use in the synthesis of alpha-pyrrolidone from which was derived the synthetic blood plasma substitute, polyvinyl pyrrolidone or "Periston" (see page 81). Production of gamma-butyrolactone at Ludwigshafen was approximately 40 metric tons or 88,000 pounds per month.

Liquid Phase Synthesis of Butyrolactone[32]

Reactor. The reaction chamber consisted of a 500-mm diameter cylinder fitted with 40 to 50 tubes, each 20 mm in diameter and 6 m long through which steam at 200 atm was passed. The capacity of the reactor was 450 liters of catalyst. The reaction was carried out at atmospheric pressure.

Catalyst. The BBE catalyst used was copper activated with chromium and deposited on 2 to 3-mm particles of Oppau grade silica gel B as a carrier. Three dippings in the saturated nitrate impregnating solutions were required for proper pick-up. The catalyst composition was: 20 per cent copper, 0.5–1.0 per cent chromium, and 79–80 per cent silica gel B.

Activation of the catalyst was carried out after charging the reactor by

[31] *D.R.Pat. 699,945; 704,287.*
[32] *PB 60902.*

heating at 200°C in a stream of hydrogen at atmospheric pressure until reduction was completed.

Catalyst life was two to four weeks, and regeneration was not possible because hydrogen evolution during the reaction caused the catalyst particles to be broken into a fine powder.

Process Operation. Pure butanediol-1,4 (99 per cent from the Buna Werke) was kept molten at 40°C in an aluminum storage vessel and pumped in at the bottom of the reactor at the rate of 60 to 80 liters per hour. The liquid hourly space velocity was 0.133 to 0.178. The lower part of the reactor was at 200°C and the upper part at 160°C. The product from the top of the chamber was passed through a condenser and the non-condensed portion was vented.

The liquid product had the following percentage composition: 90 to 92 gamma-butyrolactone, 1 to 2 tetrahydrofuran, and 3 to 5 water and traces of acetone and butyraldehyde. The yield of gamma-butyrolactone was about 90 per cent.

Vapor-Phase Synthesis of Butyrolactone

The liquid phase process was superseded by a vapor-phase process which was found to be superior.

Reactor. A general utility cast-iron reactor, which was not designed for this reaction, was used at atmospheric pressure. The main part of the reactor was about one and one half m in diameter; it had a volume of three cubic m and the total volume was four cubic m.

Catalyst Preparation An ordinary concrete mixer was used for the catalyst preparation. Into it was placed 450 liters of pumice pellets, 18 to 20 mm in size. While rotating the blender, a stirred mixture of 30 kg of basic copper carbonate, 16 kg of sodium silicate solution (30 per cent) and 30 kg of distilled water was added, at room temperature.

All liquid was absorbed by the pumice and the wet stones were poured into the reactor. Nine batches were required to fill the reactor. A current of nitrogen was admitted and the mass was heated to 100°C; then during two to four hours in a stream of hydrogen to 200°C. This temperature was maintained, as was the hydrogen stream until all water and carbon dioxide were removed. The total operation required about forty-eight hours. The catalyst was then ready for use. The life of the catalyst was quite long, about two years, the original charge still being in the reactor. It was regenerated simply by air oxidation at 200 to 300°C, every four to eight months, as the tetrahydrofuran content of the product rose to 5 to 10 per cent. Reduction was carried out as described above.

Process Operation. The endothermic reaction, −14,700 cal/mole, was carried out at atmospheric pressure. Preheated hydrogen (140 to 260°C), at the rate of 1,200 to 1,400 cubic m per hour and preheated (40°C) pure

butanediol-1,4 (99 per cent from Buna werke) at the rate of 60 to 80 liters per hour were mixed in a copper-lined vaporizing chamber at 200°C. This gaseous mixture was passed in at the bottom of the catalyst chamber which was heated to 230 to 250°C. The liquid hourly space-velocity was 0.015 to 0.020 The products at 200°C were removed at the top, led into a cooler, and the condensed liquid withdrawn into storage tanks provided with vents.

The non-condensed material from the cooler was passed into a knock-out tank. Part of the gas, 50 cu m per 90 kg of product, was vented to the air, and the rest returned through the hydrogen pump as recycle gas. The trapped-out liquid went to the product storage tank.

The production rate was 80 liters per hour of liquid, having the following percentage composition: 90 to 93 gamma-butyrolactone 1 to 3 tetrahydrofuran, and, 4 to 8 water.

The yield of gamma-butyrolactone was about 90 per cent Butyrolactone was determined by titration with base, tetrahydrofuran by distillation, and water by distillation with benzene

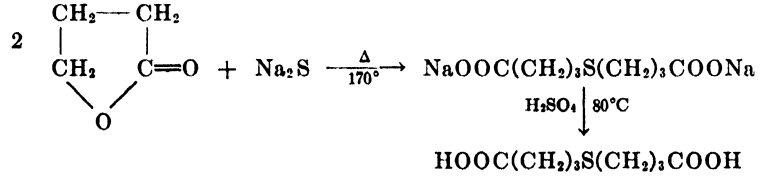
Purification of gamma-Butyrolactone. Tetrahydrofuran, water, and traces of impurities (acetone and butyraldehyde) were removed by simple distillation at atmospheric pressure in a cast-iron apparatus Pure butyrolactone was then obtained by vacuum distillation at a pressure of 2 to 20 mm of Hg. The 40-plate, bubble-cap column (plates 250 mm apart) was operated at a reflux ratio of 1:1

The product boiled at 65°C at 4 mm pressure and was collected at the rate of 500–1,000 liters per hour, it was 99 per cent pure and contained one per cent water. gamma-Butyrolactone is a colorless liquid which boils at 203°C at atm pressure, and which melts at about −41°C; n_D^{20} 1.4366, d_{20}^{20} 1.1297.

Reactions of gamma-Butyrolactone

Reaction with Sodium Sulfide

The reaction of anhydrous sodium sulfide with gamma-butyrolactone at 170°C, or higher, opens the lactone ring and couples two molecules through a sulfur linkage to form the disodium salt of thiodibutyric acid (di-*n*-propyl sulfide-3,3′-dicarboxylic acid) Acidification gives the free acid [33]



[33] *PB* 58440 (*FIAT* 946).

Manufacture of this acid was started at Ludwigshafen in 1942, and by 1944 was at the rate of 12 to 15 tons per month. Thiodibutyric acid in the form of its esters was of considerable importance as plasticizers for polyvinyl chloride resins. One report states:[34]

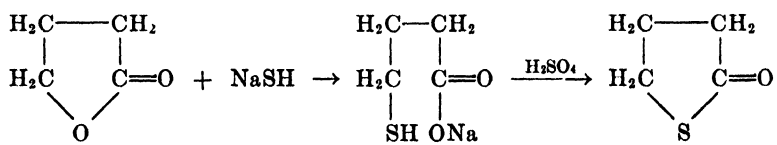
"It was proved in extensive experiments that some esters of thioether carboxylic acids are 'Igelit' (polyvinyl chloride), plasticizers with outstanding qualities. From this series of products, some have proved to be the qualitatively best 'Igelit' plasticizers known at present. 'Plastomoll TV' and 'TAH', two products which have been produced and marketed for some time, are the most important."

The trade name, chemical constitution and usage of three esters of thiodibutyric acid are listed:

Name	Ester	Tons Used in	
		1942	1943 (1st half)
"Plastomoll TAH"	Ethyl hexyl	—	2.0
"Plastomoll TB"	Butylene glycol	1 0	2.1
"Plastomoll TV"	Fischer Tropsch alcohols ($C_5 - C_7$)	65 2	39.3

Batch Preparation of Disodium Thiobutyrate. *Raw Materials.* The gamma-butyrolactone used was of 99 per cent purity, while the sodium sulfide was 95 per cent pure and contained 5 per cent salts. It was necessary to use anhydrous sodium sulfide to get best results. Since the common hydrate could not be dried readily, sodium sulfide prepared at Leverkusen from the hydrogenation of Glauber's salt was used.[35] The material was a red powder. The presence of water would cause undesirable side reactions as shown below:

$$Na_2S + H_2O \rightarrow NaSH + NaOH$$



Thus, with wet sodium sulfide thiobutyrolactone was obtained as by-product. This material has an extremely foul odor.

Reactor. The reaction vessel was a venuleth, a standard German apparatus. The one used for thiodibutyric acid was a 3-cu m, cast-steel, jacketed cylinder, four m long and one m inside diameter. It was built for vacuum and six atm pressure.

[34] *Modern Plastics*, **23**, 168–9 (1945).
[35] *PB* 58266 (*BIOS* 855); *PB* 63695 (*BIOS* 561).

Process Description. Into the reactor was charged: 700 kg (8.1 kg-moles) of butyrolactone, and 160 kg (2.1 kg-moles) of sodium sulfide. The reaction was carried out at atmospheric pressure. This charge was first heated at about 130 to 140°C with steam (four atm) in the jacket for four hours, then at about 160 to 170°C with six to eight atm of steam for four hours.

At the end of this time, a sample was removed, dissolved in water, and tested with ten per cent hydrochloric acid. If hydrogen sulfide was evolved, the reaction was not yet completed. Generally, however, the sodium sulfide had reacted completely at this point

When the reaction was over, the remaining excess butyrolactone was distilled using four atm of steam pressure for heating and a distillation pressure of about 720 mm of Hg. A greater vacuum would cause entrainment of product. Constant stirring was maintained and the disodium salt was obtained as a powdery material.

Of the 860-kg total charge, 350 kg of butyrolactone was recovered, leaving 510 kg of product. This was a yield of over 97 per cent for the disodium salt. Thus, for a 100-kg yield of disodium salt, 69 kg of butyrolactone was required. This product was obtained in the form of dry, gray-colored pellets, about one to two mm in diameter.

Acidification of the Disodium Salt to the Free Acid. In a 12,000-liter mixing vessel was dissolved 1,400 kg of the disodium salt in 7,000 kg of water by boiling for one hour with stirring The solution was cooled to 80°C and 1,000 kg of 65 per cent sulfuric acid was added during one hour, while maintaining constant agitation; 100 to 150 kg of activated carbon (carboraffin) was added during one half hour at a temperature of 80 to 90°C. This mixture was filtered hot, the cake was washed with 100 liters of hot water, and the combined filtrates were cooled with stirring to 15°C in a 12-cu m vessel. The precipitated material was filtered cold, and washed with 100 liters of water; the filtrates were discarded. The crystalline product was dried in a tray dryer at 40 to 50°C. Removal of water required about ten hours.

The yield was 900 to 950 kg, 77 to 82 per cent for the acidification step. The purity of the white, crystalline product was 98 to 99 per cent; its color number was 8–10, its melting point, 99°C. Most of the loss in yield was due to the solubility of the acid in water, from which it was precipitated.

A study had been initiated on the development of a continuous process for the preparation of thiodibutyric acid, but apparently had not been completed.

Oxidation of Thiodibutyric Acid to Sulfone Dibutyric Acid. Thiodibutyric acid is readily oxidized to the sulfone dibutyric acid (di-*n*-propyl sulfone-3,3′-dicarboxylic acid) with hydrogen peroxide, or other oxidizing

agents: On a commercial scale the oxidation can be carried out in almost quantitative yield by chlorination in aqueous solution at room temperature.[36]

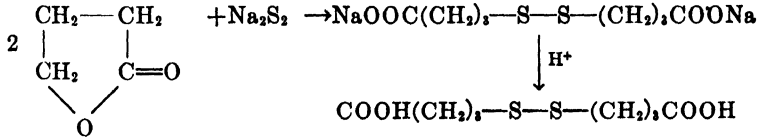
$$HOOC(CH_2)_3S(CH_2)_3COOH + 2Cl_2 + 2H_2O \xrightarrow{20\text{-}40^\circ C} HOOC(CH_2)_3SO_2(CH_2)_3COOH + 4HCl$$

A pure, chlorine-free acid of melting point 196°C is thus obtained. Instead of using a purified thiodibutyric acid, the crude fused mass from the butyrolactone-sodium sulfide reactor may be dissolved directly in water and chlorinated until the melting point of the precipitated sulfone dibutyric acid reaches 196°C. The acid may be recrystallized from water in which it is soluble to the extent of about 10 per cent at 100°C, but very insoluble in the cold.

It is claimed that the sulfone dibutyric acid is a good softener for cellulose acetate. A series of esters have been prepared. Those from the monohydric alcohols are generally crystalline solids; esters of dihydric or polyhydric alcohols are resinous, tough products resembling alkyd resins and are generally harder than the corresponding products prepared from other dicarboxylic acids.

Reaction with Sodium Disulfide

Reaction of sodium disulfide with gamma-butyrolactone takes place in a manner similar to that described previously for the reaction of sodium sulfide to yield the disodium salt of dithiodibutyric acid (di-*n*-propyl disulfide-3,3′-dicarboxylic acid).[37]



The free acid has a melting point of 108°C. Very little has been reported on reactions or uses of this acid. Upon chlorination, it is converted to *w*-sulfobutyric acid (see page 158).

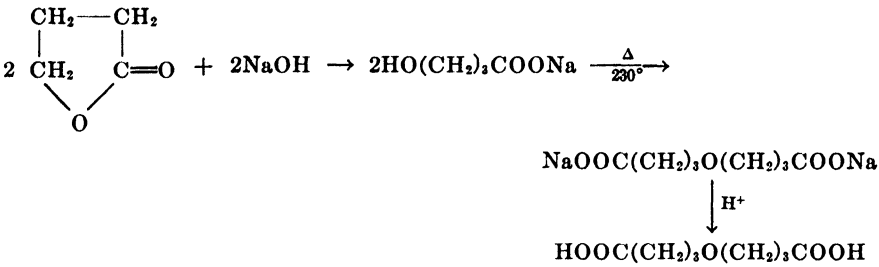
Reaction with Sodium Hydroxide

The fusion of sodium hydroxide with gamma-butyrolactone at 220 to 230°C produces the disodium salt of oxydibutyric acid (di-*n*-propyl ether-

[36] I.G. Farbenindustrie patent proposal *O.Z -12,404; PB* 605; *PB* 58440; *Fr.Pat. 883,638; SwissPat. 230,500; D.R.Pat. 759,483.*

[37] *Fr Pat. 883,638; SwissPat. 230,500; D.R.Pat. 759,483; PB* 58440.

3,3′-dicarboxylic acid). Acidification gives oxydibutyric acid, the oxygen analog of thiodibutyric acid.



The free acid and its salts are very soluble in water and considerable losses occur in the acidification step. Oxydibutyric acid boils at 196 to 223°C/1.1 to 1.2 mm and melts at 81°C.

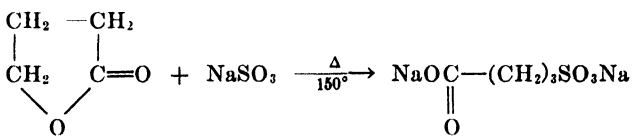
Esters of oxydibutyric acid were of interest as plasticizers for polyvinyl chloride. Although the esters of the thiodibutyric were generally preferred, there was some belief that they oxidized too readily and that eventually the esters of the oxydibutyric, although somewhat more volatile, might prove superior. The use of oxydibutyric acid as a component in nylon synthesis was not considered promising because the oxygen bridge was thermolabile and tended to split back to gamma-butyrolactone which acts as a chain terminator in the nylon process.

Oxydibutyric acid has a good taste and is tolerated well by the human body. It appeared to have promise as a substitute for citric acid in beverages and for tartaric acid in baking powder.

This acid was apparently never manufactured on a commercial scale, although quantities of several hundred pounds were prepared for evaluation.

Reaction with Sodium Sulfite

Butyrolactone is readily converted to the *w*-sulfobutyric acid by heating with aqueous sodium sulfite at 150°C or higher[38]



The course of the reaction may be followed by titration of the sulfite used up. With the usual sodium bisulfite solution (probably 30 per cent concentration) neutralized with sodium hydroxide to the neutral salt, the reaction is completed in 2 to 3 hours at 180°C.

The sodium salt may be converted to the free acid via the barium salt and decomposition with sulfuric acid. However, a better synthesis of the

[38] I.G. Farbenindustrie patent proposal *O.Z -13,355; PB* 633.

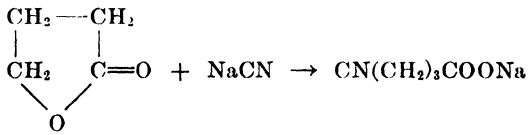
sulfobutyric acid is by chlorination in aqueous solution of the dithiodibutyric acid[39].

$$HOOC(CH_2)_3S—S(CH_2)_3COOH + 5Cl_2 + 6H_2O \rightarrow 2HOOC(CH_2)_3SO_3H + 10HCl$$

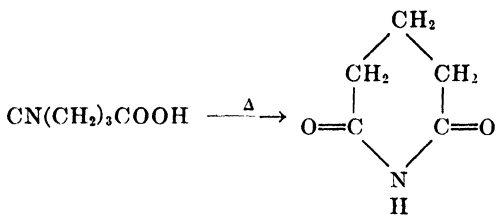
After saturating the aqueous solution with chlorine at room temperature, the water and hydrochloric acid are distilled off under reduced pressure. The pure sulfobutyric acid hydrate crystallizes in almost quantitative yield

Reaction with Alkali Cyanides

Fusion of gamma-butyrolactone with sodium or potassium cyanide at 180°C gives the alkali salt of gamma-cyanobutyric acid in 90 per cent yield.

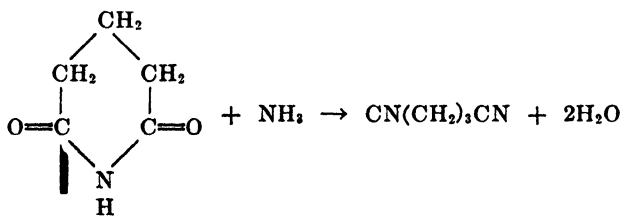


However, no satisfactory method of isolating the free cyanobutyric acid was developed. Cyanobutyric acid is unstable and when heated above its melting point easily rearranges to its cyclic isomeride, glutarimide.



Cyanobutyric acid could be converted to glutaric acid dinitrile by catalytic dehydration in the presence of ammonia. The results obtained were not satisfactory due to the ease of rearrangement to glutarimide with the formation of resinous impurities which plugged up the apparatus and deactivated the catalyst.

Glutarimide, however, may be isolated in good purity by distillation of the free cyanobutyric acid, or by heating of the cyanobutyric acid followed by recrystallization of the residue.

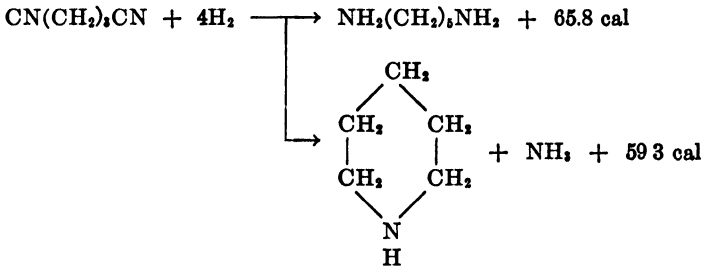


[39] I.G. Farbenindustrie patent proposal *O.Z -13,324; PB* 632.

The conversion of this glutarimide to the dinitrile can then be carried out in the vapor phase at 320 to 400°C.

With 12 moles of ammonia per mole of imide the yield of dinitrile was 90 per cent. Aluminum oxide, aluminium phosphate, and boron phosphate were satisfactory catalysts.

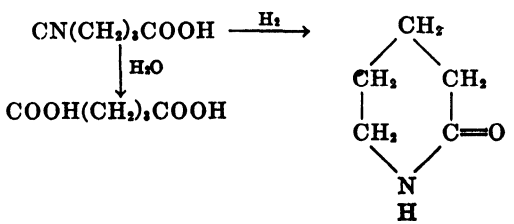
Catalytic reduction of the glutaric dinitrile gave pentamethylene diamine, piperidine and higher amines. Various types of cobalt catalysts, in particular Raney cobalt, were effective.



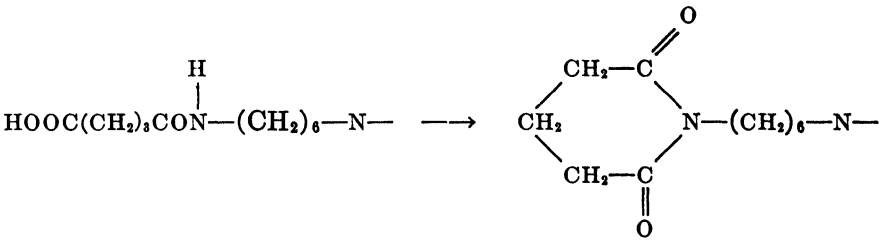
To prepare pentamethylene diamine, reduction is best carried out without a solvent. The yield depends essentially upon the rate of hydrogenation. The more rapid the reduction, the less piperidine is formed. Hence, a purified starting material and an active catalyst are necessary. The formation of the higher amines can be largely suppressed by the addition of ammonia. Apparently, the tendency toward formation of the six-membered ring is so great that even tremendous excesses of ammonia have only an insignificant effect on the yield of piperidine. Temperature, likewise, has a very small effect between 60 and 120°C. At 80°C, which was the most favorable reaction temperature, the yield of pentamethylene diamine was 62 per cent with 34 per cent of piperidine formed simultaneously.

The use of organic solvents such as methanol, tetrahydrofuran, and dioxane favored the formation of piperidine as well as the higher amines. Addition of ammonia repressed the higher amine formation and thus increased the piperidine yield at the expense of the higher amine yield. In this manner, it is possible to obtain 85 per cent piperidine with 10 per cent of pentamethylene diamine as the by-product. The presence of water increases the yield of the higher amines.

Reduction of cyanobutyric acid or its esters leads to alpha-piperidone, while hydrolysis gives glutaric acid.



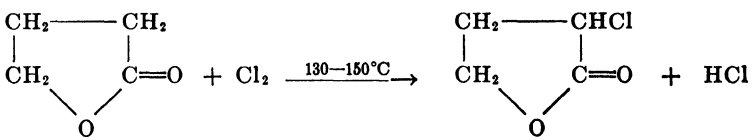
The use of 5 to 10 per cent glutaric acid-hexamethylene diamine salt in the production of 66 nylon is claimed to give more thermally resistant polymers which do not discolor so readily, although tenacity is reduced slightly. The advantages claimed are ascribed to chain termination by formation of a stable six-membered ring by elimination of water. Polymers so formed are more reproducible.



No experimental details for these reactions have been located.

Reaction with Halogens

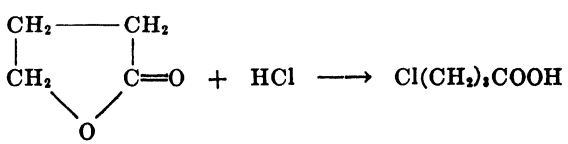
Reaction of chlorine with butyrolactone at 130 to 150°C gives good yields of alpha-chloro-gamma-butyrolactone[40].



The alpha-chloro-gamma-butyrolactone is a water-white liquid, insoluble in water, and when pure is completely stable. Its boiling point is 90 to 93°C/0 5 mm. It has been used as a starting material for the synthesis of substituted butyric acids and pyrrolidones.

Reaction with Halogen Acids

Aqueous hydrochloric acid opens the lactone ring with the formation of gamma-chlorobutyric acid[41],

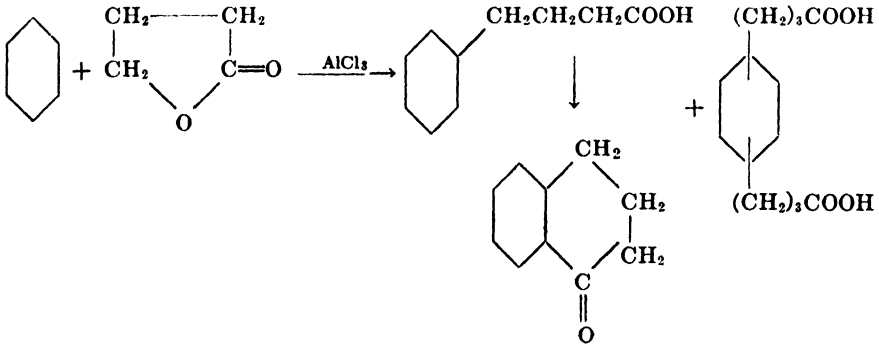


which has been used as an acid-splitting agent in the preparation of urea condensation resins.

[40] *PB* 610.
[41] *PB* 610; *PB* 13366.

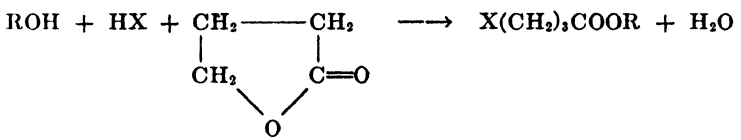
Reactions with Hydrocarbons

Butyrolactone reacts easily with aromatic compounds under the influence of catalysts of the Friedel-Crafts type.[42] For example, benzene, butyrolactone, and aluminum chloride give phenylbutyric acid and phenylenedibutyric acid. The phenylbutyric acid may be cyclized to tetralone



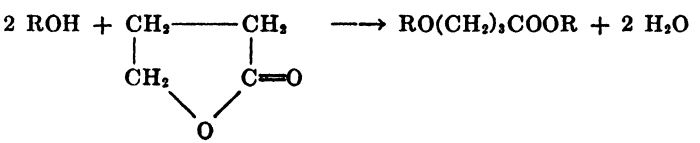
Reactions with Alcohols and Phenols

With Molar Quantities of Hydrogen Halides. Alcohols react with gamma-butyrolactone in the presence of molal quantities of hydrogen halides to furnish gamma-halobutyric acid esters.[43]



Apparently no uses for the gamma-halobutyric acid esters per se were developed. By heating with secondary amines, gamma-dialkyl (or dicycloalkyl) aminobutyric acid esters were formed. A series of these amino-esters were prepared and found to be of interest as softening agents and stabilizers for polyvinyl chloride.

With Sulfuric Acid or Sulfonic Acids. The reaction of alcohols with butyrolactone in the presence of about 2 per cent of sulfuric acid, sodium acid sulfate, or an aromatic sulfonic acid produces gamma-alkoxybutyric acid esters[44].



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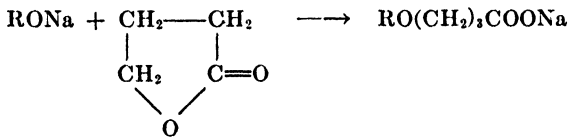
[42] *PB* 13366

[43] *PB* 610; *PB* 634.

[44] I.G. Farbenindustrie patent proposal *O.Z.-13,044.*

The alkoxy butyric acid esters are generally oily liquids if the alcohol is monohydric; water-soluble resins if dihydric, and water-insoluble resins if polyhydric.

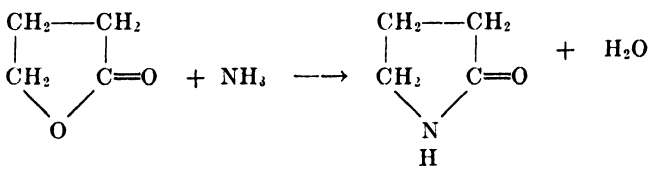
With Sodium Alkoxides. The sodium salt of gamma-alkoxybutyric acid is formed when butyrolactone reacts with a molal equivalent of a sodium alkoxide dissolved in an alcohol.



With phenolates, the salts of phenoxybutyric acid are formed. The cobalt, manganese, zinc and lead salts are of interest as siccatives (Saligins) Esters of polyfunctional alcohols had some value as dyeing assistants.

Reactions with Ammonia and Amines

Pyrrolidone and N-Substituted Derivatives. Butyrolactone is readily converted by reaction with anhydrous ammonia under pressure in an autoclave to alpha-pyrrolidone



Batch Process. Butyrolactone and anhydrous ammonia in the molar ratio of 1:1.25 were heated in a stirred iron autoclave of 1.7 cu m capacity at 230°C for 8 hours. Initially, the pressure attained was approximately 40 atm, decreasing to 20 to 25 atm as the reaction proceeded. The alpha-pyrrolidone was purified by vacuum distillation. The yield based on butyrolactone was as high as 89 per cent Approximately 6 tons/month were manufactured although capacity was somewhat more than 30 tons/month.

Continuous Process. Although the batch process was never operated to full capacity, it was believed that new applications of the polyvinyl pyrrolidones, and of interpolymers of vinyl pyrrolidone and other vinyl polymers were so promising that a continuous process for the preparation of the necessary alpha-pyrrolidone would eventually be required. The following process was worked out.

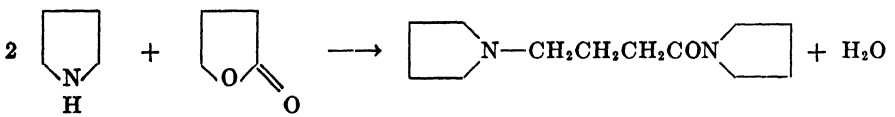
Ten liters of butyrolactone and 4.5 liters of anhydrous ammonia, previously cooled to −15°C, were mixed in a pressure vessel. The ensuing reaction which produces gamma-hydroxy butyramide raises the temperature to 40°C, sufficient to keep the amide (m.p. 40°C) molten and increases

the pressure to 8 to 10 atm. The mixture is pumped through a preheater, 4 m long and 10 mm inside diameter, where it is heated to 180°C by 20 atm steam. It then passes to a stirred horizontal pressure reactor, 150 cm long and having a volume of 17 liters. The discharge valve is located so that the reactor is only half filled. The reaction mixture is heated to 250°C and continuously discharged to a vertical high pressure pipe of 10 liters capacity where the reaction was completed at 250°C. The operating pressure in both reactors is approximately 80–90 atmospheres. The product passes to a low pressure separator from which it is continuously discharged. At present, the excess ammonia is vented.

The yield of alpha-pyrrolidone is 90 to 95 per cent of theoretical at a throughput of 15 liters per hour, or 8 tons/month.

N-Substituted Pyrrolidones

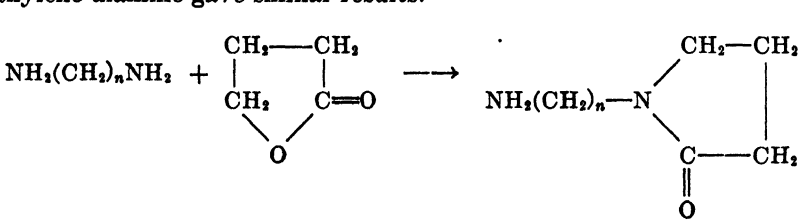
Primary amines react similarly to ammonia to yield gamma-hydroxybutyric acid amides which readily cyclize to the N-substituted alpha-pyrrolidone. With one mole of a secondary amine, reaction usually stops at the hydroxybutyric amide stage. However, with two moles of certain amines such as pyrrolidine, further reaction may occur to give the gamma-pyrrolidyl butyric acid pyrolidide.



The latter reaction can be effected with both primary and secondary amines by carrying out the reaction at 160 to 200°C in the presence of acids, or salts having an acid reaction in aqueous solution.

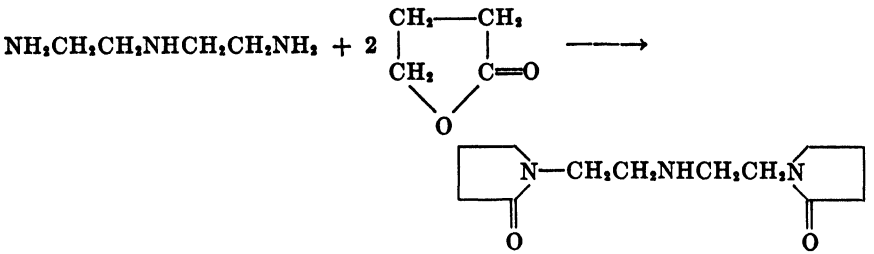
The introduction of a pyrrolidone ring into a molecule imparts a hydrophilic character which in some cases may even extend as far as causing solubility in water. The introduction of the pyrrolidone residue can be accomplished in several ways.

Aminoethylpyrrolidone can be prepared in 85 per cent yield by the reaction of a fivefold excess of ethylene diamine with butyrolactone. Hexamethylene diamine gave similar results.



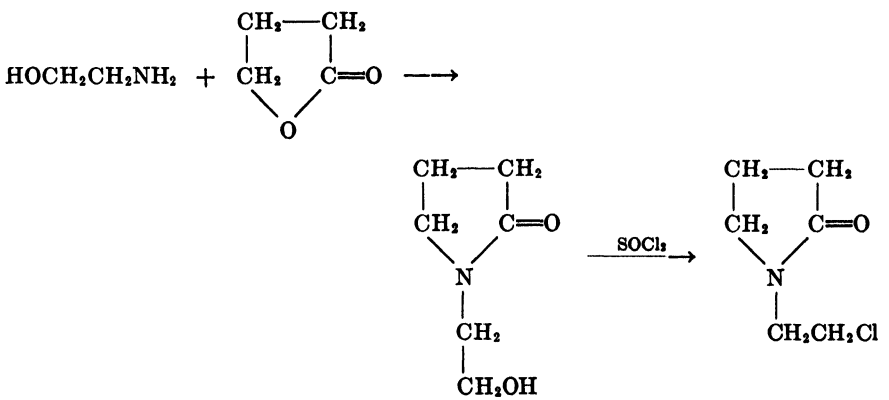
On the other hand, by using two moles of butyrolactone per mole of diamine,

two pyrrolidone residues can be introduced. For example with diethylenetriamine,



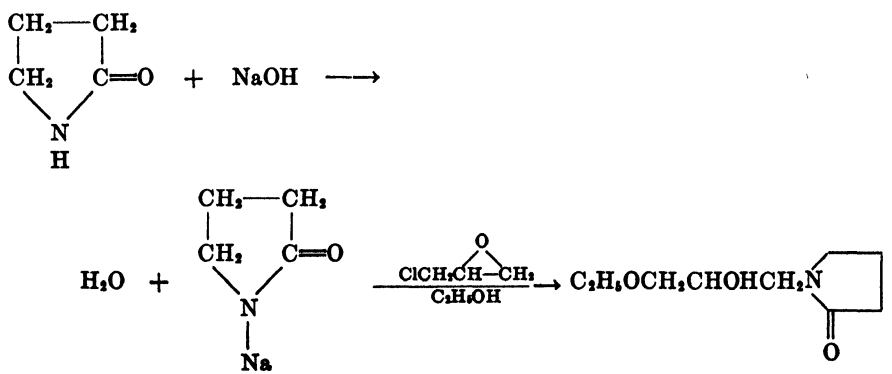
With these compounds, the presence of the amino or imino group offers a possibility of further reaction.

Ethanolamine reacts readily with butyrolactone to give N-hydroxyethyl pyrrolidone which with thionyl chloride gives beta-chloroethyl pyrrolidone,



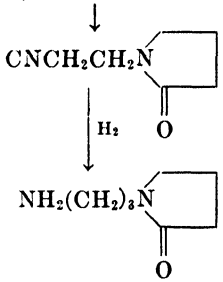
which may be used to introduce a pyrrolidone group by alkylation.

Pyrrolidone reacts with concentrated sodium hydroxide solution in acetone to give N-sodium pyrrolidone which reacts with alkyl halides, for example with epichlorohydrin in alcohol.

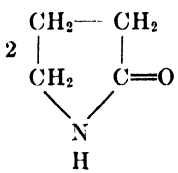


The addition of gamma-aminobutyric acid to acrylonitrile gives beta-cyanoethyl-gamma-carboxypropylamine which readily cyclizes to beta-cyanoethyl-N-pyrrolidone; this on reduction gives gamma-aminopropyl pyrrolidone.

$$NH_2(CH_2)_3COOH + CNCH{=}CH_2 \longrightarrow CNCH_2CH_2NH(CH_2)_3COOH$$



gamma-Aminobutyric Acid Derivatives. Although gamma-aminobutyric acid has a great tendency to cyclize to alpha-pyrrolidone by elimination of water, it can be prepared by hydrolysis of alpha-pyrrolidone which proceeds smoothly with aqueous calcium hydroxide at 120°C.



$$2 + Ca(OH)_2 \rightarrow (NH_2(CH_2)_3COO)_2Ca \xrightarrow{H_2SO_4}$$

$$2NH_2(CH_2)_3COOH$$

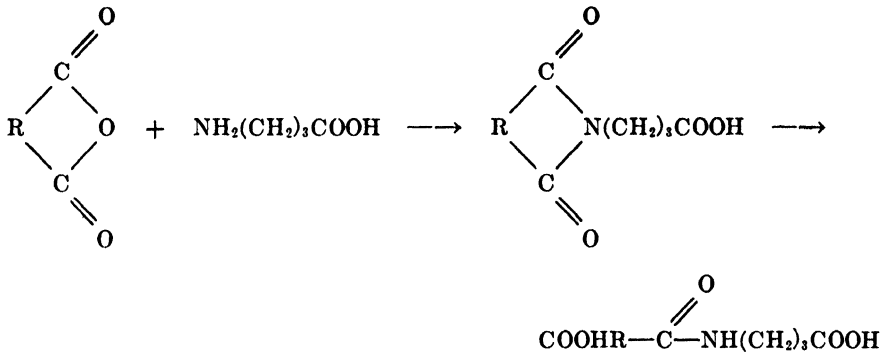
The calcium salt was used in the preparation of "Retardan N," a setting retarder for plaster of Paris.

gamma-Aminobutyric acid reacts readily with cyanates and with acrylonitrile.

$$NH_2(CH_2)_3COOH + KCNO \longrightarrow NH_2\overset{\overset{O}{\|}}{C}{-}NH(CH_2)_3COOH$$

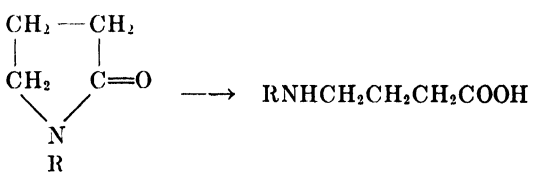
$$NH_2(CH_2)_3COOH + CNCH{=}CH_2 \longrightarrow CNCH_2CH_2NH(CH_2)_3COOH$$

Acetylation with acetic anhydride gives N-acetyl-gamma-aminobutyric acid. With the anhydrides of dicarboxylic acid, diacyliminobutyric acids are obtained,



which on saponification yield dibasic amido acids. The possibility of utilizing these acids and their esters for superpolyamides, as softening agents, and for similar purposes was under investigation.

Saponification of N-substituted pyrrolidones to the substituted aminobutyric acid is more difficult and must be carried out under more drastic conditions



The di-N-substituted aminobutyric acid derivatives may be prepared from gamma-chlorobutyric acid or its esters by heating with secondary amines

$$Cl(CH_2)_3COOH + {}_2\ R_2NH \rightarrow R_2N(CH_2)_3COOH + R_2NH\cdot HCl$$

$$Cl(CH_2)_3COOR + {}_2\ R'NH \rightarrow R'N(CH_2)_3COOR + R_2NH\cdot HCl$$

An extensive series of dialkyl and dicycloalkyl aminobutyric acid esters were prepared and found to be of interest as softening agents and stabilizers for "Igelit"

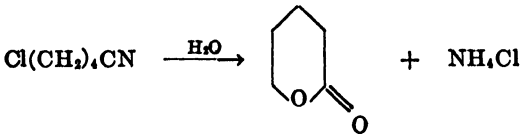
δ-Valerolactone

In the reaction of 1,4-dichlorobutane with alkali cyanides to prepare adiponitrile, δ-chlorovaleronitrile is a by-product; if desired, its yield may be increased by altering the experimental conditions.

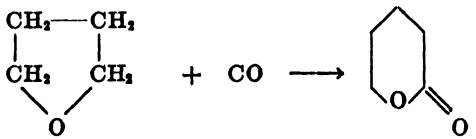
$$Cl(CH_2)_4Cl + NaCN \rightarrow Cl(CH_2)_4CN$$

Hydrolysis of δ-chlorovaleronitrile with water under pressure at 150 to 180°C gives almost quantitative yields of a mixture of approximately

70 per cent monomeric and 30 per cent polymeric lactone. δ-Valerolactone boils at 110 to 115°C/18 mm and gives a hydrazide melting at 107°C.

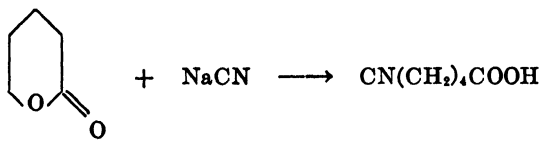


δ-Valeroactone can also be formed by the addition of carbon monoxide to tetrahydrofuran (see page 277).



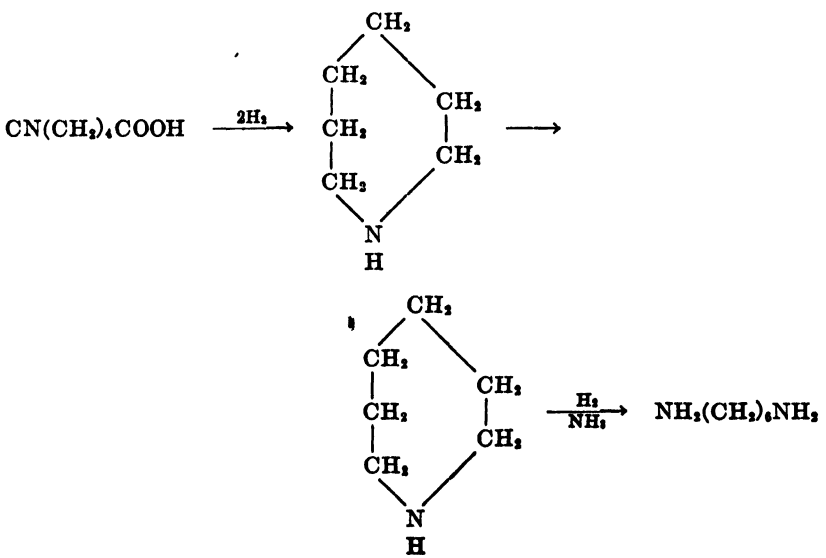
It undergoes all the previously described reactions of gamma-butyrolactone.

Of particular interest was the splitting of δ-valeronitrile with alkali cyanides:



The resulting δ-cyanovaleric acid boiled at 160°C/0.1 mm and gave an ethyl ester boiling at 138 to 140°C/18 mm.

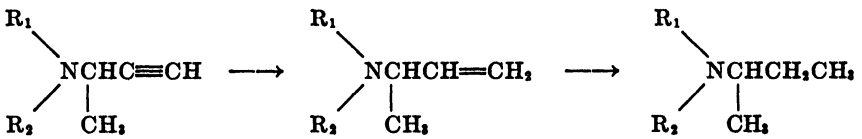
Esters of cyanovaleric acid could be reduced in good yield to δ-caprolactam with Raney cobalt, but reduction of the free acid proceeded with



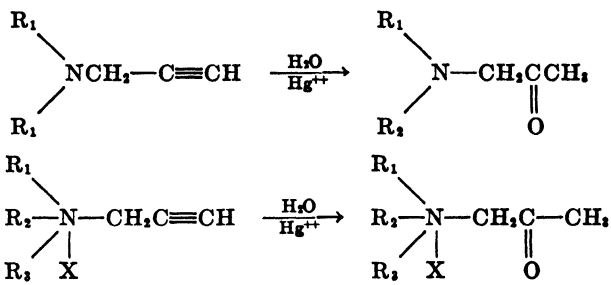
greater difficulty. Hexamethylene imine is formed as a by-product and in the presence of ammonia is aminated by ring opening to hexamethylene diamine[45].

Reactions of Aminopropynes and Aminobutynes

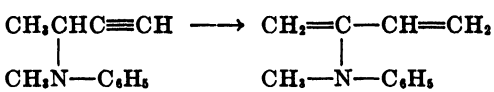
In general, the normal reactions of both the —C≡CH bond and the amino group can be carried out with the aminopropynes and aminobutynes. Partial hydrogenation to the vinyl amino compound or complete hydrogenation to the saturated amine are both possible.[46]



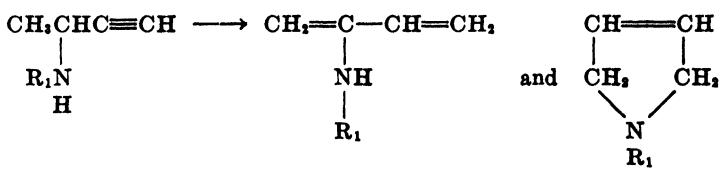
Water may be added in the presence of mercury salts to either the amine or the quaternary base derived therefrom:[47]



The addition of alcohols, hydrogen cyanide, hydrogen halides, etc., is also claimed. The acetylenic amines can act as vinylating agents for alcohols, mercaptans, etc. Substituted 2-aminobutadienes are formed by catalytic rearrangement of aminobutynes:[48]

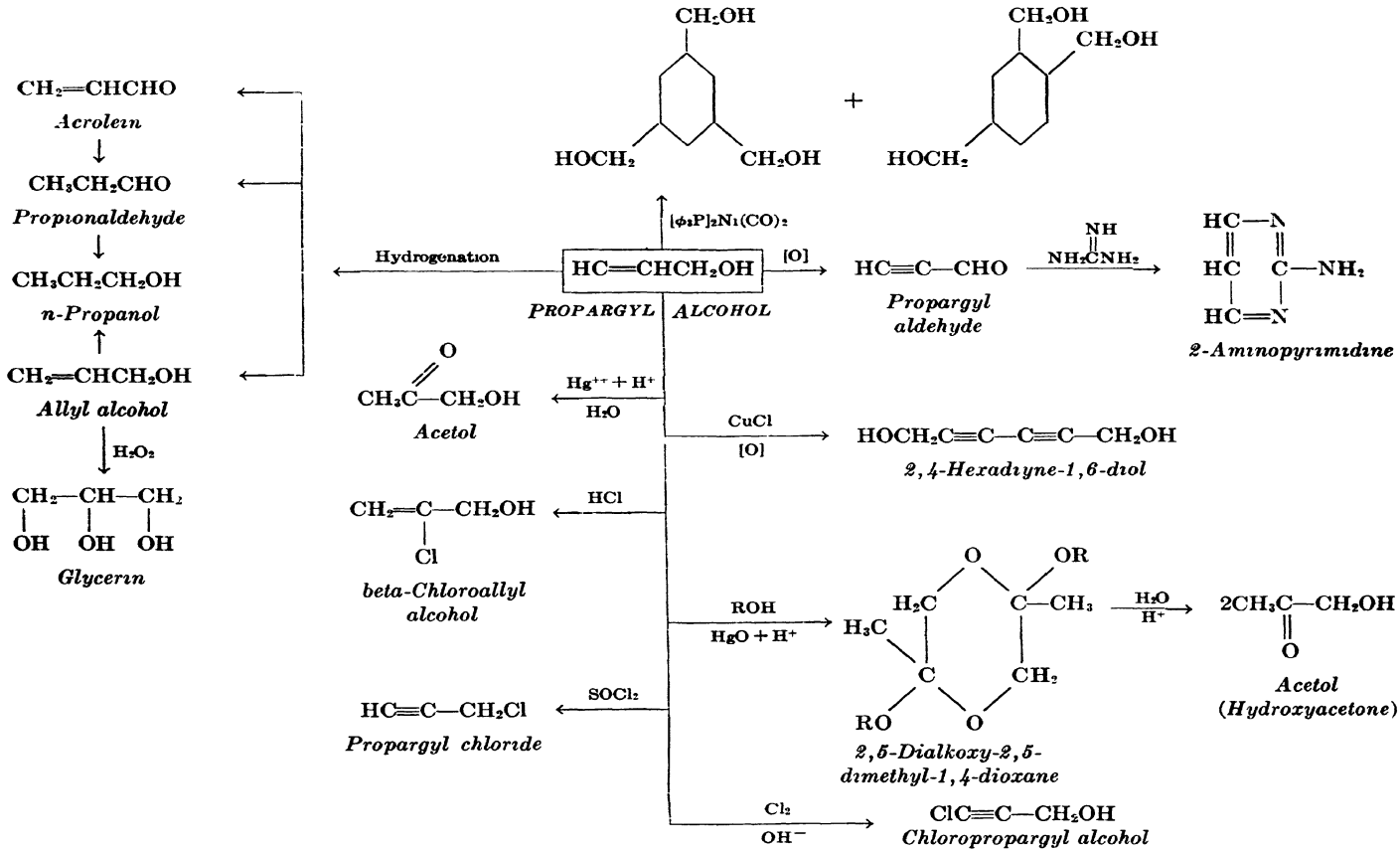


A small quantity of the isomeric pyrroline may be formed at the same time from the secondary aminobutynes:

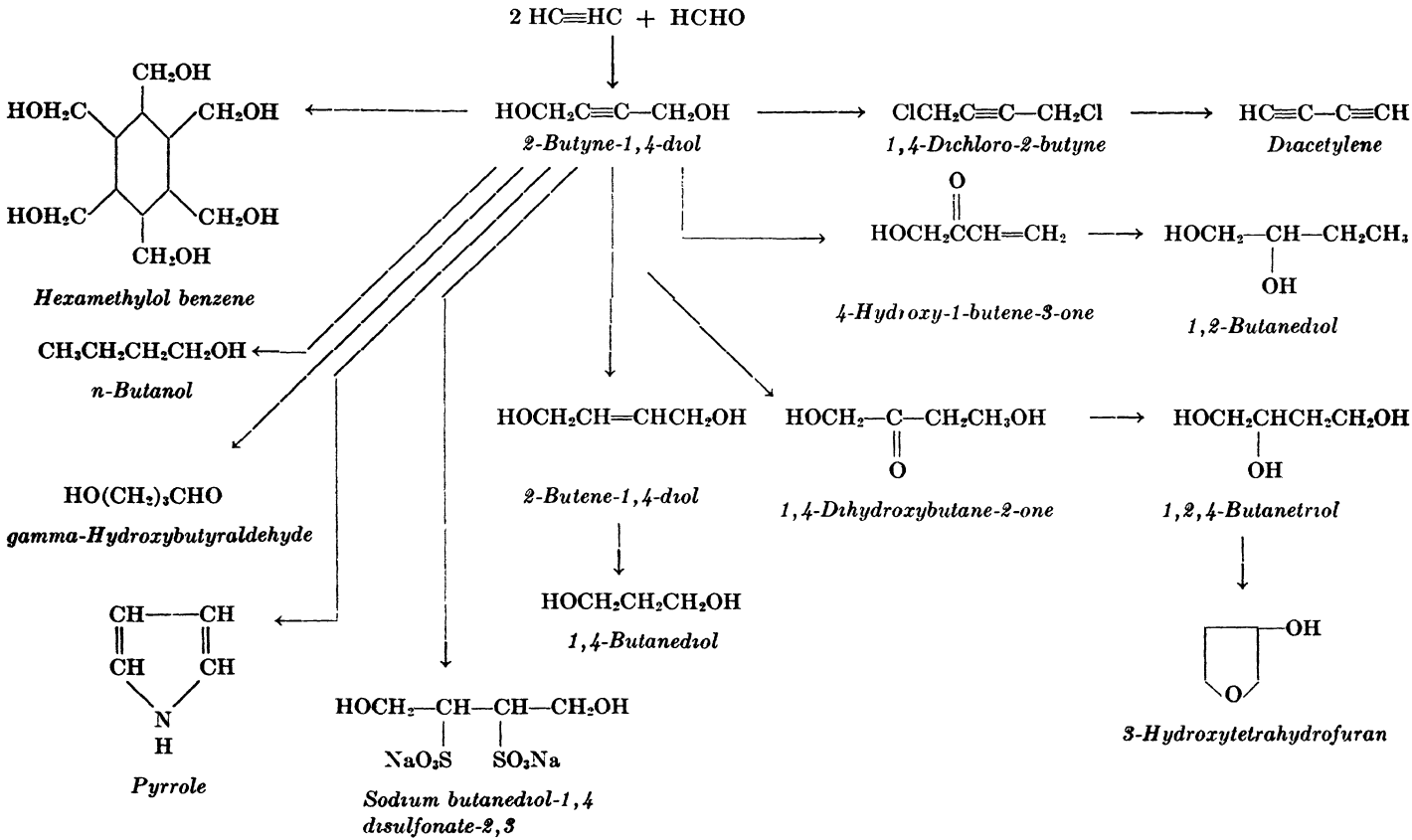


[45] I.G. Farbenindustrie patent proposal *O.Z.-13,089*.
[46] *D.R.Pat. 765,063; Fr.Pat. 846,475*.
[47] *Fr.Pat. 510,876*.
[48] *Fr.Pat. 880,878*.

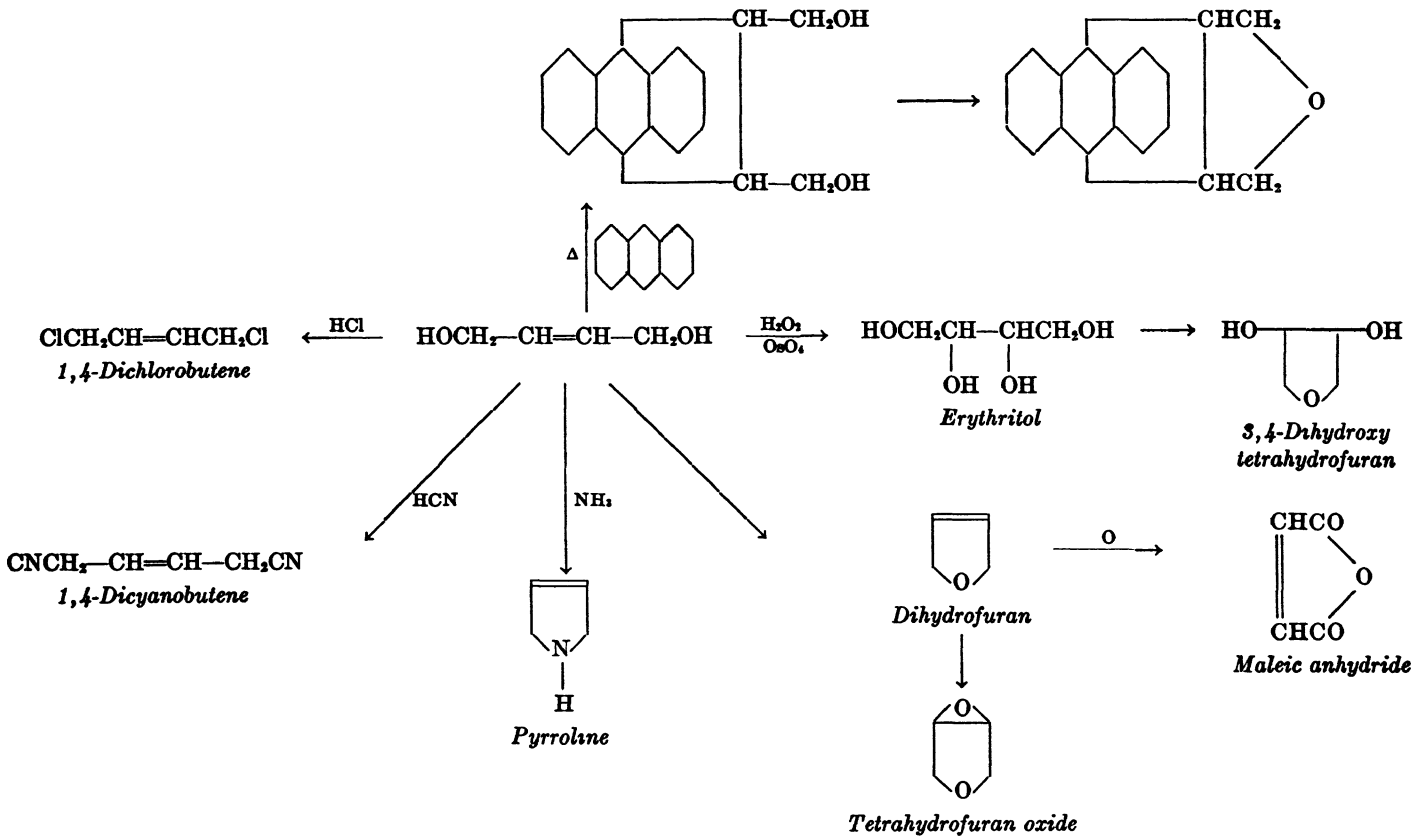
Propargyl Alcohol and Its Reactions



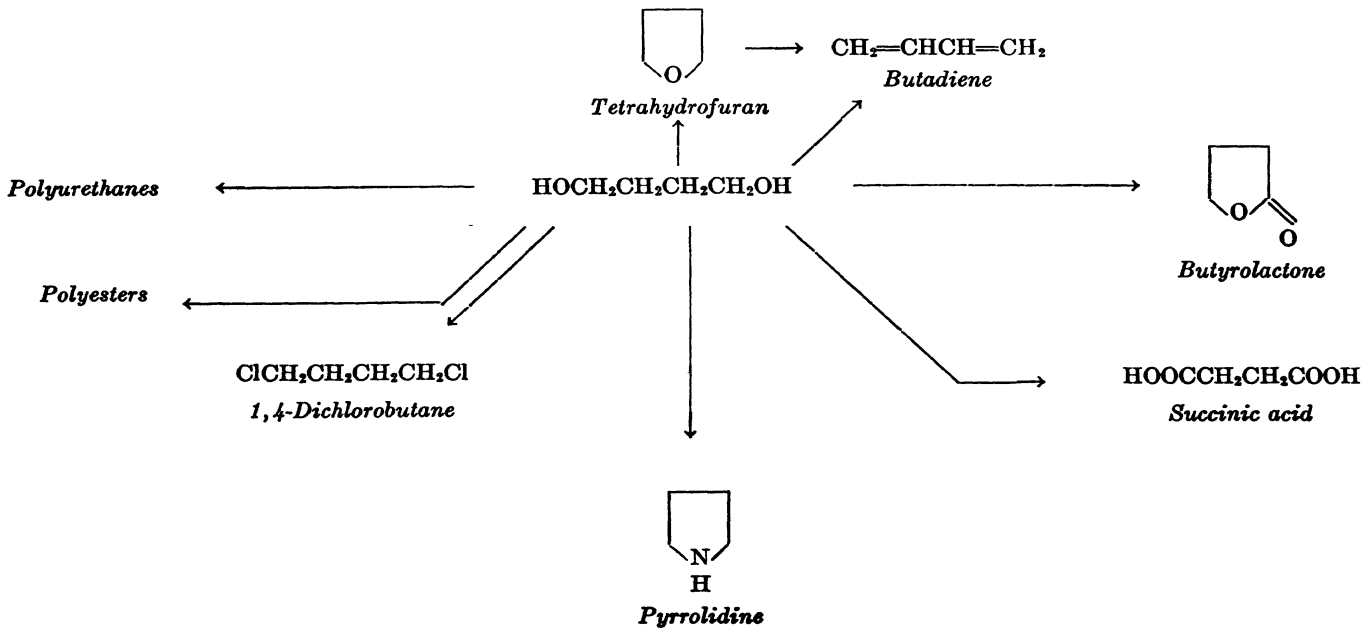
Reactions of Butynediol



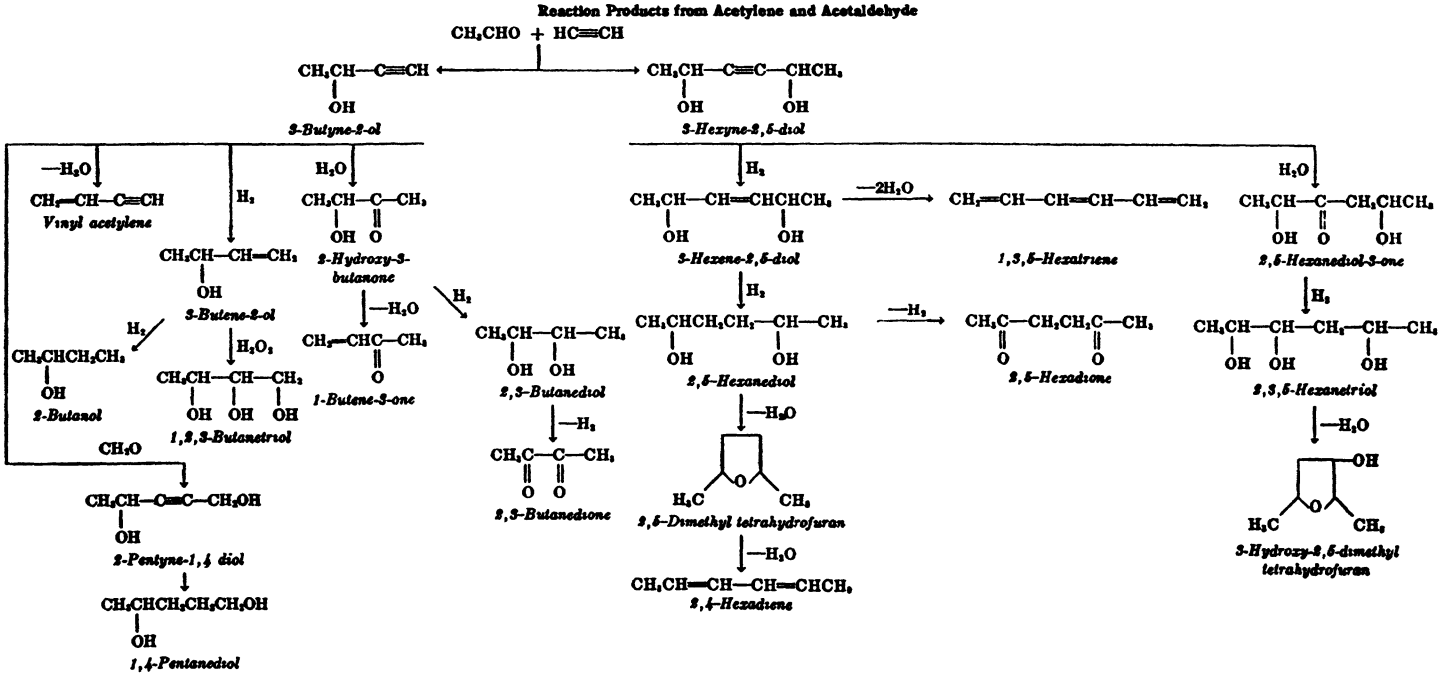
Reactions of Butenediol

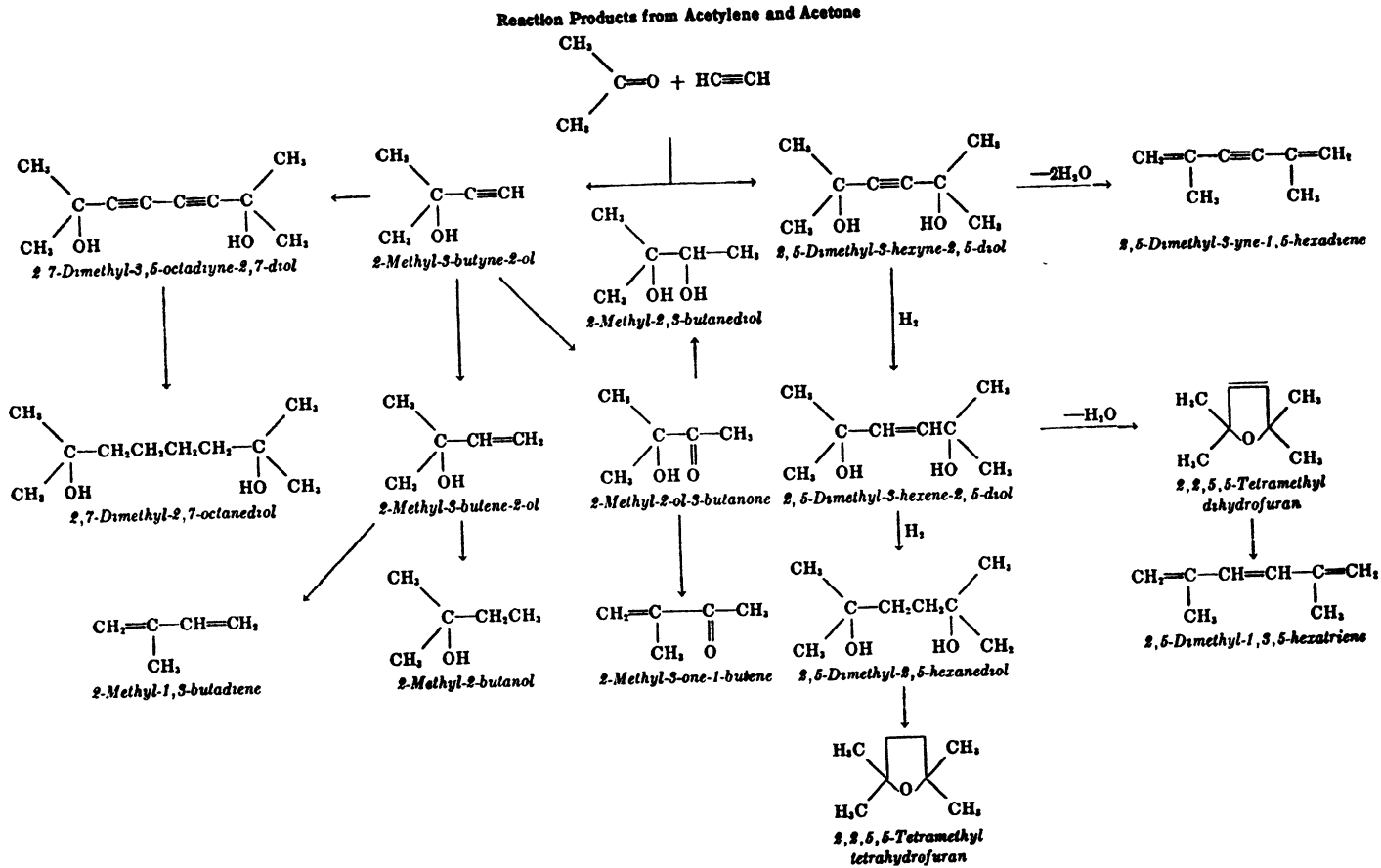


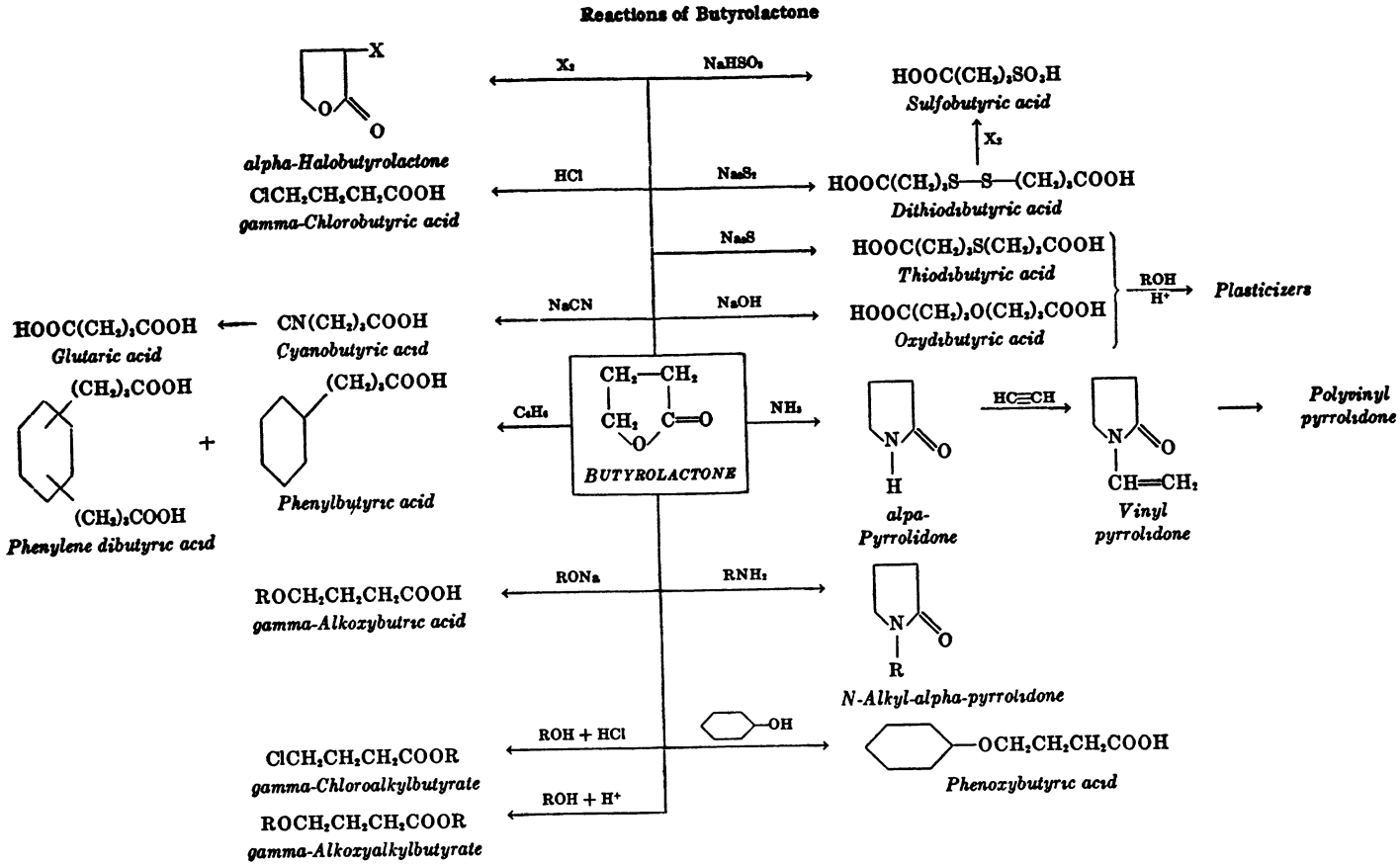
Reactions of Butanediol



Reaction Products from Acetylene and Acetaldehyde




Reaction Products from Acetylene and Acetone
CH3
C=O + HC≡CH
CH3
2,7-Dimethyl-3,5-octadiyne-2,7-diol
2-Methyl-3-butyne-2-ol
2-Methyl-2,3-butanediol
2,5-Dimethyl-3-hexyne-2,5-diol
—2H2O
2,5-Dimethyl-3-yne-1,5-hexadiene
2,7-Dimethyl-2,7-octanediol
2-Methyl-3-butene-2-ol
2-Methyl-2-ol-3-butanone
2,5-Dimethyl-3-hexene-2,5-diol
—H2O
2,2,5,5-Tetramethyl dihydrofuran
2-Methyl-1,3-butadiene
2-Methyl-2-butanol
2-Methyl-3-one-1-butene
2,5-Dimethyl-2,5-hexanediol
2,5-Dimethyl-1,3,5-hexatriene
2,2,5,5-Tetramethyl tetrahydrofuran


Reactions of Butyrolactone
alpha-Halobutyrolactone
ClCH2CH2CH2COOH
gamma-Chlorobutyric acid
X2
NaHSO3
HOOC(CH2)3SO3H
Sulfobutyric acid
X2
HCl
Na2S2
HOOC(CH2)3S—S—(CH2)3COOH
Dithiodibutyric acid
Na2S
HOOC(CH2)3S(CH2)3COOH
Thiodibutyric acid
ROH
H+
Plasticizers
NaCN
NaOH
HOOC(CH2)3O(CH2)3COOH
Oxydibutyric acid
HOOC(CH2)3COOH
Glutaric acid
CN(CH2)3COOH
Cyanobutyric acid
(CH2)3COOH
(CH2)3COOH
Phenylene dibutyric acid
+
(CH2)3COOH
Phenylbutyric acid
C6H6
NH3
BUTYROLACTONE
HC≡CH
Polyvinyl pyrrolidone
alpa-Pyrrolidone
Vinyl pyrrolidone
RONa
RNH2
ROCH2CH2CH2COOH
gamma-Alkoxybutric acid
N-Alkyl-alpha-pyrrolidone
ROH + HCl
OH
OCH2CH2CH2COOH
Phenoxybutyric acid
ClCH2CH2CH2COOR
gamma-Chloroalkylbutyrate
ROH + H+
ROCH2CH2CH2COOR
gamma-Alkoxyalkylbutyrate

Chapter V

Cyclopolyolefins

Introduction

Perhaps the most intriguing development in the whole field of acetylene chemistry was the discovery by Reppe in 1940 that acetylene under pressure in the presence of certain nickel catalysts could be polymerized to cyclic hydrocarbons consisting primarily of cyclooctatetraene and higher polymerides.*

Previously, the classical work of Berthelot[1] had shown that at high temperatures, acetylene would polymerize to form benzene, naphthalene, diphenyl and other aromatic hydrocarbons. Later, Mayer[2], Zelinski[3] and Schwarz[4] obtained good yields of benzene and toluene by shock-chilling the products from the pyrogenic treatment of acetylene.

Aliphatic polymers of acetylene, including vinyl acetylene, divinyl acetylene, had been produced by Nieuwland and his coworkers[5] by passing acetylene through aqueous solutions of ammoniacal cuprous salts.

Willstätter and his coworkers[6] synthesized cyclooctatetraene for the first time in order to investigate its unsaturated character with particular reference to Theile's theory of partial valencies, and to compare its stability and reactivity with that of benzene. Their synthesis was extremely tedious and painstaking and has usually been regarded as one of the classics of organic degradative studies. Starting with pseudopelletierine, an alkaloid found in the bark of the pomegranate tree, they were able by hydrogenation, exhaustive methylations, and decompositions of the quaternary ammonium salts to obtain cyclooctatriene. The triene was brominated, and reacted with dimethylamine; the amine was methylated, and the quaternary ammonium hydroxide decomposed to give cyclooctatetraene. The steps involved are as follows:

* This work has just been published by Reppe, Schlichting, Klager and Topel, *Ann*, **560**, 1 (1948).

[1] *Compt. rend.*, **111**, 471 (1890), *Ann. chim. phys* (4), **9**, 446 (1866), *Ann chim. phys.* (4), **12**, 54 (1867); *Ann.*, **139**, 273 (1866).

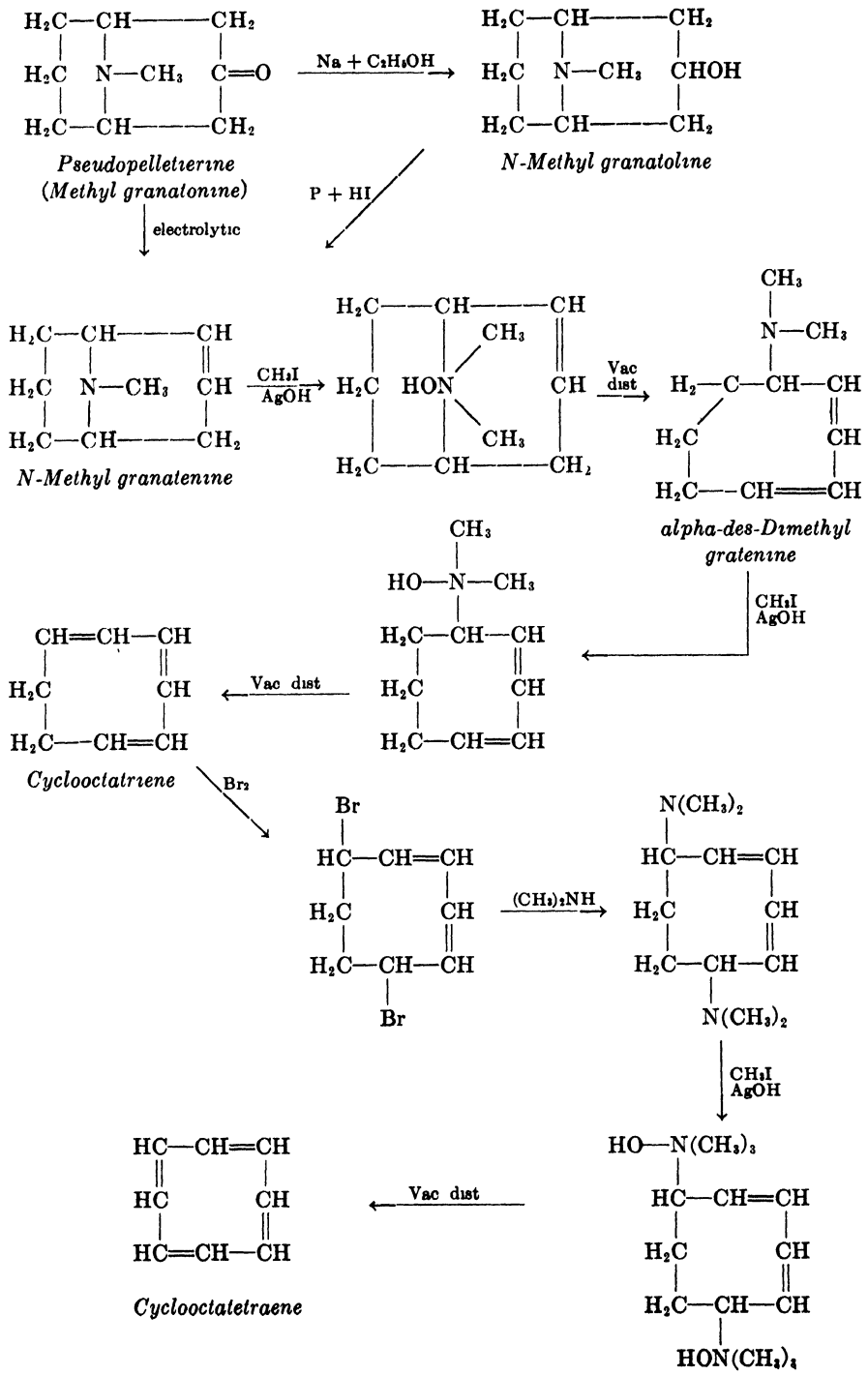
[2] *Ber.*, **45**, 1609 (1912); **46**, 3183 (1913); **47**, 2765 (1914), **50**, 422 (1917); **51**, 5171 (1918), **53**, 1261 (1920).

[3] *Chem. Centr.*, **1923**, I, 1170; *Ber.*, **57**, 264 (1924); *Compt. rend.*, **177**, 882 (1924).

[4] *J. prakt. Chem.* (2), **156**, 205 (1940); **158**, 2 (1941); **161**, 137 (1942).

[5] *J. Am. Chem. Soc.*, **53**, 4197 (1931).

[6] *Ber.*, **44**, 3442 (1911); **46**, 517 (1913).


Pseudopelletierine
(Methyl granatonine)
Na + C2H5OH
N-Methyl granatoline
P + HI
electrolytic
CH3I
AgOH
N-Methyl granatenine
Vac dist
alpha-des-Dimethyl
gratenine
CH3I
AgOH
Vac dist
Cyclooctatriene
Br2
(CH3)2NH
CH3I
AgOH
Vac dist
Cyclooctatetraene

From 100 kg of bark, the world's supply at that time, they obtained 100 g of pseudopelletierine, which in turn gave 3 to 4 g of cyclooctatetraene.

In 1940 Reppe made the surprising discovery that acetylene under pressure and the influence of certain nickel compounds, especially nickel halides and nickel cyanide, in the presence of solvents (*e.g.*, tetrahydrofuran), polymerized to cyclopolyolefins; the major component in the reaction mixture was found to be cyclooctatetraene.[7]

Cyclooctatetraene is a golden-colored liquid which was analyzed as follows:

C_8H_8	%C	%H	Mol. Wt.	Hydr. No
Calculated.. .	92.25	7 75	104.06	769
Found	92.11	7 97	103	762

The physical constants determined by Reppe differ slightly from those determined by Willstätter. These differences may be accounted for by the fact that Reppe had available larger quantities of the chemical, hence higher purity, and greater accuracy in physical measurements could be attained.

Physical Data on Cyclooctatetraene

	Reppe	Willstätter
B.p./760 mm	142 –143°	
B.p./17 mm	42 0– 42 5°	42.2–42.4°
F.p.	−7.0°	−27°
d_4°	0.9382	0.943
d_4^{20}	0 9206	0 925
N_D^{20}	1.5290	1.5389
Mol refraction	35.17	35 20 [MD (calc.) C_8H_8 = 35 08]
Mol. exaltation	0 09	0.12
Dielectric constant	2 74/20°	
	1 5 × 10^6 Hertz	
Heat of combustion Q_p	1069 02	
	K cal/mol	
Dipole moment	0 069 × 10^{-18}	
	E.S.U.	

Reppe concluded, on the basis of these data, that there could be no doubt that his product prepared from acetylene was identical with Willstätter's cyclooctatetraene and, furthermore, that cyclooctatetraene is indeed 1,3,5,7-cyclooctatetraene.

As substantiating evidence for the symmetrical structure for cyclooctatetraene, Reppe cites the following:

(1) Chemical properties (to be described later): The olefinic character of cyclooctatetraene had already been demonstrated by Willstätter. This

[7] *PB* 62593; *PB* 46996 (*BIOS* 137).

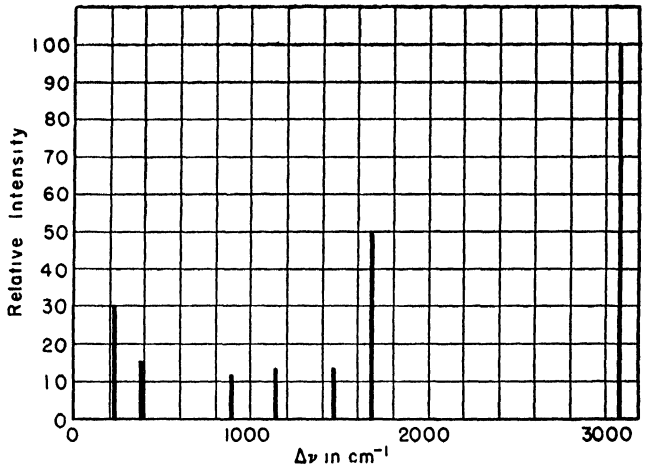


FIGURE V-1 Raman spectrum of cyclooctatetraene.

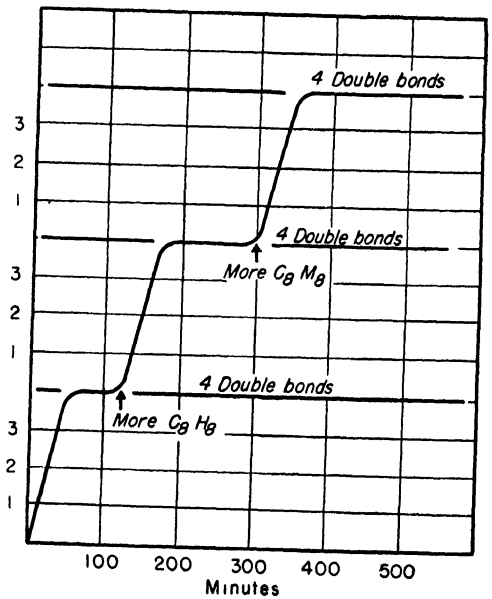


FIGURE V-2. Hydrogenation of cyclooctatetraene in acetic acid

is theoretically possible, according to Huckel[8], because the electron shell of cyclooctatetraene is not closed as is that of benzene. Cyclooctatetraene has 8 electrons in contrast to the 6 electrons of benzene, which form a closed

[8] *Z. phys. Chem.*, 70, 204 (1921).

shell. This arrangement, combined with a non-planar eight-membered carbon ring, is responsible for the olefinic nature of cyclooctatetraene[9].

(2) The practically zero dipole moment.

(3) The Raman spectra (Fig. V-1) which show only seven lines out of a possible forty-two. The two strongest lines (Raman frequencies 1673 and 3068 cm^{-1} correspond to the normal values for =C=C= and C—H linkages. For comparison, the corresponding frequencies for benzene are 1605 and 3060 cm^{-1}.

(4) Hydrogenation with palladium on charcoal catalysts in glacial acetic acid solution, which demonstrates the equivalence of the four double bonds in cyclooctatetraene as shown in Fig. V-2. Hence the double bonds must be conjugated rather than cumulative, and the molecule must have a high degree of symmetry.

It has been noted that some of the physical and chemical properties of the cyclooctatetraene obtained by Willstatter are very much like the properties of styrene as shown by the following table[10].

Properties of Cyclooctatetraene and Styrene

	Styrene	Willstätter's Cyclooctatetraene
M p	−33°	−27°
d_4^{20}	0 907	0 925
N_D^{20}	1 5450	1 5389
B p. (17 mm)	43°	42.2–42.4
Dibromide ($C_8H_8Br_2$) (m p)	72–73°	70–71 5°

Furthermore, Hurd and Drake found that the decomposition of model open-chain quaternary ammonium hydroxides derived from the diaminobutanes did not give exclusively 1,3-butadiene[11]. Since these models closely resembled the quaternary ammonium hydroxide in the final step of the Willstätter synthesis, they believed that their results cast serious doubt on the structure of the Willstätter product. The correctness of this viewpoint is now doubtful as a result of Reppe's hydrogenation experiments.

The reports that cyclooctatetraene had been synthesized by Reppe from acetylene renewed interest in cyclooctatetraene and in the validity of the Willstatter synthesis. Cope and Overberger repeated the Willstätter synthesis from pseudopelletierine which they synthesized by the condensation of glutaraldehyde with methyl amine hydrochloride and acetone dicar-

[9] *Ber.*, **67**, 1870 (1934); **67**, 2078 (1934); *Z. phys. Chem.*, **39**, 59 (1938); **41**, 287 (1938); **44**, 185 (1939); *Z. Electrochem.*, **43**, 853 (1937); **45**, 548 (1939); *Proc. Roy. Soc.* (A) **158**, 297 (1937); *Z. angew. Chem.*, **52**, 223 (1939).

[10] *J. Org. Chem.*, **3**, 603 (1938–1939); *J. Am. Chem. Soc.*, **61**, 1261 (1939).

[11] *J. Am. Chem. Soc.*, **61**, 1943 (1939).

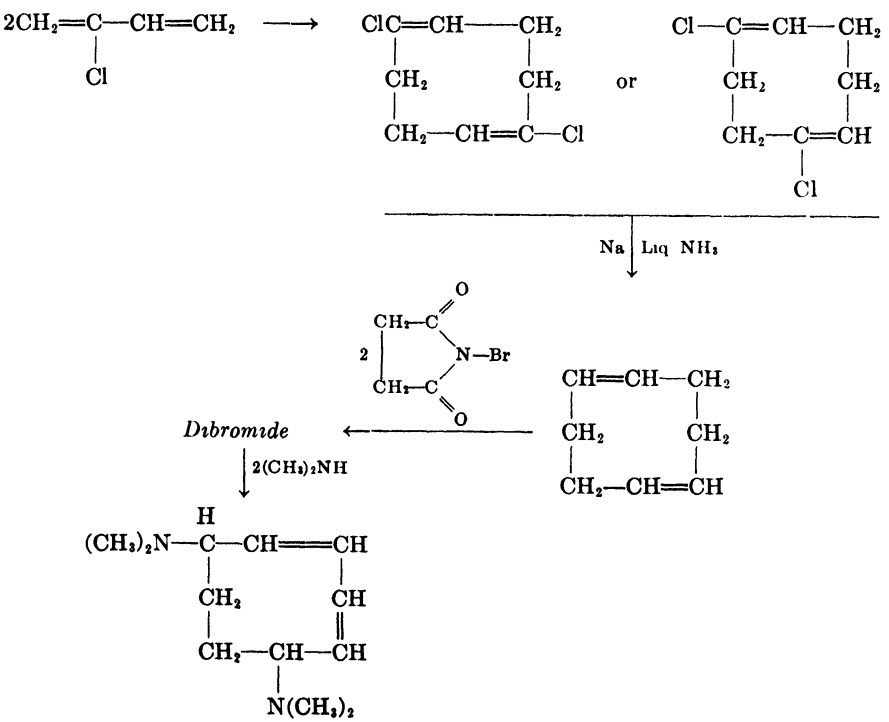
boxylic acid[12]. At the same time they prepared cyclooctatetraene by the Reppe process from acetylene polymerization. The properties of the two preparations and of Willstätter's original preparation are as follows:

Properties of Cyclooctatetraene

	Cope and Overberger's Preparations		Willstätter's Product
	From Pseudopelletierine	From Acetylene	
M p. (capillary)	−5 8 to −5 4	−5 9 to −5 3	−27
Mixed m.p	−6 0 to −5 3		
N_D^{25}	1 5342	1.5342	1.5389 (20°)
Maleic anhydride adduct, m.p	166 7–168 2	166 7–167 8	
Mixed m.p	165.4–167		

The ultraviolet absorption spectra of Cope and Overberger's two samples were identical.

More recently, Cope and Bailey have described a third synthesis of cyclooctatetraene from 2-chloro-1,3-butadiene, involving seven steps:[13]



[12] *J. Am. Chem. Soc.*, **70**, 1433 (1948).
[13] *J. Am. Chem. Soc.*, **70**, 2305 (1948).

The 1,6-bis-dimethylamino-2,4-cyclooctadiene so prepared was identical with the corresponding intermediate in the Willstätter synthesis as shown by correspondence of melting points of the dipicrates and dimethyl iodides, and of ultraviolet absorption spectra.

The remaining steps in the synthesis followed the sequence of reactions originally used by Willstätter. The cyclooctatetraene so prepared was identical with a sample prepared from acetylene on the basis of correspondence in index of refraction, melting point, mixed melting points, ultraviolet and infrared absorption spectra.

Cope and coworker's results completely substantiate the synthesis of cyclooctatetraene reported by Willstätter and furthermore prove that cyclooctatetraene prepared from pseudopelletierine, or from 2-chlorobutadiene is identical with the cyclooctatetraene prepared by the Reppe method from acetylene.

The Molecular Configuration of Cyclooctatetraene

Cyclooctatetraene has attracted considerable attention because of the relationship of its structure to that of benzene. Since it behaves chemically as an olefin, it has been suggested that its 135° bond angle involves considerable strain in the molecular structure, at the expense of the expected resonance energy[14].

Heat of combustion measurements lead to a value of 28 k cal/mole for the resonance energy, compared with 41 k cal/mole for benzene[15]. The calculated resonance energy for a planar, non-strained molecule would be 1.17 times that of the benzene molecule[16,17]; the difference between the calculated and observed resonance energy, 20 k cal/mole, has been attributed to strain (Kovner[18] calculated the resonance energy for the noncyclic octatetraene as 24 k cal/mole, about the same magnitude as that observed for the cyclic compound.)

The energy change for the transition of cyclooctatetraene to styrene has been measured by Prosen, Johnson and Rossini[19] to be $-34.5 + 0.34$ k cal/mole, indicating that cyclooctatetraene is considerably less stable than styrene, and indicating the absence of any considerable amount of resonance energy.

A number of investigations have been made to determine the actual structure of the cyclooctatetraene molecule, using infrared and Raman spectroscopy, electron and x-ray diffraction, and ultraviolet spectroscopic

[14] Pauling, L "Nature of the Chemical Bond," p. 133, Cornell University Press, 1939.

[15] Reppe, "Report on Cyclopolyolefins," *PB* 46996.

[16] Penney, *Proc Roy. Soc.* A, **146**, 223 (1934).

[17] Wheland, G., *J. Chem. Phys.*, **3**, 230 (1935)

[18] Kovner, *Acta Physicochim.* (*U.R.S.S.*), **19**, 385 (1944).

[19] Prosen, Johnson and Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947).

methods. Samples used by the different investigators have been derived from numerous sources, but for the most part their identity has been confirmed by making use of the infrared absorption spectra[20].

Infrared and Raman spectra fail to show the presence of phenyl groups, triple bonds, methylene, or methyl groups, and indicate that the H atoms are equivalent[21]. This, together with the low dipole moment value of 0.07–0. 0D*[22], is consistent with a cyclic molecule having some symmetry.

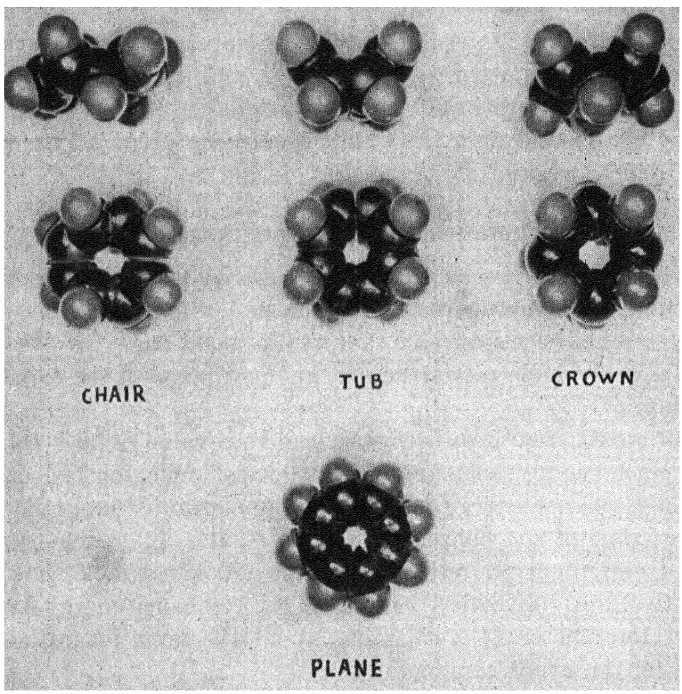


FIGURE V-3. Forms of cyclooctatetraene.

The possible molecular configurations which have been considered for cyclooctatetraene are: C_{2h} (chair, or cradle form), D_{2d} (tub, or boat form), D_{4d} and D_4 (crown forms) and D_{4h} (planar form). Photographs of models of these structures are shown in Figure V-3. Of these symmetry types, only the D_{2d} could involve a strainless configuration with no resonance (provided normal single and double bond dimensions are used).

[20] Cope, *J. Am. Chem. Soc.*, **69**, 976 (1947); Cope and Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948); Cope and Bailey, *J. Am. Chem. Soc.*, **70**, 2305 (1948).

[21] Lippincott and Lord, Jr., *J. Am. Chem. Soc.*, **68**, 1868 (1946).

* One Debye unit represents 10^{-18} electrostatic units.

[22] Measurement by Binkele of I.G. Farbenindustrie, Ludwigshafen, 1941.

One powerful method of investigating molecular symmetry is through comparison of the infrared and Raman spectra of a material. The selection rule requirements[23] make it possible to eliminate certain symmetry types by the appearance or nonappearance of the same frequency values in the two types of spectra Several such investigations have been made of cyclooctatetraene[24]

Lippincott, Lord and McDonald[25] have summarized the most complete data available, including the Raman and infrared spectra for completely deuterated cyclooctatetraene, and have concluded that (1) the number of Raman lines and infrared bands strong enough to be called fundamentals is small, so that considerable symmetry must be present; (2) the number of definite coincidences between relatively strong infrared bands and Raman lines renders a symmetry center unlikely; and (3) that several strong infrared bands appear at positions where no Raman lines could be found. Structures C_{2h}, D_{4d} and D_{4h}, as well as those of low symmetry, can be eliminated from consideration under (1) and (2), (3) indicates that the spectroscopic data favor the D_4 over the D_{2d} form.

The result of x-ray diffraction analysis[26, 27] indicates the D_{2d} structure; the crown configuration will not satisfy the observed intensity data. Electron diffraction investigations[28] favor the D_{2d} type of structure for cyclooctatetraene.

The golden yellow color of cyclooctatetraene has been considered as one evidence of a resonance structure[29, 30]. Measurements of a very carefully purified sample made at Ludwigshafen, however, did not show any distinct absorptions in the ultraviolet but only an increasing general absorption

[23] The selection rule requirements for the postulated structures are summarized below:

Structure	Fundamental Frequencies Permitted		
	Infrared	Raman	Common to Both Types
C_{2h}	21	21	0
D_{2d}..	15	27	15
$D_{4d} = V_d$...	8	15	0
D_4 ..	14	28	10
D_{4h} .	8	15	0

[24] Lippincott and Lord, Jr., *J. Am. Chem. Soc.*, **68**, 1868 (1946); Flett, *Nature*, **159**, 739 (1947).

[25] Lippincott, Lord, Jr., and McDonald, *J. Chem. Phys.*, **16**, 548 (1948).

[26] Kaufman, Fankuchen, and Mark, *J. Chem. Phys.*, **15**, 414 (1947).

[27] Kaufman, H. S., Fankuchen, I., and Mark, H., *Nature*, **161**, 165 (1948).

[28] Bastiansen and Hassel, *Tids, Kjemi, Bergvesen Met.*, **7**, 55 (1947).

[29] Forster, *Z. Elect.*, **45**, 548 (1939).

[30] Maccoll, *Nature*, **157**, 695 (1946).

toward the shorter wave lengths[31]. The absence of such absorption maxima would indicate the absence of any appreciable amount of resonance energy.*

The lack of a discrete absorption in the ultraviolet absorption spectra, the D_4** structure indicated by Raman and infrared methods; the D_{2d} structure suggested by x-ray and electron diffraction methods; the combustion measurements showing essentially the amount of resonance energy calculated for the non-cyclic compound; and the chemical reactivity all indicate the absence of any considerable amount of resonance energy.

Discovery and Theory of the Polymerization of Acetylene

Just as in the case of the vinylation and ethinylation reactions, the discovery of the polymerization of acetylene to cyclopolyolefins was made accidently during the attempted synthesis of 3-hexyne-1,6-diol from 2 moles of ethylene oxide and 1 mole of acetylene in the presence of a nickel cyanide catalyst[32].

$$\underset{\backslash/}{\overset{}{CH_2CH_2}}\underset{O}{} + HC{\equiv}CH + \underset{\backslash/}{\overset{}{CH_2CH_2}}\underset{O}{} \xrightarrow{Ni(CN)_2} HOCH_2CH_2C{\equiv}C{-}CH_2CH_2OH$$

However, the reaction product was found to be a mixture of hydrocarbons C_8H_8, $C_{10}H_{10}$, $C_{12}H_{12}$ and $C_{10}H_8$. This discovery, no doubt, also explains the continued use of ethylene oxide in subsequent polymerizations of acetylene to cyclopolyolefins.

Very unstable acetylene-nickel compounds are presumed to be the actual catalyst; they are generated by the action of acetylene under pressure upon the nickel compounds present. The formation of those very reactive nickel

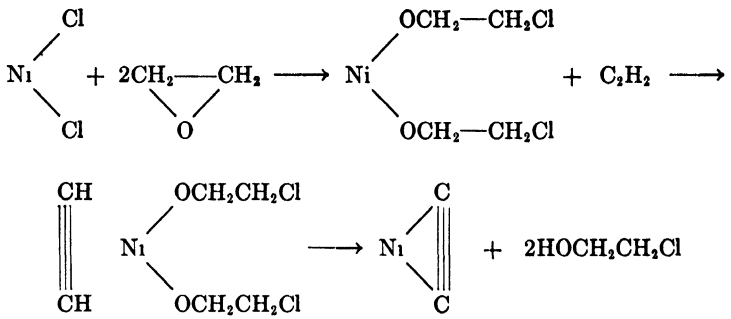
[31] Topel of Ludwigshafen, May 26, 1941 (document from I.G files) The sample was triply distilled under nitrogen, crystallized under nitrogen and preserved at a low temperature until used. A 0 02% solution of the cyclooctatetraene in ligroin was used for the examination

* Forster[29] has shown that resonance between the two Kekule forms for cyclooctatetraene should lead to an absorption maximum at 4100 Å U. Maccoll[30], using the complete set of fourteen structures and neglecting the second excited structures, calculated a value of 3550 Å.U. for the maximum. No explanation for the color, other than as a resonance phenomenon of the cyclooctatetraene, has been suggested

** The D_4 structure is not a puckered ring with identical bonds Rather it involves two types of bonds appearing alternately; hence it would be inconsistent with complete resonance such as is observed with benzene The D_{4d} crown structure, which involves identical bonds, is the structure usually depicted as the crown form, and is not favored by either infra-red and Raman, or x-ray diffraction methods. The D_4 structure cannot be constructed with ordinary atomic models, and so would involve some strain or resonance if it existed.

[32] *PB* 25560 (*BIOS* 352).

acetylides, which are doubtless very unstable, can be facilitated by the addition of cyclic oxides such as ethylene oxide. Theoretically, the unstable nickel salts of ethylene halohydrins, which are probably formed by the action of halides and ethylene oxide, are decomposed by reaction with acetylene to form unstable nickel acetylides and ethylene halohydrins.

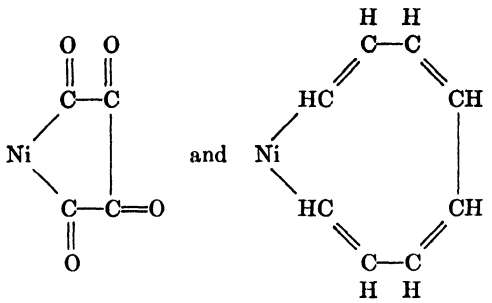


Ethylene chlorohydrin can actually be isolated in the expected quantity if the reaction mixture is worked up properly. It has been mentioned that formation of cyclopolyolefins occurs if tetrahydrofuran is used as a diluent. This observation has been interpreted to mean that tetrahydrofuran, the ring of which can be easily opened, reacts like ethylene oxide. Tetrahydrofuran is, so to speak, regarded as an "extended ethylene oxide." Butylene chlorohydrin could not be isolated in this case, possibly because it splits out hydrogen chloride and reforms tetrahydrofuran.

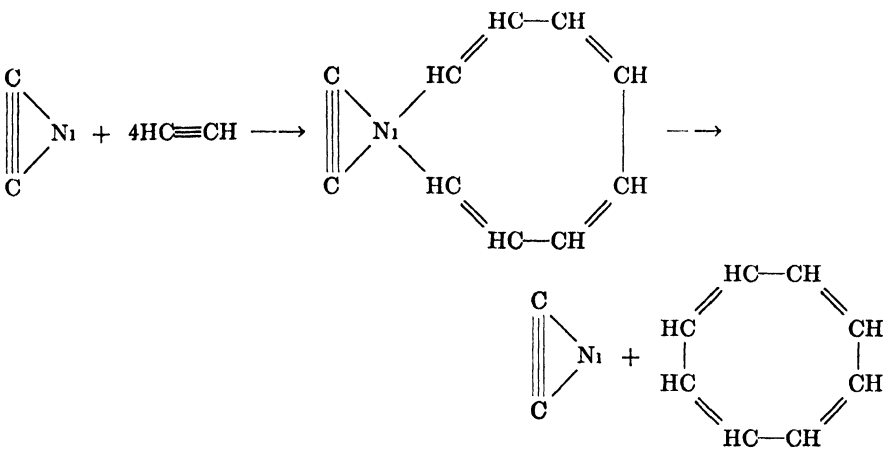
Only those nickel compounds in which the nickel is weakly linked to the anion are catalysts. Therefore, it is obvious that nickel halides and other similar salts are not catalysts; nickel compounds in which the nickel is bound in the form of stable complex (such as nickel phthalocyanine) are also unsuitable for the production of cyclopolyolefins. Acetylene is polymerized only if the nickel, which is strongly bound, as in the halides, is transformed into a much weaker combination, for instance, by means of ethylene oxide. Such a loose bond is already present in nickel thiocyanate and nickel cyanide ($Ni(CNS)_2$ and $Ni(CN)_2$), and the nickel can form complexes and bind acetylene by free van der Waals' forces. Other nickel salts in which nickel is bound very loosely, *e.g.*, as in the nickel salts of acetoacetic ester, acetylacetone, benzoyl-, oxalyl, terephthaloyl- and cyanoacetic esters, and of di-*o*-aminophenol, are efficient catalysts for the polymerization of acetylene to cyclopolyolefins.

The mechanism of the reaction which leads to the formation of cyclopolyolefins is not yet clear. Acetylene reacts similarly to carbon monoxide in many cases, and Reppe assumed that nickel or nickel acetylide binds

four molecules of acetylene just as it holds four molecules of carbon monoxide in nickel carbonyl:*



The nickel-acetylene complex thus formed decomposes, giving cyclooctatetraene and regenerating nickel acetylide which may react the same way again.



Regardless of the mechanism, the formation of cyclooctatetraene is surprising in view of thermodynamic considerations, since cyclooctatetraene has a higher energy content than benzene, as shown in the following tables.

Heat of Combustion and Heat of Formation

	Heat of Combustion Q_p	Heat of Formation $C = 94.3$, $H = 34.2$
Vinyl acetylene	569 K cal/mole	−57 K cal/mole
Benzene	783 K cal/mole	−12.4 K cal/mole
Cyclooctatetraene	1069 K cal/mole	−40 K cal/mole

* The authors must confess that this analogy seems completely illogical to them, but it is presented here since it was a part of Reppe's original manuscript.

Energetics of the Formation from Acetylene

	Q (liquid) K cal/mole	Q (gas) K cal/mole	Q/mole C_2H_2 K cal/mole
2 C_2H_2 Vinyl acetylene	+55.8	+49 6	+25
3 C_2H_2 Benzene	+153.8	+146.4	+49
4 C_2H_2 Cyclooctatetraene	+180.6	+170.6	+42.6

The formation of cyclopolyolefins from acetylene is claimed to be extremely sensitive to catalytic impurities. Although the different autoclaves used in this work were of the same structural steel (V2A or V4A, they gave widely varying results. No polymerization could be obtained in certain autoclaves, and it became necessary to keep a record of those autoclaves in which the polymerization was successful. This behavior was thought to be due to the previous history of the autoclave.

In all these experiments it was found that the presence of water must be carefully avoided. Reppe has always insisted that even with nickel cynide, ethylene oxide was an essential component in the formation of intermediate products which, with acetylene, gave nickel acetylide in very active form. However, some of his coworkers claim that the function of the ethylene oxide is simply that of a dehydrating agent; finely powdered calcium carbide can replace the ethylene oxide, if all reagents are rigorously dried.

The process has until now been carried out discontinuously; suitable catalysts and working conditions have not yet been developed for continuous production. The experiments are still in the initial stage. The average yield is 70 per cent of the theoretical; in some cases 90 per cent yields are obtained, the balance consisting of a little benzene and 5 to 10 per cent of higher polyolefins ($C_{10}H_{10}$, $C_{12}H_{12}$, and others), as well as resins soluble in tetrahydrofuran and insoluble cuprene.

Preparation of Cyclooctatetraene (C_8H_8)

Twenty grams of nickel cyanide (see below) and 50 grams of powdered calcium carbide are suspended in 2 liters of tetrahydrofuran and charged to an autoclave of 4- to 5-liter capacity. The autoclave is freed from air-oxygen by flushing with nitrogen and then heated to 60 to 70° inside temperature under 5 atm of nitrogen pressure. The contents are agitated by stirring or shaking the vessel while introducing acetylene to a total pressure of 15 to 20 atm. The degree of reaction is observed by the pressure drop, and acetylene is pumped in from time to time until the absorption stops.

The reaction is stopped after 48 to 60 hours. Cuprene and the catalyst

are separated by filtration from the brown solution. The filtrate is then subjected to distillation under reduced pressure to protect the product. The crude cyclooctatetraene obtained is rectified under normal pressure and separated from the residue; 320 to 400 grams of cyclooctatetraene, 30 to 50 grams of resins and 50 grams of benzene are obtained under these conditions.

Production of the Catalyst. The most effective catalyst is nickel cyanide made from nickel chloride and hydrocyanic acid; it gives good conversion of the acetylene with formation of only a little benzene and resinous material. Nickel chloride is dissolved in alcohol to form the nickel cyanide catalyst. The solution is chilled to 0 to $-10°$, and a 10 per cent alcoholic solution of hydrocyanic acid is added with stirring. The mixture is left standing for 12 hours, keeping it cold. Precipitation is then completed by another addition of hydrocyanic acid solution; after another 12 hours, the precipitated nickel cyanide is filtered off. It is washed well with water until neutral. The pale blue nickel cyanide is then converted into the yellowish-brown anhydrous salt at 175°. Nickel cyanide made in any other way proved to be less effective.

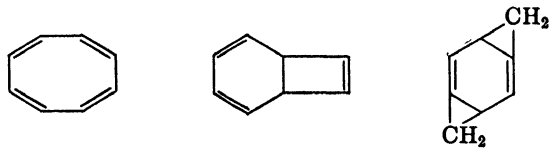
If the catalyst is made in this way and is perfectly neutral, and if, furthermore, the tetrahydrofuran and the acetylene gas are kept absolutely dry, a satisfactory yield of cyclooctatetraene is obtained, even without addition of calcium carbide. Under these conditions, no hydrocarbons boiling higher than C_8H_8 or, at most only traces of them and of azulene are formed.

Reactions of Cyclooctatetraene

Due to its olefinic character, cyclooctatetraene is unstable to some chemical reagents. It is attacked by oxidants; when exposed to air, it gradually deposits yellow flakes. Halogens add to it readily. It undergoes diene synthesis, with the formation of characteristic addition products. Upon long standing, particularly when warm, it apparently polymerizes to a mixture of a dimeric compound and a resin-like substance. It forms crystalline addition compounds with silver nitrate or copper ammonium chloride.

The study of the reactions of cyclooctatetraene shows that under the influence of different reagents it reacts as if it had different structures. In some of the reactions the 8-membered ring is left intact; in others, aromatization occurs with formation of derivatives of ethyl benzene or *p*-xylene. There are other reactions in which compounds are formed having a 4-membered ring fused to a 6-membered ring.

Cyclooctatetraene is, therefore, able to react according to the following three fundamental structures: (1) as an 8-membered ring; (2) as a bicyclo (0,2,4)-octatriene (2,4,7); and (3) as a 1,2,4,5-dimethylene cyclohexadiene-2,5. These structures are illustrated below.



(I) *Cyclooctatetraene*

(II) *Bicyclo-(0,2,4)-octatriene-(2,4,7)*

(III) *1,2,4,5-Dimethylene cyclohexadiene-2,5*

Reactions of Cyclooctatetraene with Retention of Eight-Membered Ring. *Catalytic Hydrogenation.* Willstatter has demonstrated that cyclooctatetraene, when hydrogenated in the presence of platinum catalysts, yields cyclooctane. This perhydrogenation is possible not only with precious metal catalysts but also with base metals, such as nickel, under pressure[33]. It was observed that the cyclooctane thus obtained had a melting point lower than that previously mentioned in the literature. Instead of melting at 13° as reported for pure cyclooctane, Reppe's sample melted at 11.8°. This discrepancy is attributed to the presence of minute quantities of aromatization products according to reactions of type (2) and type (3) referred to in an earlier paragraph. These contaminants are believed to be *p*-xylene or ethyl benzene, or the hydrogenated products thereof, and bicyclooctane.

By oxidizing cyclooctane with nitric acid, suberic acid is obtained, the yield being approximately 40 per cent.

Cyclooctatetraene may be partially hydrogenated to cyclooctene if the process is conducted in non-ionizing solvents such as methanol, ethanol, and tetrahydrofuran, with palladium on calcium carbonate as the catalyst[34]. Under these conditions three moles of hydrogen are absorbed rapidly, while the fourth mole requires nearly ten times as long. (Figure V-4)

If the hydrogenation is stopped after the absorption of three moles of hydrogen, cyclooctene (b. p. 140°) is readily isolated in a 90 per cent yield.

Comparative hydrogenations of cyclooctene carried out in alcoholic and in acetic acid solutions proved that the absorption of hydrogen was ten times faster in the acid solution. The influence of solvents in selective catalytic hydrogenations has been observed in other cases[35]. Rates of hydrogenation in the two solvents are shown in Figure V-5.

Bromination of cyclooctene yields the dibromide, $C_8H_{14}Br_2$, boiling at 123 to 124°C (5 mm). Perbenzoic acid reacts with cyclooctene to yield the known crystalline cyclooctene oxide, $C_8H_{14}O$, melting at 45°. When oxidized with nitric acid, cyclooctene gives a better yield of suberic acid

[33] *D.R.Pat. Anmeldung I-69,547* IVc/12o.
[34] *D.R.Pat. Anmeldung I-73,871* IVc/12o.
[35] *Helv. Chim. Acta*, **14**, 1327 (1931).

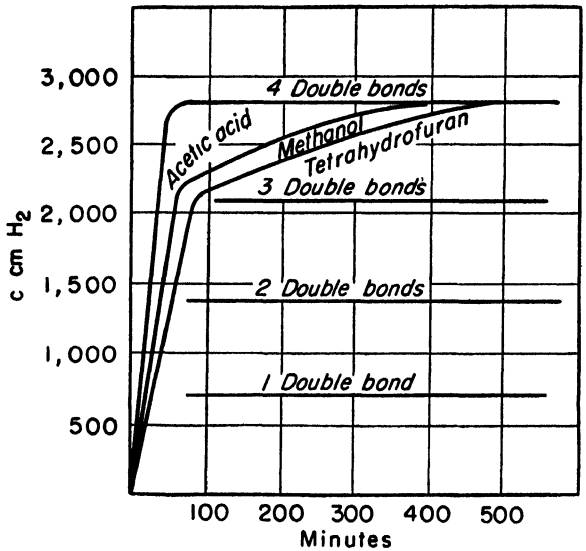


FIGURE V-4 Hydrogenation curves of cyclooctatetraene in various solvents

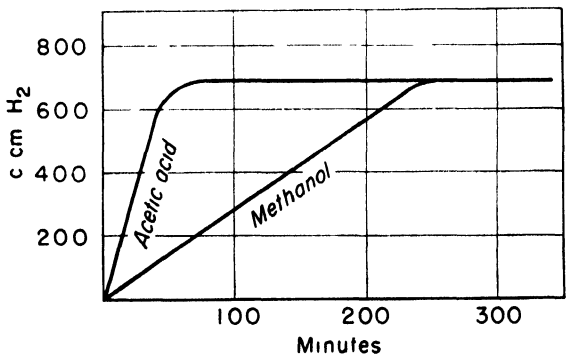
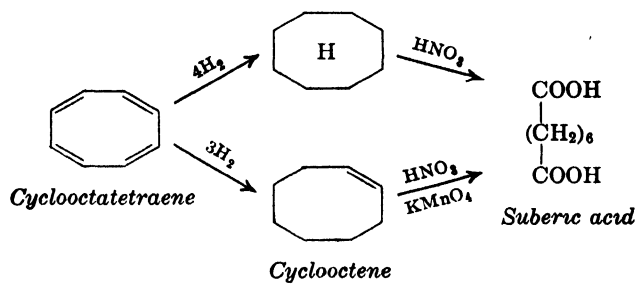


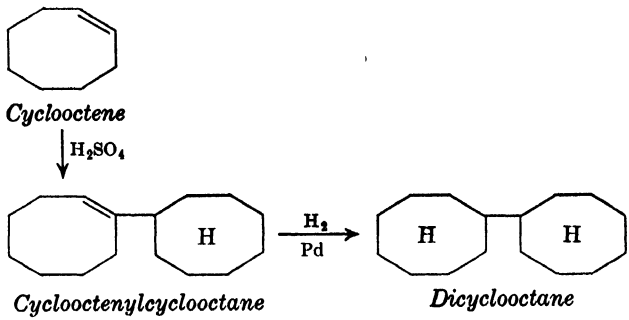
FIGURE V-5 Hydrogenation curves of cyclooctene.

than cyclooctane[36]. Reactions involving hydrogenation and subsequent oxidation are shown in the following illustration.

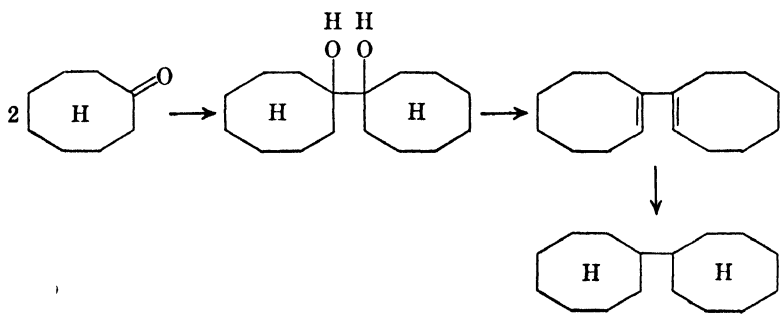


[36] *Helv. Chim. Acta*, **14**, 1327 (1931).

Cyclooctatetraene when subjected to the well-known olefinic reactions becomes a convenient starting point for the preparation of substituted cyclooctanes and cyclooctenes. Under the influence of dilute acids, such as sulfuric acid, cyclooctene is condensed to cyclooctenyl cyclooctane[37], which upon hydrogenation yields dicyclooctane[38].

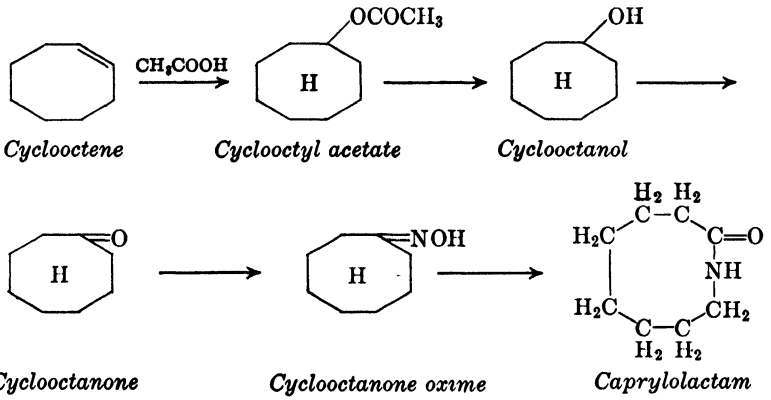


Ruzicka had previously obtained dicyclooctane in the following manner from cyclooctanone:

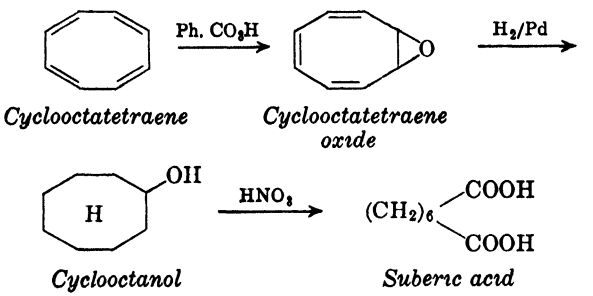


Cyclooctyl acetate can be made from cyclooctene by treatment with glacial acetic and sulfuric acids. Saponification yields cyclooctanol, which on dehydrogenation yields cyclooctanone. Conversion to the oxime and rearrangement yield caprylolactam, which is a new basic material for polyamides.

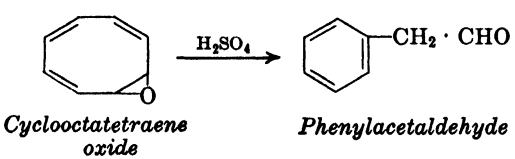
[37] *D.R.Pat Anmeldung I-75,480* IVd/12o.
[38] *D.R.Pat. Anmeldung I-73,915* IVc/12o.



Reactions with Peracids. When cyclooctatetraene dissolved in chloroform is treated with one or several moles of perbenzoic acid, only one oxygen atom reacts, to form an almost colorless oxide with the composition C_8H_8O. Upon catalytic hydrogenation, the oxide absorbs four moles of hydrogen; the resulting cyclooctanol, upon oxidation with nitric acid, yields suberic acid.



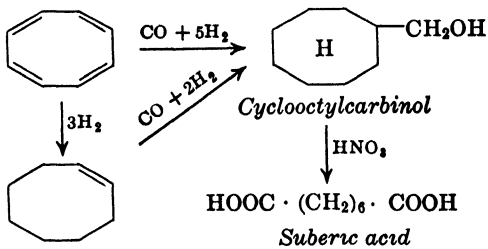
If cyclooctatetraene oxide is heated with a few drops of dilute sulfuric acid, a violent reaction ensues and aromatization occurs, forming phenyl acetaldehyde quantitatively[39].



Reactions with Water Gas (H_2 and CO). Under the catalytic influence of cobalt, only one double bond of cyclooctatetraene reacts with hydrogen and carbon monoxide in the oxo reaction (see page 000), with the formation of cyclooctyl carbinol; the other three double bonds are reduced. The

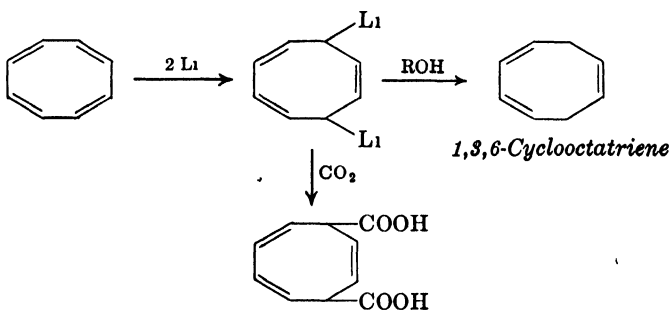
[39] *D.R.Pat. Anmeldung I-70,709* IVd/12o.

course of the reactions leading to the formation of cyclooctyl carbinol (b.p. 106°C, 7 mm), is as follows:



Cyclooctyl carbinol may also be made by the Oxo reaction from cyclooctene and water gas.

Reactions with Alkali Metals. Cyclooctatetraene will add two atoms of alkali metals, the 8-membered ring structure being retained[40]. The resulting compound reacts with carbon dioxide, forming a crystalline dicarboxylic acid of yellow color, which sublimes at 220° (1.5 mm). The alkali-metal adducts react with alcohol, generating cyclooctatriene.



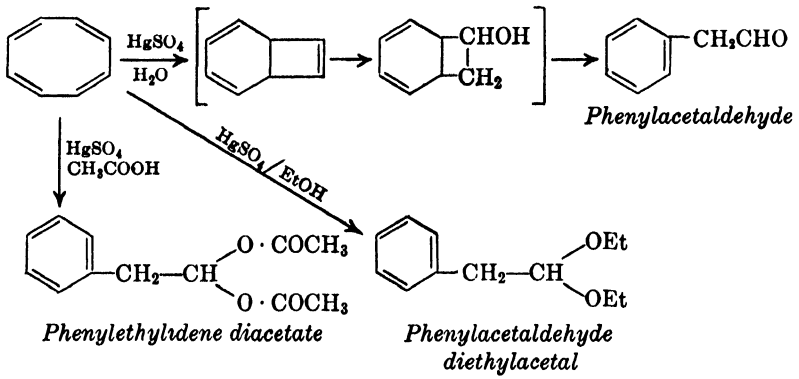
(No evidence has been found for the assignment of these structures to either the acid or the triene.)

Aromatization of Cyclooctatetraene. Cyclooctatetraene aromatizes to give derivatives of ethyl benzene, presumably through the intermediate bicyclo-(0,2,4)-octatriene-(2,4,7) which then undergoes fission of the 4-membered ring. Oxidizing agents, with the exception of perbenzoic acid, accomplish the aromatization.

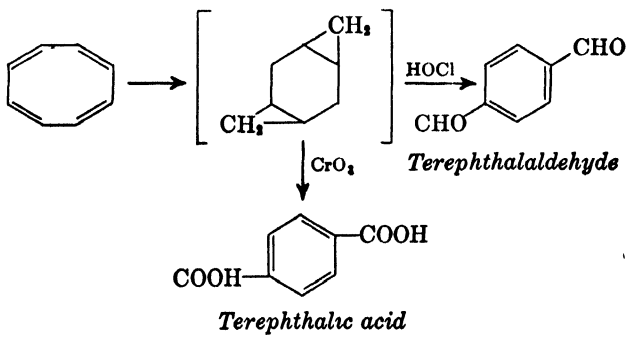
If an aqueous suspension or emulsion of cyclooctatetraene is treated with a solution of a mercury salt such as the sulfate, a white precipitate (which turns black due to formation of metallic mercury) and a colorless oil (boiling at 221°) having the composition C_8H_8O are formed. The oil is phenyl acetaldehyde, and the yield is nearly stoichiometric. The composition of the oil was proven by converting it to the oxime, the semi-carbazone, and

[40] *D.R.Pat. Anmeldung I-72,515* IVc/12o.

to stilbene, and phenylacetic acid. If the water is replaced with glacial acetic acid, or by absolute alcohol, phenylethylidene diacetate, or the diethyl acetal of phenyl acetaldehyde, respectively, are formed.



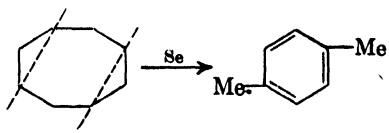
Cyclooctatetraene, in the gaseous phase, is oxidized quantitatively to benzoic acid by air in the presence of catalysts such as vanadium pentoxide. Oxidation in aqueous media yields benzaldehyde and benzoic acid. Hypochlorous acid in alkaline media yields derivatives of *p*-xylene. In this reaction it is presumed that 1,2,4,5-dimethylene cyclohexadiene-2,5 is formed as an intermediate compound. Terephthal aldehyde is formed, along with some benzaldehyde and benzoic acid. Oxidation of cyclooctatetraene by chromic acid in glacial acetic acid yields mostly terephthalic acid plus a small amount of benzaldehyde. These reactions are illustrated below.



Ruzicka probably observed the first aromatization of cyclooctatetraene[41]

[41] *Helv. Chim. Acta*, 19, 432 (1936).

when dehydrogenating cyclooctane to *p*-xylene with selenium. This reaction is illustrated in the following figure.



Cyclooctane *p-Xylene*

Aromatization of Cyclooctatetraene to Bicyclo-(0,2,4)-octatriene-(2,4,7) with Conservation of the Four-Membered Ring. A large number of reactions of cyclooctatetraene involve structural rearrangement of the 8-membered ring, forming derivatives of bicyclo-(0,2,4)-octatriene-(2,4,7). Reactions of cyclooctatetraene with halogens[42] and with dienophils[43] belong to this group.

By a careful study of the reactions of primary addition products and by the analysis of the decomposition products, the constitution of the addition products was established and shown to be derived from bicyclo-(0,2,4)-octane as the parent hydrocarbon.

Halogenation of Cyclooctatetraene. The halogenation products of cyclooctatetraene which have been made and isolated are listed as follows

$C_8H_8Br_2$	Br_2 in $CHCl_3$ at −20° (Willstatter)	m p. 71°C
$C_8H_8Br_2$	Br_2 in $CHCl_3$ at 0–5°	b p. 90°C/1 mm.
$C_8H_8Br_4$	$2Br_2$ in $CHCl_3$	m p. 94°C
$C_8H_8Br_4$		m.p. 147–148°C
$C_8H_8Br_6$	$3Br_2$ in $CHCl_3$	m.p. 156°C + liq. isomers
C_8H_8Cl	SO_2Cl_2 in $CHCl_3$	b p. 62°C/0 5 mm
$C_8H_8Cl_4$	$2SO_2Cl_2$ in $CHCl_3$ or CH_2Cl_2	m p. 111–112°C
$C_8H_8Cl_4$		b p. 126–128°C/1 mm
$C_8H_8Cl_6$	Cl_2 in $CHCl_3$ at 0–5°	m p. 126–127°C + liq isomers

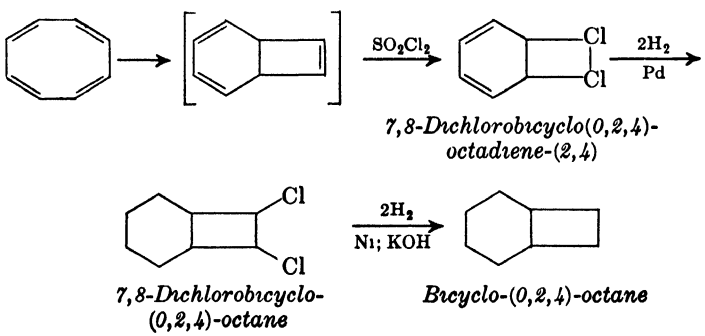
Willstätter found that chlorination of cyclooctatetraene gave a pentachloride in addition to hydrochloric acid. Bromination of cyclooctatetraene in chloroform at −20°C gave a crystalline dibromide melting at 71°C. This dibromide was found by Reppe to be very unstable and easily resinified. Reppe, by varying the temperature of bromination, also iso

[42] *D.R.Pat. Anmeldung I-73,918* IVd/12o; *I-74,070* IVd/12o.
[43] *D.R.Pat. Anmeldung I-71,228* IVc/12o; *I-74,029* IVc/12o.

lated a liquid dibromide ($C_8H_8Br_2$) which had a boiling point of 90°C (1 mm). With several moles of bromine, cyclooctatetraene yields two crystalline tetrabromides ($C_8H_8Br_4$) melting at 94° and 147 to 148°C, respectively. A hexabromide ($C_8H_8Br_6$), a crystalline product melting at 156°C, which is entirely saturated and represents the highest stage of bromination, also exists. An octabromide could not be produced.

Chlorination of cyclooctatetraene yields products which are readily identified. With one mole of sulfuryl chloride a liquid dichloride ($C_8H_8Cl_2$) boiling at 62°C (0.5 mm) is formed. With two moles of sulfuryl chloride a solid tetrachloride ($C_8H_8Cl_4$) melting at 111 to 112°C, and a liquid tetrachloride (b.p. 126–8°C/1 mm) are formed. A liquid hexachloride (melting at 126 to 127°C) is also formed by introducing chlorine into a chloroform solution at 0 to −5°C. Mixed halogenated products were made, but Reppe was unsuccessful in producing any iodine derivatives.

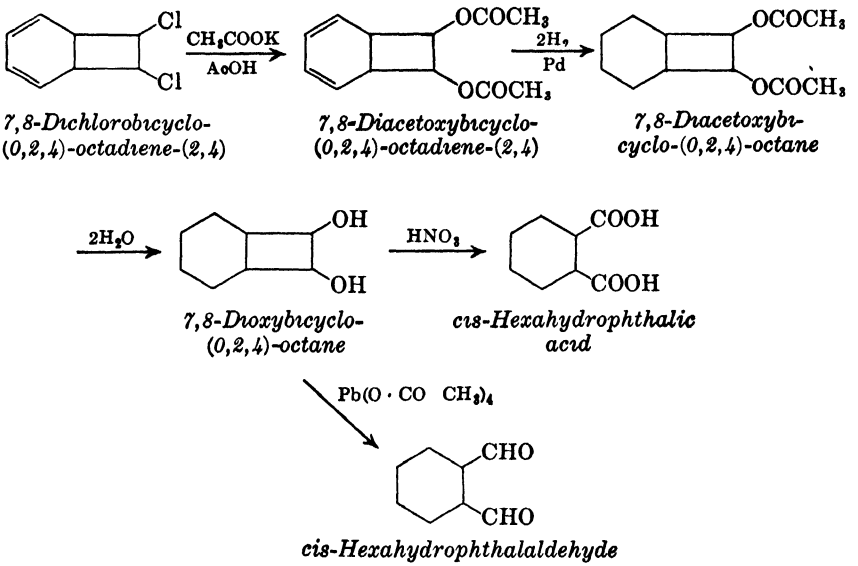
The observation that the highest stage of halogenation is the hexahalide, and that the dihalogen compound absorbs catalytically only two moles of hydrogen instead of the expected three, led to the assumption that the halogenation of cyclooctatetraene creates a fundamental change in structure of the cyclooctatetraene. A saturated hydrocarbon (C_8H_{14}) which is the basic structure for the octahydrocarbon must be bicyclic in structure, the 8-membered ring has been converted into a bicyclic compound which contains a 6-membered and a 4-membered ring This rearrangement is shown graphically in the following figure.



The hydrocarbon C_8H_{14}, bicyclo-(0,2,4)-octane (melting at 136°C) can be produced by hydrogenating the dichloride ($C_8H_{12}Cl_2$) in alkaline solution under pressure. The stability of this reaction product is remarkable. It is known that cyclobutane is readily split open to *n*-butane by hydrogenation, but it is impossible to split open the 4-membered ring in bicyclo-

position of the halogen atoms in halogenated cyclooctatetraene was accomplished as follows:

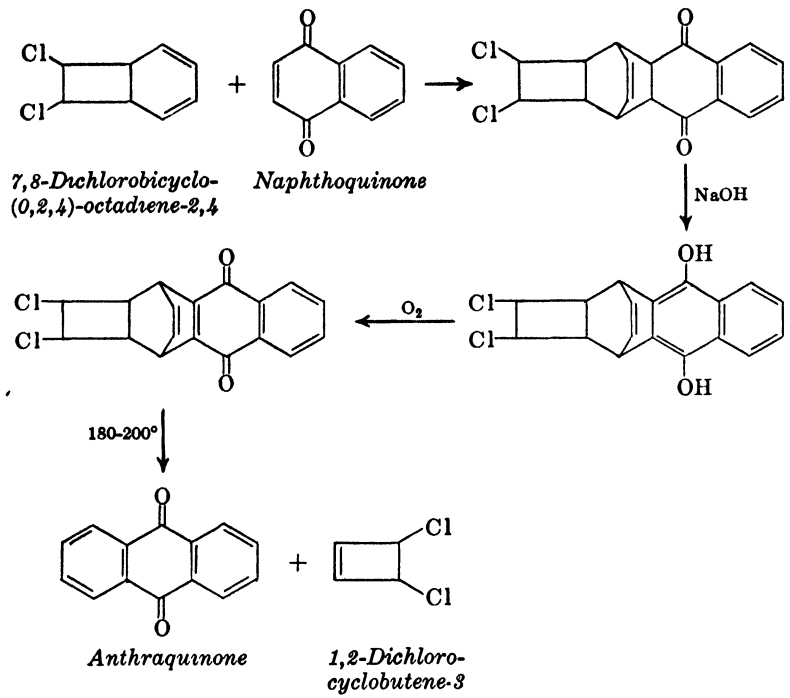
The dichloride ($C_8H_8Cl_2$) was reacted with potassium acetate in glacial acetic acid. The diacetate, m.p. 66°C, absorbs two moles of hydrogen, producing the saturated diacetate, (b.p. 105°C/0.4 mm), which upon hydrolysis forms the glycol $C_8H_{14}O_2$, melting at 142°. The yield is quantitative. Upon oxidation it is converted to *cis*-hexahydrophthalic acid, proving the *ortho*-condensation of the 6- and 4-membered ring, as well as the position of the chlorine atoms. Further proof is the formation of the *cis*-hydrophthalic aldehydes when the glycol ($C_8H_{14}O_2$) is oxidized with lead tetraacetate.



The existence of the 4-membered ring can be shown in another way. The dichloride ($C_8H_8Cl_2$), which still contains two conjugated double bonds in the 6-membered ring, was reacted with naphthaquinone in a typical diene synthesis. The resulting crystalline product melts at 221° and is soluble in caustic, forming a red solution; oxidation of this solution with air yields a crystalline anthraquinone derivative of yellow color. It decomposes thermally at 170 to 180°C, forming a volatile substance. If heated to 220°C, it re-solidifies, giving a crystalline compound which melts at 275 to 280°C. The decomposition products are anthraquinone and a product identified as 1,2-dichlorocyclobutene-3, boiling at 133° and melting at 44°C.[44]

[44] *D.R.Pat. Anmeldung I-74,070* IVd/120.

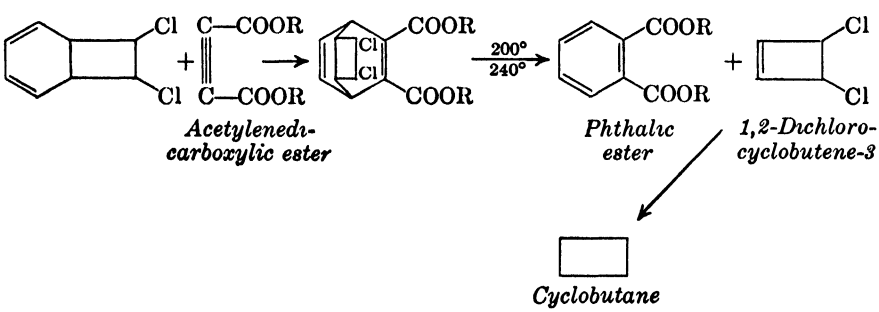
The reaction is believed to proceed as shown in the following illustrations:



7,8-Dichlorobicyclo-(0,2,4)-octadiene-2,4 *Naphthoquinone*

Anthraquinone *1,2-Dichloro-cyclobutene-3*

Similarly, the thermal decomposition of the addition product of the dichloro compound of cyclooctatetraene with acetylene dicarboxylic ester gives phthalic acid esters and 1,2-dichlorocyclobutene-3 quantitatively[45]. This reaction is illustrated in the following diagram:



Acetylenedicarboxylic ester *Phthalic ester* *1,2-Dichloro-cyclobutene-3*

Cyclobutane

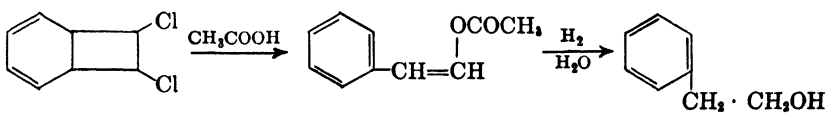
The addition product of 7,8-diacetoxybicyclo-(0,2,4)-octadiene-2,4 and acetylenedicarboxylic acid dimethyl ester or naphthoquinone likewise undergoes thermal decomposition to dimethyl phthalate or anthraquinone, and 1,2-diacetoxycyclobutene-3.

[45] *D.R.Pat. Anmeldung I-74,070* IVd/12o.

These results confirm the observations of Diels[46] and of Alder-Rickert[47] that the addition products of cyclic dienes with naphthoquinone, or acetylene dicarboxylic acid ester, containing one endoethylene bridge, are unstable to heat and are split into aromatics and the endo group.

The structure of the cyclic dichloride ($C_4H_4Cl_2$) which was split out was proven as follows: By the absorption of only one mole of bromine it was converted into the saturated dibromide ($C_4H_4Cl_2Br_2$), boiling at 119 to 120°C (18 mm), proving that it contains just one double bond and hence is evidently cyclic. Oxidation with nitric acid formed fumaric acid, the carbon atoms connected to the chlorine atoms being oxidized to carboxyl groups. Three moles of hydrogen are absorbed in catalytic alkaline hydrogenation forming cyclobutane. This proves with certainty the presence of the 4-membered ring.

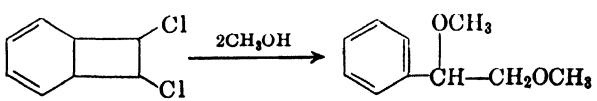
The behavior of the dihalogen compound of cyclooctatetraene toward glacial acetic acid, alcohols and alcoholates is remarkable. In the first two cases mentioned aromatization occurs, but in the third case there is a surprising structural change. If the dichloro compound ($C_8H_8Cl_2$) is heated with glacial acetic acid, hydrochloric acid is split out and styryl acetate in a good yield results. Hydrogenation and saponification converted the styryl acetate to beta-phenylethyl alcohol which was identified as the phenylurethane.



7,8-Dichlorobicyclo-(0,2,4)-octadiene-2,4

Phenylethanol

If the same reaction is carried out with alcohols at elevated temperature, aromatization and splitting off of the 4-membered ring takes place and the dimethyl ether of phenyl glycol is formed.



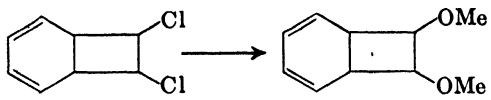
7,8-Dichlorobicyclo-(0,2,4)-octadiene-2,4

β-Phenylglycol dimethyl ether

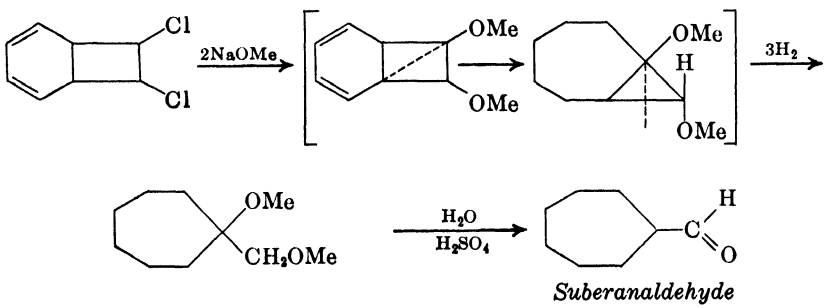
The readiness with which the 4-membered ring can be split to a derivative of ethyl benzene is surprising in these simple reactions. As stated before, the 4-membered ring in the bicyclooctane system is exceedingly stable toward reducing agents and, in saturated form, toward oxidizing

[46] *Ber.*, **62**, 2345 (1929)
[47] *Ann.*, **524**, 185 (1936).

agents. However, if the carbons of the 4-membered ring are substituted by oxygen atoms, the ring system becomes unstable and is split easily. When the dichloride ($C_8H_8Cl_2$) is treated with alcoholates, the expected replacement of halogen atoms by alkoxy groups, as indicated below, does not take



place. The dialkyl ether formed absorbs three moles of hydrogen instead of two on catalytic hydrogenation and does not react with dienophilic components, as is normally the case when the first reaction takes place as anticipated. Careful study of hydrogenation reactions has proved that in the reaction of the dichloride with alcoholates, an unexpected ring enlargement which forms suberane aldehyde takes place as illustrated below[48].



Suberanaldehyde

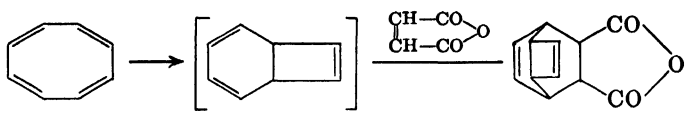
The suberane aldehyde was identified by its semicarbazone, melting at 154°C[49]. Oxidation and amidation convert it to the suberane carboxylic acid amide, melting at 194°C[50].

Diene Syntheses with Cyclooctatetraene. It would normally be expected that cyclooctatetraene, because of its four double bonds, would react with two moles of a dienophilic component. However, this does not happen. In all diene syntheses which were studied (addition of maleic acid anhydride, acrylic acid, quinone and naphthoquinone), the cyclooctatetrane reacted only in the ratio of 1:1 with the dienophilic component[51]. Nor do the addition products undergo a further diene synthesis. The temperature of the reaction is in general fairly high; usually, heating to 100° is required, and in some cases the reaction must be forced to take place under pressure at elevated temperatures. All the diene addition

[48] *D.R.Pat Anmeldung I-77,901* IVd/12o
[49] *Ann* , **345**, 149 (1906).
[50] *Ber.*, **35**, 2691 (1902)
[51] *D.R.Pat. Anmeldung I-71,228* IVc/12o.

products of cyclooctatetraene upon perhydrogenation absorb one mole of hydrogen less than might be expected.

This, of course, indicates that a change in structure of the 8-membered ring must have taken place, in the course of which one double bond disappeared. A close study has been made of the crystalline adduct (m.p. 167 to 168° C) made from cyclooctatetraene and maleic acid anhydride in molten mass at 150° or in solution in boiling mono- or dichlorobenzene. The yield obtained was stoichiometric. It was found that the diene synthesis, like halogenation, proceeds through an intermediate state of the bicyclo-(0,2,4)-octatriene-(2,4,7).



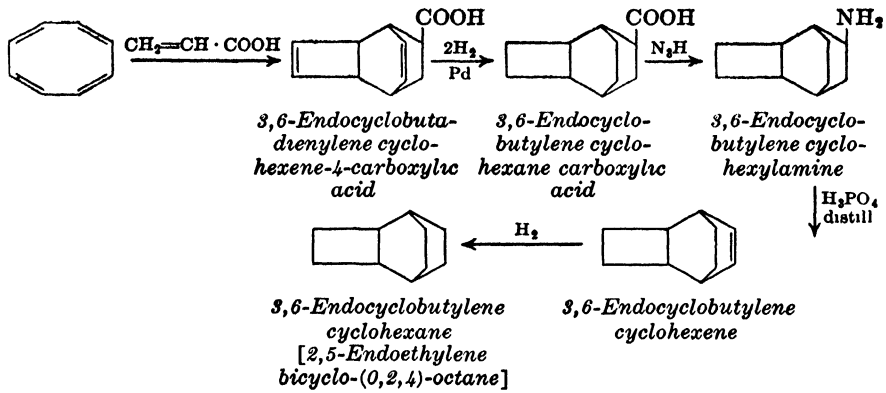
Cyclooctatetraene — *Bicyclo-0,2,4-octatriene-2,4,7* — *3,6-Endocyclobutadienylene cyclohexene-4-dicarboxylic acid-1,2-anhydride*

This new compound dissolves in dilute potassium hydroxide, forming a dicarboxylic acid ($C_{12}H_{12}O_4$) which can be converted into a crystalline dimethyl ester melting at 52 to 55°C. On catalytic hydrogenation with palladium catalysts it absorbs two moles of hydrogen; one double bond is readily saturated, the other one only with difficulty. Hydrogenation can, therefore, be controlled. If only one double bond is saturated, an unsaturated dicarboxylic acid ($C_{12}H_{14}O_4$), is formed, which by distillation is converted to the anhydride ($C_{12}H_{12}O_3$) melting at 142°C Distillation under vacuum of the saturated dicarboxylic acid ($C_{12}H_{16}O_4$) readily converts it to the anhydride of formula $C_{12}H_{14}O_3$, melting at 128 to 129°C. This new tetrahydro acid is perfectly stable toward bromine or potassium permanganate. Nitric acid (specific gravity 1.40) converts it to the anhydride without further attack.

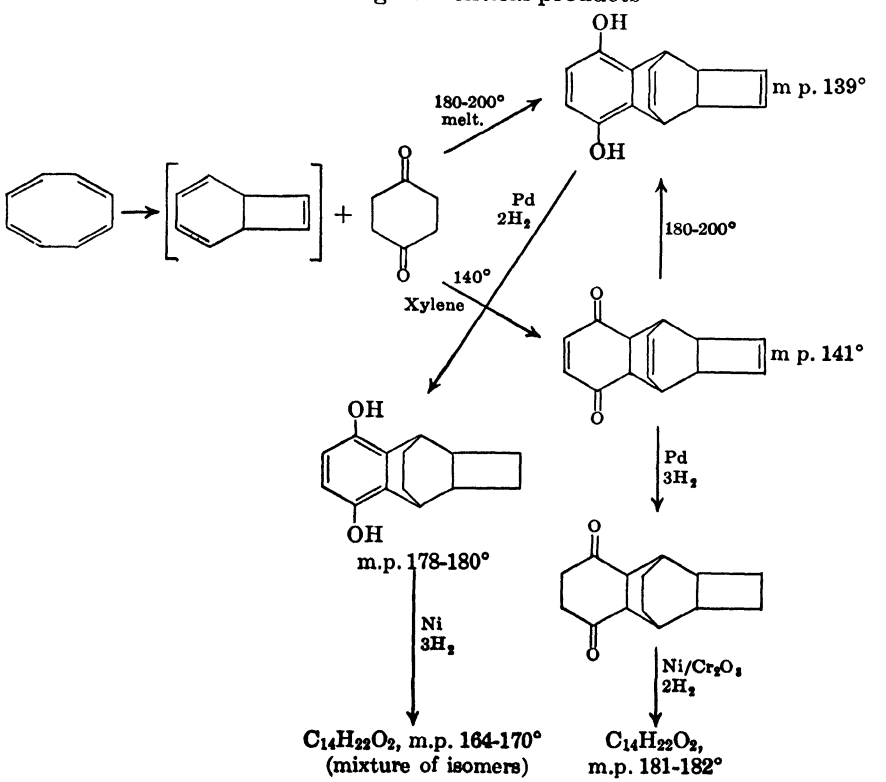
Hydrogenation can also be accomplished with nickel catalysts under pressure[52]. Again, instead of the three double bonds expected, only two can be found in the addition products, meaning that one disappeared in the diene synthesis. This result, which was originally noted in the adduct with maleic acid, was confirmed for all other addition products as well. The result of the catalytic hydrogenations can be explained only by the presence of a tricyclic ring system in the addition products.

To further prove the constitution of the adducts, the acrylic acid addition product (melting at 113°C) was prepared, perhydrogenated, converted to the acid azide, and to the amine which was decomposed and reduced to the saturated tricyclic hydrocarbon $C_{10}H_{16}$.

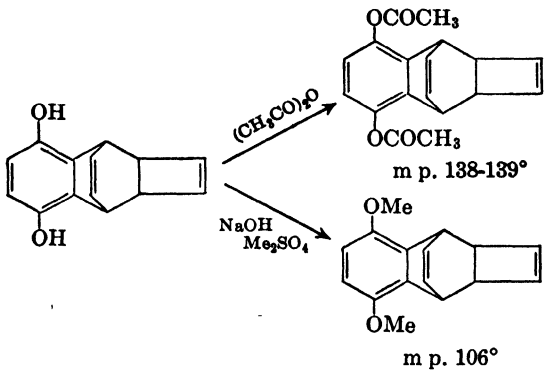
[52] *D.R.Pat. Anmeldung I-74,097* IVc/12o.



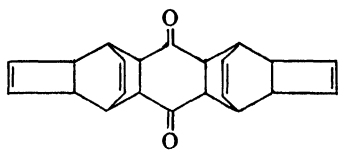
The primary product of the diene synthesis from benzoquinone and cyclooctatetraene was prepared by condensation of the components in dichlorobenzene at 140°. It melts at 141°C, has a quinoid structure, is difficultly soluble in alcohol and easily soluble in benzene The hydroquinone form was obtained directly by condensing without solvents at 180 to 200°C, or by heating the adduct itself to 180 to 200°C. Quinone was produced simultaneously, probably due to splitting of the addition product Reduction of the two adducts did not give identical products



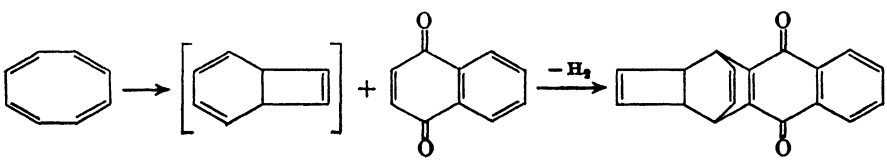
The new adducts were characterized as the acetates and the methyl ethers.



Benzoquinone adds two molecules of cyclooctatetraene to a limited extent according to the diene synthesis, yielding the following product:



Addition products with naphthoquinone and with acetylene dicarboxylic acid ester were also made. At first the condensation was effected with naphthoquinone at 180 to 200°C, but anthraquinone was obtained. If condensation is performed in solvents at 140°C, however, a product of the formula $C_{18}H_{12}O_2$ results. This substance melts at 192°, is yellow in color, and can be used as a vat dye with sodium hyposulfite and caustic. This is evidently not the primary product; two hydrogen atoms which were originally present in the diene synthesis have been lost by dehydrogenation. 1,4-Dihydroxynaphthalene was isolated as a by-product. A compound of unknown constitution (melting at 243 to 247°C) was also formed.

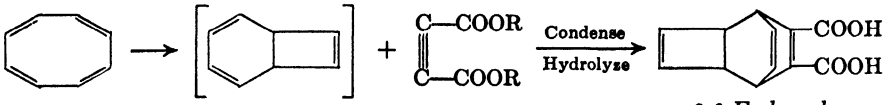


1,4-Endocyclobutadienylene-1,4-dihydroanthraquinone

In the preparation of the addition product of cyclooctatetraene and acetylene dicarboxylic acid ester, small quantities of phthalic acid esters

are formed as by-products. If condensation is carried out at a higher temperature, phthalic acid esters are the main product.

The free acid of the addition product of cyclooctatetraene to acetylene dicarboxylic acid ester melts at 158 to 159°C.



3,6-Endocyclobutadienylene cyclohexadiene-1,4-dicarboxylic acid-1,2

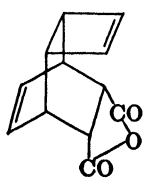
When subjected to thermal decomposition according to the Alder-Rickert method, these decompose to anthraquinone and phthalic acid esters, respectively. This proves that condensation occurs in the 1,4-position of cyclooctatetraene. The number four position comes from the third 6-membered ring of the anthraquinone which is produced by thermal decomposition. However, instead of the unknown cyclobutadiene, whose formation might be expected, only resinous polymerization products are formed, probably due to polymerization of decomposition products at high temperature.

In all these pyrolysis or cracking experiments, neither acetylene (which should have been formed, as cyclobutadiene cannot exist according to Willstatter) nor vinyl acetylene (which might be produced according to the formula) was isolated.

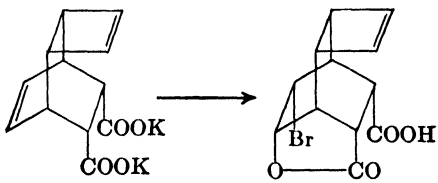
In spite of the fact that this last link is missing, it can be assumed with certainty, based on the results of hydrogenation and of decomposition by the Alder-Rickert method, that the diene synthesis of cyclooctatetraene passes through an intermediate stage of bicyclooctane from which the tricyclic ring system is formed.

Configuration of Diene Addition Products. Work on the configuration of various diene addition products of cyclooctatetraene was started but had to be stopped owing to war conditions. Research on configuration is essential because of the formation of new ring systems and the conversion of one ring system into another; it is necessary also to permit conclusions about the unknown course of some reactions such as dimerization.

The first product dealt with was the maleic anhydride addition product of cyclooctatetraene, which according to Alder is probably formed as an "endo-*cis*-compound".



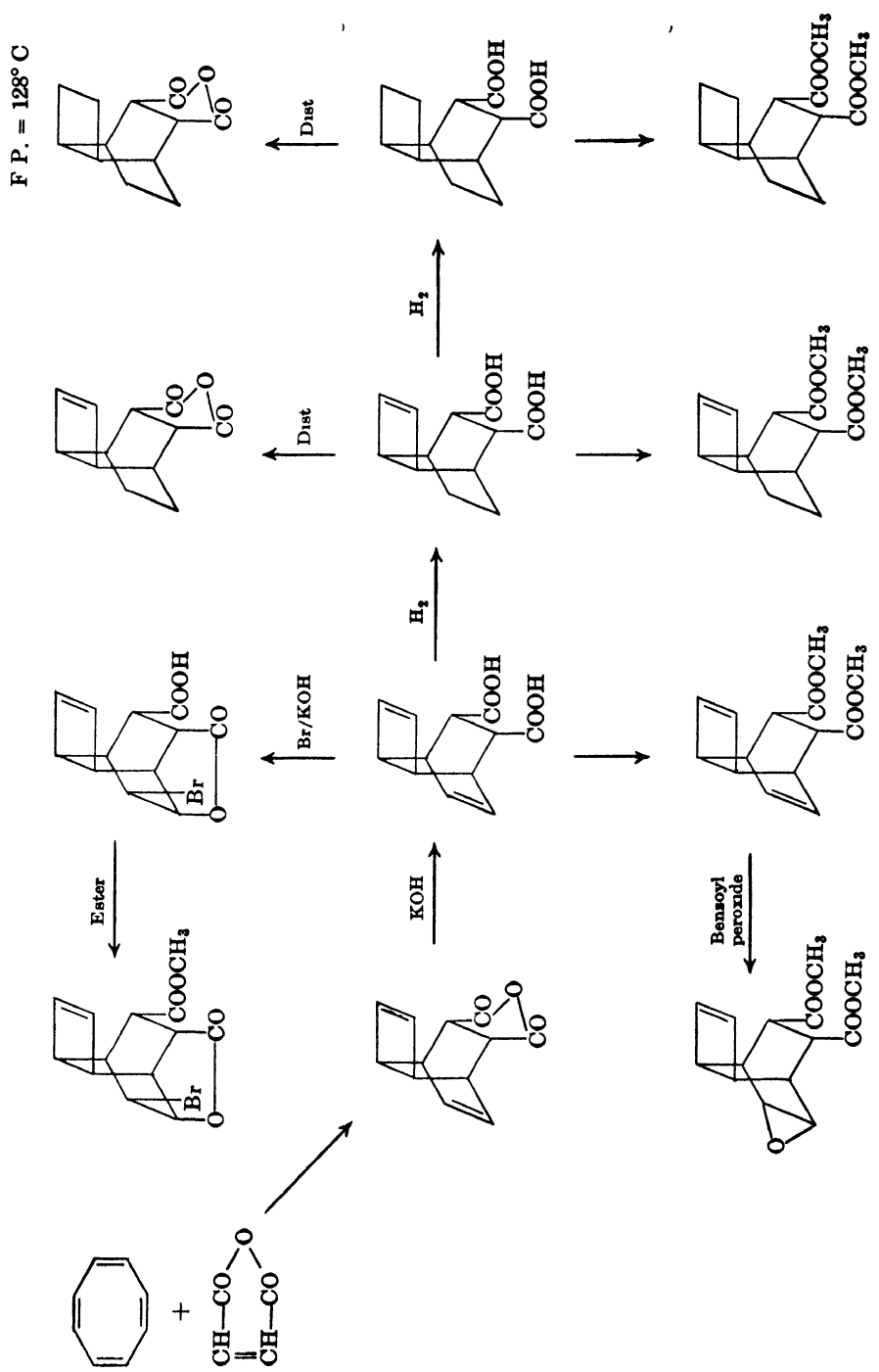
This was proved as follows: The sodium salt of the dicarboxylic acid, produced when the maleic addition product is saponified with caustic soda, was reacted with one mole of chlorine or bromine to form a monohalolactone-monocarboxylic acid. As is known, the double bond of the 6-membered ring is more reactive and halogen is added there. One carboxyl of the maleic addition product is now closed to give the lactone; this is effected by splitting off the hydrogen halide originating from halogen in the *cis* position and the hydrogen of the carboxyl group.



The formation of a lactone ring is possible only if the two carboxyl groups of the maleic addition product are in the "endo position," the *cis* position of the carboxyls being proved by the formation of an anhydride. The fact that the dihydro adduct and its dicarboxylic acid do not react with bromine under the same conditions is further proof of the constitution of partially hydrogenated addition products Confirming the results of Diels and Alder, the "endo-*cis*" configuration is thus proved for addition products of cyclooctatetraene. The dilactone has not been made, which should indicate the position of the second halogen atom which is not split off, without changing the conclusions about the "endo position."

A number of configurative changes of the maleic addition product were made; these indicated a number of possible isomers. The "endo-*cis*-dicarboxylic acid" of the maleic addition product can be rearranged to "*trans*-dicarboxylic acid" (m.p. 220°C) by heating the crystallized dimethylester (m.p. 52 to 55°C) with sodium methylate, according to Heuckel and Groth.

The dihydro and tetrahydro acids of the *trans* series can be made by partial, or exhaustive hydrogenation of the *trans* acid. They can be made also from esters of *cis* acids by rearrangement, according to Hueckel and Groth. One representative of the "exo" series was made by catalytic hydrogenation of the anhydride of the addition product with acetylene dicarboxylic acid. It was the "exo" tetrahydromaleic addition product, melting at 154 to 155°C. The "endo" tetrahydromaleic addition product melts at 128 to 129°C. The *trans* acid is, of course, incapable of forming an anhydride.


F P. = 128° C
Dist
Dist
H_2
H_2
Br/KOH
Ester
KOH
Benzoyl peroxide
COOH
$COOCH_3$
Br
CO
O

NaOCH₃
Ester.
H₂
Br₂
Dist
F.P. = 154-155° C

Among other reactions, the more reactive double bond of the maleic addition product, *i.e.*, the "endo-*cis*" ester, was also reacted with perbenzoic acid, thus forming the oxide. It was formulated without additional proof as *trans*-oxide, similarly to Alder's. Bromination of the ester is more complicated, producing the monomethylester of "bromo-lactonic acid" and "dibromoester" (melting at 225 to 227°C), which after saponification with caustic potash gives the free acid (melting at 234 to 236°C). If the dibromoester is saponified with concentrated sulfuric acid, it readily yields the anhydride of the "dibromo acid," which melts at 277 to 278°C. Since "bromo-lactonic acid" was not formed by alkaline saponification, it is likely that the bromine atoms are in the *trans* position.

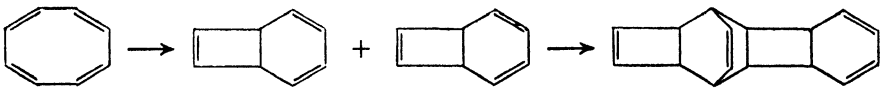
Research on configurations is still being carried out. This is the case not only for the diene addition products (position of the 4-membered ring is still doubtful; in the above formulas it was pictured in a chair-like structure of cyclooctatetraene) but for all derivatives of cyclooctatetraene which can be obtained by chemical reactions.

Polymerization of Cyclooctatetraene and Its Dihalogen Derivatives. *Dimerization.* Cyclooctatetraene and its dihalogen compounds polymerize if they are left standing for a long time, or more quickly when heated[53]. Only the dimeric cylooctatetraene, which can be obtained if cyclooctatetraene is refluxed with admission of air for several hours, has been closely examined. A mixture of at least two isomeric hydrocarbons of the formula $C_{16}H_{16}$ is formed, one of which melts at 43°, whereas the other is a viscous oil boiling at 298° (separated by addition of ether and chilling)[54]. The solid hydrocarbon has three double bonds by catalytic hydrogenation; the liquid isomeride, however, has only two. The dimerization can be made homogeneous by exclusion of air (nitrogen)[55], and only the liquid hydrocarbon $C_{16}H_{16}$ is formed. On perhydrogenation the solid hydrocarbon $C_{16}H_{16}$ gives a liquid hydrocarbon, $C_{16}H_{22}$, which boils at 140°C/1 mm, whereas perhydrogenation of the liquid hydrocarbon produces a solid $C_{16}H_{20}$ with a melting point of 30 to 35°C[56].

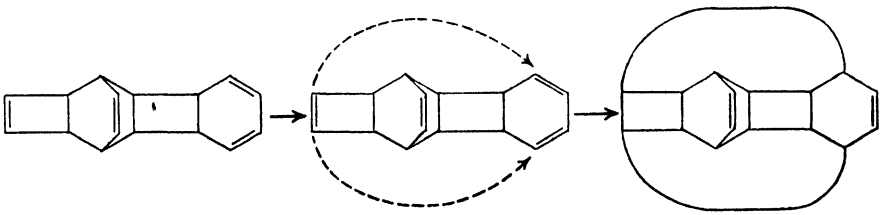
Dimerization of cyclooctatetraene is without doubt a diene synthesis, for some double bonds disappear; this can be explained only by the formation of new rings. Moreover, there is absolutely no aromatization because no decomposition products of an aromatic nature, such as benzoic acid or phthalic acid, can be found. No aromatization could be detected on dehydrogenation. It may be assumed that the unsaturated hydrocarbon is formed by diene condensation of two molecules of cyclooctatetraene. Primarily, conversion of the 8-membered ring into the bicyclooctane-

[53] *D.R.Pat. Anmeldung I-70,996* IVd/12o
[54] *D.R.Pat. Anmeldung I-73,901* IVd/12o.
[55] *D.R.Pat. Anmeldung I-74,028* IVd/12o.
[56] *D.R Pat. Anmeldung I-74,006* IVc/12o.

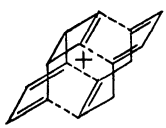
(0,2,4) system will probably occur; this undergoes a diene synthesis with itself as the dienophil component:



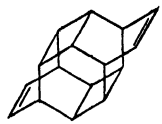
The dimeric compounds have only two or three double bonds, however; hence the end product of dimerization cannot have such a simple formula. It must undergo further cyclization by a second diene synthesis which may occur intramolecularly:



Accordingly, a product of dimerization would result which would contain only two double bonds, corresponding to the dimer produced in an atmosphere of nitrogen. It is presumed that the reaction in its primary stage passes through the "exo" stage, as has been proved for the thermal polymerization of cyclooctatetraene by Alder

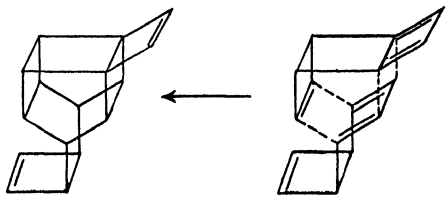


2 Cyclooctatetraenes as Bicyclo-(0,2,4)-octatriene-(2,4,7)



$C_{16}H_{16}$ (Liquid)

Intramolecular diene synthesis may, however, take place in such a way that the double bond of the 6-membered ring, which was produced in the first diene synthesis, acts as dienophil component for the second diene synthesis. Dimerization would then proceed in the following way primarily over the "endo" stage:



This formulation is impossible for the hydrocarbon containing three double bonds.

The reactivity of dimeric cyclooctatetraene with carbon monoxide and water under the catalytic influence of nickel carbonyl is remarkable. The liquid modification gives a dicarboxylic acid, the dimethyl ester of which boils at 200 to 205°C at 0.6 mm. The solid compound which contains three double bonds also gives a dicarboxylic acid when treated similarly. The boiling point of the dimethyl esters is practically the same. These dicarboxylic acids are produced when cyclooctatetraene is subjected to the same reaction, probably due to dimerization.

The liquid halogenation products change to the well crystallized dimerides, $C_{16}H_{16}Cl_4$ and $C_{16}H_{16}Br_4$, melting point 190 and 218°, respectively.

Polymerization of Cyclooctatetraene with Catalysts. Attempts were made to polymerize cyclooctatetraene by means of oxidizing agents such as benzoyl peroxide and hydrogen peroxide, and with acid catalysts such as boron fluoride dihydrate, boron fluoride etherate, phosphotungstic acid, and iodine. No positive results were obtained. A small amount of rubber-like polymer was obtained at the liquid-air interface under the influence of light. The presence of peroxides gives only dimeric compounds. Treatment with gaseous oxygen yields oil-soluble resins (softening at 114°C) which, according to molecular weights, are tetrameric compounds.

Experiments indicate that cyclooctatetraene in acid or alkaline emulsions polymerizes to a hydrocarbon, $C_{16}H_{16}$. This colorless, viscous dimer boils at 130 to 132°C at 0.8 mm. It is spontaneously generated if cyclooctatetraene is left standing for some time, even in an ice box. This dimerization is accelerated very slightly by such catalysts as benzoyl peroxide.

Emulsion Polymerization of Cyclooctatetraene. Cyclooctatetraene was redistilled *in vacuo* under a current of nitrogen. Experiments were conducted in pressure test tubes of 50 cc volume. The proportion of organic phase to water was 1:1. The quantity of amphoteric soap was 4 per cent; the persulfate content was 0.3 per cent. Resinification of cyclooctatetraene due to the influence of acids was repressed by adjusting the pH to 10 with sodium hydroxide. After polymerization the pH was 7.5.

Experiments included (1) cyclooctatetraene 66 per cent, butadiene 34 per cent (mole 1:1); (2) cyclooctatetraene 30 per cent, butadiene 70 per cent; and (3) cyclooctatetraene 100 per cent. Corresponding experiments were conducted for check and comparison using butadiene and styrene in equimolar proportions, and in a proportion of 70:30. All experiments were run for 62 hours at 50°C with agitation.

The experiment involving 30 per cent of cyclooctatetraene and 70 per cent of butadiene exploded. Only traces of polymer were formed with the 66:34 mixture; no polymerization occurred with 100 per cent cyclooctatetraene. The mixture of equimolecular quantities of butadiene and

styrene gave 85 per cent polymer, while the 70:30 ratio yielded 55 per cent polymer.

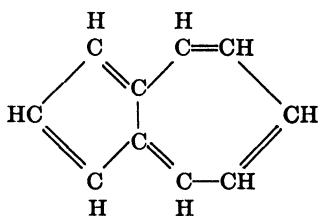
Experiments were conducted to determine the influence of boron trifluoride as a catalyst. The results were negative. These experiments were carried out as follows: Three grams of cyclooctatetraene were mixed with 1, 5 and 10 per cent of boron trifluoride. No heat was evolved nor did polymerization take place at low temperatures after 24 hours. After heating for 1 hour to 95°, the sample containing 10 per cent of boron trifluoride polymerized to a black gelatinous mass. The activity of the boron trifluoride was checked by polymerizing a vinyl ether. One-half cc of 1.25 per cent solution of boron trifluoride in tetrahydrofuran added to 25 cc of the ether brought about complete polymerization.

Azulene ($C_{10}H_8$) and Higher Cyclopolyolefins, $C_{10}H_{10}$ and $C_{12}H_{12}$

In the experiments to produce cyclooctatetraene, small amounts of other hydrocarbons boiling from 195 to 240°C were formed, the quantity depending largely upon the temperature of the reaction, and amounting to roughly 5 to 10 per cent of the yield It was assumed that these products were cyclopolyolefins, mainly cyclodecapentaene and cyclododecahexaene.

The war interrupted the study of these products, the separation of which proved extremely difficult. Separation by distillation was not feasible, but chromatographic adsorption methods were useful in identifying the compounds By using petroleum ether as a solvent and fused aluminum oxide as an absorbent, azulene was separated and crystallized. It was purified by sublimation and recrystallization from methanol. It melted at 99 to 100°C and was identified by conversion to the trinitrobenzolate (m p. 167 to 168°C). This product was identical with that produced synthetically from hydrindene and diazoacetic acid ester.

The formula of azulene was found by Plattner and Pfau to be bicyclo-(0,3,5)-decapentaene-(1,3,5,7,9)[57].



As soon as it was established that the blue color was due to azulene, it was possible to isolate this product by means of its addition products with trinitrotoluene or picric acid, rather than by chromatographic methods[58]. The blue-colored fractions were simply mixed with a methyl alcohol solu-

[57] *Helv. Chim. Acta*, **19**, 865 (1936).
[58] *Helv. Chim. Acta*, **20**, 224 (1937).

tion of trinitrotoluene or picric acid to give the derivative. The trinitrotoluene addition complex could be obtained by recrystallization from alcohol in the form of brownish needles melting at 167 to 168°C, and the picrate as violet needles melting with decomposition at 144 to 148°C.

Azulene was also isolated by the phosphoric acid method described by Sherndall[59], Kremers[60], and Plattner and Pfau[61]. The blue distillates were diluted with petroleum ether and shaken with phosphoric acid, the azulene reacting with the acid, while the other chemicals remained dissolved in the petroleum ether. The azulene is precipitated in crystalline form when the red phosphoric acid solution is decomposed with ice water. It is pressed on a clay dish, sublimed and recrystallized from methanol to give dark blue glittering tablets melting at 99 to 100°C. Once azulene was obtained in pure form, it was possible to estimate the quantity of azulene present in other distillates by colorimetric comparison with a solution of known azulene content.

The quantity of azulene formed under conditions which are suitable for the production of cyclopolyolefins is very small. In an autoclave holding four liters and charged with two liters of tetrahydrofuran and catalyst, there are obtained approximately 250 grams of cyclooctatetraene, 30 grams of higher polyolefins, and 0.5 gram of azulene.

Dark-colored distillates of the $C_{12}H_{12}$ fraction, boiling at 240 to 242°C (753 mm), contained 3 to 5 per cent of azulene. However, azulene isolated by means of the picric or phosphoric acid method was not recovered in quantities equivalent to that known to be present by colorimetric analysis. The phosphoric acid method gives a recovery of 60 to 65 per cent, the picric acid method only 45 to 50 per cent of the theoretical quantity, indicating that the phosphoric acid method is preferable.

Isolation of Azulene ($C_{10}H_8$) from the Blue Hydrocarbon Fraction $C_{10}H_{10}$ and $C_{12}H_{12}$. Thirty-five grams of blue hydrocarbon, boiling at 71 to 94°C (5 mm), are dissolved in 140 cc of low-boiling petroleum ether, which is cooled and shaken with 40 cc of 80 per cent phosphoric acid until the ether is decolorized. The red-brown phosphoric acid solution is then separated from the yellow petroleum ether solution and washed with several portions of petroleum ether. The phosphoric acid solution is mixed with ice water and ether, and the ether solution washed neutral and dried with sodium sulfate. Ether is distilled off, leaving azulene as a blue solid which is dried on a clay dish and sublimed. The yield is 0.583 g of azulene, melting at 97 to 99°. The colorimetric analysis of the 35 g of blue hydrocarbon

[59] *J. Am. Chem. Soc.*, **37**, 167, 1537 (1915).
[60] *J. Am. Chem. Soc.*, **45**, 717 (1923).
[61] *Helv. Chim. Acta*, **9**, 131 (1926).

indicated 0.970 g present. Recrystallization from methanol gave blue tablets melting at 99 to 100°C.

C_8H_8 (128.06) Calcd.: C, 93.71; H, 6.29
Found: C, 93 71; H, 6 38

Azulene distills at atmospheric pressure at 237 to 239°C.

The discovery that the blue color of the high-boiling fractions in cyclooctatetraene production is caused by a minute quantity of azulene throws some light upon the presence of blue color in similar processes. Schlaepfer and Stadler[62] obtained blue distillates, the color of which they attributed to azulene, from cuprene tar. It is doubtful, however, if they proved this by isolating the compound in pure form. Their hydrocarbon was not believed to be pure but rather a mixture. Herzenberg and Ruhemann[63] isolated a dark blue oil from brown coal tar. They did not isolate azulene and assumed the color to be due to sesquiterpenes. Ruzicka and Rudolp[64] doubted the conclusions drawn by Herzenberg and Ruhemann, and are of the opinion that since Schlaepfer and Stadler demonstrated the formation of blue hydrocarbons from acetylene, Herzenberg's theory needs further proof because blue hydrocarbons may be produced by pyrogenic decomposition.

This was confirmed quite recently when Schwarz[65] polymerized acetylene in a shock-chilling tube and obtained blue distillates. It is believed that the blue color hitherto attributed to various substances has always been due to azulene, that is, unsubstituted $C_{10}H_8$; the formation of substituted azulenes is considered unlikely. It may be mentioned that when Walter[66] tried to synthesize cyclodecapentaene by dehydrogenation of cyclodecadiene, he obtained a blue distillate at 250°C.

Apparently the deep blue color frequently observed in the vinylation of high-boiling alcohols and glycols is also due to the presence of traces of azulene. Thus it appears likely that azulene is produced by thermally induced condensations of acetylene rather than by catalytic reactions in the presence of nickel salts.

Experiments to increase the azulene content in reactions involving cyclopolyolefins were projected, but the defeat of Germany interrupted this work.

Isolation of $C_{10}H_{10}$ and $C_{12}H_{12}$ Cyclopolyolefins. When it was found that azulene was always present in reactions involving the preparation of higher cyclopolyolefins, and that it could be removed by the phosphoric

[62] *Helv. Chim. Acta*, **9**, 186 (1926).
[63] *Ber.*, **58**, 2249 (1926).
[64] *Helv. Chim. Acta*, **9**, 118 (1926).
[65] *J. prakt Chem.* (2), **156**, 205 (1940); (2), **158**, 2 (1941).
[66] W. Walther, Dissertation, Karlsruhe, 1939

acid method, the separation of the two hydrocarbons, $C_{10}H_{10}$ and $C_{12}H_{12}$, in pure form became possible. These higher olefins were prepared using the cyclooctatetraene reaction, but the yield was increased by raising the reaction temperature. The reaction temperature for maximum production of cyclooctatetraene is 60 to 70°C. If the temperature is increased to 90 to 100°C, there is an increased production of the orange-colored hydrocarbon, $C_{10}H_{10}$, which boils at 47 to 50°C (2 mm) or at 195 to 197°C (755 mm). The yellow colored hydrocarbon, $C_{12}H_{12}$, is formed in appreciable amounts at a reaction temperature of 120 to 130°. In all these reactions naphthalene is also formed.

Production of $C_{10}H_{10}$ (orange-colored hydrocarbon). Eighteen hundred cc of tetrahydrofuran (perfectly dry), 100 grams of ethylene oxide and 30 grams of nickel cyanide (anhydrous) are reacted with acetylene in a 5-liter autoclave at 90 to 100°C and under 15 to 20 atm pressure, 5 of which are nitrogen, as described above. The catalyst and cuprene are separated by filtration; solvent and cyclooctatetraene are distilled off leaving a blue-green fraction boiling between 42 and 60°C at 2 mm. Traces of glycol and diglycol are removed by water-washing and drying. (The glycol is from ethylene oxide and water.) In order to remove the azulene, which is the cause of the blue-green color, the distillate is mied with petroleum ether and shaken with 80 per cent phosphoric acid. The petroleum ether is washed neutral, dried with sodium sulfate, the solvent distilled off, and the residue then fractionated. To remove minor quantities of oxygenated compounds (peroxides ?), the hydrocarbon (b.p. 43 to 50°C at 2 mm) is dissolved in low-boiling petroleum ether, contacted with aluminum oxide, freed from solvent and the residue vacuum-distilled. The orange colored hydrocarbon, $C_{10}H_{10}$, is then obtained with a boiling point of 47 to 50° at 2 mm.

Production of $C_{10}H_{10}$ (pale yellow hydrocarbon). The pale yellow hydrocarbon $C_{10}H_{10}$ is obtained from the last runnings of the C_8H_8 fraction and from the first runnings of the $C_{12}H_{12}$ fraction Its boiling point is practically identical with the orange-colored $C_{10}H_{10}$.

Production of $C_{12}H_{12}$ (yellow). The reaction is carried out exactly as described above, except that the temperature is 120 to 140°C. After the solvent, benzene and cyclooctatetraene have been distilled off, and glycols, azulene, and oxygen compounds have been removed, as described above, two fractions, $C_{10}H_{10}$ (pale yellow), boiling at 33 to 36°C at 0.4 mm, and $C_{12}H_{12}$, boiling at 77°C at 0 8 mm and 240 to 242°C at 753 mm, can be obtained by fractionation.

Properties of Orange-Colored $C_{10}H_{10}$ Cyclopolyolefin. This cyclopolyolefin has the following properties.

$C_{10}H_{10}$ (mol wt. 130.08)	Calculated	C, 92.26; H, 7 74
	Found:	C, 92 47; H, 7.73

Boiling point:	47 to 50° at 2 mm
	195 to 197° at 755 mm
Refractive index:	$N_D^{20} = 1\ 5755$
	$D_4^{20} = 0.9344$
R_D (calculated)	43 85 ($C_{10}H_{10}$ with 5 double bonds)
R_D (observed)	46 05

Hydrogenation number (as iodine number) at 50° = 838

For $C_{10}H_{10}$ with four double bonds, the calculated value is 781 and for five double bonds, 977. Evidently, there are more than four double bonds.

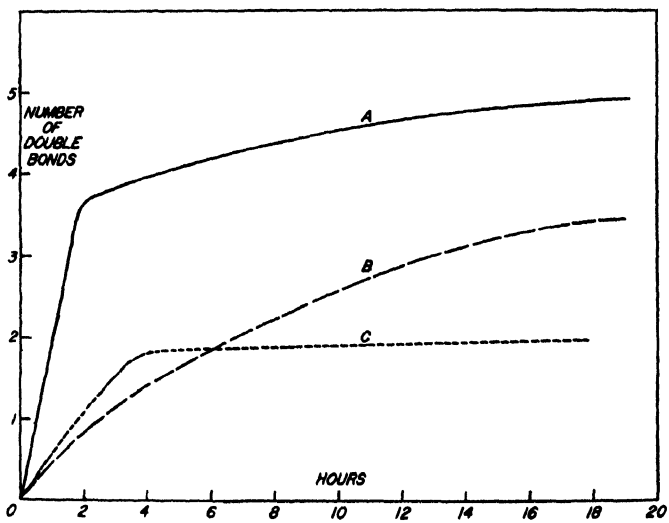


FIGURE V-6 Hydrogenation curves of $C_{10}H_{10}$

Curve A—$C_{10}H_{10}$ (orange) with PtO_2 in glacial acetic acid
Curve B—$C_{10}H_{10}$ (orange) with palladium on $CaCO_3$ in CH_3OH
Curve C—$C_{10}H_{10}$ (yellow) with palladium on $CaCO_3$ in CH_3OH

The orange-colored hydrocarbon, $C_{10}H_{10}$, gives a solid addition product with cuprous chloride dissolved in ammonium chloride. Addition products are obtained with both two and three moles of maleic anhydride. Partial hydrogenation with palladium-calcium carbonate catalyst in methanol showed a steady absorption of hydrogen equivalent to 3½ double bonds. Then the hydrogen absorption dropped rapidly and finally stopped as shown in curve B, Figure V-6; this hydrogenation behavior is similar to that observed in the reduction of cyclooctatetraene to cyclooctane. Upon hydrogenation with platinum oxide in glacial acetic acid, a steady absorption of hydrogen equivalent to four double bonds takes place in three hours. The fifth double bond is hydrogenated very slowly, the reaction taking twenty hours (Curve A, Fig. V-6). Analysis of this hydrogenated product,

which boils at 179 to 201°C, conforms, however, to the formula $C_{10}H_{18}$ rather than to $C_{10}H_{20}$. By perhydrogenation with Raney nickel catalyst at 20 atm and 130 to 140°C, a quantity of hydrogen equivalent to five double bonds is readily absorbed. The product $C_{10}H_{20}$ boils at 175 to 179°C. It is colorless and saturated.

Oxidation of the various hydrogenation products, using permanganate or nitric acid, did not give conclusive results; either the conditions of oxidation or the oxidizing agents were chosen wrongly. While all experimental data indicated that the orange-colored hydrocarbon was cyclodecapentaene, the possibility that it is vinyl cyclooctatetraene is not yet excluded.

Properties of Yellow-Colored $C_{10}H_{10}$ Cyclopolyolefin. The properties of the yellow hydrocarbon $C_{10}H_{10}$ are as follows:

$C_{10}H_{10}$ (mol wt 130 08)	Calculated C, 92 26; H, 7 74
	Found· C, 92.15, H, 8.07
Boiling point.	46–51° at 2 mm
	195–196° at 758 mm
N_D^{20}	1.5790
d_4^{20}	0 9400
R_D (observed)	46 00
R_D (calcd)	43 85 ($C_{10}H_{10}$ with 5 double bonds)

In contrast to the orange colored $C_{10}H_{10}$, it gives no addition products with cuprous chloride. It reacts with maleic anhydride like the orange-colored product, although the yield is inferior. The colorless addition product with three moles of maleic acid anhydride is insoluble, or nearly so, in most solvents. It dissolves in hot sodium hydroxide solution, forming the sodium salt of a hexacarboxylic acid. The addition product with two moles of maleic anhydride can be recrystallized from acetone.

Analytical data of these products are as follows:

$C_{10}H_{10}\cdot 3\ C_4H_2O_3$	Calculated. C, 62 26; H, 3 80; O, 33.94
(mol wt. 424)	Found. C, 62 23; H, 4.10; O, 33 9
$C_{10}H_{10}\ 2\ C_4H_2O_3$	Calculated. C, 66 25, H, 4.33
(mol wt 376)	Found· C, 66 25; H, 4 74

In contrast to the orange-colored $C_{10}H_{10}$, on hydrogenation with palladium-calcium carbonate catalyst at 24°C and 720 mm in methanol solution, the hydrogen equivalent to only two double bonds is readily absorbed (curve C, Fig. V-6). Perhydrogenation with Raney nickel catalyst yields the same product obtained from the orange-colored substance. This product is $C_{10}H_{20}$, boiling at 23 to 25°C at 0.4 mm or 175 to 179°C at 755 mm.

$C_{10}H_{20}$	Calculated: C, 85.62; H, 14.37
(mol wt. 140.16)	Found: C, 85.62; H, 14.07
N_D^{20}	1.4522

Oxidation of the hydrogenation products gave no useful results.

The appearance of two hydrocarbons $C_{10}H_{10}$ with practically the same boiling points but different gravities and refractive indexes is noteworthy. The complete agreement of molecular refraction is probably more than coincidental. Possibly, they are stereoisomeric or mesomeric compounds. Experiments with Stuart's atomic models proved that $C_{10}H_{10}$ can exist in two stereoisomeric forms. This may explain the different boiling points of the perhydrogenated products $C_{10}H_{20}$.

Properties of the Yellow $C_{12}H_{12}$ Cyclopolyolefin. Analytical and physical data are as follows:

$C_{12}H_{12}$	Calculated: C, 92 26; H, 7.74
(mol wt. 156 096)	Found· C, 92 28; H, 7 88
Boiling point·	77° at 0 8 mm
	240–242° at 753 mm
Mol wt (in benzene)	159
$d_4^{20} = 1\ 0213$	R_D (calculated) 52.62 (for 6 double bonds)
$N_4^{20} = 1\ 5893$	R_D (observed) 51 54

Professor Klemm (Danzig) determined the magnetic susceptibility of $C_{12}H_{12}$ which was contaminated with 3 per cent azulene and obtained 87.9 $\times 10^{-6}$ cgs.

Hydrogenation experiments were conducted with hydrogen both with and without pressure. No conclusive results were obtained. On hydrogenation without pressure the absorption of hydrogen was not quite equivalent to two double bonds It was not possible to hydrogenate exhaustively to $C_{12}H_{24}$; the highest absorption of hydrogen yielded $C_{12}H_{22}$, a terpene-like oil boiling at 64 to 65°C at 0.5 mm and 240° at 753 mm.

The hydrocarbon $C_{12}H_{12}$ readily absorbs one mole of bromine when treated at 0 to 5°C with bromine dissolved in methylene chloride. No more bromine is absorbed even after 24 hours at room temperature. The dibromide is a yellowish viscous oil incapable of being distilled without decomposition.

With perbenzoic acid (chloroform solution), an oxide with the formula $C_{12}H_{12}O$ and boiling at 110 to 113°C is formed.

The yellow hydrocarbon $C_{12}H_{12}$ when passed over palladium-carbon catalysts in vacuum at 250 to 260°C gave a colorless liquid which reacted with picric acid to form a picrate crystallizing in yellow needles, melting at 127 to 129°C. Analytical data indicated this material to be the picrate of 1,2-dimethylnaphthalene; a mixed melting point with an authentic sample confirmed this.

Without additional evidence, the structure of this hydrocarbon must remain unsettled. Reppe believes that it must be cyclododecahexaene.

Uses of Cyclooctatetraene and Higher Cyclopolyolefins

On the basis of preliminary work, it is possible to prophesy that cyclooctatetraene will be of considerable technical importance in the near future.

It cannot be doubted that it will be possible to produce this interesting and reactive product in good yield by a continuous technical procedure. This would give a new and relatively cheap basic chemical for industrial organic chemistry which should be the key not only to the chemistry of the 8-membered rings, which have been so inaccessible until now, but it should also make possible the production of some benzene derivatives, which are difficult to make, and the synthesis of interesting new compounds, many of which will prove to be of considerable importance.

Some possible future fields of use for cyclooctatetraene can be anticipated. Its diene addition products are starting materials for outstanding lacquers; suberic acid, which can be obtained from cyclooctatetraene by way of cyclooctane or cyclooctene, is of interest for polyamide chemistry. Cyclooctene, the double bond of which is capable of undergoing all the reactions of ethylene chemistry, offers a new approach to the chemistry of the 8-membered ring and its derivatives. It is possible, for instance, to synthesize caprylo-lactam, a fundamental structural element for polyamides, via cyclooctene → cyclooctanol → cyclooctanone → cyclooctanone-oxime → caprylo-lactam. It is furthermore expected that the new synthesis of cyclooctatetraene supplies a new starting material for alkaloid syntheses and will make possible the production of new and valuable pharmaceuticals. Cyclooctatetraene may lead to new synthetic perfumes

Cyclooctatetraene absorbs ultraviolet rays, even in dilute solution and may be used in cases where protection from the action of ultraviolet light is desired. Cyclooctatetraene can, therefore, be used in skin-protecting cold creams or as a component of plastics (polymethacrylates, allyl resins, etc.) which are desired to be impermeable to ultraviolet rays

Accordingly, it is safe to predict that cyclooctatetraene will have considerable importance in the future.

Nothing can be predicted about the future use of the $C_{10}H_{10}$ and $C_{12}H_{12}$ polyolefins. They may have a field of application in medicine. Prof. Kuhn of Heidelberg found that a preparation of $C_{12}H_{12}$, which was blue in color and contaminated with 3 per cent of azulene, stopped inflammation of tissues. According to Kuhn, the growth of certain pathogenic bacteria was checked completely by dilute solutions (1:100,000). This result was not confirmed by the pharmacological section of I G. Hochst and Elberfeld. It was possible that Kuhn had been using very sensitive bacteria. It cannot be stated with certainty whether or not all the testing laboratories obtained the same preparation; this is not surprising, considering the terrible conditions under which the work had to be done. It was believed that the effect observed by Kuhn might be attributed to azulene, and arrangements were made to isolate the chemicals $C_{10}H_{10}$, $C_{12}H_{12}$ and $C_{10}H_8$ and to test them separately. Recently, it was learned that these tests gave negative results. Neither the individual chemicals nor their mixtures

exhibited any inflammation-checking properties. There is still the possibility that in purification (phosphoric acid, chromatographic methods) minute quantities of exceedingly active chemicals may have been removed, or that polyolefins $C_{10}H_{10}$ and $C_{12}H_{12}$ had already undergone structural changes. In any case, the observation of Kuhn is so interesting that it deserves to be looked into more closely.

Further research on the cyclopolyolefins C_8H_8, $C_{10}H_{10}$, $C_{12}H_{12}$, etc., will prove to be a rich mine of scientific discoveries. It is to be expected that it will bring about important contributions to the knowledge of the behavior and structure of organic ring compounds. All experience points to the fact that this field is the theoretical bridge linking aliphatic and aromatic chemistry.

Theory of Cuprene Formation

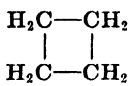
It is probable on the basis of the mode of formation and the reactivity of cyclopolyolefins that the products of thermal condensation of acetylene, acetylene tar and cuprene (as found by Berthelot and later by many others) are formed through the cyclopolyolefins as intermediates. The simplest cyclopolyolefin, cyclobutadiene, is incapable of existence; it is likely that it decomposes as soon as it is formed. The next higher cyclopolyolefin is cyclohexatriene, the extremely stable benzene. The formation of cyclooctatetraene from acetylene was never previously observed in products formed by pyrogenic condensation at high temperature. However, in view of the instability of that hydrocarbon, this is not surprising. By assuming the formation of cyclooctatetraene as an intermediate it is possible to explain the formation of the aromatics normally isolated in this reaction by aromatization forming bicyclo-(0,2,4)-octatriene and subsequent splitting of the two 3-membered rings forming toluene, xylene, styrene, etc. The next higher homolog, the hydrocarbon $C_{10}H_{10}$ (cyclodecapentaene) forms naphthalene, which appears in cuprene tar and in all products of condensation at higher temperature. The hydrocarbon $C_{12}H_{12}$ is the intermediate for the methylnaphthalene fraction (methylnaphthalene and dimethylnaphthalene); $C_{14}H_{14}$ could not be isolated, but its presence in the higher fractions is probable; it would give anthracene and phenanthrene (experiments to isolate those two compounds from the soluble resinous residues of cyclopolyolefin production are still incomplete). By further condensation and aromatization, cuprene is finally produced; its structure has a decidedly aromatic character, as Kauffmann[67] has proved. Further research in the field of cyclopolyolefin chemistry will go far toward elucidating the problem of cuprene formation.

[67] *Ber.*, **55**, 267 (1922); **56**, 2633 (1923).

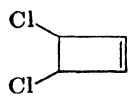
Appendix to Chapter V

Physical Properties of Derivatives of Cyclooctatetraene

(1) C_4H_8 *Cyclobutane*

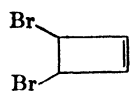


(2) $C_4H_4Cl_2$ *1,2-Dichlorocyclobutene-3*



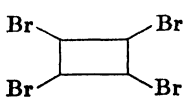
Small white plates from ligroin M.p. 44°C; b.p 133°C/760 mm, D_4^{20} 1 2692; N_D^{20} 1 5121 Obtained by thermal decomposition of the addition product of $C_8H_8Cl_2$ (15) and naphthoquinone

(3) $C_4H_4Br_2$ *1,2-Dibromocyclobutene-3*



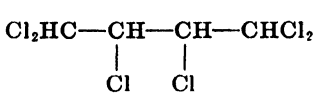
Colorless oil. B p. 174 to 175°C/760 mm. Obtained by thermal decomposition of the addition product of $C_8H_8Br_2$ (18) and acetylene dicarboxylic acid ester

(4) $C_4H_4Br_4$ *1,2,3,4-Tetrabromocyclobutane*



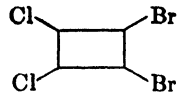
Colorless oil. B.p. 110°C/1.5 mm; N_D^{20} 1.6303. Obtained by brominating $C_4H_4Br_2$ (3) with one mole of bromine in chloroform.

(5) $C_4H_4Cl_6$ *1,1,2,3,4,4-Hexachlorobutane*



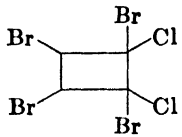
Colorless prisms from ether, glacial acetic acid or benzene. M p. 109 to 110°C. Obtained by introducing chlorine into a chloroform solution of $C_4H_4Cl_2$ (2) at 25 to 30°C.

(6) $C_4H_4Cl_2Br_2$ *1,2-Dichloro-3,4-dibromocyclobutane*



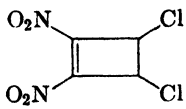
Colorless liquid. B.p. 79°C/0 6 mm, N_D^{20} 1 5757, D_4^{20} 2 0784. Obtained from the reaction of one mole of bromine with 1,2-dichlorocyclobutene (2) in chloroform.

(7) $C_4H_2Cl_2Br_4$ *Possibly 1,2-dichloro-1,2,3,4-tetrabromocyclobutane*



Prisms from glacial acetic acid. M.p. 128 to 129°C Obtained by reacting two moles of bromine with $C_4H_4Cl_2$ (2) in carbon tetrachloride.

(8) $C_4H_2O_4N_2Cl_2$ *Possibly 1,2-dichloro-3,4-dinitrocyclobutene-3*



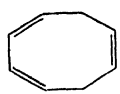
Yellow prisms from methanol. M p. 127°C

(9) $C_7H_{12}O_4$ *Pimelic acid*

HOOC—CH_2·CH_2·CH_2 CH_2 CH_2—COOH

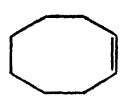
White crystals from benzene. M.p. 104 to 105°C Obtained by the oxidation of perhydrogenated ethers, from the reaction of sodium methylate with $C_8H_8Cl_2$ (15).

(10) C_8H_{10} *Cyclooctatriene (1,3,6)*



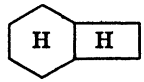
Colorless liquid B p 147 to 148°C/760 mm. From the lithium addition product of cyclooctatetraene and alcohol

(11) C_8H_{14} *Cyclooctene*



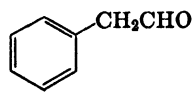
Colorless liquid. B.p. 140°C/760 mm. From cyclooctatetraene by hydrogenation with palladium-calcium carbonate catalyst in methanol, dioxan, tetrahydrofuran.

(12) C_8H_{14} *Bicyclo-(0,2,4)-octane*



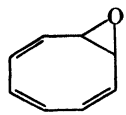
Colorless liquid. B.p. 136°C/760 mm; N_D^{20} 1.4613, D_4^{20} 0 8573. From $C_8H_{12}Cl_2$ (24) through hydrogenation in alkaline solution with nickel catalyst

(13) C_8H_8O *Phenylacetaldehyde*



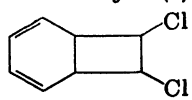
B.p. 194°C/760 mm. From cyclooctatetraene and mercury salts.

(14) C_8H_8O *7,8-Epoxycyclooctatriene-(1,3,5)*



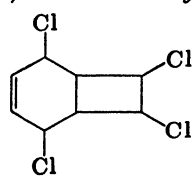
Colorless liquid. B.p. 73°C/12 mm; N_D^{20} 1.539; D_4^{20} 1.063. From cyclooctatetraene and perbenzoic acid in chloroform.

(15) $C_8H_8Cl_2$ *7,8-Dichlorobicyclo-(0,2,4)-octadiene-(2,4)*



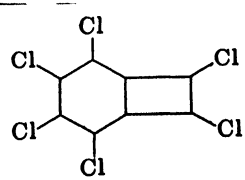
Colorless liquid. B.p. 62°C/0 5 mm, N_D^{20}1 5417; D_4^{20} 1.2468. (I) From reaction of cyclooctatetrane with one mole of sulfuryl chloride in chloroform or methylene chloride. (II) By reaction with one mole of chlorine in methylene chloride at 0 to 30°C.

(16) $C_8H_8Cl_4$ *2,5,7,8-Tetrachlorobicyclo-(0,2,4)-octene-3*



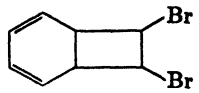
Plates. M.p. 111 to 112°C; also exists as colorless oil. B P. 126 to 128°C/1 mm.

(17) $C_8H_8Cl_6$ *2,3,4,5,7,8-Hexachlorobicyclo-(0,2,4)-octane*



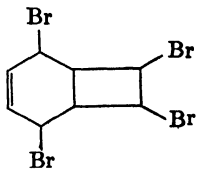
Colorless plates from isobutanol. M.p. 126 to 127°C; also exists as an oil. B.p. 153 to 160°C/1 mm.

(18) $C_8H_8Br_2$ *7,8-Dibromobicyclo-(0,2,4)-octadiene-(2,4)*



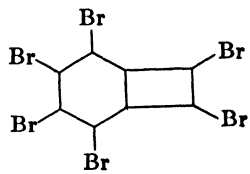
Colorless liquid. B p. 90°C/1 mm N_D^{20} 1.5951; D_4^{20} 1 7755 Obtained by reacting cyclooctatetraene with one mole of bromine in chloroform or methylene chloride at 0 to 20°C

(19) $C_8H_8Br_4$ *,5,7,8-Tetrabromobicyclo-(0,2,4)-octene-3*



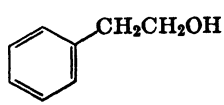
High melting-point types are colorless prisms from benzene. M.p. 147 to 148°C. Intermediate form: prisms from ligroin. M.p. 94°C. Obtained by reacting two moles of bromine with cyclooctatetraene in chloroform.

(20) $C_8H_8Br_6$ *2,3,4,5,7,8-Hexabromobicyclo-(0,2,4)-octane*



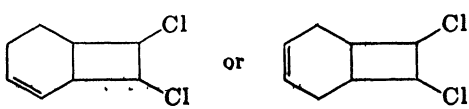
Colorless prisms from benzene. M p. 153 to 154°C. Obtained by reacting 3 moles of bromine with cyclooctatetraene in chloroform

(21) $C_8H_{10}O$ *beta-Phenylethyl alcohol*



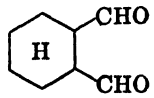
Liquid. B p. 219 to 221°C/750 mm. Obtained from styryl acetate through hydrogenation and saponification. Phenylurethane m.p. 80 to 81°, *p*-nitrobenzoate m.p 60 to 61°C.

(22) $C_8H_{10}Cl_2$ *7,8-Dichlorobicyclo-(0,2,4)-octene-(2 or 3)*



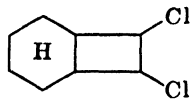
Colorless liquid. B.p. 104°C/13 mm; N_D^{20} 1.5242. Obtained from $C_8H_8Cl_2$ (15) by catalytic hydrogenation with palladium-calcium carbonate in diisopropyl ether.

(23) $C_8H_{12}O_2$ *Hexahydro-phthalaldehyde*



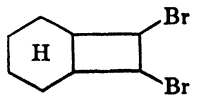
Colorless liquid. B.p. 91 to 94°C/3 mm. Made from $C_8H_{14}O_2$ (28) by oxidation with lead tetraacetate It polymerizes very quickly.

(24) $C_8H_{12}Cl_2$ *7,8-Dichlorobicyclo-(0,2,4)-octane*



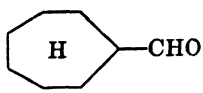
Colorless liquid. B.p. 104°C/12 mm; N_D^{20} 1.5069; D_4^{20} 1 1887. Made from $C_8H_8Cl_2$ (15) by hydrogenation with palladium or nickel catalyst.

(25) $C_8H_{12}Br_2$ *7,8-Dibromobicyclo-(0,2,4)-octane*



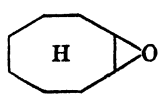
Colorless liquid. B.p. 91°C/1.2 mm; N_D^{20} 1.5583; D_4^{20} 1.7050. Made by hydrogenating $C_8H_8Br_2$ (18)

(26) $C_8H_{14}O$ *Cycloheptyl formaldehyde*



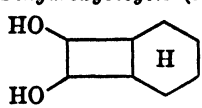
Colorless liquid. B p. 61°C/8 mm. Semi-carbazone; m.p. 155 to 156°C. Made by reacing dimethylether (57) with dilute sulfuric acid.

(27) $C_8H_{14}O$ *Cyclooctene oxide*



White crystals. M.p. 38 to 40°C. B.p. 88°C/25 mm. Made from cyclooctene and perbenzoic acid in chloroform.

(28) $C_8H_{14}O_2$ *7,8-Dihydroxybicyclo-(0,2,4)-octane*



Plates from benzene. M.p. 142°C. Made by saponifying diacetate $C_{12}H_{18}O_4$ (76) with methyl alcoholic HCl.

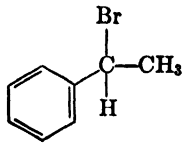
(29) $C_8H_{14}O_4$ *Suberic acid*

$HOOC—CH_2·CH_2·CH_2·CH_2·CH_2·CH_2—COOH$

M.p. 138–140°. (I) From cyclooctene by oxidation

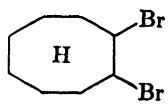
with HNO_3, $KMnO_4$, chromic acid. (II) From cyclooctane by oxidation with HNO_3. (III) From cyclooctanol by oxidation with HNO_3.

(30) C_8H_9Br *alpha-Bromoethylbenzene*



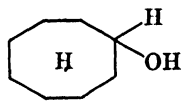
Liquid. B p. 85°C/13 mm. From cyclooctatetraene and HBr in glacial acetic acid.

(31) $C_8H_{14}Br_2$ *1,2-Dibromocyclooctane*



Colorless liquid B.p. 123 to 124°C/5 mm. From cyclooctene and 1 mole of bromine in chloroform.

(32) $C_8H_{16}O$ *Cyclooctanol*



B.p. 74°C/3 mm , 100 to 101°C/15 mm; N_D^{20} 1.4871; D_4^{20} 0.9740. From the oxide C_8H_8O (14) by hydrogenation

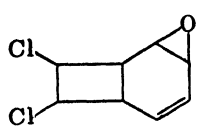
(33) $C_8H_7O_2Cl$ *Constitution unknown*

White needles from CH_3OH. M p. 139 to 141°C. From the dichloride $C_8H_8Cl_2$ (15) with perbenzoic acid in chloroform.

(34) $C_8H_7O_2Br$ *Constitution unknown*

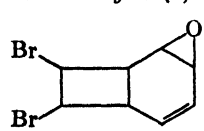
Colorless needles from benzene M.p. 144°C. From the dibromide (18) with perbenzoic acid in chloroform

(35) $C_8H_8OCl_2$ *7,8-Dichlorobicyclo-(0,2,4)-octene-2-oxide-(4,5)*



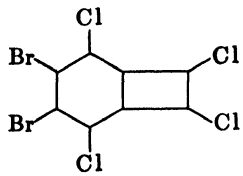
Colorless needles from petroleum ether. M.p. 72 to 75°C. From the dichloride $C_8H_8Cl_2$ (15) with perbenzoic acid in chloroform.

(36) $C_8H_8OBr_2$ *7,8-Dibromobicyclo-(0,2,4)-octene-2-oxide-(4,5)*



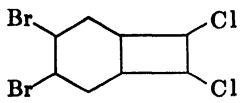
Colorless needles from ligroin. M.p. 88°C. From the dibromide $C_8H_8Br_2$ (18) with perbenzoic acid in chloroform.

(37) $C_8H_8Cl_4Br_2$ *2,5,7,8-Tetrachloro-3,4-dibromobicyclo-(0,2,4)-octane*



Colorless prisms from methanol. M p. 100 to 101°C. From the bromination of the tetrachloride $C_8H_8Cl_4$ (16).

(38) $C_8H_{10}Cl_2Br_2$ *7,8-Dichloro-3,4-dibromobicyclo-(0,2,4)-octane*



Colorless needles from CH_3OH. M.p. 124 to 125°C. From the dichloride $C_8H_{10}Cl_2$ (22) with one mole of bromine in methylene chloride

(39) $C_8H_{10}O_2Cl_4$ *Constitution unknown*

Colorless needles from benzene. M.p. 140°C. From oxidation of the tetrachloride $C_8H_8Cl_4$ (16) with $KMnO_4$

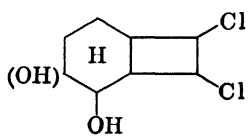
(40) $C_8H_{10}O_4Cl_2$ *Constitution unknown*

Colorless needles from benzene M p 129 to 130°C A dibasic acid formed by oxidation with HNO_3 of hydrogenated oxide (42).

(41) $C_8H_{10}O_5Cl_2$ *Constitution unknown*

Needles from water. M.p. 218 to 220°C. A dibasic acid made from $C_8H_8Cl_4$ (16) by oxidation with $KMnO_4$ in acetone

(42) $C_8H_{12}OCl_2$ *2 or 3-Hydroxy-7,8-dichlorobicyclo-(0,2,4)-octane*

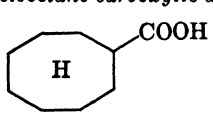


M.p. 80 to 81°C. Made by hydrogenating the oxide $C_8H_8OCl_2$ (35) with palladium

(43) C_8H_8ONCl *Constitution unknown*

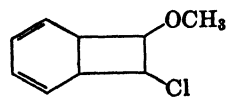
Colorless powder. M.p. 87 to 88°C. Made from nitrosylchloride on cyclooctatetraene.

(44) $C_9H_{16}O_2$ *Cyclooctane carboxylic acid*



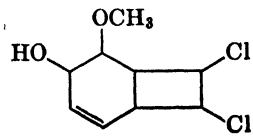
Liquid. B.p. 135 to 138°C/3.3 mm. From cyclooctene by reaction with CO and H_2O in presence of nickel carbonyl.

(45) $C_9H_{11}OCl$ *Possibly: 7-Methoxy-8-chlorobicyclo-(0,2,4)-octadiene-(2,4)*



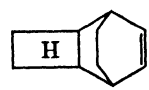
Colorless liquid. B.p. 87 to 90°C/10 mm. From the dichloride (15) with sodium methylate at 5 to 10°C.

(46) $C_9H_{12}O_2Cl_2$ *4-Hydroxy-5-methoxy-7,8-dichlorobicyclo-(0,2,4)-octene-2*



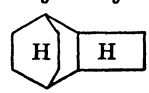
Plates. M.p 80 to 81°C. From $C_8H_8OCl_2$ (35) and warm CH_3OH

(47) $C_{10}H_{14}$ *3,6-Endocyclobutylene cyclohexene-1*



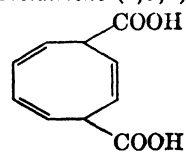
Colorless oil. B p 80 to 82°C/30 mm. From the phosphate of 3,6-endocyclobutylene cyclohexylamine-1 by distillation

(48) $C_{10}H_{16}$ *3,6-Endocyclobutylene cyclohexane*



Liquid. B.p 100 to 120°C/15 mm By hydrogenation of $C_{10}H_{14}$ (47).

(49) $C_{10}H_8O_4$ *Cyclooctatriene-(1,3,6)-dicarboxylic acid-(5,8)*



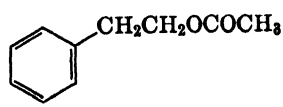
M.p. 240 to 260°C. Made from cyclooctatetraene and CO_2 with lithium catalyst.

(50) $C_{10}H_{10}O_2$ *Styryl acetate*

$C_6H_5 \cdot CH{=}CH{-}O \cdot COCH_3$

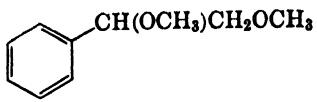
B.p. 80°C/0.5 mm. N_D^{20} 1.5513 From the dichloride $C_8H_8Cl_2$ (15) and glacial acetic acid.

(51) $C_{10}H_{12}O_2$ *beta-Phenylethylacetate*



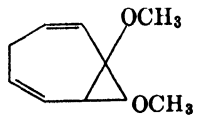
B.p. 118 to 120°C/13 mm. Made by hydrogenating $C_8H_8Cl_2$ (15) in glacial acetic acid, or by hydrogenating styryl acetate (50).

(52) $C_{10}H_{14}O_2$ *Phenylglycol dimethyl ether*



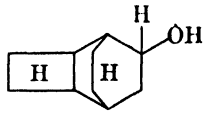
Colorless liquid. B.p. 93°C/10 mm; N_D^{20} 1 4946, D_4^{20} 1 0047. From $C_8H_8Cl_2$ (15) and CH_3OH.

(53) $C_{10}H_{14}O_2$ *Possibly 7,8-dimethoxybicyclo-(0,1,5)-octadiene-(2,5)*



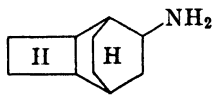
Colorless liquid B.p. 79°C/8 mm, N_D^{20} 1.5088; D_4^{20} 1.0206 From $C_8H_8Cl_2$ (15) and CH_3ONa.

(54) $C_{10}H_{16}O$ *Possibly 3,6-endocyclobutylene cyclohexanol-1*



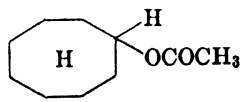
White crystals from ligroin M p 138 to 140°C From amine (55) with HNO_2.

(55) $C_{10}H_{17}N$ *3,6-Endocyclobutylene cyclohexylamine-1*



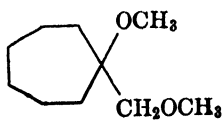
B.p. 110 to 111°C/16 mm From decomposition of acid azide of corresponding acid (59).

(56) $C_{10}H_{18}O$ *Cyclooctanol acetate*



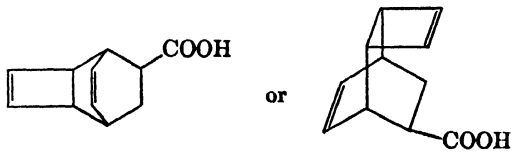
Colorless liquid. B.p. 75 to 76° C/3mm. From cyclooctene and glacial acetic acid in presence of H_2SO_4.

(57) $C_{10}H_{20}O_2$ *1-Methoxy-1-methoxymethyl cycloheptane*



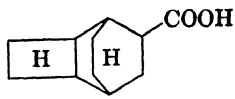
Colorless liquid. B.p. 80°C/13 mm; 74 to 75°C/8 mm; N_D^{20} 1.4546; D_{20} 0.9494. By catalytic hydrogenation of ether (53).

(58) $C_{11}H_{12}O_2$ *3,6-Endocyclobutadienylene cyclohexene-4-carboxylic acid-1*



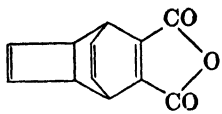
Colorless crystals from water. M.p. 112 to 113°C. From cyclooctatetraene by condensation with acrylic acid at 150°C.

(59) $C_{11}H_{16}O_2$ *3,6-Endocyclobutylene cyclohexane carboxylic acid-1*



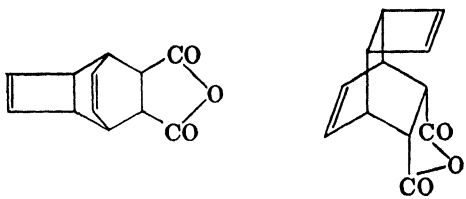
Needles from water. M p 85 to 86°C. Reduction of the adduct $C_{11}H_{12}O_2$ (58) with H_2 and palladium

(60) $C_{12}H_8O_3$ *3,6-Endocyclobutadienylene cyclohexadiene-1,4-dicarboxylic acid-1,2-anhydride*



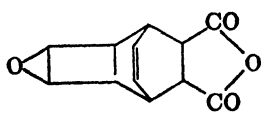
White crystals. M p. 168 to 170°C. Anhydride of adduct of cyclooctatetraene and acetylene dicarboxylic acid.

(61) $C_{12}H_{10}O_3$ *3,6-Endocyclobutadienylene cyclohexene-4-cis-dicarboxylic acid-1,2-anhydride*



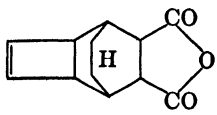
White crystals from monochlorobenzene. M.p. 167°C. From cyclooctatetraene and maleic anhydride.

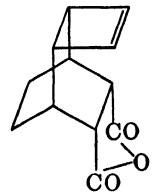
(62) $C_{12}H_{10}O_4$ *Adduct of cyclooctatriene-(1,3,5)-7,8-oxide and maleic anhydride*



White needles from monochlorobenzene. M.p. 205 to 206°C.

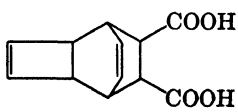
(63) $C_{12}H_{12}O_3$ *3,6-Endocyclobutadienylene cyclohexane-cis-dicarboxylic acid-1,2-anhydride*



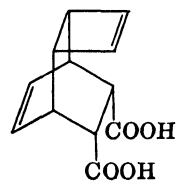


White crystals from benzene. M.p. 140 to 142°C. From catalytic hydrogenation of the maleic addition product $C_{12}H_{10}O_3$ (61) in alkaline solution.

(64) $C_{12}H_{12}O_4$ *3,6-Endocyclobutadienylene cyclohexene 4-trans-dicarboxylic acid-(1,2)*

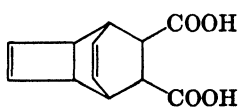


or

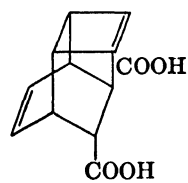


White crystals from water. M.p. 208°C. Made by heating the dimethyl ester of 3,6-cyclobutadienylene cyclohexene-4-cis-dicarboxylic acid-1,2 (93) with CH_3ONa, and hydrolyzing the trans ester so produced.

(65) $C_{12}H_{12}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-cis-dicarboxylic acid-1,2*

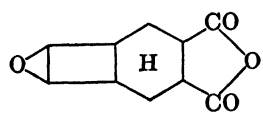


or



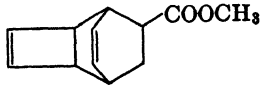
White needles from water. M.p. 167°C. By action of dilute NaOH on anhydride $C_{12}H_{10}O_3$ (61).

(66) $C_{12}H_{12}O_4$ *Possibly 3,6-endocyclobutylene-3,4-oxide-cyclohexane dicarboxylic acid-(1,2)-anhydride*



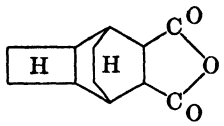
White prisms from benzene. M.p. 140 to 145°C Made by catalytic hydrogenation of the addition product of cyclooctatriene oxide and maleic anhydride (62).

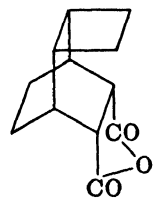
(67) $C_{12}H_{14}O_2$ *3,6-Endocyclobutadienylene cyclohexene-4-carboxylic acid-1-methyl ester*



B p. 135 to 140°C/12 mm By esterification of adduct (58)

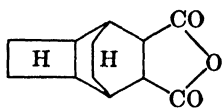
(68) $C_{12}H_{14}O_3$ *3,6-Endocyclobutylene cyclohexane-cis-dicarboxylic acid-1,2-anhydride*

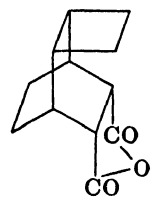




Colorless crystals. M.p. 130 to 132°C. Distillation of the acid (73) in vacuum.

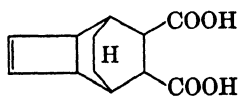
(69) $C_{12}H_{14}O_3$ *Possibly 3,6-endocyclobutylene cyclohexane-cis-dicarboxylic acid-1,2-anhydride*

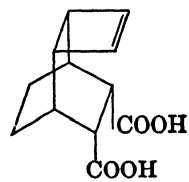




White crystals from cyclohexane. M p. 154 to 155°C. From adduct (60) by catalytic hydrogenation

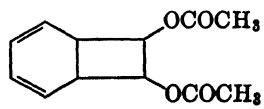
(70) $C_{12}H_{14}O_4$ *3,6-Endocyclobutadienylene cyclohexane-cis-dicarboxylic acid-(1,2)*





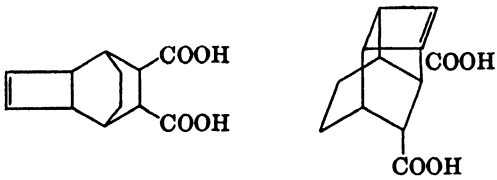
White crystals from benzene. M.p. 149°C. From adduct (61) by hydrogenation in alkaline solution.

(71) $C_{12}H_{14}O_4$ *7,8-Diacetoxybicyclo-(0,2,4)-octadiene-(2,4)*



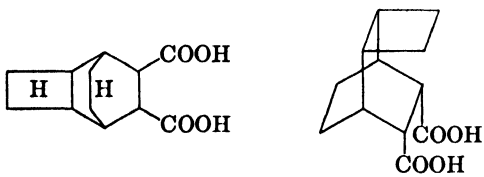
White needles from ligroin. M.p. 66°C. From the dichloride $C_8H_8Cl_2$ (15) with potassium acetate in glacial acetic acid.

(72) $C_{12}H_{14}O_4$ *3,6-Endocyclobutadienylene cyclohexane-trans-dicarboxylic acid-(1,2)*



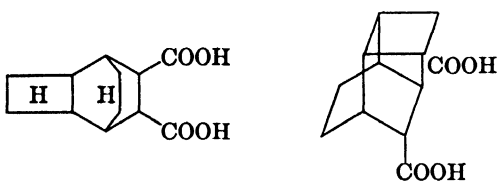
White crystals from dilute CH_3OH. M p. 212 to 213'C Made by partial hydrogenation of 3,6-endocyclobutadienylene cyclohexene-4-trans-dicarboxylic acid-1,2 (72)

(73) $C_{12}H_{16}O_4$ *3, 6 - Endocyclobutylene cyclohexane - cis - dicarboxylic acid-1,2*



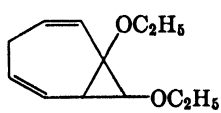
White crystals from CH_3OH. M p 172°C From adduct (61) by hydrogenation in alkaline solution.

(74) $C_{12}H_{16}O_4$ *3 , 6 - Endocyclobutylene cyclohexane - trans-dicarboxylic acid-1,2*



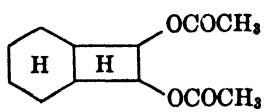
White powder. M p 228 to 229°C Hydrogenation of adduct (72)

(75) $C_{12}H_{16}O_4$ *Possibly 7,8-Diethoxybicyclo-(0,1,5)-octadiene-(2,5)*



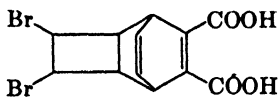
Colorless liquid. B p. 101 to 102°C/8 mm. From $C_8H_8Br_2$ (18) and sodium ethoxide

(76) $C_{12}H_{18}O_4$ *7,8-Diacetoxybicyclo-(0,2,4)-octane*



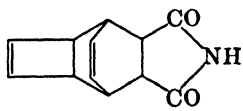
Colorless liquid. B.p. 105°C/0.5 mm. N_D^{20} 1.4662; D_4^{20} 1.1025. Hydrogenation of (71).

(77) $C_{12}H_{10}O_4Br_2$ *3,6-Endo-(3'4'-dibromo)-cyclobutylene cyclohexadiene-4-dicarboxylic acid-1,2*



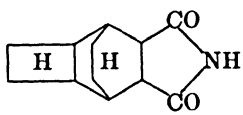
From glacial acetic acid. M.p. 205 to 207°C. From hydrolysis of adduct (101).

(78) $C_{12}H_{11}O_2N$ *3,6-Endocyclobutadienylene cyclohexene-4-dicarboxylic acid-1,2-imide*



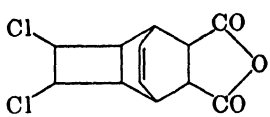
Crystals. M.p. 252 to 253°C. Action of ammonia on adduct (61).

(79) $C_{12}H_{15}O_2N$ *3,6-Endocyclobutylene cyclohexane dicarboxylic acid-1,2 imide*



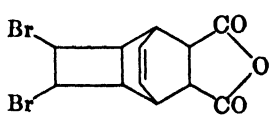
Colorless crystals M.p. 212 to 213°C. Made by reacting the anhydride with ammonia at 120°C.

(80) $C_{12}H_{10}O_3Cl_2$ *3,6-Endo-(3'4'-dichloro)-cyclobutylene cyclohexene-4-dicarboxylic acid-(1,2)-anhydride*



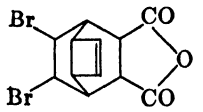
Crystal plates from monochlorobenzene M.p. 267 to 268°C. From $C_8H_8Cl_2$ (15) and maleic anhydride.

(81) $C_{12}H_{10}O_3Br_2$ *3,6-Endo-(3'4'-dibromo)-cyclobutylene cyclohexene-4-dicarboxylic acid-(1,2)-anhydride*



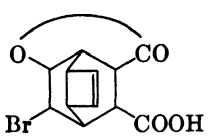
Prisms from monochlorobenzene. M.p. 205°C. Formed by reacting the dibromide $C_8H_8Br_2$ (18) with maleic anhydride.

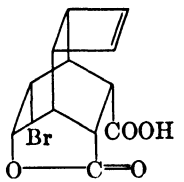
(82) $C_{12}H_{10}O_3Br_2$ *3,6-Endocyclobutadienylene-4,5-dibromocyclohexane dicarboxylic acid-1,2-anhydride*



White crystals from glacial acetic acid. M.p. 277°C. From hydrolysis of adduct (103) with conc. sulfuric acid

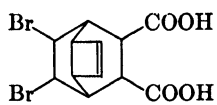
(83) $C_{12}H_{11}O_4Br$ *3,6-Endocyclobutadienylene cyclohexane-4-bromo-1,5-lactone-2-carboxylic acid*





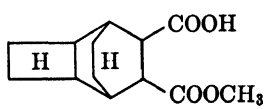
Colorless crystals from CH_3OH—H_2O. M p 238°C Action of bromine on potassium salt of (65).

(84) $C_{12}H_{12}O_4Br_2$ *3,6-Endocyclobutadienylene-(4,5)-dibromocyclohexane dicarboxylic acid*



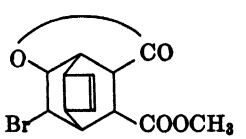
Colorless rosettes from CH_3OH—H_2O M p 234 to 236°C. Hydrolysis of adduct (103)

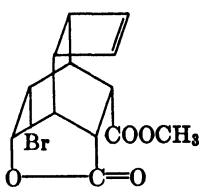
(85) $C_{13}H_{14}O_4$ *3,6-Endocyclobutylene cyclohexane-cis-dicarboxylic acid-1,2-monomethyl ester*



Colorless needles from benzene. M p. 95 to 96°C. By action of methanol on anhydride (69).

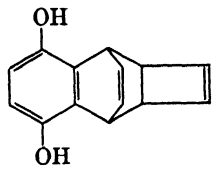
(86) $C_{13}H_{13}O_4Br$ *3,6-Endocyclobutadienylene cyclohexane-4-bromo-(1,5)-lactone-carboxylic acid-2-methyl ester*





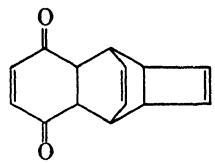
Crystals from chloroform and ligroin. M.p. 177 to 178°C. From bromine and (93).

(87) $C_{14}H_{12}O_2$ *1,4-Dihydroxy-5,8-endocyclobutadienylene-(5,8)-dihydronaphthalene*



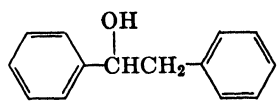
White crystals from benzene. M.p to 133°C. From cyclooctatetraene and benzoquinone at 180 to 200°C.

(88) $C_{14}H_{12}O_2$ *5,8-Endocyclobutadienylene-5,8,9,10-tetrahydro-1,4-naphthoquinone*



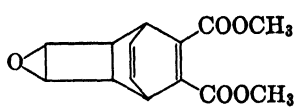
Yellow crystals from alcohol M p. 141°C. As in (87) except in dichlorobenzene at 140°C.

(89) $C_{14}H_{14}O$ *Phenylbenzylcarbinol*



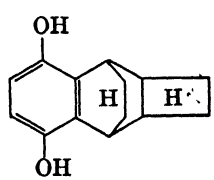
Crystals. M.p. 69 to 71°C.

(90) $C_{14}H_{14}O_5$ *Addition product of cyclooctatriene-(1,3,5)-7,8-oxide- and acetylene dicarboxylic acid dimethyl ester.*



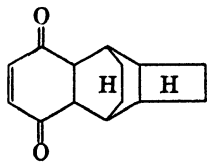
Colorless crystals. M.p. 103°C.

(91) $C_{14}H_{16}O_2$ *1,4-Dihydroxy-5,8-endocyclobutylene-5,6,7,8-tetrahydronaphthalene*



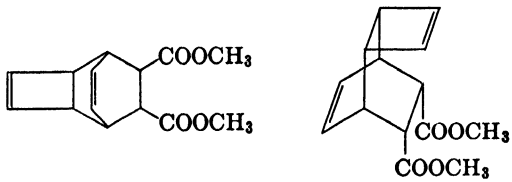
White crystals from benzene. M.p. 178 to 180°C. Hydrogenation of (87).

(92) $C_{14}H_{16}O_2$ *5,8-Endocyclobutylene-5,6,7,8,9,10-hexahydronaphthoquinone*



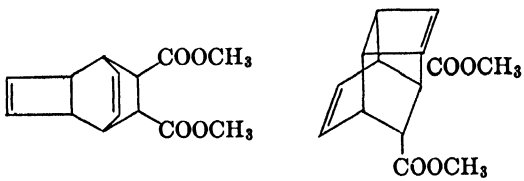
White crystals from monochlorobenzene M.p. 251 to 252°C. Hydrogenation of (88).

(93) $C_{14}H_{16}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-cis-dicarboxylic acid-(1,2)-dimethyl ester*



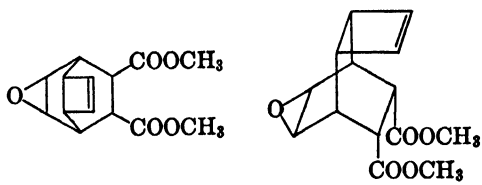
Colorless crystals. M.p. 52 to 55°C. B.p 149°C/1 mm. Esterification of (65)

(94) $C_{14}H_{16}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-trans-dicarboxylic acid-(1,2)-dimethylester*



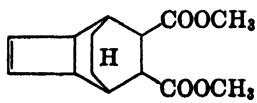
Colorless oil. B.p. 160°C/10mm. Esterification of (64)

(95) $C_{14}H_{16}O_5$ *3,6-Endocyclobutadienylene cyclohexene-4,5-oxido-cis-dicarboxylic-1,2-dimethyl ester*



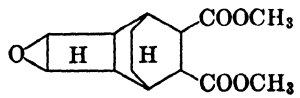
Crystals from cyclohexane. M.p. 85 to 86°C. From (93) and perbenzoic acid.

(96) $C_{14}H_{18}O_4$ *3,6-Endocyclobutadienylene cyclohexane-cis-dicarboxylic acid-1,2-dimethyl ester*



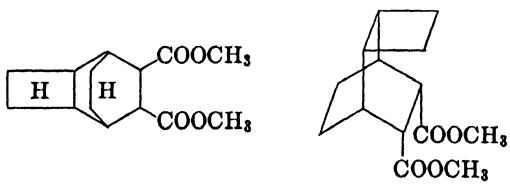
Colorless crystals. M.p. 25 to 30°C. B.p. 158 to 160°C/2 mm. Made from the anhydride and CH_3OH + H_2SO_4.

(97) $C_{14}H_{18}O_6$ *3,6-Endo-(3'4'-oxido)-cyclobutylene-cyclohexane dicarboxcylic acid-1,2-dimethyl ester*



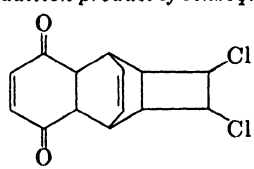
Colorless needles from ether M p 86 to 87°C. From catalytic hydrogenation of the addition product of cyclooctatriene oxide and acetylene dicarboxylic acid dimethyl ester (95)

(98) $C_{14}H_{20}O_4$ *3,6-Endocyclobutylene cyclohexane-cis-dicarboxylic acid-1,2-dimethyl ester*



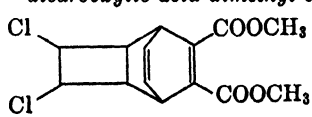
Colorless rosettes. M p. 62 to 63°C; b.p. 166°C/4 mm Formed by reacting the anhydride, $C_{12}H_{14}O_3$ (69), with CH_3OH + H_2SO_4

(99) $C_{14}H_{12}O_2Cl_2$ *Addition product of benzoquinone and dichloride ($C_8H_8Cl_2$)*



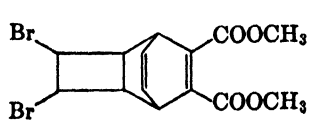
Colorless needles from benzene. M.p 174°C. Made by condensing $C_8H_8Cl_2$ (15) and benzoquinone in benzene.

(100) $C_{14}H_{14}O_4Cl_2$ *Addition product of dichloride ($C_8H_8Cl_2$) and acetylene dicarboxylic acid dimethyl ester*



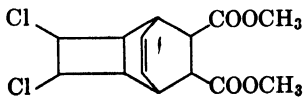
Colorless tablettes from CH_3OH. M.p. 125 to 126°C. Made by condensing $C_8H_8Cl_2$ (15) and acetylene dicarboxylic acid dimethyl ester in benzene.

(101) $C_{14}H_{14}O_4Br_2$ *Addition product of dibromide ($C_8H_8Br_2$ (18) and acetylene dicarboxylic acid dimethyl ester*



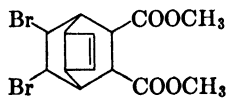
Colorless plates from CH_3OH. M.p. 134 to 135°C. Made by condensation of $C_8H_8Br_2$ and acetylene dicarboxylic acid dimethyl ester in benzene

(102) $C_{14}H_{16}O_4Cl_2$ *Addition product of dichloride, $C_8H_8Cl_2$ (18), and maleic acid dimethyl ester*



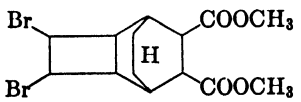
Plates from CH_3OH. M.p. 126 to 127°C

(103) $C_{14}H_{16}O_4Br_2$ *3,6-Endocyclobutadienylene-4,5-dibromocyclohexane dicarboxylic acid-(1,2)-dimethyl ester*



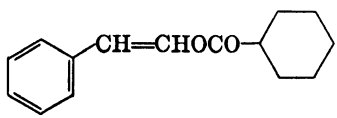
Crystals from chloroform or ligroin M p 225 to 227°C. Bromination of (93).

(104) $C_{14}H_{18}O_4Br_2$ *3,6-Endo-(3'4'-dibromo)-cyclobutylene cyclohexane dicarboxylic acid-1,2-dimethyl ester*



Plates from CH_3OH. M.p 148°C Hydrogenation of adduct (101).

(105) $C_{15}H_{12}O_2$ *Styryl benzoate*



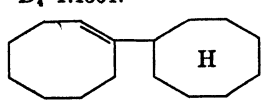
Colorless oil. B p. 150°C/0.1 mm. N_D^{20} 1.6087. Made from $C_8H_8Cl_2$ (15) + benzoic acid in chlorobenzene

(106) $C_{16}H_{16}$ *Dimeric cyclooctatetraene (liquid)*
Colorless oil. B p 136°/1 mm D_4^{20} 1.1844; N_D^{20} 1 5868

(107) $C_{16}H_{16}$ *Dimeric cyclooctatetraene (crystalline)*
Colorless crystals. M p. 43 to 44°C.

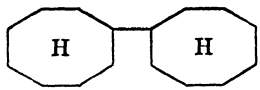
(108) $C_{16}H_{20}$ *Perhydrogenated $C_{16}H_{16}$ (liquid) (106)*
Colorless cyrstals M p 30°C.

(109) $C_{16}H_{22}$ *Perhydrogenated $C_{16}H_{16}$ (solid) (107)*
Colorless oil. B p. 127 to 128°C/0 5 mm. N_D^{20} 1.5668, D_4^{20} 1.1364.



(110) $C_{16}H_{28}$ *Cyclooctenyl cyclooctane*
Colorless oil. B p. 130 to 131°C/1 mm. N_D^{20} 1.4994; D_4^{20} 0.9291.

(111) $C_{16}H_{30}$ *Cyclooctyl cyclooctane*

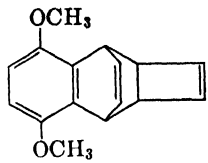


Colorless oil. B.p. 135 to 140°C/1 mm. By hydrogenation of cyclooctenyl cyclooctane (110).

(112) $C_{16}H_{14}Cl_2$ *Constitution unknown*

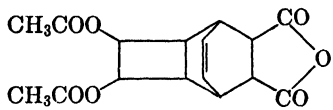
Colorless crystals. M.p 249 to 250°C. From $C_8H_8Cl_2$ (15) with zinc dust and methanol.

(113) $C_{16}H_{16}O_2$ *Dimethyl ether of quinone addition products*



Crystals from benzene. M p 106°C. Methylation of (87).

(114) $C_{16}H_{16}O_7$ *Addition product of 7,8-diacetoxybicyclo-(0,2,4)-octadiene-(2,4) and maleic anhydride*



Colorless prisms from benzene. M p. 131°C.

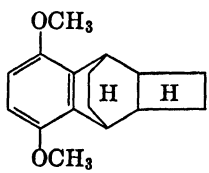
(115) $C_{16}H_{16}Cl_4$ *Dimeric dichloride $C_8H_8Cl_2$ (15) (constitution unknown)*

Colorless prisms from glacial acetic acid. M p. 109°C

(116) $C_{16}H_{16}Br_4$ *Dimeric dibromide $C_8H_8Br_2$ (18) (constitution unknown)*

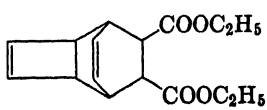
Colorless prisms from chlorobenzene. M.p. 218°C.

(117) $C_{16}H_{20}O_2$ *1,4-Dimethoxy-5,8-endocyclobutylene-5,6,7,8-tetrahydronaphthalene*



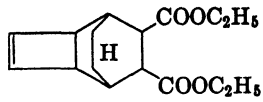
Crystals from methanol. M.p. 119 to 120°C. Hydrogenation of (112).

(118) $C_{16}H_{20}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-cis-dicarboxylic acid-(1,2)-diethyl ester*



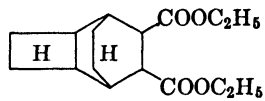
Colorless crystals. M.p. 57 to 58°C. Esterification of adduct (61) with ethanol.

(119) $C_{16}H_{22}O_4$ *3,6-Endocyclobutadienylene cyclohexane-cis-dicarboxylic acid diethyl ester*

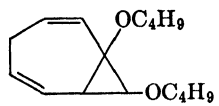


Colorless liquid. B.p. 164 to 167°/2 mm. Esterification of $C_{12}H_{12}O_3$ (63).

(120) $C_{16}H_{24}O_4$ *3,6-Endocyclobutylene cyclohexane dicarboxylic acid-1,2-diethyl ester*



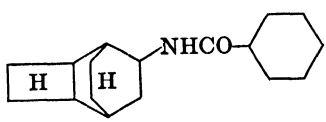
Colorless liquid. B p. 177 to 178°C/3 mm. From anhydride (69) by esterification.



(121) $C_{16}H_{26}O$ *Possibly 7,8-dibutoxybicyclo-(0,1,5)-octadiene-(2,5)*

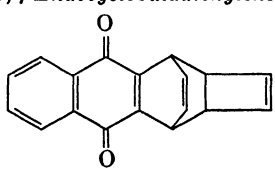
Colorless liquid. B.p. 126 to 127°C/2 mm. From $C_8H_8Br_2$ (18) and sodium butoxide.

(122) $C_{17}H_{21}ON$ *3,6-Endocyclobutylene cyclohexyl benzoyl amine-1*



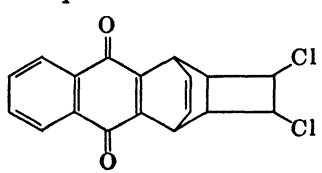
Crystalline. M p 164°C. Benzoylation of (55).

(123) $C_{18}H_{12}O_2$ *1,4-Endocyclobutadienylene-1,4-dihydroanthraquinone*



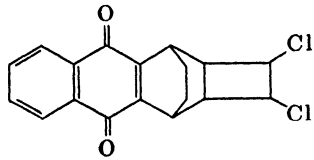
Yellow crystals from butanol. M.p. 192°C. Adduct of cyclooctatetraene and anthraquinone air oxidized in alkaline solution.

(124) $C_{18}H_{12}O_2Cl_2$ *1,4-Endo-(3'4'-dichlorocyclo)-butylene-1,4-dihydroanthraquinone*



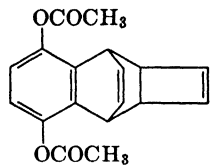
Bright yellow needles. M p. 170 to 180°C. Air oxidation of adduct (125).

(125) $C_{18}H_{14}O_2Cl_2$ *Naphthoquinone addition product of dichloride,* $C_8H_8Cl_2$ *(14)*



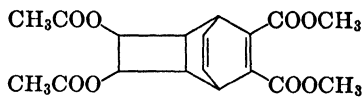
Colorless needles M.p. 221°C.

(126) $C_{18}H_{16}O_4$ *Diacetate of benzoquinone addition product of cyclooctatetraene (87).*



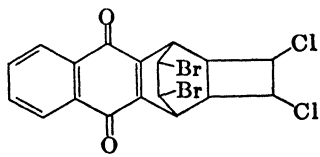
Needles from CH_3OH. M p. 137 to 138°C.

(127) $C_{18}H_{20}O_8$ *Addition product of 7,8-diacetoxybicyclo-(0,2,4)-octadiene-(2,4) and acetylene dicarboxylic acid dimethyl ester*



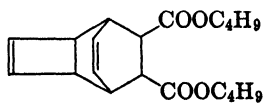
Colorless prisms from benzene M p. 84°C.

(128) $C_{18}H_{12}O_2Cl_2Br_2$ *Dibromide of naphthoquinone addition products* ($C_{18}H_{12}O_2Cl_2$) *(124)*



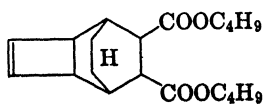
Prisms from trichlorobenzol. M p 300°C.

(129) $C_{20}H_{28}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-dicarboxylic acid-1,2-dibutyl ester*



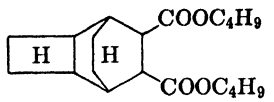
Liquid. B.p. 178 to 179°C/1 mm. From anhydride (61) and butanol.

(130) $C_{20}H_{30}O_4$ *3,6-Endocyclobutadienylene cyclohexane dicarboxylic acid-1,2-dibutyl ester*



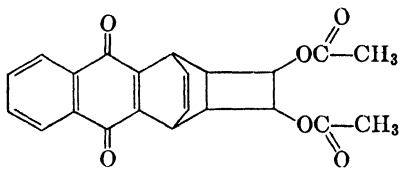
Colorless oil. B.p. 180 to 190°C/2 mm. From anhydride (63) and butanol.

(131) $C_{20}H_{32}O_4$ *3,6-Endocyclobutylene cyclohexane dicarboxylic acid-1,2 dibutyl ester*



From anhydride (69) and butanol

(132) $C_{22}H_{18}O_6$ *Dehydrogenated addition product of naphthoquinone an diacetate* $C_{12}H_{14}O_4$ (71)

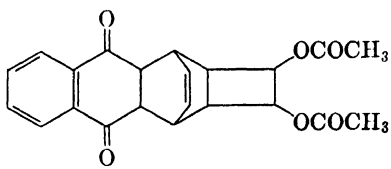


Bright yellow plates from CH_3OH M p 190 to 200°C

(133) $C_{22}H_{28}O_4$ *Constitution unknown*

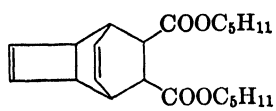
Viscous oil. B p 200 to 205°C/3 mm From $C_{16}H$ (106 and 107) and CO + H_2O + $Ni(CO)_4$.

(134) $C_{22}H_{20}O_6$ *Addition product of napthoquinone and diacetat* $C_{12}H_{14}O_4$ (71)



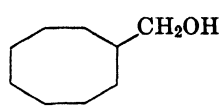
Prisms from CH_3OH. M.p. 160 to 161 C.

(135) $C_{22}H_{34}O_4$ *3,6-Endocyclobutadienylene cyclohexene-4-cis-carboxyli acid-1,2-diamyl ester*



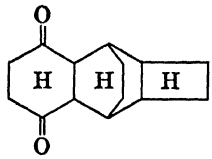
Crystals. M.p. 58 to 60°C. From adduct (61) an amyl alcohol.

(136) $C_9H_{16}O$ *Cyclooctyl carbinol*



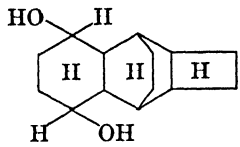
Colorless liquid. B.p. 106°C/7 mm. From C_8H_8 o C_8H_{14} by action of CO + H_2 in presence of cobal catalyst.

(137) $C_{14}H_{18}O_2$ *1,4-Endocyclobutylene-5,8-diketodecalin*



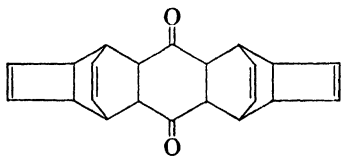
Colorless crystals. M.p. 134 to 135°C. Hydrogenation of adduct (88) with Pd

(138) $C_{14}H_{22}O_2$ *1,4-Endocyclobutylene-5,8-dihydroxy decalin*



Crystals M p 181°C Hydrogenation of (88) with Ni catalyst under pressure

(139) $C_{22}H_{20}O_2$ *Addition product of 2 moles of cyclooctatetraene with 1 mole of naphthoquinone*



Yellow crystals. M.p. 223°C.

Chapter VI

The Chemistry of Carbon Monoxide—Carboxylation and Related Processes

Carboxylation

Introduction

In addition to the vinylation, ethinylation, and polymerization reactions of acetylene, Reppe embarked upon a completely new field of chemistry involving the reactions of acetylene with carbon monoxide His successful work in the acetylene field led him to the idea of combining acetylene with cheap and reactive carbon monoxide to produce in a simple way new and interesting chemicals. In addition to the low potential cost of chemicals based on these reactants, the possibility of finding some use for carbon monoxide which is generated with an equal volume of acetylene in the carbide process was attractive since there was no other use for this carbon monoxide than for heating purposes.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$CaC_2 \xrightarrow{H_2O} HC{\equiv}CH + CaO$$

The new field of acetylene-carbon monoxide chemistry is characterized by the introduction of catalysts never before used in chemical syntheses, and by new reactions quite as audacious as those used in the synthesis of vinyl ethers, alkynols, alkynediols and cyclooctatetraene.

In general, these new catalysts are the metal carbonyls such as cobalt, nickel, and iron carbonyls, or the salts of carbonyl-forming metals in the presence of carbon monoxide. However, in many cases the metal carbonyls are not true catalysts but are reactants which are used in stoichiometric amounts as a source of carbon monoxide, and as such undergo conversion to the salts of the metal.

These new reactions and catalysts are of great interest and potential value, but as yet have not been developed sufficiently to permit large scale commercial production. Most of these reactions have been discovered

since the very late thirties, and the continuation of research during the war years was beset with many difficulties. The principal obstacle to future development appears to be the very difficult corrosion problems arising from the use of metal carbonyls, metallic halides, and carbon monoxide under pressure. It is also apparent that the catalyst problem has not been satisfactorily solved in some cases, and many questions can be answered only by further research.

Some confusion relating to the terms used for the designation of the general reaction of carbon monoxide with organic compounds unfortunately exists in the present literature. Originally, the term "carbonylation" was used by the Germans, and by early investigators of the wartime German chemical industry, to denote reactions of carbon monoxide with an organic compound in the presence of a metal carbonyl. Although the term "carbonylation" would seem to imply the introduction of a carbonyl group into the molecule, the reaction product in many carbonylation reactions was actually a carboxylic acid, or a derivative thereof, rather than a true carbonyl-containing compound such as an aldehyde or ketone. Preferred usage now, at least in this country, is to designate all reactions in which carbon monoxide reacts with an organic compound to produce a carboxylic acid, or a derivative thereof, by the term "carboxylation," even though a metal carbonyl may be a reactant or catalyst in the reaction.

Synthesis of Acrylic Acid Derivatives

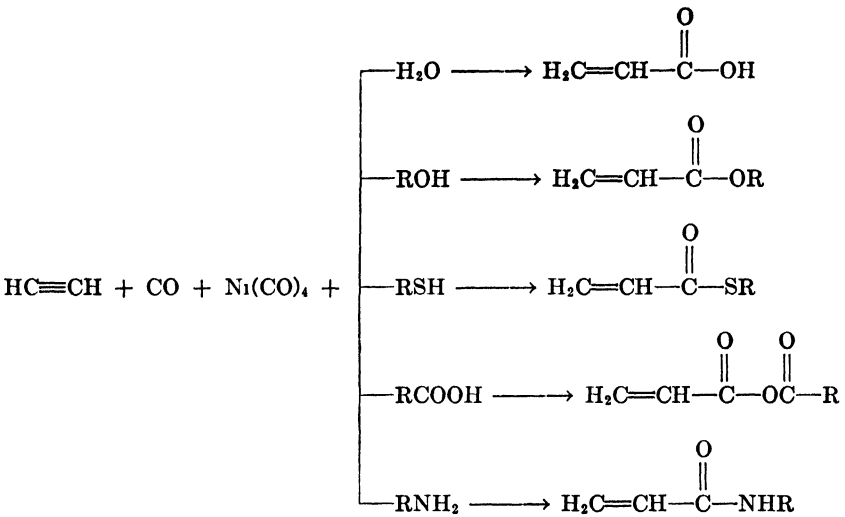
At first Reppe intended to react carbon monoxide with acetylene to form acetylene mono- or dialdehyde. It was a fortunate choice that from the very beginning nickel and nickel carbonyl were used as transferring agents for carbon monoxide, for it soon became evident that only metal carbonyls, or metals capable of forming carbonyls, are catalysts for the reaction between carbon monoxide and acetylene.

Experiments carried out in the summer of 1939 in an attempt to produce acetylene mono- or dialdehyde from carbon monoxide and acetylene did not proceed according to the formulation:

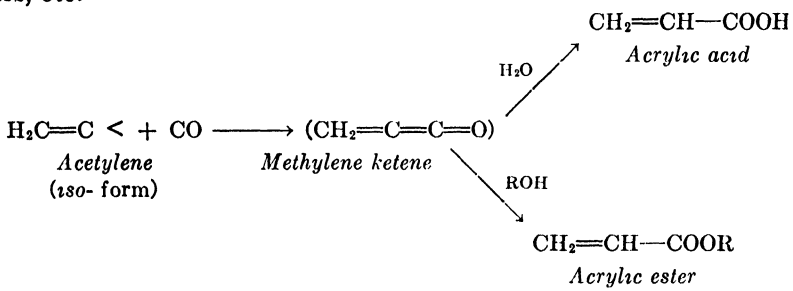
$$HC{\equiv}CH + CO \longrightarrow HC{\equiv}C{-}CHO \xrightarrow{CO} OCH{-}C{\equiv}C{-}CHO$$

Instead, in the presence of water, acrylic acid was formed in a surprisingly smooth reaction.[1] Other compounds with reactive hydrogen atoms behaved similarly with acetylene and carbon monoxide. Alcohols, acetylene, and carbon monoxide gave acrylic acid esters; amines gave acryl amides, mercaptans gave acrylic acid thioesters, or tautomeric thioacrylic esters, while mixed anhydrides with acrylic acid were obtained from organic acids. These transformations are shown on page 248.

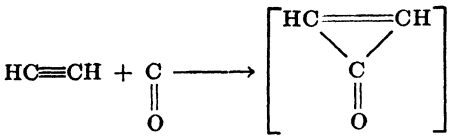
[1] *PB* 1345; *PB* 11396; *PB* 27713 (*BIOS* 355).



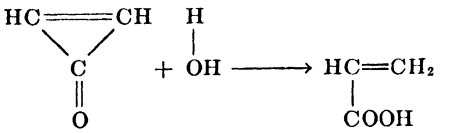
The course of the reaction was initially explained as follows. Acetylene in its *iso-* form reacts with carbon monoxide and forms methylene ketene, which further reacts with water, alcohols, etc., to give acrylic acid, acrylic esters, etc.



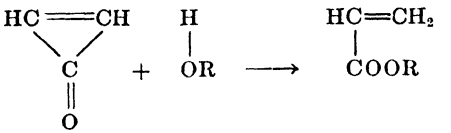
It is of course known that ketenes readily combine with water or alcohols at fairly low temperatures, forming acids, or acid esters The formation of acrylic esters from acetylene, alcohols, and carbon monoxide or metal carbonyls under exceedingly mild conditions is thus possible This theory does not, however, explain the reactivity of acetylenes which are unilaterally or bilaterally substituted In the first case, products are generated, the formation of which cannot be explained by the ketene theory. Phenylacetylene, for example, gives alpha-phenyl acrylic acid instead of cinnamic acid, which would be expected if the ketene theory were true. In the case of bilaterally-substituted acetylenes which have no reactive hydrogen atom, ketene formation is impossible; yet di-substituted acetylenes give two different reaction products. It became necessary, therefore, to assume the intermediate formation of a hypothetical cyclopropenone ring from acetylene and carbon monoxide, which is then split open by compounds with an



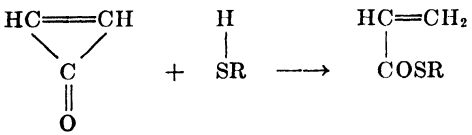
Cyclopropenone (hypothetical)



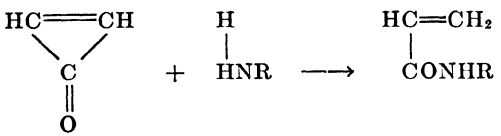
Acrylic acid



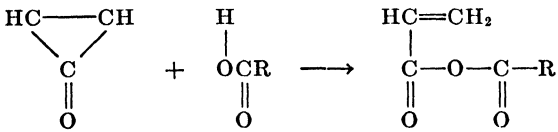
Acrylic acid ester



Acrylic acid thioester



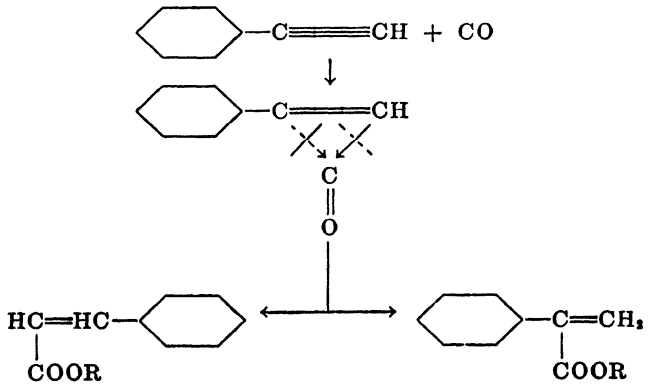
N-Substituted acrylic acid amide



Mixed acrylic-carboxylic acid anhydride

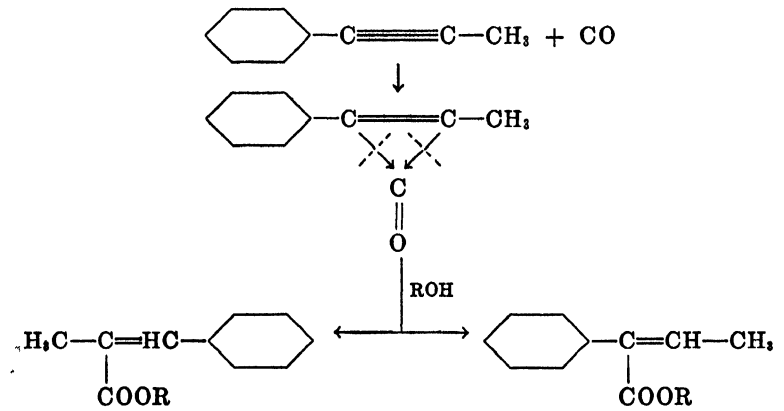
Efforts to split the hypothetical cyclopropenone with molecular hydrogen gave negative results.

According to this theory, phenylacetylene, carbon monoxide and alcohols might react to give either alpha-phenyl acrylic esters or cinnamic esters.



Cinnamic acid ester *alpha-Phenyl acrylic ester*

Actually, only alpha-phenyl acrylic esters could be isolated. However, methyl phenylacetylene yielded two different carboxylic acids—alpha-phenyl crotonic acid and alpha-methyl cinnamic acid:



alpha-Methyl cinnamic acid ester *alpha-Phenyl crotonic acid ester*

The above-described reactions between acetylene, carbon monoxide and compounds containing reactive hydrogen atoms, such as water, alcohols, amines, mercaptans and carboxylic acids, can be carried out with all acetylenic compounds, either by a stoichiometric procedure with metal carbonyls, or by a purely catalytic method using carbonyl-forming metals or their compounds as catalysts.

Stoichiometric Procedure. *Synthesis of Acrylic Esters from Nickel Carbonyl and Acetylene Under Pressure.* The first experiments producing acrylic acid and its esters from nickel carbonyl and acetylene were carried out in an autoclave at 12 atm pressure (6 atm acetylene and 6 atm nitrogen) with glacial acetic acid (2 moles), ethanol (11 moles) and nickel carbonyl (1 mole). The reaction temperature was 35 to 40°C. Frequently, the reaction was very vigorous and the calculated quantity of acetylene was absorbed in a very short time. The yield of ethyl acrylate was 94 per cent or better, based on nickel carbonyl.

For reasons unknown, in some experiments the reactions did not start until heated to 60°C. In other experiments, some decomposition of the nickel carbonyl occurred without any absorption of the acetylene. In those experiments which had run successfully, it was found that the quantity of acetylene absorbed agreed only fairly well with the quantity which had been calculated for the nickel carbonyl used. Thus in one experiment carried on until no more acetylene was absorbed, a pressure drop of 42 atm of acetylene had occurred, whereas the calculated figure was 30 atm. A part of this additional consumption must be attributed to cuprene, which always formed to some extent. If the absorption of acetylene was stopped as soon

as the main reaction was over, the ratio of total acetylene consumed to that combined in the desired reaction product was more favorable.

Synthesis of Acrylic Esters from Nickel Carbonyl and Acetylene at Atmospheric Pressure. The formation of acrylic acid and its esters from metal carbonyls and acetylene without pressure is also possible.[2] Acetylene is simply bubbled into, or passed over a solution of the carbonyl in water or alcohol, in the presence of an acid. The reaction is very vigorous and strongly exothermic.

Carpenter[3] describes the batch process for the preparation of ethyl acrylate using a 100-liter enameled kettle as follows:

"The charge was 25 kg of ethyl alcohol (30 liters) and 48 kg of 20 per cent hydrochloric acid (1 to 5 per cent excess of theoretical). About 0.1 to 0.2 per cent of catechol (50 g) is added, and the charge heated up to 40°C after purging carefully with nitrogen. The stoichiometric amount of nickel carbonyl (23.2 kg) is now added slowly from a graduated cylinder where it is stored under water (nickel carbonyl is very poisonous and forms an explosive mixture with air). After a small amount of nickel carbonyl has been added, the acetylene flow is started, and the equimolar flow of reactants adjusted so that the temperature never exceeds 45°C. Theoretical acetylene (14.1 kg) is used and no excess is necessary.

"The yield on alcohol is 90 per cent of theoretical; the principal by-product is vinyl acetic acid.* The yield on nickel carbonyl and acetylene is also 90 per cent or better."

The acrylic ester synthesis, according to the above-described stoichiometric procedure from nickel carbonyl, concentrated aqueous hydrochloric acid and alcohol, can be carried out continuously in liquid phase in a tower on a large scale. This process has been described in some detail in the report of Gartshore and Rose,[4] which includes flowsheets for the process and for the recovery of the nickel carbonyl as well as process data.

Nickel carbonyl is the most generally useful carbonyl. Cobalt carbonyl gives similar results, but is much harder to produce. The reaction fails entirely with iron carbonyl; in a mixture of nickel carbonyl with iron carbonyl, only a part of the iron carbonyl reacts. With metal carbonyls as the source of carbon monoxide, the presence of acids (or halogen) is imperative in order to combine with the metal of the carbonyl to form a salt. The course of the reaction can be seen from the following formulas which show

[2] I.G. Farbenindustrie patent proposal *O.Z.-11,813; D.R.Pat. Anmeldung I-65,757* IVc/12o.

[3] *PB* 58447 (*FIAT* 933)

* As will be shown on page 253, the by-product is probably ethyl beta-vinyl propionate).

[4] *PB* 25648 (*BIOS* 358).

the reactions which result when using nickel carbonyl:

$$H_2O + C_2H_2 + \tfrac{1}{4}\,Ni(CO)_4 + \tfrac{1}{2}\,HCl_{aq} \rightarrow H_2C{=}CH{-}COOH + \tfrac{1}{4}\,NiCl_{2aq} + \tfrac{1}{4}\,H_2$$

$$ROH + C_2H_2 + \tfrac{1}{4}\,Ni(CO)_4 + \tfrac{1}{2}\,HCl_{aq} \rightarrow H_2C{=}CH{-}COOR + \tfrac{1}{4}\,NiCl_{2aq} + \tfrac{1}{4}\,H_2$$

$$RSH + C_2H_2 + \tfrac{1}{4}\,Ni(CO)_4 + \tfrac{1}{2}\,HCl_{aq} \rightarrow H_2C{=}CH{-}COSR + \tfrac{1}{4}\,NiCl_{2aq} + \tfrac{1}{4}\,H_2$$

The quantity of acid needed to convert the nickel of the carbonyl into a nickel salt should be added. A slight surplus of acid is favorable during the reaction, but is undesirable later when the ester is worked up. Therefore, the quantity of acid theoretically required is usually added. Slow formation of ester may be obtained in neutral solutions, but a large amount of cuprene is also formed.

The rate of the reaction is determined primarily by the acid used; the reaction is most rapid in the presence of hydrochloric acid It is considerably slower with sulfuric acid, which is stated to be out of the question for technical use under the conditions which have been worked out. The use of acetic acid gives more favorable results. The reaction is not quite as fast as with hydrochloric acid but it is still rapid enough, and, above all, it runs more evenly. Experiments with other acids, such as formic acid, did not give good results.

The synthesis of acrylic esters was carried out both in the presence and absence of water. The presence of water is thought to help in eliminating hydrogenation of the acrylic acid ester by the hydrogen released in the reaction of the nickel with the acid. In the absence of water, as much as 25 per cent of the total acrylic ester is hydrogenated to propionic ester, a reaction which is almost entirely absent if water is present. On the other hand, closely checking ester and hydrogenation numbers indicating no formation of propionic esters were also obtained in some experiments in the absence of water by using alcoholic hydrochloric acid or glacial acetic acid.

No one seems to know exactly what happens to all the hydrogen which should be formed on the basis of the reaction equation. The theoretically calculated amount of hydrogen cannot be found in the waste gases. From the hydrogenation number of the reaction product, it is evident that the small quantity of propionic acid, or propionic ester, present is not equivalent to the missing hydrogen. Reduction of carbon monoxide to methanol is a possible explanation.

Favorable as the presence of water may be in preventing hydrogenation, it also has the disadvantage of giving some free acrylic acid. Less acid is formed and better conversion of carbon monoxide to acrylic acid ester is obtained, if the conversion is carried out slowly and evenly and if acetylene is absorbed uniformly. A large excess of alcohol is helpful, as nickel carbonyl is not completely decomposed by theoretical quantities of alcohol.

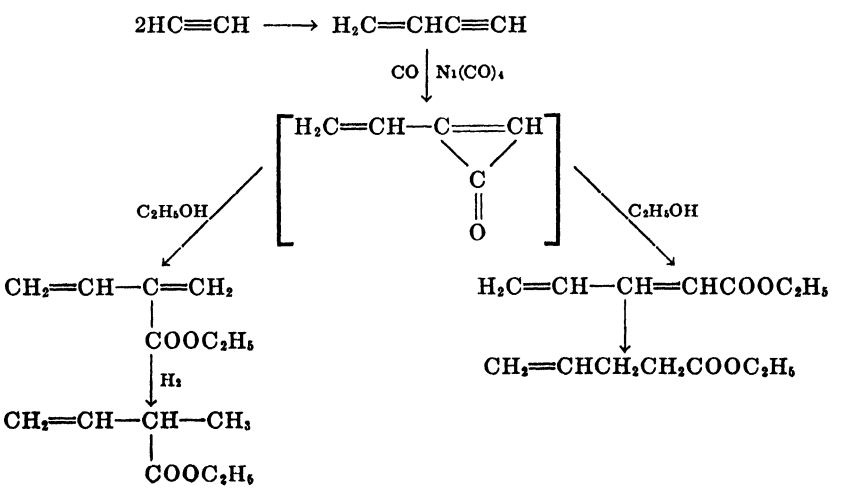
The optimum temperature seems to be between 38 and 41°C. Heating

to 38 to 40°C is needed to start the reaction, but as soon as some ester is formed, the reaction becomes vigorous and strong cooling is required. The start of the reaction can be facilitated by adding some acrylic acid ester right at the beginning, or even better, a small quantity of a previous reaction product. The solution becomes brown as soon as the reaction starts to proceed rapidly, especially in hydrochloric acid solution, then turns dark green, and later pale green as the reaction continues. Absorption of acetylene decreases at the same time, and finally stops. If fresh nickel carbonyl is added, the brown coloration reappears and rapid absorption of acetylene ensues. The sequence of brown coloration and acetylene absorption is very evident; brown coloration always occurs first.

It is assumed by German chemists that the added nickel carbonyl forms some colloidal nickel which starts the reaction. The brown color has also been attributed to an intermediate, such as $Ni(CO)_n \cdot (C_2H_2)_n$, which may be formed from $Ni(CO)_4$ and dissolved acetylene, or to traces of cuprene. The brown coloration occurs only in the presence of nickel carbonyl and never in a solution where all nickel carbonyl has already decomposed.

More acetylene than calculated theoretically is absorbed in all experiments. The surplus consumption is 20 per cent on an average. A large part of it seems to be dissolved in the reaction mixture.

Working up the crude solution still causes some difficulty, and it has not been possible to isolate the total quantity of ester from the crude solution by distillation. The ester if not carefully fractionated contains a small quantity of a higher-boiling substance (boiling at 144 to 148°C), which adversely affects its polymerization. The constitution of this impurity has not been completely determined. It is stated not to be the adduct of alcohol to the double bond of the acrylic acid ester; more probably, it is the ethyl ester of a vinyl propionic acid formed by the following side reactions:



Since its boiling point agrees fairly well with the literature value for ethyl beta-vinyl propionate, it is thought that this isomer is the more likely. The formation of this ester may account, in part, for the excess consumption of acetylene and also for the disappearance of some of the hydrogen.

Recent research has shown that the presence of nickel chloride causes trouble during distillation because part of the ester is hydrolyzed by the acid reacting liquid, thus causing a comparatively high loss. Removal of the ester quickly by direct distillation of the raw solution with steam, or in a column was attempted, as was distillation at low temperature *in vacuo*; some polymerization always occurred. These problems are the subject of present study.

Regeneration of Nickel Carbonyl

Regeneration of nickel carbonyl from the nickel chloride solution is a simple process.[5] Ammonia in excess of that necessary for the formation of the complex hexamine nickelous chloride is added to the nickel chloride solution; the solution is treated with carbon monoxide at 80°C and under 50 to 100 atm pressure. Nickel carbonyl is formed quantitatively and separated from the aqueous solution containing excess ammonia and ammonium-chloride; the ammonium carbonate-ammonium chloride solution is treated with lime to recover the combined ammonia for recycling. This novel and simple conversion of nickel salts to nickel carbonyl in aqueous solution can be done continuously in trickling towers. In contrast to the metallurgical process—precipitation of nickel chloride solution with soda ash, filtration, drying, ignition, and reaction of the dry oxide with carbon monoxide in a batch process—the new procedure represents considerable technical progress. Formulation of the recovery of nickel carbonyl from aqueous nickel chloride solution is as follows:

$$NiCl_2 + 6NH_3 \rightarrow Ni(NH_3)_6Cl_2 \xrightarrow{5CO + 2H_2O} NiCO_4 + 2NH_4Cl + (NH_4)_2CO_3 + 2NH_3$$

Summary of the Syntheses of Acrylic Acid Derivatives by the Reaction of Nickel Carbonyl, Acetylene, and Active Hydrogen Compounds. The reaction of nickel carbonyl with acetylene at atmospheric pressure and moderate temperatures (40 to 45°C) in the presence of an acid, preferably aqueous hydrochloric acid, and an organic compound containing active hydrogen atoms produces derivatives of acrylic acid in high yields The reaction may be formulated:

$$Ni(CO)_4 + 2HCl + 4HC{\equiv}CH + 4RQH \rightarrow 4H_2C{=}C(-C(=O)-QH) + NiCl_2 + H_2$$

This new procedure permits the production of numerous derivatives of

[5] *PB* 25594 (*BIOS* 371).

acrylic acid, such as esters, amides, acid anhydrides, thioesters, etc., in a very simple manner in a single cycle. The process may also be applied to any substituted acetylene such as methyl-, ethyl- and phenylacetylene; to vinyl acetylene, divinyl acetylene, and diacetylenes; to alkynols, alkynediols; and to ethers, esters, amines, and mercaptans containing an acetylenic group.

Reppe claims that this new process has a very good chance for large-scale application in the synthesis of acrylic esters due to the perfectly smooth reaction at low temperatures without pressure. The high yields of acrylic esters and the development of a new method of regenerating nickel carbonyl from the nickel chloride makes the procedure substantially cheaper than previous methods which involved the following series of reactions:

$$H_2C{=}CH_2 \xrightarrow[Cl_2,\ H_2O]{HOCl} Cl{-}CH_2{-}CH_2OH \xrightarrow{Ca(OH)_2}$$

$$CH_2{-}CH_2 \xrightarrow{HCN} HOCH_2{-}CH_2{-}CH_2CN \xrightarrow[\text{hydrolyzed}]{-H_2O,\ ROH} CH_2{=}CH{-}COOR$$

(O bridges the two CH$_2$ groups)

Catalytic Procedure. *Catalytic Production of Acrylic Esters from Acetylene, Carbon Monoxide and Alcohols.* The production of acrylic esters by reaction of acetylene, carbon monoxide, and an alcohol in the presence of catalysts and at increased temperature and pressure is disclosed in a patent application dated October 6, 1939.[6] The salts of bivalent nickel, especially the chloride, bromide, iodide and sulfide, are stated to be suitable catalysts.

The reaction disclosed required temperatures between 130 and 180°C, and 30 atm pressure; under these conditions, polymerization of the acrylic ester formed was likely to occur, and even spontaneous decomposition of acetylene was possible. An attempt was made to find more active catalysts which would enable the reaction to proceed under milder conditions. Various nickel salts and heavy-metal salts in pure form, or in admixtures, were tested for catalytic activity on a laboratory scale. There is no evidence that this work led to the development of a successful catalytic procedure for the synthesis of acrylic esters. Therefore, the various materials tested as catalysts and the results obtained will not be detailed here. However, since these data may possibly be of interest and value to those engaged in, or contemplating work in this field, they are tabulated in part one of the appendix to this chapter, on page 295.

The method used in testing the catalytic activity of the various salts was as follows. The catalyst to be tested and 40 g of absolute ethyl alcohol were charged to a shaking autoclave of 200-cc volume make from V2A steel The air was displaced and the mixed gas (1:1 acetylene-carbon monoxide, pumped in at 30 atm and at the desired temperature. The experiment

[6] I.G. Farbenindustrie patent proposal *O.Z.-11,814; D.R.Pat. Anmeldung I-65,758* IVc/12o.

was stopped after 100 atm pressure drop, and the contents of the autoclave were filtered and distilled. A weighed sample was neutralized with sodium hydroxide and hydrolyzed by refluxing one hour with an excess of *N* NaOH, and the caustic was back-titrated (1 cc. of *N* NaOH = 0.1 g of ethyl acrylate). The conversion of alcohol was calculated from the ester content, and also the conversion which would be obtained after 100 hours.

The results of these autoclave experiments may be briefly summarized as follows: Qualitative results were obtained with regard to the temperature at which the catalyst was active, and the rate of reaction. Not much can be concluded from the quantitative viewpoint, because there were several sources of error—chiefly fluctuations of temperature and pressure, composition of the gas, and leaks in the apparatus. The best catalysts were nickel halides, gamma-nickel sulfide, and steam-treated nickel halides on siliceous extrudings. Addition of other salts to the nickel salts did not effect any improvement. The iron, cobalt and nickel salts of the oxygen acids such as sulfuric, phosphoric, etc., are not catalysts

In the middle of January, 1940, experiments were initiated to study the use of these selected catalysts in a continuous process. The apparatus consisted of a V2A high-pressure steel pipe, 5 meters long, 30 mm inside diameter, which could be heated to 350°C, and which was packed with the catalyst (3 liters). Alcohol and the gas mixture were introduced into the top of the tower. The liquid trickled down over the catalyst in intimate contact with the gas mixture and was collected in a separator at the tower base from which it could be expanded to a storage tank by way of a cooler. The uncondensed gas was recycled into the tower. The inside temperature of the reactor was measured by thermocouples. The reaction product was discontinuously discharged from the reactor and analyzed for ester content.

Some difficulty was caused by the formation of cuprene, and by decomposition of acetylene. Cuprene formation was later eliminated completely by the addition of 0.8 g of mercuric chloride per liter of feed stock.

Acetylene decomposition always occurred if the catalyst became dry in any place because of poor distribution of the liquid, or because catalysts such as gamma-nickel sulfide on catalyst supports, or gelatin-treated nickel bromide, are hard to wet. Decomposition of the acetylene was prevented by filling the tower with liquid before each run, and by the use of supports with 3-mm channels.

The largest number of tests were carried out with butanol because its vapor pressure is only 6.5 atm at 180°C, whereas that of ethanol is 19.5 atm at that temperature. It was found that a satisfactory rate of reaction was obtained with only 20 atm partial pressure of the mixed gas. In some cases, the butanol contained up to 17 per cent of ester in an attempt to decrease the solubility of the nickel salt in butanol. Solubility tests of nickel bromide in butanol-ester mixtures showed, however, that nickel bromide is insoluble only at 90 per cent ester content. Pure butanol and

intermediate mixtures with ester dissolve approximately 12 g of nickel bromide per liter when cold.

In all the tower experiments, it was found that useful catalyst life was extremely short. The higher the yield of ester in the finished product, the shorter the catalyst life. After some experiments, only traces of nickel could be detected on the catalyst support. Analysis of the waste gas and reaction products revealed that most of the nickel had been converted to nickel carbonyl. A considerable amount of nickel carbonyl was released when the reaction mixture was expanded to normal pressure; more was obtained by vacuum distillation and freezing out the first runnings with solid carbon dioxide. In this way, two-thirds of the nickel which was theoretically contained in the catalyst could be isolated.

Recycling of the reaction product containing nickel carbonyl did not improve the ester yield, thus showing that nickel carbonyl without addition of acid was not capable of forming acrylic esters. The addition of 10 per cent of acetic acid was also unsuccessful because, under the working conditions, it was immediately converted to butyl acetate.

The use of hydrochloric acid or hydrobromic acids was impossible because no sufficiently corrosion-resistant steels were available for construction of the pressure reactors. Tests in V2A reactors with 1.5 per cent of hydrobromic acid in butanol containing mercuric chloride at 150°C were underway, but the work was not finished

Despite the short catalyst life, it was established that acrylic ester formation is definitely a catalytic reaction as shown by the fact that the quantity of acrylic ester formed in several experiments was more than ten times the quantity which would result from stoichiometric reaction of the catalyst used

Liquid phase catalytic synthesis of acrylates Most nickel salts have a comparatively high solubility in alcohols. Therefore, experiments were initiated to carry out the reaction between carbon monoxide and acetylene in liquid phase.

Carpenter[7] has described this liquid-phase catalytic procedure for the synthesis of butyl acrylate. A solution containing 91.5 per cent of butanol, 5 per cent of water, 2 per cent of butyl bromide* and 1.5 per cent of nickel bromide is fed to the reactor (72-liter volume) at 400 cc per hour so as to give a contact time of about 20 hours. The feed is preheated to 170 to 180°C. Mixed gas (CO/CH≡CH equals one) was compressed to 30 atm and pressed into the catalytic solution at a rate of about 900 liters per hour by a gas circulating pump by way of a preheater and a porous plate. This effects some agitation because of the rising gas bubbles. A side vent at the top of the reactor recycled the liquid to the base, thus providing con-

[7] *PB* 58447 (*FIAT* 933).

* Carpenter states that the butyl bromide is present to suppress conversion of butanol to butyl bromide. This appears questionable in view of later work.

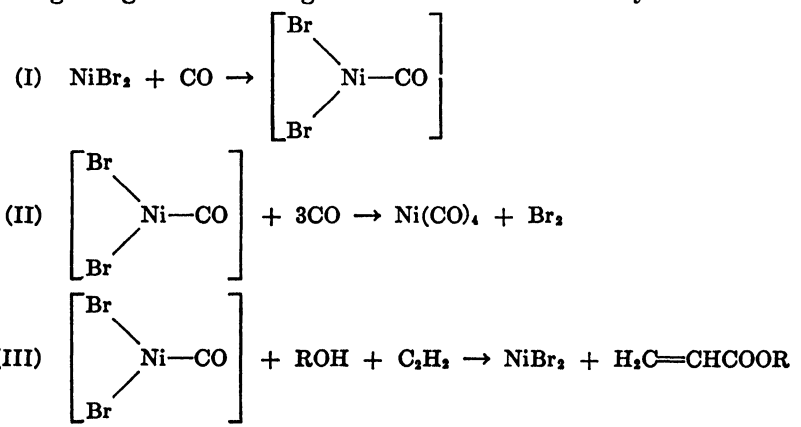
tinuous circulation and good mixing. The gas passed a dephlegmator and a cooler which liquefied the condensable components and was then recycled. About 30 liters of gas per hour was vented from the top of the reactor. Condensed liquid was drawn off from time to time.

The liquid product contained 15 to 20 per cent of butyl acrylate. The concentration could be increased to 40 to 50 per cent by continued recycling, but at the higher concentrations polymerization was apt to take place. The butyl acrylate was separated by distillation, the catalyst remaining in the still bottoms together with high-boiling material. The catalyst may be reused, but a purge must be taken and some new catalyst added. Approximately one mole of nickel bromide is consumed for every 70 moles of butyl acrylate formed.

Ethyl acrylate may be prepared similarly. The procedure is not applicable to methyl acrylate because of the high vapor pressure of methanol at 170 to 180°C. Data on yields, throughputs, etc., are not available.

The true catalyst in the catalytic syntheses using nickel salts is believed to be the hypothetical addition compound of the nickel salt and carbon monoxide, and not nickel carbonyl as might be supposed on the basis of the stoichiometric procedure previously described.

This belief is based on the prior work of Hieber[8] who found that cobalt iodide adds 1 mole of carbon monoxide at 150° and 200 atm, forming the unstable compound ($CoI_2 \cdot CO$). A similar reaction should take place with nickel halides, and the compounds should also be unstable and capable of existence only at a certain pressure and temperature. It is known that nickel halides are easily converted to nickel carbonyl at high carbon monoxide pressures. Under the experimental conditions it was assumed, therefore, that the formation of nickel halide-carbon monoxide compounds of the type $NiBr_2 \cdot CO$ occurred. These compounds may react further with acetylene and alcohol to form esters directly, or with carbon monoxide, liberating halogen and forming non-reactive nickel carbonyl.



[8] *Z. anorg. Chem.*, **243**, 145-63 (1939).

(II) and (III) are competing reactions which might be governed by adjusting the concentration of the reacting components. If this formulation is correct, it should be possible to suppress reaction (II) by reducing carbon monoxide pressure and to promote reaction (III) by increasing the concentration of acetylene and alcohol. No data have been located which would indicate that this theory was ever tested.

On the basis of the information available to the authors, it appears doubtful that Reppe succeeded in developing a satisfactory, continuous, catalytic process for the synthesis of acrylic esters using nickel halides as the catalyst. In December of 1940 in his report to the Kuko committee, Reppe stated:[9]

"We naturally also endeavored to carry out the newly discovered reaction catalytically which proved to be quite feasible.

"Metallic nickel or cobalt are suitable catalysts, but their salts, especially the halides and sulfides, are better. Nickel iodide is the most active and is most effective in combination with metallic nickel as well as other activators. The catalytic process operates at 120 to 150°C and requires pressure. In batch production in autoclaves, the catalytic conversion to acrylic esters proceeds perfectly. The continuous production is, at present, still in the preliminary stage; there are some difficulties with regard to catalyst life. But, on the other hand, the formation of acrylic amides according to the catalytic method is more advanced. Here, the catalysts show longer life, so that there are prospects that in case a larger demand for acrylic amides should arise this method could soon be applied on a commercial scale."*

Role of triphenylphosphine nickel bromide catalysts in acrylic ester synthesis from alcohol, carbon monoxide and acetylene. As shown earlier (page 256), all nickel salts of oxygen containing organic compounds had little, if any, catalytic activity in the reaction of acetylene with carbon monoxide. However, some organic complexes of nickel chloride and nickel bromide are apparently more active than the nickel halides alone. Such a complex formed by the reaction of triphenyl phosphine with nickel halides or nickel carbonyl was particularly promising. The following is a translation of a report by Dr. Schweckendiek, dated November 27, 1944, which attempts to explain the role of such catalysts.‡

[9] *PB* 1345

* The authors present this somewhat long and involved discussion with certain misgivings. No data relating to the actual method of operation with the various triphenyl phosphine-nickel halide or nickel carbonyl complexes have been located, so that it is impossible to evaluate the importance of this type of catalyst. However, since general statements in Reppe's speeches indicate that he was apparently enthusiastic about the potentialities of these novel complexes, this section is recorded in the hope that it may prove of value to workers in this field of chemistry.

‡ *Note Added in Proof*

Reppe and Schweckendiek, *Ann.*, **560**, 104 (1948), have just described the use of such catalysts in the cyclization of acetylene to benzene and styrene, the cyclization

Triphenylphosphine reacts in alcoholic solution with nickel carbonyl at room temperature with the replacement of one molecule of carbon monoxide:

$$(C_6H_5)_3P + Ni(CO)_4 \xrightarrow{20°C} [(C_6H_5)_3P]Ni(CO)_3 + CO \quad (1)$$

If excess triphenylphosphine is present and the temperature is raised, there is an almost quantitative formation of a nickel carbonyl complex with two molecules of triphenylphosphine:

$$2(C_6H_5)_3P + Ni(CO)_4 \xrightarrow{50°C} [(C_6H_5)_3P]_2Ni(CO)_2 + 2CO \quad (2)$$

This same product results if the triphenylphosphine nickel carbonyl complex is heated at its melting point (123°C); nickel carbonyl splits off. In alcohol solution this reaction occurs below 123°.

$$2[(C_6H_5)_3P]Ni(CO)_3 \xrightarrow{123°C} [(C_6H_5)_3P]_2Ni(CO)_2 + Ni(CO)_4 \quad (3)$$

Thus, two well-defined compounds may be isolated from the reaction of triphenylphosphine and nickel carbonyl:

(A) $[(C_6H_5)_3P]Ni(CO)_3$ m.p 123° C
(B) $[(C_6H_5)_3P]_2Ni(CO)_2$ m p 192–194° C (decomposes)

These two complexes have been used as catalysts for acrylic acid ester synthesis, though with little success in the beginning. In addition to a little acrylic ester, a considerable quantity of high-boiling residue was formed, mainly by the high temperature of the reaction which takes place only at 180 to 190°C. It was surprising that both compounds gave 50 per cent of acrylic ester in a very short time (10 hours), and at 140 to 150°C if butyl bromide was present in the shaking autoclave. There was a slight difference between (A) and (B) because the (A) compound gave a much larger quantity of high-boiling products. This is evident if one considers equation (3), because nickel carbonyl which is released at higher temperature will certainly undergo side reactions, especially in the presence of butyl bromide. The high-boiling residue with complex (A) amounted to 10 to 20 per cent; with complex (B), 3 to 5 per cent based on acrylic ester.

Larger scale experiments in an autoclave without the use of mixed gas (C_2H_2 + CO) were carried out. A mixture of butanol, butyl bromide and the substituted nic' el carbonyl compounds (A and B) was heated to 150°C under pressure. A strong exothermic reaction occurred at 150° and the temperature rose to approximately 200°, although heating of the autoclave

of propargyl alcohol to trimethylol benzene and other new cyclization reactions of vinyl compounds (See page 126)

was immediately checked when the reaction started. A dark green crystalline substance (C) was obtained which melted at 177 to 178°C and was easily soluble in alcohol and butanol. Methanol, however, decomposes the complex with separation of triphenylphosphine The analysis of the compound indicated the following composition

(C) $[(C_6H_5)_3P]_2NiBr_2 \cdot C_4H_9Br$ m.p. 177–178° C

which can only have been generated by reaction of butyl bromide with (A) or (B), since additional gas was excluded.

(4) $$[(C_6H_5)_3P]_2Ni(CO)_2 \xrightarrow[150°C]{C_4H_9Br} [(C_6H_5)_3P]_2NiBr_2\ C_4H_9Br + CO$$

A substantial quantity of the butyl ester of valeric acid was always found; it is probable that it had been formed from released carbon monoxide, butyl bromide and butanol [compare formula (4)]. When the autoclave was opened, the presence of gas was evidenced by the formation of bubbles.

Triphenylphosphine nickel bromide (m.p. 222 to 223°C) was tried as a catalyst; this compound was previously unknown. The high yield of ester in these experiments (70 to 80 per cent) was surprising. Best yields were obtained if heavy-metal halides (such as $HgBr_2$) were present and if triphenylphosphine nickel bromide was used in the presence of an alkyl halide (to get a slightly acid reaction) at 150 to 160°C. This knowledge became interesting when there was successfully produced a triphenylphosphine nickel bromide-butyl bromide complex [compound (C)(4)] by way of the above-mentioned complexes (A) and (B) in the presence of butyl bromide, which is obviously the real catalyst in the synthesis of acrylic esters with triphenylphosphine compounds.

There are apparently two methods which yield the same basic compound. It is also possible that reactive intermediates are formed if mixed gas under pressure is used. Triphenylphosphine may be reversibly substituted by carbon monoxide, and acetylene may be added as well. (Compare addition of acetylene to copper acetylide in Reppe's alkynol synthesis in which these unstable and reversible addition products are the real catalysts.) As stated above, one method gives reactive compounds with the mixed gas via triphenylphosphine nickel bromide (as well as in the presence of butyl bromide). It could be anticipated that both compounds might have the same composition and properties (solubility, color, etc.) after they had been used as catalysts in the presence of acetylene and carbon monoxide. The research on this subject has not been concluded because some samples were lost as a result of bombings.

There is the possibility that triphenylphosphine nickel bromide is decomposed in the presence of carbon monoxide with formation of nickel

carbonyl through active intermediates. It remains to be determined what will happen if the nickel carbonyl exists in addition to triphenylphosphine nickel bromide (with or without butyl bromide). If nickel carbonyl is reacted with an alcoholic solution of triphenylphosphine nickel bromide at low or high temperature, the nickel carbonyl disappears immediately (just as if triphenylphosphine were present). Substituted nickel carbonyls are formed; carbon monoxide is released and nickel bromide is set free from the triphenylphosphine nickel bromide:

$$(5)\quad [C_6H_5)_3P]_2NiBr_2 + Ni(CO)_4 \xrightarrow{80°C} [(C_6H_5)_3P]_2Ni(CO)_2 + NiBr_2 + 2CO$$

The nickel carbonyl in equation (5) reacts immediately and releases two moles of carbon monoxide. From equation (4) it was learned that substituted nickel carbonyl compounds can be readily converted to the corresponding nickel bromide compound in the presence of alkyl halide (*e.g.*, butyl bromide); even at 150°C, equilibrium is shifted far to the left side, and a stable triphenylphosphine nickel bromide-butyl bromide compound is obtained [compare (4) and (5)].

$$[(C_6H_5)_3P]_2NiBr_2 + Ni(CO)_4 \underset{150\text{-}160°C}{\overset{C_4H_9Br}{\rightleftharpoons}} [(C_6H_5)_3P]_2Ni(CO)_2 + NiBr_2 + 2CO$$

This means that nickel carbonyl *in statu nascendi* releases activated carbon monoxide and is regenerated from carbon monoxide in the mixed gas. Nickel carbonyl is the real catalyst in this case. (Compare stoichiometric acrylic ester synthesis after Reppe from nickel carbonyl, alcohol and acetylene in acid solution.)

It is probable that all these assumptions are far too complicated and that the triphenylphosphine nickel bromide-butyl bromide complex C [compare (4)] is the effective agent. It exchanges the butyl bromide which is bound by subsidiary valencies to carbon monoxide (or acetylene) and recycles this added and activated carbon monoxide by a new exchange of bromide. It is furthermore to be considered that besides the triphenylphosphine nickel bromide compounds (m.p. 221 to 223°C) there exist two other nickel bromide compounds with variable triphenylphosphine content, the properties of which are very similar; this makes formation of active intermediates in the presence of carbon monoxide or acetylene very likely. Besides the compound melting at 221 to 223°C, there was isolated a red compound melting at 335 to 360°C, which is probably

$$\{[(C_6H_5)_3P]NiBr_2\}_2,$$

and another one melting at 98 to 102°C, the formula of which is probably:

$$\{[(C_6H_5)_3P]_3NiBr_2\}_2$$

Corresponding mercury and cadmium compounds have been known for a considerable time.[10]

All these compounds are, so to speak, members of a series, and it may be assumed that one compound can be generated from any other one under the conditions of acrylic ester synthesis, or that there is at least formation of an equilibrium such as:

$$\underset{\text{(1a)}}{[(C_6H_5)_3P]_2NiBr_2} + \underset{\text{(2a)}}{[(C_6H_5)_3P]NiBr_2} \quad \text{(7)}$$

$$\downarrow \text{ 150–160°C, 30 atm, mixed gas } \uparrow$$

$$\underset{\text{(3a)}}{[(C_6H_5)_3P]_3(NiBr_2)_2}$$

The unsaturated stages (2a) and (3a) will add carbon monoxide in the presence of mixed gas and form the stable compound (1a), adding carbon monoxide or butyl bromide instead of the missing triphenylphosphine. If carbon monoxide is added to such an unsaturated state, it becomes richer in energy and is unstable in the next complex, which can be expressed in the following formula:

$$[(C_6H_5)_3P]NiBr_2 \xrightarrow{(C_6H_5)_3P} [(C_6H_5)_3P]_2NiBr_2 \text{ [stable (1a)]} \quad \text{(8)}$$

$$[(C_6H_5)_3P]NiBr_2 \xrightarrow{CO} [(C_6H_5)_3P](CO)NiBr_2 \text{ [unstable]}$$

$$[(C_6H_5)_3P]NiBr_2 \xrightarrow{C_4H_9Br} [(C_6H_5)_3P](C_4H_9Br)NiBr_2 \text{ [unstable]}$$

Theoretically, it should be possible to replace all triphenylphosphine radicals of a nickel bromide complex by carbon monoxide, and a pure nickel bromide carbon monoxide complex should be obtained:

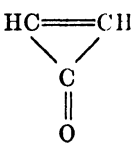
$$[(C_6H_5)_3P]_2NiBr_2 + 2CO \rightarrow (CO)_2NiBr_2 + 2(C_6H_5)_3P$$

It is very likely that such intermediates occurred in acrylic acid ester synthesis with nickel bromide catalysts, especially since stable cobalt-carbon monoxide-iodine compounds were isolated by H. Hieber. In alcoholic solution solvates probably exist with alcohol molecules. In acrylic ester synthesis from butanol, carbon monoxide and acetylene, the compound $Ni(C_4H_9OH)_4(CO)_2Br_2$ may be present. The solvated compound $[Ni(C_4H_9OH)_4]Br_2$ was isolated.

[10] Evans, Frederic, Mann, Peizer, Purdie, *J. Chem. Soc.*, **1940**, 1209.

Not only unstable intermediates but also nickel carbonyl will frequently be formed at the end. This explains the large quantity of nickel carbonyl which appears if nickel bromide is the only catalyst used, and the temperature is kept below 180°C. This disadvantage is absent if triphenylphosphine stabilized active intermediates of nickel bromide are used because there is generally no formation of free nickel carbonyl and no decomposition of the effective nickel catalysts. If nickel carbonyl should be formed, the interfering side reaction is stopped immediately by reformation of an active nickel bromide compound with the release of carbon monoxide [(4) and (6)]. With phosphine catalysts and butyl bromide, some nickel carbonyl was formed only at the start of the experiments.

With other nickel catalysts, such as nickel bromide between 150 and 160°C, there is usually formation of much nickel carbonyl because equilibrium is far on the left side of the equation $Ni(CO)_4 \rightarrow Ni + 4CO$ at this temperature and pressure The discharge from the reactors did not smell of nickel carbonyl in the triphenyl phosphine experiments. Acrylic ester formation must therefore be attributed to carbon monoxide activation; the activated carbon monoxide undergoes cyclization together with the acetylene, thus forming the 3-membered ring cyclopropenone, which has been discussed by Reppe and which reacts with the alcohol to yield acrylic esters.



The phosphine compounds have the advantage of precipitating quantitatively when unreacted alcohol and acrylic ester are distilled off. They may be separated by filtration at low temperatures and reused with new alcohol-butyl bromide mixtures. They are therefore ideal catalysts which are permanently effective without becoming exhausted. Their life depends on how the reaction is carried out. In the presence of slightly acid butyl bromide, much iron (2 per cent) may dissolve due to corrosion (iron bromide). Triphenylphosphine will combine, forming iron complexes which have a damaging effect upon the catalyst in long runs.

It should also be noted that active nickel compounds which are able to add carbon monoxide or acetylene can also be formed if the valency of nickel changes from the bivalent to the univalent stage by reduction. Univalent nickel compounds have a general tendency to add carbon monoxide and acetylene. If one assumes that the change of valency occurs with special readiness in triphenylphosphine nickel compounds in alcoholic

solution and in the presence of acetylene and carbon monoxide under pressure, then the formation of univalent nickel compounds is obvious. The red color of the compound obtained from triphenylphosphine and nickel bromide at 320°C proves that these nickel compounds exist since red nickel compounds almost always contain monovalent nickel. This does not interfere with the above-described conceptions. The extent of reaction between alcohol and the applied nickel compound is still to be investigated. One may recall the decomposition of substance C (triphenylphosphine nickel bromide-butyl bromide) by methanol, and former experiments to produce solvates of nickel bromide. It would be useful to study closely these reactions of phosphine-nickel halide compounds which could only partly be realized by experiment and which will be of importance for questions in catalytic chemistry in general.

The following schematic representation for the role of triphenyl phosphine-nickel halide catalysts in the synthesis of acrylic esters from acetylene and carbon monoxide is indicated:

$$2[(C_6H_5)_3P]_2(NiBr_2)C_4H_9Br \xrightarrow{C_4H_9Br}$$

Substance C

$$[(C_6H_5)_3P]_3(NiBr_2)_2\ C_4H_9Br + [(C_6H_5)_3P]\cdot C_4H_9Br$$

$$[(C_6H_5)_3P]_3(NiBr_2)_2\ C_4H_9Br + CO \longrightarrow [(C_6H_5)_3P]_3(CO)\cdot(NiBr_2)_2\ C_4H_9Br$$

$$[(C_6H_5)_3P]_3(CO)(NiBr_2)_2\ C_4H_9Br + (C_6H_5)_3P\cdot C_4H_9Br \xrightarrow[HC\equiv CH]{ROH}$$

$$H_2C{=}CH{-}COOR + 2[(C_6H_5)_3P]_2NiBr_2\cdot C_4H_9Br$$

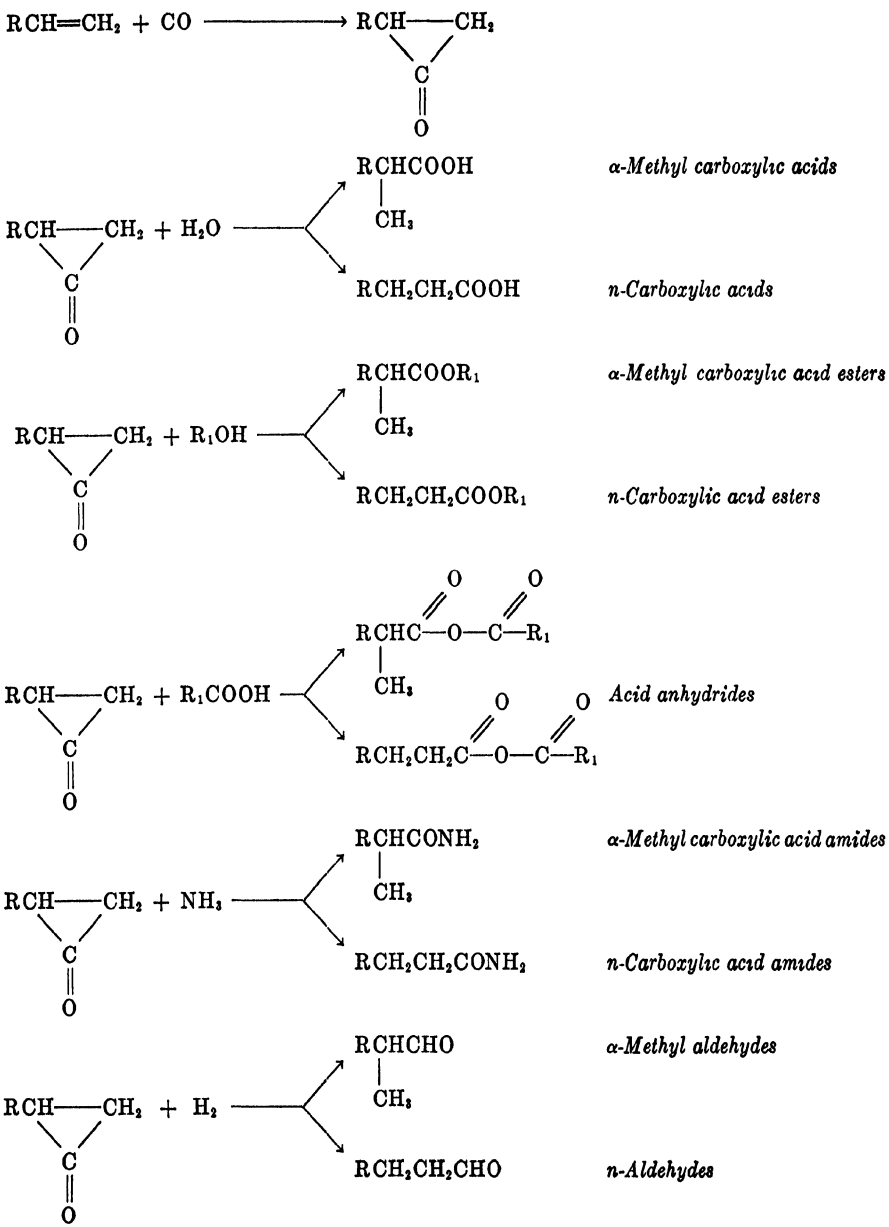
Substance C

Other triphenyl phosphine complexes. A handwritten list of other triphenyl phosphine-metal carbonyl and triphenyl phosphine-metal salt complexes was found attached to the above report. It is not clear whether these complexes had been prepared and tested as catalysts or whether they were simply possibilities for future work In view of this uncertainty, they are not presented here but, as a matter of record, are listed on page 297.

Synthesis of Saturated Carboxylic Acids and Their Derivatives from Olefins and Olefinic Compounds

Reppe tried immediately to transfer the new knowledge gained from his experience with acetylene and carbon monoxide to olefinic compounds. It was expected that carbon monoxide would add to the olefinic double bond, forming the intermediate hypothetical cyclopropanone ring. This should then react with active hydrogen atoms, *e.g.*, with water, alcohols, amines, mercaptans, etc., to give aliphatic carboxylic acids, esters, amides,

thioesters, etc. Reppe could, in fact, realize all the reactions which would be anticipated on account of this theory, as the following formulas show:



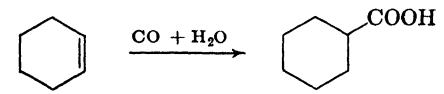
Actual reactions prove that splitting of the cyclopropanone ring occurs in both possible ways, and straight-chain compounds as well as alpha-methyl substituted compounds are obtained. With olefins, just as with

acetylene, various reaction possibilities can be realized by use of stoichiometric quantities of metal carbonyls and acid, or by catalytic methods.

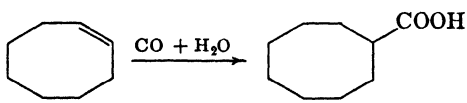
Synthesis of Carboxylic Acids from Olefins, Carbon Monoxide and Water. The synthesis of carboxylic acids from olefins, carbon monoxide, and water can be carried out very smoothly with carbonyl-forming metals or nickel carbonyl catalysts at 200 to 300°C under 150 to 300 atm. For example, Carpenter[11] states that the reaction may be carried out as follows: a reactor is charged with one liter of catalyst made by depositing nickel from nickel carbonyl at 200°C on silica gel. The reactor was then charged with a mixture of C_{12} to C_{16} olefins containing 80 to 90 per cent of total olefins. The reaction temperature is 180°C, and a mixture of carbon monoxide and steam is circulated through the reactor. Conversion and yield are approximately 100 per cent.

The reaction works with both the lower olefins like ethylene, propylene and butylene, and the higher, and even the highest members of this series with 5 to 25 carbon atoms, as long as the olefins contain a terminal double bond. However, the conversion of the lower olefins such as ethylene, propylene, and butylene is considerably slower than that of the higher olefins. Furthermore, the lower aliphatic acids in the presence of nickel carbonyl presented very serious corrosion problems which apparently had not been solved in Germany during the war years; hence, little progress had been made towards commercial installations of this process.

In a similar way, carboxylic acids can be obtained from cyclic olefins, carbon monoxide and water. Cyclohexene gives hexahydrobenzoic acid, and cyclooctene gives cyclooctylcarboxylic acid.



Hexahydrobenzoic acid



Cyclooctylcarboxylic acid

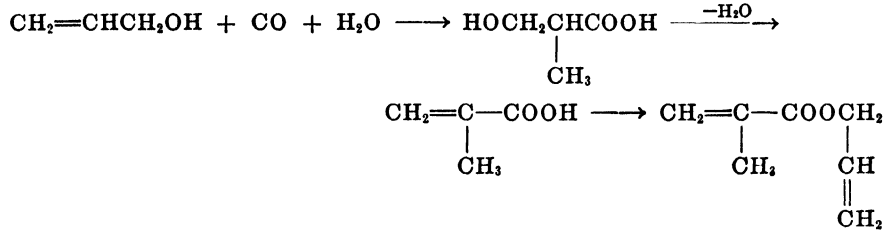
Diolefins also react, although not simply; butadiene undergoes cyclization to vinyl cyclohexene, which then reacts to form a mixture of isomeric mono- and dicarboxylic acids.

Many unsaturated compounds such as olefinic mono- and polyalcohols, olefinic carboxylic acids, and unsaturated ketones also react with carbon monoxide and water under the influence of metal carbonyls with the introduction of a carboxylic group.[12] Allyl alcohol adds carbon monoxide and

[11] *PB* 58447 (*FIAT* 933).

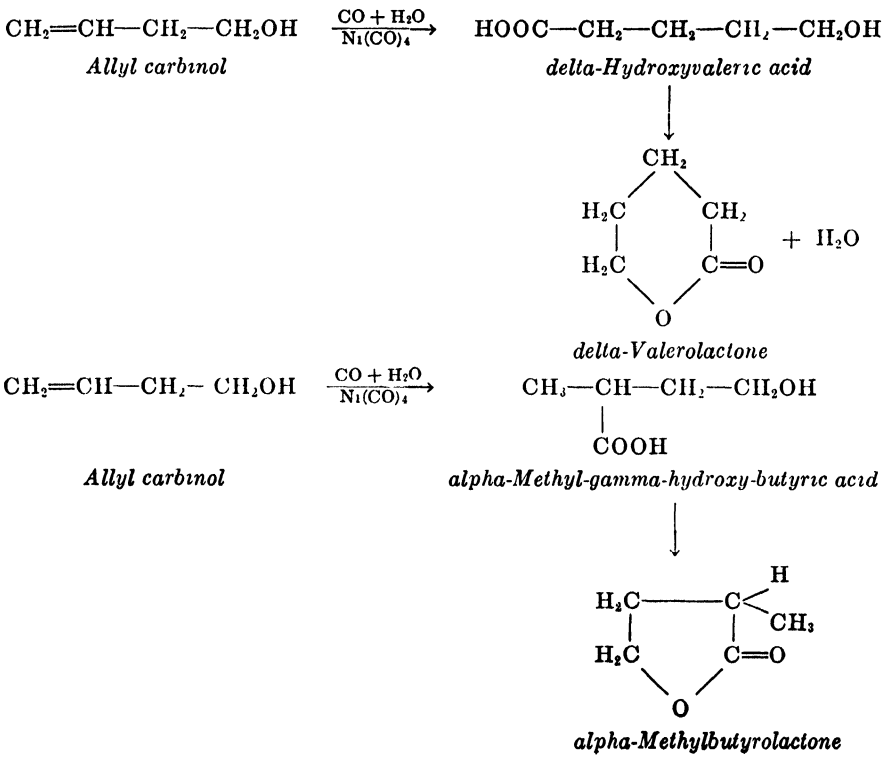
[12] I.G. Farbenindustrie patent proposal *O.Z.-14,216*.

water, producing beta-hydroxy isobutyric acid which is dehydrated to methacrylic acid during the reaction; part of the methacrylic acid is esterified by the allyl alcohol, while part apparently dimerizes:



A mixture of 115 parts of allyl alcohol, 30 parts of water and 60 parts of nickel carbonyl were heated in a pressure vessel at 170°C for 16 hours under a carbon monoxide pressure of 50 atm. The reaction product consisted primarily of the allyl ester of methacrylic acid together with some dimeric methacrylic acid.

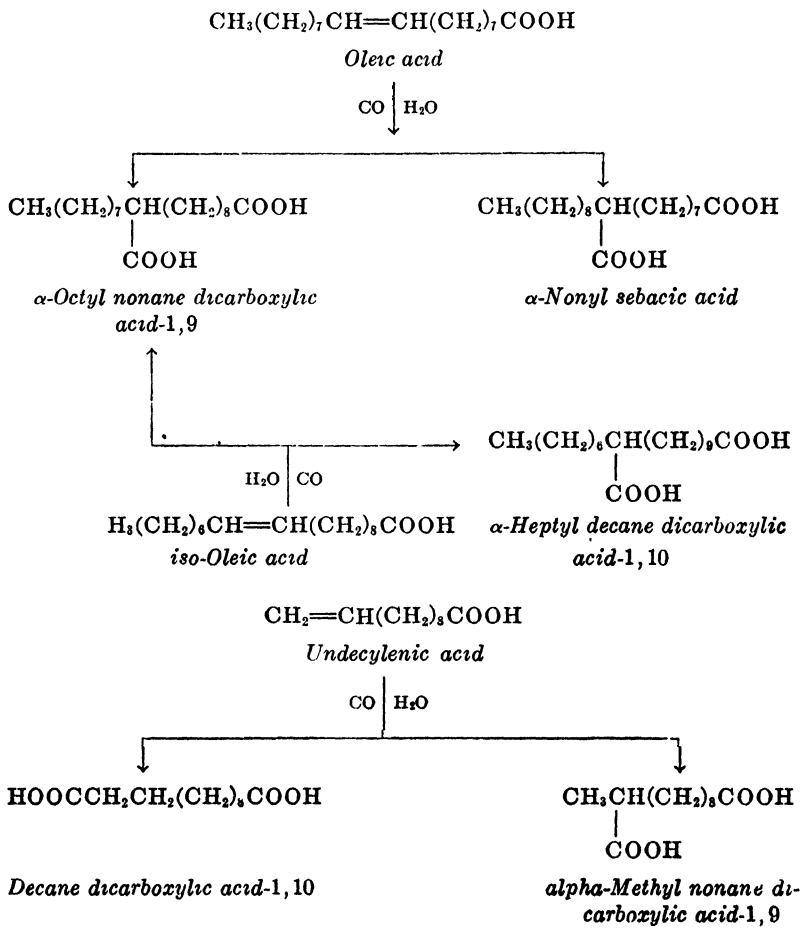
Allyl carbinol, carbon monoxide, and water give primarily the unstable hydroxy acids, alpha-methyl-gamma-hydroxybutyric acid and delta-hydroxyvaleric acid, which readily form alpha-methyl-butyrolactone and delta-valerolactone:



300 parts of allyl carbinol, 75 of water, and 60 of nickel carbonyl were heated for 16 hours at 270°C. The reaction product contained 45 per cent of alpha-methyl butyrolactone, about 5 per cent of delta-valerolactone, and the remainder unchanged allyl carbinol.

In the presence of about 1.5 per cent of added nickel iodide, the yield of alpha-methyl butyrolactone was 64 per cent and of delta-valerolactone, 20 per cent. Using 3 per cent of bismuth hydroxide in place of the nickel iodide, the yield was 64 per cent alpha-methyl butyrolactone and about 10 per cent delta-valerolactone.

Study of the behavior of olefinic carboxylic acids toward carbon monoxide and water, or other compounds with active hydrogen atoms, was of great interest. Reppe succeeded in adding carbon monoxide and water to oleic acid and to undecylenic acid, and obtained valuable dicarboxylic acids which may prove to be useful for the manufacture of polyamides, plasticizers, etc. The reactions were formulated in the following manner:



These reactions were carried out as follows: A mixture of 14 parts of oleic acid, 3.6 of water, 4 of nickel carbonyl and 0.5 of nickel iodide was heated for 18 hours at 270°C under 200 atm of carbon monoxide to give an 80 per cent yield of nonodecane dicarboxylic acids.

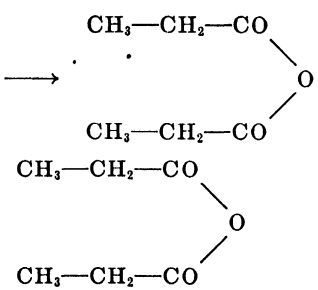
A mixture of 18.4 parts of undecylenic acid, 61 of nickel carbonyl and 36 of water were heated for 15 hours at 170°C in a pressure vessel. At 53 per cent conversion, the yield of dodecanedicarboxylic acids was essentially 100 per cent.

If desired, the reaction could be carried out with the ester of the unsaturated acid in the presence of an alcohol to produce the diester of the dibasic acid, for example: A mixture of 9 parts of methyl undecylenate 3.7 of ethanol, 10 of nickel powder and 3 of cupric iodide was heated at 270°C for 16 hours under 200 atm of carbon monoxide pressure. The reaction product contained 73 per cent of the diethyl ester of dodecane dicarboxylic acid. The conversion was 66 per cent, the yield quantitative.

It is also claimed that by carrying out the reaction of nickel carbonyl with unsaturated acids in the presence of ammonia or formamide, the diamide of the dicarboxylic acid results. Thus undecylenic acid and ammonia or formamide in the presence of nickel carbonyl at 270° and 200 atm of carbon monoxide pressure gave the diamide of dodecane dicarboxylic acid.

The synthesis of carboxylic acid anhydrides under the influence of nickel carbonyl is of great potential importance. In a single cycle from ethylene, carbon monoxide and water, it is possible to prepare propionic acid anhydride, which is used in the production of cellulose propionate. The formation of propionic acid and its anhydride from ethylene may be formulated.

(1) $H_2C{=}CH_2 + CO + H_2O \longrightarrow CH_3{-}CH_2{-}COOH$

(2) $H_2C{=}CH_2 + CO + CH_3{-}CH_2{-}COOH \longrightarrow$ 

$2\,H_2C{=}CH_2 + 2\,CO + H_2O \longrightarrow$

It is interesting to note that a paper by Mailhe describes the reverse of reaction (2); that is, the splitting of acid anhydrides to olefins, carbon monoxide and carboxylic acids under the influence of finely divided nickel catalysts.[18]

Properties of the Fatty Acids Produced. Based upon the boiling point, the constitution of the fatty acids produced from the carboxylation of

[18] *Bull. soc. chim.* (4), **5**, 815–9 (1909).

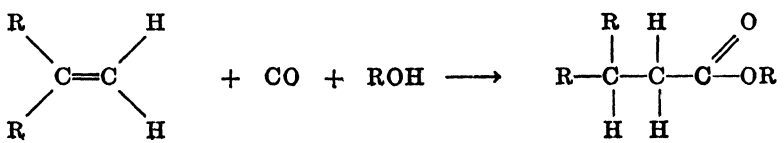
olefins was assumed to be that of alpha-methyl carboxylic acids. The fatty acids from octadecylene consisted of a liquid and a solid part (composition and physical constants of the liquid and solid acids are identical). It was difficult to decide whether this fact was due to the starting material, or whether it must be attributed to the formation of isomeric compounds from olefins, due to migration of the double bond under the reaction conditions. The esters of the synthetic fatty acids, especially of the liquid acids, are hard to hydrolyze. The melting point of solid methyl stearic acid mixed with an acid synthesized from cetylbromide via methyl malonic acid ester was unchanged. The ketone obtained by distillation of the nickel, or thallium salt of the acid from octylene is not identical with the ketone obtained from the synthetic acid in the same way. However, since a uniform acid is not formed in the synthesis, it is uncertain which one of the ketones has been isolated by crystallization.

Properties of Soaps from Synthetic Fatty Acids. Soda and potash soaps can be manufactured from methyl-substituted fatty acids in the usual way. These soaps are softer than soaps from natural fatty acids of the same molecular weight. They are stated to be superior to soaps from natural fatty acids with regard to solubility, ability to lather, and plasticizing ability for rayon. The decreased hardness will be found advantageous in milling the soaps.

Alcohol sulfonates prepared from the alcohols obtained by hydrogenation of these fatty acids are also claimed to have properties superior to those of the straight-chain alcohols.

Higher olefins are cheap only in low percentage mixtures with paraffins; consequently, synthesis of carboxylic acids from such mixtures, carbon monoxide, and water is a convenient way to produce fatty acids and their corresponding alcohols in pure form. Obviously, the paraffin can easily be separated if the fatty acids are converted into soaps. The acids may be subjected to distillation and purification by fractionation, after which they are hydrogenated to alcohols which serve as starting materials for the manufacture of detergents.

Synthesis of Carboxylic Acid Esters from Carbon Monoxide, Olefins and Alcohols. The reaction of a low molecular weight olefin with carbon monoxide and water in the presence of a carbonyl-forming metal or a metal carbonyl is frequently slow, and the carboxylic acid produced also causes difficulty due to corrosion. It was thought possible that the replacement of the water by an alcohol might lead to an improved reaction which would produce the carboxylic acid ester as shown in the formula:



The yields of esters obtained in the first experiments were much more favorable than those published in the prior patents; hence, it was hoped that after a thorough study of the reaction, preliminary results might be improved upon and a useful technical procedure developed. Patent applications[14] covering the reaction of olefins with stoichiometric amounts of nickel carbonyl as well as the catalyzed reaction of carbon monoxide, alcohols and olefins were submitted.

U. S. Patent 1,979,717 which claims poorer results with quite different catalysts and under much less advantageous conditions (pressure 700 atm, 300°C) is stated to anticipate these patent applications.*

The authors have not found it possible to correlate or evaluate satisfactorily the results of the scattered laboratory records which they have seen describing the results of this phase of carbon monoxide chemistry. Apparently, the work for the most part had not progressed beyond the exploratory laboratory scale. It is not clear whether this status was the result of incomplete research, lack of time, or corrosion difficulties.

The pertinent observations noted which relate to the synthesis of esters from alcohols and olefins by reaction with metal carbonyls or by catalytic reaction with carbon monoxide are as follows:

Catalysts. Nickel carbonyl alone does not react with olefins in the presence of alcohols. However, in the presence of halogens, particularly iodine, good yields of esters can be obtained. Metals capable of forming carbonyls are not catalysts for the reaction of carbon monoxide with olefins and alcohols. However, cobalt activated with other metals was somewhat more active and gave up to 20 per cent of ester.

The halides of carbonyl-forming metals, particularly cobalt and nickel, are catalysts for the reaction. The reactivity increases from fluorides (no reactivity) to chlorides (poor, up to 30 per cent yields), to bromides (poor), to iodides (73 per cent yields). Salts other than halides are ineffective. Halides of other carbonyl-forming metals ($MoCl_5$, MoI_2, $CrCl_3$, WCl_4, WO_2Cl_2, etc.) gave no yields or very poor yields. Halides of non-carbonyl-forming metals had little or no activity.

The addition of carbon monoxide and an alcohol to an olefin in the presence of a metal halide is a catalytic reaction as shown by the fact that 0.16 mole per cent of nickel iodide gave a 58 per cent yield of ester. It is not known definitely that nickel carbonyl occurs as an intermediate; whether a compound ($NiI_2 \cdot CO$) exists which splits off activated carbon monoxide and is continuously regenerated was not determined.

[14] I G Farbenindustrie patent proposals *O Z.-12,304* and *O Z -12,060.*

* Reppe, in one of his papers, lists numerous patents issued to such companies as DuPont, I C. I., Celanese, etc., which disclose the synthesis of carboxylic acids or derivatives thereof by reaction of carbon monoxide with olefins or alcohols, but states that he did not consider it possible to develop them into technically feasible processes. The reader will, of course, recognize that certain of the above-mentioned companies have successfully operated such processes.

A combination of metallic nickel with heavy metal halides (preferably iodides, *e.g.* silver or cupric iodide) gave olefin conversions up to 90 per cent of theoretical. For higher olefins such as octadecylene, a combination of nickel stearate and a heavy metal halide was apparently the preferred catalyst.

Reactivity of Various Alcohols and of Ammonia. Methanol generally gives poor conversion; the maximum yield of methyl ester was 52 per cent; dimethyl ether and acetic acid are usually formed as by-products. Ethanol, propanol, and butanol react more readily; while octyl alcohol and phenol react less readily. Ammonia instead of alcohol does not form the carboxylic amide.

Reactivity of Olefins. Butylene, octylene, dodecylene, octadecylene, cracked olefins, and synthetic olefins from the hydrogenation of carbon monoxide were also used. The lower olefins react with greater difficulty than do the higher olefins, octylene and octadecylene. Butylene did not react with metal iodide catalysts.

Course of the Reaction. A number of reactions are possible under the conditions shown below:

Chief Reaction

(I) $R{-}CH{=}CH_2 + C_2H_5OH + CO \longrightarrow$

$$R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOC_2H_5 \text{ or } RCH_2CH_2COOC_2H_5$$

Side Reactions

(II) $$C_2H_5OH \longrightarrow C_2H_5COOH$$

(III) $$C_2H_5OH + C_2H_5COOH \longrightarrow C_2H_5{-}COOC_2H_5 + H_2O$$

(IV) $$R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOC_2H_5 + C_2H_5COOH \rightarrow C_2H_5{-}COOC_2H_5 + R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$$

(V) $$R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOC_2H_5 + H_2O \longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH + C_2H_5OH$$

(VI) $$R{-}CH{=}CH_2 + H_2O + CO \longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$$

(VII) $$2\ C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$$

(VIII) $$C_2H_5OC_2H_5 + CO \longrightarrow C_2H_5{-}COOC_2H_5$$

(IX) $$C_2H_5OH \longrightarrow CH_2{=}CH_2 + H_2O$$

(X) $$CH_2{=}CH_2 + H_2O + CO \longrightarrow C_2H_5COOH$$

(XI) $$C_2H_5OH \longrightarrow CH_3CHO + H_2$$

Reactions (II) and (III) depend upon the type and quantity of iodide used, time of reaction and temperature. Ester interchange between fatty acid ester and free propionic acid leads to the formation of free fatty acid (IV). The formation of fatty acid from olefin and water (VI) which comes from the formation of esters, ethers, or olefins (III, VII, IX) is of minor importance only. The same holds true for the hydrolysis of esters with water, which will be a subject of closer study (V). The formation of ethers (VII) was especially observed with methanol, and under suitable conditions, with butanol and ethanol. Butylene and ethylene were found also (IX) as was acetaldehyde (XI) by dehydrogenation of alcohol. The presence of acetaldehyde does not interfere with the reaction.

Synthesis of Acetic Acid from Methanol and Carbon Monoxide. The synthesis of acetic acid by the high-temperature high-pressure reaction of methanol and carbon monoxide has been the subject of many patents As catalysts for the reaction, phosphoric acid, phosphates, activated carbon, heavy metal salts such as zinc and cuprous chlorides, oxides and silicates of chromium, molybdenum, tungsten, uranium, oxides of thorium, zirconium, titanium, aluminum, and magnesium, and boron fluoride have been suggested.

In the synthesis of fatty acid esters by the reaction of olefins with carbon monoxide and an alcohol in the presence of metal carbonyls, large quantities of carboxylic acids having one carbon more than the alcohol used were often isolated; in some cases, as much as 40 to 45 per cent of the alcohol charged might be converted to the carboxylic acid or its ester. It was obvious, therefore, that the metal carbonyls, or metals capable of forming carbonyls in the presence of carbon monoxide, were also catalysts for the reaction of an alcohol with carbon monoxide.

$$ROH + CO \rightarrow RCOOH$$

An extensive investigation of the synthesis of acetic acid from the reaction of carbon monoxide with methanol was carried out. The results of this research indicated: The formation of acetic acid from methanol and carbon monoxide is an endothermic reaction which is favored by high pressure. All experiments were done under a total pressure of 200 to 300 atm and a partial pressure of methanol of 80 to 120 atm. The temperature

range of the reaction is between 260 and 360°C, and the most advantageous range is between 270 and 290°C. The carbonyl-forming metals, especially nickel, iron, and cobalt, showed satisfactory catalytic activity when used in conjunction with metal halides or free halogens. The activity of the metals decreases in the order nickel, iron, cobalt; the activity of the halogens, in the order iodine, bromine, chlorine.

The best catalysts in the batch experiments were nickel iodide, Raney nickel, or nickel gravel with cuprous iodide, either free or on catalyst supports. A conversion of 70 to 82 per cent total acetic acid with 50 to 77 per cent free acetic acid was obtained. Cuprous iodide, however, is not stable as a catalyst. The use of copper-nickel alloys in combination with cuprous iodide did not prove advantageous.

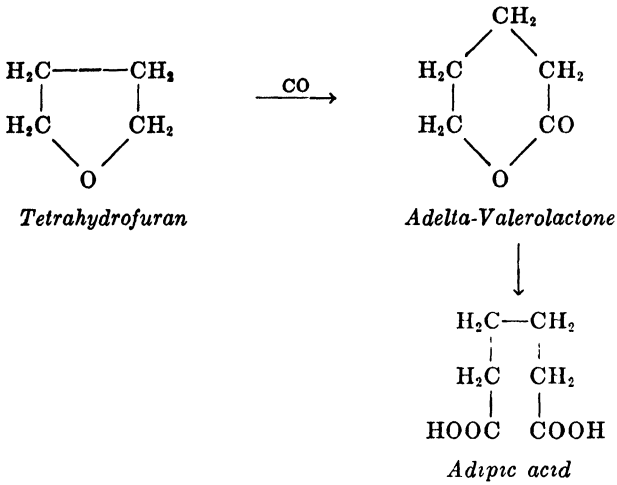
The catalytic action of cuprous iodide can be explained by continuous cleavage, releasing free iodine which is effective in the catalytic reaction. Part of this iodine is afterward found as nickelous iodide, which is dissolved in the acetic acid, and part on the copper walls of the reactor, where it is precipitated as difficultly soluble cupric iodide. It therefore lasts only a limited time in a continuous process. The quantity of iodine which is withdrawn in solution is 1 kg per 1000 kg of methanol throughput. In a continuous process, therefore, it would be necessary to replace the iodine continuously by addition to the feed of small amounts of iodine in the form of soluble iodine salts or hydriodic acid.

An undesired side reaction in acetic acid synthesis is the formation of dimethyl ether which occurs chiefly in silver autoclaves, whereas this reaction is very limited in copper and V4A autoclaves unless chlorides are used. Experiments to produce acetic acid by way of the dimethyl ether stage give exceedingly poor yields consisting chiefly of the ester. Phenols and aromatic ethers do not react.

Sufficient data are not available, at least to the authors, to permit an appraisal of the final conclusions arrived at by the German chemists. Great difficulty due to the corrosive nature of the reactants and reaction products was experienced; ordinary autoclaves of various stainless steels were so badly corroded after a few experiments that the contents of the autoclave sometimes solidified due to formation of the metal acetates. Copper was more corrosion-resistant than the ferrous alloys, but required the use of higher temperatures to obtain satisfactory results. Tantalum-lined autoclaves were apparently satisfactory, but not readily available in a wartime economy such as Germany's.

Synthesis of Acids and Lactones from Cyclic Ethers. It is comparatively easy to introduce carbon monoxide into aliphatic and particularly cyclic ethers with the aid of metal carbonyls, especially of nickel carbonyl, in the presence of halogen. Reppe was interested primarily in the con-

version of cheap tetrahydrofuran to adipic acid according to the following reaction:



Tetrahydrofuran *Adelta-Valerolactone* *Adipic acid*

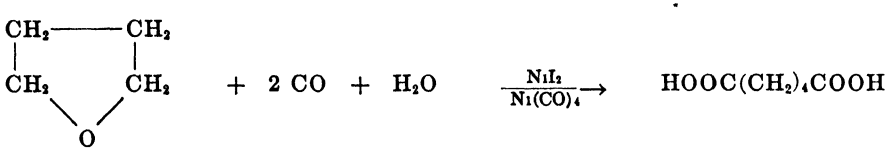
Reppe claims that this synthesis is the cheapest and simplest way to produce adipic acid in good yield in a single cycle. Adipic acid which is an important starting material for polyamides thus can be produced on a large scale without using phenol. If suitable catalysts are chosen, it is possible to add only one mole of carbon monoxide to tetrahydrofuran and to stop the reaction at delta-valerolactone. This lactone can easily be converted into epsilon-caprolactam, which is important for polyamide synthesis. Tetrahydropyran may be converted in a similar way into pimelic acid.

The diols which are the precursors of the cyclic ethers, *e.g.*, butanediol-1,4 and pentanediol-1,5, also undergo the reaction. Suberic acid can be made from hexanediol-1,6 and higher diols behave accordingly.

Reaction of Carbon Monoxide with Tetrahydrofuran

Nickel Catalysts[15]

The reaction of carbon monoxide with tetrahydrofuran at 270° and 200 atm in the presence of nickel iodide as a catalyst and nickel carbonyl as the carbon monoxide carrier gave 80 per cent yields of adipic acid.



The reactor, constructed of steel and lined with platinum to resist corrosion, is 70 mm in diameter and 3 meters high. An overflow is located

[15] *PB* 25655 (*BIOS* 351).

approximately 2.5 meters from the bottom so the liquid volume is about 7 liters.

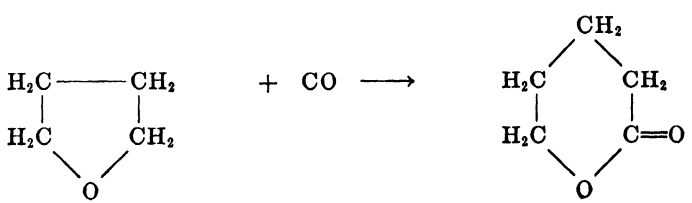
The reactor is first filled with molten adipic acid at 270°C. A mixture of 93 per cent by weight of tetrahydrofuran and 7 per cent nickel carbonyl is pumped at a rate of 7 to 14 liters per 24 hours to the base of the reactor where it meets two other liquid streams: (1) catalyst solution, a concentrated solution of nickel iodide in water, fed at such a rate that nickel iodide amounts to 1 per cent on the tetrahydrofuran and (2) recycle condensate. Carbon monoxide is pumped in to maintain a pressure of 200 atm.

Under steady conditions, the liquid overflowing consists of 80 per cent adipic acid, 5 per cent delta-valerolactone and 15 per cent valeric acid with a small amount of tetrahydrofuran and all the nickel iodide. The vapors above the overflow consist of carbon monoxide saturated with tetrahydrofuran, water and nickel carbonyl, and are recycled.

The procedure for working up the reaction product is not available. Although Reppe claims that this is the cheapest method for the preparation of adipic acid, it is not evident that the work in Germany had been carried past the scale detailed here.

Cobalt Catalysts

In the search for catalysts for the reaction of carbon monoxide with tetrahydrofuran, it was found that this reaction can be accomplished with cobalt catalysts at temperatures between 140 and 200°C. The course of the reaction, however, differs from the synthesis of adipic acid by the reaction of carbon monoxide with tetrahydrofuran in the presence of nickel catalysts and water. In the presence of cobalt catalysts only one molecule of carbon monoxide reacts with the tetrahydrofuran, with the formation of delta-valerolactone:



The action of water gas upon tetrahydrofuran in the presence of cobalt catalysts gave delta-valerolactone in yields of approximately 40 per cent. It was hoped that this substance could be obtained in higher yield when using pure carbon monoxide because one mole of tetrahydrofuran with one mole of carbon monoxide should, according to the equation above, give delta-valerolactone without hydrogen in the reaction. The reaction using carbon monoxide yielded delta-valerolactone in 80 per cent of theoretical yield. Conversion took place very slowly, however, and could not be sub-

stantially improved by activators. This slow conversion was not caused by the fact that the catalyst was spent or that the reaction was inhibited, as proved by stopping the experiments from time to time and analyzing the contents of the autoclave. Sixteen per cent of tetrahydrofuran had been converted after 18 hours; 34 per cent after 36 hours.

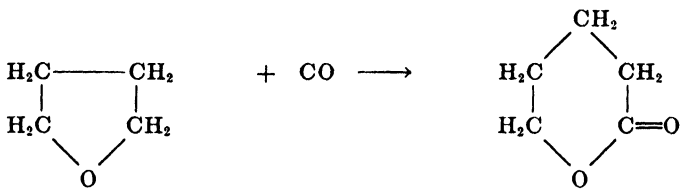
Process Description. Fifty parts of siliceous catalyst containing 13.2 per cent of cobalt (from cobalt nitrate) and 0.7 per cent of tin oxide were reacted with a mixture of 200 parts of tetrahydrofuran and 50 of water under 200 atm of carbon monoxide pressure for 18 hours at 160°C. Slow absorption of carbon monoxide (66 atm) was observed. The reaction product was a liquid, colored dark brown by cobalt carbonyl. It was worked up by adding caustic potash solution and heating one hour in a water bath, the carbonyl decomposing to cobalt hydroxide, which was filtered off. The filtrate was now acidified with sulfuric acid (decomposing the last traces of cobalt carbonyl hydride) and extracted with ether for 24 hours. The ether extract was concentrated and distilled under vacuum; thus 51 g of 76 per cent delta-valerolactone, or 39 g of pure delta-valerolactone and 12 g of by-products were obtained from 200 g of tetrahydrofuran. No contamination of the delta-valerolactone by other isomeric lactones was found.

Catalysts, Activators, and Quantity of Catalysts. Suitable catalysts are cobalt salts of weak acids, as well as finely divided cobalt metal (*e.g.*, by reduction of cobalt carbonate) or cobalt precipitated on supports. It is likely that the real catalyst is cobalt carbonyl or cobalt carbonyl hydride formed therefrom. Reactions with pure cobalt catalyst proceed slowly, hence, numerous experiments were carried out in a search for other activators.

Pronounced acceleration was not observed with additions of various metals or of their oxides or sulfides Variation of the pH did not accelerate the rate of the reaction; the addition of weak acids, such as carbonic acid, acetic acid or higher fatty acids, had no noticeable influence. The addition of mineral acids considerably decreased the conversion and in high concentration entirely checked the reaction. The addition of strong caustic also stopped the reaction. It was surprising that the addition of a small quantity of a weak hydroxide, such as calcium hydroxide or mercuric hydroxide, allowed some conversion, but considerable adipic acid was isolated from the converted component (up to 34 per cent).

The quantity of catalyst needed for the reaction is approximately 5 per cent of cobalt metal calculated on the quantity of tetrahydrofuran used. If this concentration is decreased, the rate of the reaction is decreased considerably. It was found, however, that a very low cobalt concentration decreased side reactions and that exceptionally pure delta-valerolactone was obtained, though in small yield. The addition of halogen had no effect.

Influence of Water or Hydrogen upon the Reaction. As with the reaction to produce adipic acid, a considerable quantity of carbon dioxide was always found in the waste gases. Little hydrogen could be found, however. This means that cobalt catalysts and water convert carbon monoxide to carbon dioxide and hydrogen, and that the hydrogen is used up during the reaction. Experiments performed in complete absence of water gave practically no conversions, although no water is needed, according to the equation:



If, however, 50 parts per weight of water were added for 200 parts of tetrahydrofuran, high conversions were generally obtained, but the purity of delta-valerolactone was not more than 50 to 60 per cent.

If 100 to 200 parts of water were added for 200 parts of tetrahydrofuran, conversion became considerably smaller, but the purity of the delta-valerolactone improved considerably (up to 80 per cent). Analysis of the waste gas in these experiments showed that the quantity of hydrogen and of carbon dioxide was the same, that is, no consumption of hydrogen had taken place. It had, evidently, not been used up for side reactions, as was shown by the purity of the delta-valerolactone formed. Increasing the water beyond the proportion tetrahydrofuran:water 1:1 gave no conversion.

The by-products of the reaction are complicated and can be characterized only with difficulty. The only well-defined by-product was a small quantity of adipic acid which was found regularly. The other by-products are similar to those obtained as chief products from the reaction of carbon monoxide and hydrogen with cobalt catalysts although they are formed in considerably smaller quantity (diols of various composition, hydroxy methyl tetrahydropyran). There are, in addition, some very high-boiling substances which are most probably polyesters and polymeric delta-valerolactones. These high-boiling compounds have the properties of factice (a rubber-like vulcanized oil similar to art gum) and proved to be very good substitutes for it.

Addition of Foreign Gases; Gas Pressure. In view of these data, activation of the reaction by a slight addition of hydrogen was tried. This experiment failed completely; nor could the reaction be accelerated by the use of cobalt carbonyl hydride. It seems that hydrogen, which is intermediately liberated during the conversion, is used up *in statu nascendi* but that a partial pressure of small amounts of molecular hydrogen is not

sufficient to cause reaction. The addition of carbon dioxide likewise had no effect.

When the pressure of carbon monoxide was increased to 300 atm, conversion was increased. It is likely that even higher pressures would be helpful.

Valerolactone from Butanediol-1,4

delta-Valerolactone can also be obtained if butanediol-1,4 is used instead of tetrahydrofuran. Conversions are much poorer, however, than with tetrahydrofuran.

Conversion of delta-Valerolactone to Adipic Acid

Experiments to convert delta-valerolactone to adipic acid in the presence of cobalt catalysts were performed under various conditions and with many catalysts. The reaction can be effected with cobalt catalysts; the best experiment succeeded in converting 44 per cent of the delta-valerolactone to adipic acid. Halogens, especially iodine, had no influence.

Oxo Process[16]

Introduction

The reaction of olefins with water gas in the presence of a Fischer-Tropsch type catalyst to give aldehydes according to the general equation

$$>C{=}C<\ +\ CO\ +\ H \longrightarrow -C-\overset{H}{\underset{|}{C}}-C{=}O$$

is now commonly known as the Oxo process. The aldehydes initially produced are hydrogenated to alcohols in a subsequent step.

The fundamental oxo reaction was apparently first discovered, but not exploited, by Smith, Hawk, and Golden who observed the formation of oxygenated compounds when ethylene, carbon monoxide and hydrogen were passed over a cobalt catalyst at elevated temperatures and pressures.[17] In 1939, the reaction of olefins with carbon monoxide and hydrogen was under active investigation by Dr. O. Roelen of Ruhrchemie A. G. Reppe, while admitting that Ruhrchemie was the first to demonstrate the utility of this reaction, insisted that he would have inevitably discovered this reaction since it is only a special case of the general reaction between olefins, carbon monoxide and other components such as water, ammonia, etc. At the time of Ruhrchemie's work, Reppe had already observed the formation of alcohols by the direct action of metal carbonyls on olefins in the presence of bases. Later, he claimed credit for demonstrating that cobalt carbonyl was the true catalyst in the oxo reaction.

[16] *PB* 81383 (*FIAT* 1000).

[17] *J. Am. Chem. Soc.*, **52**, 3221 (1930).

The large-scale development of a continuous process resulted from a cooperative effort of Ruhrchemie and the I. G. Farbenindustrie. The Chemo-Gesselschaft was a development organization formed by these two companies on an equal participation basis. The process was later licensed to the operating company, the Oxo Gesellschaft, the license covering only olefins of 10 to 20 carbon atoms.

This operating company was to receive 35,000 tons per year of Fischer-Tropsch liquid (b.p. 175 to 310°C) containing 33 per cent olefin. Conversion of this material would furnish 10,000 tons per year of fatty alcohols which were to be converted to the alcohol sulfates for detergents. The mixed alcohols are claimed to be better raw materials for this purpose than the individual pure alcohols. Extensive research on the process was carried out at Leuna where a plant of 100-ton per month design capacity operated for 1½ to 2 years. The actual production was, however, only 40 to 50 tons per month because of shortage of the preferred raw material, "Kogasin." Leuna processed a certain amount of "Gelbol," an olefinic by-product of the higher alcohols process, to supplement their "Kogasin" supplies, but it was stated that this was an inferior raw material. The process details and design were not completely settled and the full-scale plant was never put into operation.

Process Conditions

The first stage of the process is carried out at about 200 atm of pressure and 150 to 160°C in liquid phase. Finely divided Fischer-Tropsch catalyst (cobalt-thoria) is suspended in the liquid feed in a concentration of 3 to 5 per cent by weight. Most of the catalyst is recycled and the make-up requirement is said to be very small. Normally, when using "Kogasin" as the olefinic feed, the reaction time required is of the order of 20 minutes. Lower olefins reacted very readily. In the case of low molecular weight olefins, they have to be used in solution in a liquid medium.

A number of side reactions occur in the oxo stage. Aldehydes polymerize to give "Dickol," which may amount to 20 per cent of the crude product. About one-third of the aldehydes initially formed are also hydrogenated to the corresponding alcohol. It is thus not practical to isolate aldehydes from the crude product obtained in the first stage of the process. If these products are required, it is considered preferable to complete the hydrogenation in the second step, separate the alcohols and oxidize them to the corresponding aldehydes.

This second step of hydrogenation, in addition to converting the aldehydes into alcohols, breaks down about 50 per cent of the "Dickol" to alcohols of the same composition as those derived from the corresponding aldehydes. The hydrogenation is hindered by the presence of carbon monoxide. It is, therefore, necessary to let down the crude product from the first oxo stage to atmospheric pressure and to carry out the hydrogena-

tion in a separate step at about 200 atm and 170 to 195°C. The same catalyst used in the first stage can be employed, or, alternatively, this catalyst can be filtered out of the first stage crude and replaced by the more readily available copper chromite. If the Fischer-Tropsch catalyst is employed, some carbon monoxide is formed in the hydrogenation reaction as a result of reduction of cobalt carbonyl In order to keep down the concentration of carbon monoxide in the circulating hydrogen, the exit gas is treated over an iron catalyst to convert carbon monoxide to methane. The methane content of recycle gas can be as high as 10 per cent without adversely affecting the reaction. This concentration is maintained by bleeding off the requisite amount of gas from the circulating system.

The first step of the Oxo process is not affected by the presence of sulfur compounds in the raw materials, but these impurities do hinder the subsequent hydrogenation step if carried out with Fischer-Tropsch, or copper chromite catalyst. With sulfur-containing olefinic raw material, it is necessary to filter off the first-stage catalyst and to carry out the hydrogenation over fixed nickel-tungsten sulfide catalyst. A partial hydrogenation of the crude first-stage product must be carried out prior to filtration to convert any cobalt carbonyl into cobalt.

Operation at Leuna

As originally worked out by Ruhrchemie, this was a batch process, and the pilot plant at Hoten consisted of 18 units originally intended for batch operation. Work at Leuna showed that considerably higher throughputs were obtained from continuous operations.

The following description of the latest method of operation of the Leuna plant was obtained by W. A. Horne from Dr. Gemassmer, who was the chemist directly in charge of these operations.

The olefin or olefin-containing charge is mixed with 3 to 5 per cent by weight of catalyst, most of which is recycled material. This suspension is pumped through a heater at the rate of 300 to 700 liters per hour and at a pressure of 220 to 240 atm, which raises its temperature to approximately 150°C. The preheated feed enters the bottom of the first reactor and passes upward concurrently with a stream (60 cubic meters per hour) of carbon monoxide and hydrogen which has been separately preheated to 150 to 190° (maximum 200°). This synthesis gas is partly recycle gas from the process (40 to 50 cubic meters per hour) and partly make-up gas which consists of equal molecular proportions of hydrogen and carbon monoxide. The first reactor, which is constructed of carbon steel, has an internal diameter of 200 mm and a length of 8 meters. It contains six vertical steel cooling tubes (21 mm outside diameter, 17 mm inside diameter) connected to a water jacket surrounding the reactor. Cooling by these tubes is used only when very reactive olefins are charged, and the heat released

is high. A thermocouple well extends the length of the reactor, and the temperature of the exit products is normally controlled at 150°C. The temperature and feed rate depend on the concentration and molecular weight of the olefins in the charge stock. As previously stated, lower molecular weight olefins are more reactive. Low concentration of olefins in the feed necessitates the use of lower feed rates and higher temperatures in order to insure that the reaction proceeds to the required extent. Normally, about 70 per cent of the olefins charged is converted in the first reactor.

The exit products from the top of this first reactor pass to the bottom of the second reaction vessel where they come into contact with an additional 60 cubic meters per hour of synthesis gas. The second reactor has the same dimensions as the first but is fitted with baffles to increase the efficiency of contact. No cooling tubes are required. The normal operating temperature is 170°C. Essentially, all the remaining olefins are converted, and some 20 per cent of the aldehydes formed are hydrogenated to alcohols.

The exit products from the top of the second reactor now flow through a water cooler to a separator from which synthesis gas is recycled to the preheater. The liquid product is let down to atmospheric pressure, and the released gases are purged after scrubbing with crude second-stage product to prevent loss of liquid by entrainment. The crude first-stage product is now pumped under a pressure of 200 to 250 atm to the second-stage preheater from which it passes to the bottom of the first reactor of the hydrogenation stage. Sixty cubic meters per hour of a mixture of preheated fresh hydrogen and methanized recycle gas is also introduced at the bottom of this reactor. The reactor is identical with the first reactor of the oxo stage but operates at an exit temperature of 180°. The exit product from the top of this reactor passes to the top of the second hydrogenation reaction vessel and travels downward countercurrent to an additional 60 cubic meters per hour of reaction gas. The exit temperature of this second reactor is roughly 200°C The draw-off of liquid product from the bottom of the converter is regulated so as to keep the reactor full of liquid. The top of the second reactor serves as a high-pressure separator for hydrogen and liquid products. The hydrogen, containing some carbon monoxide, is water-cooled and passed to a catch-pot for separation of condensed liquid, which is returned to the hydrogenation reactors; the gas is reacted at 250°C over an iron catalyst (similar to that used in the Synol process) to convert carbon monoxide to methane.

The liquid product is let down to a pressure of 10 atm to a separator from which dissolved gases are vented. The liquid from this separator is charged under its own pressure to the filter system. The liquid, in batches of 700 liters, enters the filter vessel (which is pressured with nitrogen) and is

filtered through the porous ceramic tubes situated at the bottom of the vessel. This operation requires about 10 minutes with a new filter but can take up to 30 minutes when the filters are old When filtration is complete, fresh olefin charge is introduced and passes in the reverse direction through the filter, thereby washing off the catalyst material. The whole vessel is then rotated at 60 rpm for 2 to 3 minutes It is stopped in the inverted position, and the olefin catalyst suspension is forced out by nitrogen pressure. This suspension is then transferred to the feed mixer of the Oxo process. The cycle time for a complete operation of the filter is one hour per batch of 700 liters of crude product.

The treatment of the filtered crude product depends on the type of olefinic raw material used. If this raw material has initially a boiling range not exceeding 30°C, the alcohols can be separated from the hydrocarbons by simple distillation. If, on the other hand, a raw material of wider boiling range is employed, the alcohols must be separated by the boric acid method.

A number of variations of the above process had been tried at Leuna. The effect of introduction of liquid feed at the top of one or both of the oxo reactors was tried, as was also the operation of the Oxo process with liquid and gas flowing countercurrently. The process was also operated with only one reactor in the oxo and hydrogenation stages. According to Dr. Gemassmer, however, the method described in detail above was found to be the most satisfactory.

Any scheme for operating the Oxo process requires that the rate of introduction of the synthesis gas in both the oxo and hydrogenation stage must be sufficiently high to insure efficient stirring and complete suspension of the catalyst. A large excess of synthesis gas is, however, not necessary from the purely chemical standpoint. Research carried out by the I. G. Farbenindustrie suggests that under these conditions the throughput would be lower and the reaction temperature somewhat higher One of the difficulties sometimes encountered was that unless the conditions in the Oxo stage are carefully controlled, olefin polymerization takes place. The polymers so formed, after hydrogenation in the second step, are difficult to separate from the higher-boiling alcohols.

Catalyst Preparation. The Fischer-Tropsch catalyst used in the Oxo process was obtained from the catalyst plant of Ruhrchemie at Oberhausen-Holten. It was reported to have the following approximate percentage composition: 30 cobalt, 2 thorium oxide, 2 magnesium oxide and 66 kieselguhr.

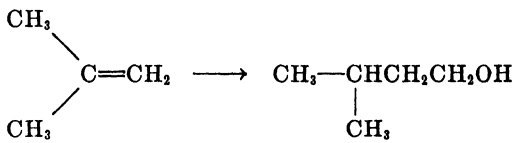
The catalyst in powder form is reduced with pure sulfur-free hydrogen. The hydrogen flow is controlled at a rate high enough to prevent settling of the catalyst powder, *i.e.*, the catalyst is fluidized by the hydrogen stream. The period of reduction is 2 to 4 hours.

Oxonation of Other Olefins

Extensive research was also carried out on the oxonation of other olefins. The production of propionaldehyde from ethylene and water gas had progressed to a point where a plant to be erected in Italy had been designed. Although practically quantitative conversion of ethylene was possible, the yield of propionaldehyde was only about 60 per cent, the remaining 40 per cent consisting of comparatively small amounts of *n*-propanol and diethyl ketone and larger amounts of higher-boiling products presumably formed by aldolization reactions.

Propylene was oxonated to a mixture of butanols normally containing about equal parts of *n*-butanol and isobutanol. It is stated in other reports that the *n*-butanol was the major component. The yield was given as 85 per cent with 15 per cent of higher-boiling products.

Isobutylene, unlike most olefins, gave almost exclusively 3-methyl butanol-1 and very little 2,2-dimethyl propanol.



The synthesis of higher alcohols (C_6—C_{11}) from C_5—C_{10} olefins was a potential source of alcohols for use in ester-type plasticizers.

The C_{30} and higher olefins (from Fischer-Tropsch hard wax, b.p. about 460°C, by chlorination and dehydrohalogenation) gave C_{31} and higher wax alcohols which were outstanding emulsifiers.

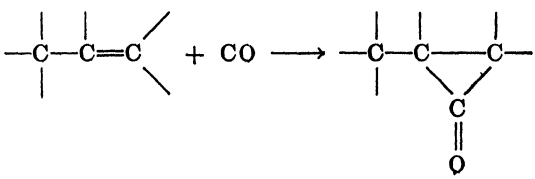
Dimethyl hexadiene-1,5 gave 35 per cent dimethyl octanediol and 65 per cent of the monoalcohol, although diolefins ordinarily did not give diols when subjected to oxonation.

Conjugated diolefins gave resins or monoalcohols, the other double bond undergoing hydrogenation. Butadiene and dicyclopentadiene both gave resins, while 1,1,4,4-tetramethyl butadiene gave 100 per cent of the C_9 alcohol.

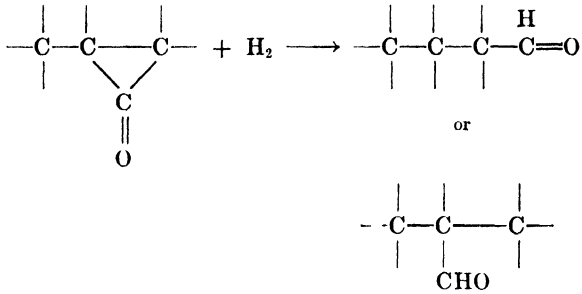
Nitriles cannot be substituted for olefins. Ammonia does not give amides with olefins and carbon monoxide.

Chemistry of the Oxo Process

The first step in the process appears to consist of the addition of carbon monoxide to the olefinic double bond according to the equation:

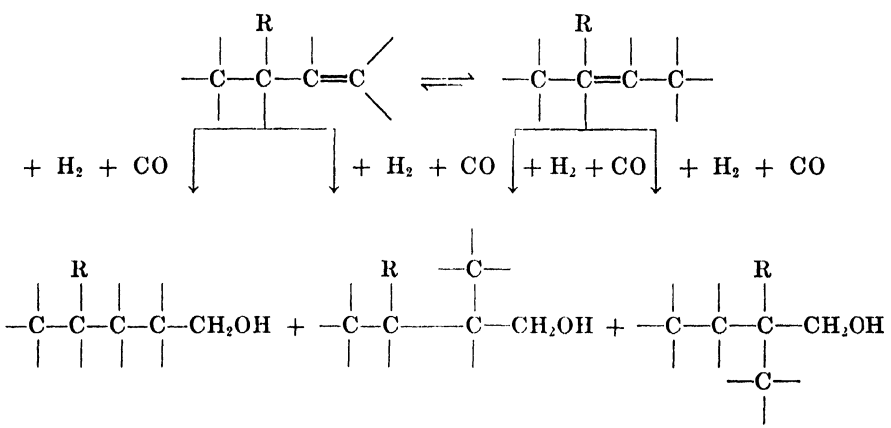


This intermediate product cannot be isolated because it is hydrogenated immediately to give aldehydes as follows:



depending on the point at which hydrogen enters the molecule. Further hydrogenation, usually carried out in a separate reaction stage, yields the corresponding *primary* alcohols.

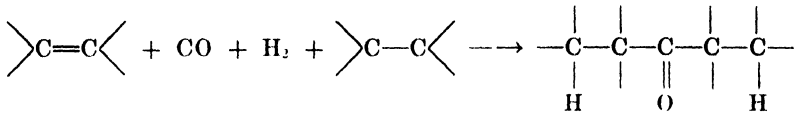
It should be noted that with the exception of symmetrical olefins the Oxo process may give a mixture of isomeric aldehydes or isomeric alcohols, as well as a mixture of both aldehydes and alcohols. This tendency toward a mixed product is further increased by isomerization of the olefin under the Oxo-process conditions:



The reaction involving the least steric hindrance predominates Thus, using isobutylene as the olefin, 3-methyl butanol-1 is obtained in greater quantity than is 2,2-dimethylpropanol-1. Similarly, using trimethyl pentenes obtained from the polymerization of isobutylene, the main Oxo process products are those derived from the isomers with terminal double bonds.

Ketone formation, which occurs to a limited extent, probably results

from the reaction of two molecules of olefin with one molecule of carbon monoxide and one molecule of hydrogen.



Reduction of the ketone would yield higher alcohols.

The aldehydes may undergo side reactions leading to acids and alcohols (Cannizarro type), or esters (interaction of acids and alcohols or Tschenko type), all of which may be present in the higher-boiling fraction.

Reactions with Carbonyl Hydrides

The success which Reppe had in introducing the metal carbonyls into organic chemistry led him to test the action of carbonyl hydrides upon unsaturated organic compounds in the hope that the carbonyl hydrides might be catalysts which would further stimulate carbon monoxide chemistry.

Carbonyl hydrides could be produced as described by Hieber by the reaction of aqueous solutions of alkali and alkaline earths with metal carbonyls, particularly iron pentacarbonyl. However, for the intended reaction with carbon monoxide, Reppe had to find basic compounds which would not yield salts of formic acid as easily as alkalis and alkaline earths do with carbon monoxide. In an attempt to produce carbonyl hydrides from iron pentacarbonyl and ammonia or secondary and tertiary bases, he made the important discovery that iron carbonyl hydride in alkaline solution can be quantitatively converted to iron pentacarbonyl and hydrogen by carbon monoxide. The iron pentacarbonyl reacts with surplus alkali with the production of iron carbonyl hydride and carbon dioxide, the reaction coming to an end when all the alkali has been converted to carbonate with the liberation of an equivalent quantity of hydrogen It is, therefore, a type of water-gas conversion (shift reaction) which runs at room temperature or slightly above under the catalytic influence of iron carbonyl hydride.

$$Fe(CO)_5 + H_2O \xrightarrow{OH^-} Fe(CO)_4H_2 + CO_2$$

$$Fe(CO)_4H_2 + CO \xrightarrow{OH^-} Fe(CO)_5 + H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

However, no study was made to find bases which would permit accomplishment of this water-gas process catalytically.

A second way to produce metal carbonyl hydrides which makes these interesting chemicals easily accessible on an industrial scale is as follows. Nickel carbonyl can easily be made by treating solutions of nickel salts with

carbon monoxide under pressure and at elevated temperatures, as was done in the recovery of nickel carbonyl in stoichiometric synthesis of acrylic esters (see page 254). If this reaction is attempted with iron and cobalt salts, the carbonyl hydrides are produced (for instance, iron carbonyl hydride from divalent iron salts, such as Mohr's salt in aqueous ammonia). However, by further action of carbon monoxide upon iron carbonyl hydride, it is transformed quantitatively into iron pentacarbonyl and hydrogen. By use of only the calculated amount of carbon monoxide, it is possible to check the reaction at the iron carbonyl hydride state. On the other hand, if cobalt is used (solution of cobaltous chloride in aqueous ammonia), the reaction with carbon monoxide stops at cobalt carbonyl hydride, which in contrast to iron carbonyl hydride is stable to carbon monoxide. Pure carbonyl hydrides can be liberated from their salts by acids such as phosphoric acid, as is known.

$$2\ CoCl_2 + 12\ NH_3 \rightarrow 2\ Co(NH_3)_6Cl_2$$

$$2[Co(NH_3)_6]Cl_2 + 11\ CO + 6\ H_2O \rightarrow 2\ Co(CO)_4H + 4\ NH_4Cl + 3\ (NH_4)_2CO_3 + 2\ NH_3$$

This also gives a convenient way of producing cobalt carbonyl because cobalt carbonyl hydrides can be converted quantitatively to cobalt carbonyl and hydrogen under suitable conditions

Reppe was now able to test the physical and chemical properties of these interesting substances. This knowledge was of great importance for carrying on his work. Cobalt carbonyl hydride is perfectly stable and easy to handle under certain conditions (pure chemical at low temperature, if diluted, also at higher temperatures). Cobalt carbonyl hydride can be heated for a considerable time at 200°C without decomposition if the solution is alkaline. Iron carbonyl hydride behaves differently and can be obtained in pure form only if special precautions are observed. Its alkaline solution hydrolyzes at 100°C in a very short time Cobalt carbonyl hydride can be determined by titration with sodium hydroxide solution and methyl orange as indicator, just as a strong inorganic acid. The transition point is equally pronounced if the neutral point is approached from either side. Titration curves for cobalt and iron carbonyl hydrides are shown in Figures VI-1 and VI-2. The acidimetric analyses check very well the figures which were obtained by titration with methylene blue. In the titration of cobalt carbonyl hydride with methylene blue, it was noted that the reduction can be determined in acid solution only in contrast to iron carbonyl hydride, which can be readily titrated with methylene blue in alkaline solution.

Reppe concluded from this behavior of metal carbonyl hydrides that cobalt carbonyl hydride is a very strong acid (also indicated by severe corrosion of technical equipment), while iron carbonyl hydride is a considerably weaker acid, as already indicated by its readiness to hydrolyze.

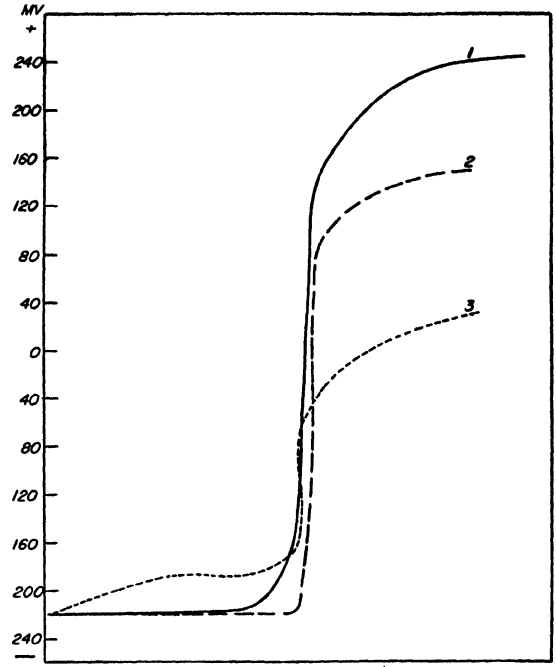


FIGURE VI-1 Titration of 0 5*N* sodium hydroxide in aqueous acetone with (1) cobalt carbonyl hydride, (2) hydrochloric acid, and (3) acetic acid Titration temperature 0° C Glass electrode/calomel electrode

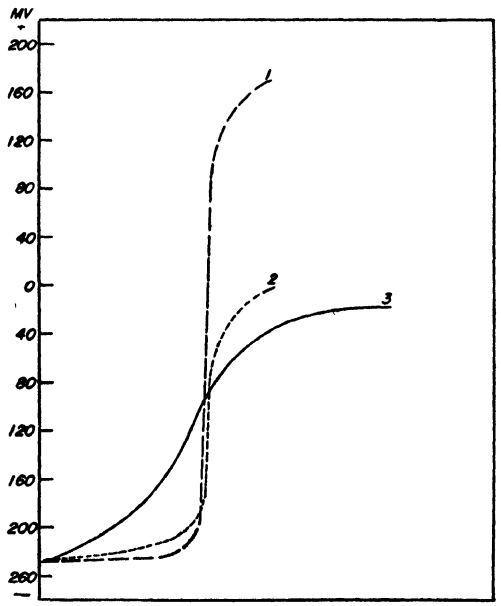


FIGURE VI-2. Titration of 0 5*N* sodium hydroxide in aqueous methanol with (1) hydrochloric acid, (2) acetic acid, and (3) iron carbonyl hydride. Titration temperature −10° C. Glass electrode/calomel electrode.

The behavior of metal carbonyl hydrides towards olefins and towards acetylenes was then studied. Surprisingly enough, Reppe found that with olefins alcohols were produced, but with acetylenes hydroquinones were the main reaction product.

Synthesis of Alcohols from Olefins, Carbon Monoxide and Water

If ethylene is reacted with an aqueous alkaline solution of iron carbonyl hydride (the reaction is much more complicated with cobalt carbonyl hydride), *n*-propanol is formed. Other products such as higher alcohols and organic acids (formic acid, propionic acid) result as well. The same effect was obtained if an alkaline solution of iron pentacarbonyl and ethylene was contacted; ferrous bicarbonate was found as a by-product. The formation of *n*-propanol can be formulated as follows:

$$Fe(CO)_4H_2 + 2CH_2{=}CH_2 + 4H_2O \longrightarrow 2CH_3{-}CH_2{-}CH_2OH + Fe(HCO_3)_2$$

or

$$FeCO_3 + H_2O + CO_2$$

The reaction can be carried out with higher olefins such as propylene, butylene, octylene, etc.; straight-chain primary alcohols are produced if the olefinic double bond is terminal.

For example, a mixture of 20 parts of iron pentacarbonyl, 27 of trimethylamine, 23 of water, and 32 parts of methanol was treated with a 2:1 mixture of propylene and carbon monoxide in an autoclave at 125 to 155°C and 180 to 200 atms pressure for 12 hours. Distillation of the reaction mixture gave 19 parts of *n*-butanol. The residue contained ferrous carbonate and the formic acid salt of the amine.

If ammonia, primary or secondary amines are used instead of the tertiary amine, a smooth alkylation results, which for ethylene can be formulated as follows:

$$H_2C{=}CH_2 + 3\ CO + H_2O + NH_3 \rightarrow H_2N{-}CH_2{-}CH_2{-}CH_3 + 2\ CO_2$$

$$H_2C{=}CH_2 + 3\ CO + H_2O + H_2N{-}CH_2{-}CH_2{-}CH_3 \rightarrow HN(CH_2{-}CH_2{-}CH_3)_2 + 2\ CO_2$$

$$H_2C{=}CH_2 + 3\ CO + H_2O + HN(CH_2{-}CH_2{-}CH_3)_2 \rightarrow N(CH_2{-}CH_2{-}CH_3)_3 + 2\ CO_2$$

For example, a mixture of 77 parts of a 50 per cent aqueous solution of dimethylamine and 20 parts of iron pentacarbonyl were treated with an ethylene-carbon monoxide mixture (ratio 2:1) in a shaking autoclave at 120 to 125°C and 190 to 200 atm for 20 hours. Distillation of the reaction mixture gave 20 parts of *n*-propyl dimethylamine; by-products were formic acid (combined as amine salt) and ferrous carbonate.

This alkylation reaction may be extended to other olefins and can be used to prepare primary, secondary, and tertiary amines. Dialkyl or trialkyl amines containing different alkyl groups are stated to be formed by allowing a mixture of olefins to react, either simultaneously, or one after the other.

The formation of alcohols from olefins, iron carbonyl hydride and carbon monoxide in the presence of ammonia or primary and secondary amines takes place only after the alkylation of the amine has been completed.

The fact that iron carbonyl hydride can be converted to iron pentacarbonyl and hydrogen by treatment of an alkaline solution with carbon monoxide led Reppe to try the reaction in a catalytic manner with a continuous carbon monoxide feed using iron carbonyl hydride as a catalyst:

$$2\,Fe(CO)_5 + (Base) + 2\,H_2O \rightarrow 2\,Fe(CO)_4H_2 + (Base) + 2\,CO_2$$
$$2\,Fe(CO)_4H_2 + 2\,CO \rightarrow 2\,Fe(CO)_5 + 2\,H_2$$
$$H_2C{=}CH_2 + CO + 2\,H_2 \rightarrow CH_3{-}CH_2{-}CH_2OH$$
$$H_2C{=}CH_2 + 3\,CO + 2\,H_2O \rightarrow CH_3{-}CH_2{-}CH_2OH + 2\,CO_2$$

This formulation does not give a true picture of the unknown intermediates of iron carbonyl which decompose under the reaction conditions to alcohols, carbon dioxide and ferrous carbonate, and which are continuously regenerated from iron carbonyl, olefin, carbon monoxide and water under the influence of the base. Undesired side reactions (formation of iron carbonate and formate and condensations) could be avoided by correct adjustment of alkalinity

The bases used must therefore meet the following conditions:

(1) They must be strong enough to react with iron pentacarbonyl as well as to combine intermediately with the carbon dioxide formed.

(2) At elevated temperature they must easily release carbon dioxide to insure continuous removal of the carbon dioxide from the reaction mixture

(3) They must be soluble in water and non-volatile to permit separation from the reaction products.

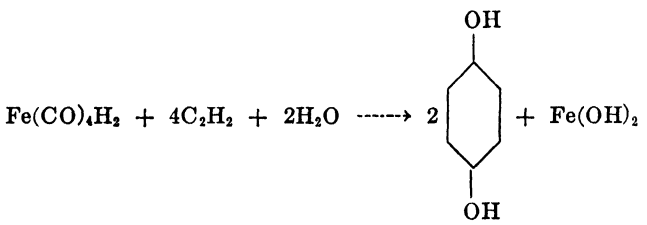
(4) They must not undergo undesired side reactions with the reactants (formation of formate, alkylation).

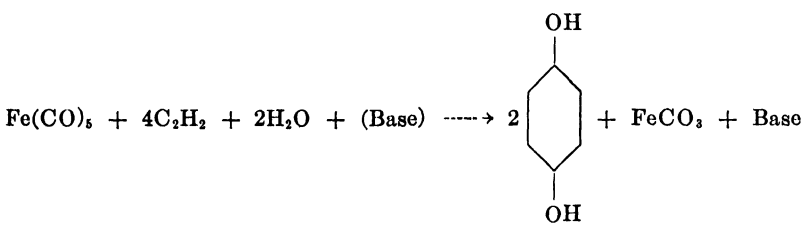
Reppe found that only tertiary organic bases were useful for this new synthesis of alcohols, and he selected those which contained carboxyl or sulfo groups in order to meet the demand for solubility in water and low volatility. The bases which are used in the Alkazid process, such as sodium dimethylaminoacetate, meet all the required conditions.

Apparently, however, this development was still in the very early stages of research, and the authors have not been able to locate any experimental details in addition to those presented. It is possible that the development of this procedure may have been overshadowed by the concurrent development of the "oxo" reaction (see page 280), which would appear to have considerable technical advantages. However, the iron carbonyl hydride-olefin-carbon monoxide procedure does give the straight chain primary alcohol exclusively, whereas the Oxo process usually produces both the normal alcohol and the alpha-methyl-substituted alcohol; additional isomers may result if rearrangement of the double bond under the catalytic influence of the catalyst occurs.

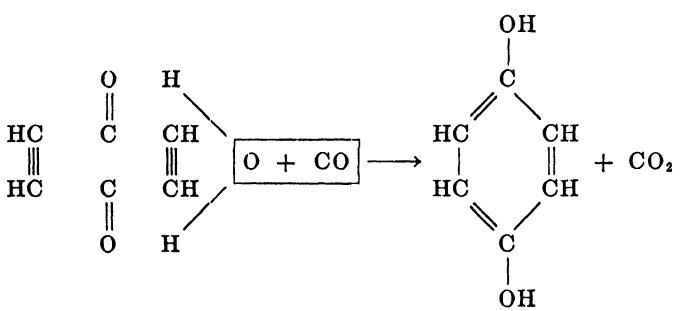
Hydroquinones from Acetylenes, Carbon Monoxide and Water

Instead of the unsaturated alcohols which Reppe expected, hydroquinone and its substituted derivatives were formed from the reaction of carbonyl hydrides with acetylene or its derivatives. The conditions of operation were similar to those previously used for olefins (see page 290), but the temperature must be considerably lower (50–70°) due to the higher reactivity of acetylene. Monoethanolamine was a suitable base for the "base reaction." The presence of a basic agent is not absolutely required; the presence of hydroxyl containing compounds such as water or alcohols is usually sufficient for the formation of carbonyl hydride. With acetylene the reaction runs in a simple way as follows:





Hydroquinone



$$2HC{\equiv}CH + 3CO + H_2O \longrightarrow C_6H_6O_2 + CO_2$$

These reactions require only sufficient pressure to avoid contact with atmospheric oxygen.

After separating the reaction mixture from precipitated iron compounds and from surplus iron carbonyl, hydroquinone was identified as the reaction

product. The yield of hydroquinone is at present only 20 to 30 per cent of theoretical (calculated for applied carbonyl hydride).

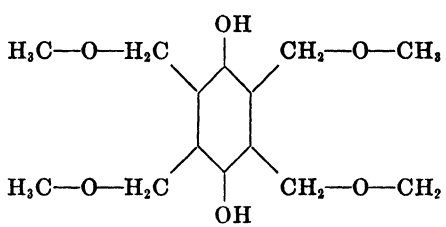
Naturally, the course of the reaction is not as simple as it looks in the formulas above. A number of well-defined iron carbonyl hydride or iron pentacarbonyl complexes with acetylene are formed as intermediates. It is certain that the metal carbonyl hydrides are active intermediates; this was proved by experiments with pure cobalt carbonyl hydride, which reacted with acetylene in caustic solution and gave hydroquinone.

It is remarkable that hydroquinone is also formed from acetylene and iron carbonyl in the presence of alcohol and in the absence of caustics. A part of the starting material is, however, converted to acrylic esters in this case.

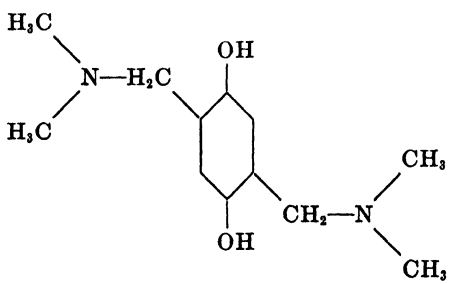
The reaction was also extended to substituted acetylenes; methyl acetylene gave 2,5-dimethylhydroquinone; dimethylacetylene, tetramethyl hydroquinone; phenylacetylene, 2,5-diphenylhydroquinone.

Other acetylene derivatives are also capable of undergoing the reaction. From 1,4-dimethoxybutyne-2, 2,3,4,5-tetramethylol hydroquinone tetramethyl ether (m.p. 88°C) was obtained.

$$2CH_3OCH_2C{\equiv}C{-}CH_2OCH_3 + 2CO + H_2O \longrightarrow$$

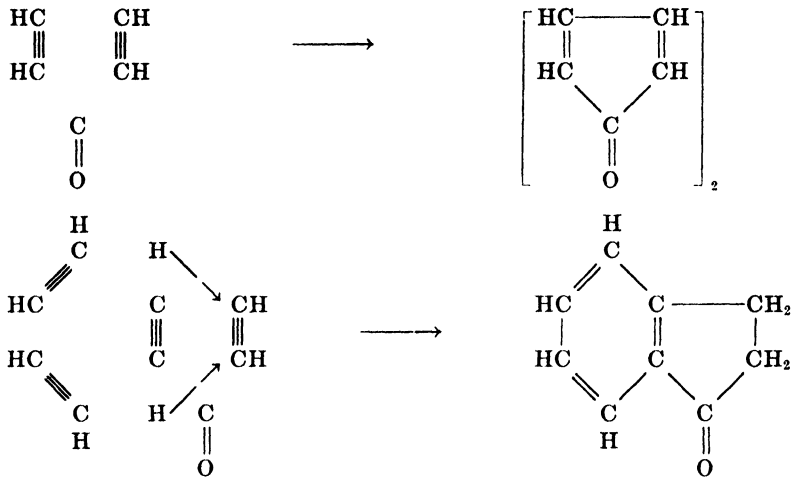


From 1-dimethylaminopropyne was prepared 2,5-bis-(dimethyl aminomethyl) hydroquinone (m.p. 187°C) of the formula:



The possible reactions of carbon monoxide with acetylene are far from exhausted. The reaction between carbon monoxide and acetylene can also run in an entirely different way. Under certain conditions, Reppe observed the formation of dimeric cyclopentadienone, and of hydrindone

which can be formulated as the reaction of one mole of carbon monoxide with 2 or 4 moles of acetylene as follows:



Aldehydes and ketones react with acetylene in the presence of metal carbonyls and acid, but the course of this reaction has not been cleared up yet. At present, no final conclusions can be drawn about the mechanism of these reactions.

It seems possible that the metal carbonyl hydrides are the real transferring agents for carbon monoxide in all these addition or substitution reactions. It is believed certain that further work in this field will not only bring about interesting results but will also explain many reactions which have already been carried out.

Appendix to Chapter VI

Part I

The results obtained in the evaluation of various metallic salts as catalysts in the synthesis of acrylic esters from acetylene, carbon monoxide and alcohols (see page 255) are summarized in the table below. Following the table is a list of chemicals which had little or no catalytic activity

Activity of Nickel Salts as Catalysts in the Catalytic Synthesis of Acrylic Esters

No	Catalyst	Quantity (g)	Temperature (°C)	% Conversion per 100 hr	Remarks
7	Ni- salt of cyclohexylbutyric acid	8	130	23 0	Badly contaminated with ethyl ester of cyclohexyl butyric acid. Catalyst decomposed.
55	NiBr dried at 130°C	4 5	180	14 1	
56	$K_2Ni_3S_4$	2 6	130	12.3	
57	NiF_2	2.0	180	16 6	
59	NiI_2, baked	6.4	120–130	25.6	Including polymerized matter.
61	$K_2Ni_{11}S_{10}$	2 14	130–140	17.8	
63	gamma-NiS	1.9	140	17.2	
64	gamma-NiS + 10% hydroquinone	1 9	180	34.0	
67	$NiCl_2$, dried at 130°C	2 6	160–170	27 0	Butyl ester.
68	10.6% $NiCl_2$ on siliceous extrudings	10 0	180	8.4–10 1	
69	10.6% $NiCl_2$ on Al_2O_3	10 0	180	23.2	Including polymerized matter.
70/68	Catalyst 68 steam-treated $NiCl_2$· conversion = 7 75%	10 0	180	7.75	
72/68	Catalyst 68 steam-treated $NiCl_2$: conversion = 19%	10 0	180	28.9	
73/68	Catalyst 68 steam-treated $NiCl_2$: conversion = 69%	10 0	180	42.0	
74/68	Catalyst 68 steam-treated $NiCl_2$: conversion = 66%	10 0	180	45.0	
85	$NiCl_2$ on pumice stone	10.0	180	22.6	
96	$NiBr_2$ on extrudings 9.9% $NiBr_2$	10.0	180	13.8	

Activity of Nickel Salts as Catalysts in the Catalytic Synthesis of Acrylic Esters—Continued

No.	Catalyst	Quantity (g)	Temperature (°C)	% Conversion per 100 hr	Remarks
97	NiI_2 on extrudings 28% NiI_2	10.0	180	21.0	
98	gamma-NiS on extrudings	10 0	180	24.0	
99	$NiCl_2$—2 NH_3 on extrudings	10 0	180	25.6	
100/96	Catalyst 96 steam-treated $NiBr_2$. conversion = 79.5%	10 0	180	20.0	
102/68	Catalyst 68 steam-treated· conversion 69.8%	10 0	180	41.0	
106	10% $NiBr_2$ on 3 mm granulated clay	10.0	180	88 5	
107	10% $NiBr_2$ on 3 mm siliceous extrudings, gelatin-coated	10 0	180	60 0	Without polymerized matter.

The following catalysts had no activity, or very slight activity

1 Ni salt of phthalic acid monoethyl ester
2 Ni salt of phthalic acid monobutyl ester
3 Ni salt of phthalic acid monocyclohexyl ester
4 Nickel palmitate
5 Nickel stearate
6 Nickel oxalate
7 Nickel phthalocyanine
8 Nickel salt of delta-4-cholestenone-3-sulfonic acid-6
9 Nickel malonate
10 Nickel succinate
11 Nickel adipate
12 Nickel suberate
13 Nickel sulfide (from elements)
14 $Ni(CN_2\ 4\ H_2O\ x\ NH_3$
15a Nickel vanadate decahydrate
15b Nickel vanadate, anhydrous
16 Nickel tungstate
17 Nickel *o*-phosphate, baked
18 Nickel *m*-phosphate
19 Nickel pyrophosphate, baked
20 Nickel pyridine chloride ($NiCl_2$-C_5H_5N)
21 Basic nickel chromate, baked
22 Cobalt sulfide
23 Cobalt chloride, anhydrous (formation of acetal)
24 Ferrous chloride
25 Ferric chloride
26 Cobalt thiocyanate
27 Platinum catalyst from factory
28 Iron sulfide

29 Nickel thiocyanate
30 Cobalt acetate
31 Cobalt formate
32 Ferrous oxalate
33 Ferric chloride, subl. (formation of acetal)
34 $NiCl_2$ with 10% $SnCl_4$
35 " " " $TiCl_4$
36 " " " $AlCl_3$
37 " " " LiCl
38 " " " NaCl
39 " " " KCl
40 " " " $CuCl_2$
41 " " " CuCl
42 " " " CuCl + NH_3
44 " " " $BeCl_2$
45 " " " $MgCl_2$
46 " " " $CaCl_2$
47 " " " $SrCl_2$
48 " " " $BaCl_2$
49 " " " $ZnCl_2$
50 " " " Hg_2Cl_2
51 " " " $HgCl_2$
52 " " " $SnCl_2$ (formation of ether)
53 " " " $PbCl_2$
58 Nickel fluoride
60 $NiCl_2$ + 10% $TiCl_2$
62 Fused product from BaO, S and $NiCl_2$
65 beta-Nickel sulfide
66 Nickel hydroxide
75 Nickel chloride with copper acetylide on siliceous extrudings
82 Nickel ferrocyanide
83 Nickel ferricyanide
84 $NiCl_2$ on Al_2O_3, steam-treated
86/87 Nickel acetate
103 10% $NiBr_2$ on silica gel
105 Mixed sulfide from NiS + V_2S_5 (hydrogenation catalysts)
108 Nickel mercaptide
109 Nickel permutite and neopermutite
115 Nickel sulfate, anhydrous

Part II

Following is a list of other triphenyl phosphine complexes referred to on page 265.

Other Complex Tertiary Phosphine Metal Carbonyl Compounds

$Ni(CO)_3[(C_6H_5)_3P]$	$Co(CO)_2[(C_6H_5)_3P_2]_2$
$Ni(CO)_2[(C_6H_5)_3P]_2$	$Fe(CO)_4[(C_6H_5)_3P]$
$Co(CO)_3[(C_6H_5)_3P]_2$	$Fe(CO)_3[(C_6H_5)_3P]_2$

Instead of tertiary phosphines, the tertiary arsins and stibins such as triphenyl arsine or triphenyl stibine may be used, for example

$$\left[\begin{matrix}Fe(CO)_3\cdot[(C_6H_5)_3P]\\(C_6H_5)_3Sb\end{matrix}\right]$$

Carbonyl hydrides also gave new complexes with triphenylphosphine, but these could not be produced in pure form.

The following series of complexes between triphenylphosphine and metal salts was apparently prepared. It is not known whether the catalytic activity of these compounds has been tested.

$Cu(I)Cl[(C_6H_5)_3P]_2$
$Cu(II)Cl_2[(C_6H_5)_3P]_2$
$Cu(I)Br[(C_6H_5)_3P]_2$
$Cu(II)Br_2[(C_6H_5)_3P]_2$
$AgCl[(C_6H_5)_3P]$
$AgBr[(C_6H_5)_3P]$
$ZnCl_2[(C_6H_5)_3P]_2$
$CdBr_2[(C_6H_5)_3P]_2$
$Hg(I)Cl[(C_6H_5)_3P]_2$
$Hg(II)Cl_2[(C_6H_5)_3P]_2$
$Hg(I)Br[(C_6H_5)_3P]_2$
$Hg(II)Br_2[(C_6H_5)_3P]_2$
$AlCl_3[(C_6H_5)_3P]_x$
(tenacious plastics)
$AlBr_3[(C_6H_5)_3P]_x$
(tenacious plastics)
$BiI_3[(C_6H_5)_3P]_x$
(could not be isolated)
$Fe(II)Cl_2[(C_6H_5)_3P]_2$
$Fe(III)Cl_3[(C_6H_5)_3P]_2$
$Fe(II)Br_2[(C_6H_5)_3P]_2$
$Fe(III)Br_3[(C_6H_5)_3P]_2$
$CoBr_2[(C_6H_5)_3P]_2$
$NiBr_2[(C_6H_5)_3P]_2$
$(NiBr_2)_2[(C_6H_5)_3P]_3$
$NiCl_2\ [(C_6H_5)_3P]_2$
(not crystallized, highly viscous)
$PdCl_2[(C_6H_5)_3P]_2$

The literature recognizes only Cu(I), Ag, Au compounds as well as Hg, Cd, and Pd compounds. The following compounds are possible according to the literature

$CdBr_2\cdot[(C_6H_5)_3P]_2$ $\quad$ $CdBr_2\ [(C_6H_5)_3P]_3$ $\quad$ $CdBr_2\cdot[(C_6H_5)_3P]_2$

Cyanide Compounds

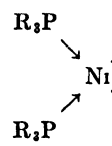
(unknown in the literature)

$Hg(CN)_2[(C_6H_5)_3P]_2$ $\quad$ $Cu(CN)\,[(C_6H_5)_3P]_2$

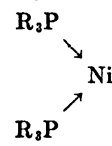
No further cyanides were investigated $Ni(CN)_2$ does not give complex compounds with *tert* -phosphines.

The complexes between triphenylphosphine and metal salts are nonionic and may be formulated as follows

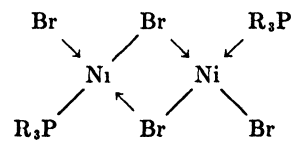
$[(C_6H_5)_3P]_2NiBr_2$



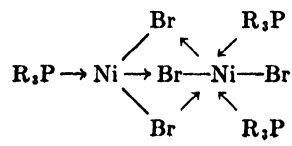
$[(C_6H_5)_3P]_2Ni(CO)_2$



$[(C_6H_5)_3P\cdot NiBr_2]_2$



$[(C_6H_5)_3P]_3(NiBr_2)_2$



Chapter VII

Synthesis and Reactions of Acetylene Homologs

Synthesis of Methyl Acetylene[1]

Two forms of magnesium carbide are known, MgC_2 and Mg_2C_3; the former hydrolyzes with water to form acetylene,

$$MgC_2 + H_2O \rightarrow MgO + HC{\equiv}CH$$

while the latter yields almost pure methyl acetylene (propyne-1)

$$Mg_2C_3 + 2\ H_2O \rightarrow 2\ MgO + HC{\equiv}C{-}CH_3$$

Methyl acetylene was of considerable interest to the Germans since carboxylation of this acetylenic homolog gave a new route to methacrylic acid or its esters[2]

$$HC{\equiv}C{-}CH_3 + CO + H_2O \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}COOH$$

$$HC{\equiv}C{-}CH_3 + CO + ROH \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}COOCH_3$$

The production of the required magnesium carbide (Mg_2C_3) was apparently worked on by several laboratories. The earliest work appears to have been done in the inorganic laboratory at Leverkusen by Dr. Kerasnik. In this work various hydrocarbon gases were passed over magnesium powder; at temperatures below 700°C, MgC_2 was formed. At 700 ±25°, Mg_2C_3 was formed; this gave methylacetylene of 99 per cent purity upon hydrolysis. This reaction, it was stated, was consistent with the work of Novak.[3] It was found that ethylene was the most satisfactory hydrocarbon gas; methane, propane, butane, pentane, etc., also reacted similarly, whereas benzene, hexahydrobenzene, and hexahydronaphthalene failed to react, and acetylene decomposed. The temperature of the reaction had to be controlled very accurately as the reaction was exothermic. Attempts to operate on a kilogram scale in an agitated vessel gave very poor yields owing to poor temperature control. Kerasnik failed to ob-

[1] *PB* 63780 (*FIAT* 1019).
[2] *PB* 58447 (*FIAT* 933)
[3] *Z. phys. Chem*, **73**: 513 (1910).

tain a magnesium carbide by reaction of calcium carbide with magnesium chloride.

Preliminary experiments indicated that a heated mixture of coal powder and magnesium powder gave approximately 60 per cent of MgC_2 and 40 per cent of Mg_2C_3, but temperature data and details are lacking.

At Griesheim, Kraus studied the formation of a number of carbides by double decomposition with calcium carbide. The work was successful only in the case of magnesium carbide.

The reaction between magnesium chloride and calcium carbide forms carbides, but is inefficient and results in poor yields owing to inability to secure good physical contact between the reactants in the solid state. This is corrected by forming a eutectic, melting below the reaction temperature, of magnesium chloride with salts such as potassium chloride or sodium chloride. A mixture of 56 per cent of sodium chloride and 44 per cent of magnesium chloride melts at 435°C, and is recommended for the reaction medium. Powdered calcium carbide is added to the fused eutectic which is maintained at constant temperature in an agitated metal vessel. Such a fusion mixture reacts with calcium carbide to form MgC_2 and Mg_2C_3 at different temperature levels:

500 to 600°C	$MgCl_2 + CaC_2 \rightarrow MgC_2 + CaCl_2$
600 to 700°C	$2\ MgCl_2 + 2\ CaC_2 \rightarrow Mg_2C_3 + 2\ CaCl_2 + C$
over 700°C	$MgCl_2 + CaC_2 \rightarrow Mg + 2\ C + CaCl_2$

For the production of Mg_2C_3, the eutectic should be held at 650°C. Yields have not been stated.

Hydrolysis was accomplished in the usual manner in a gas generator equipped to drop water at a controlled rate on the 2-mesh or finer carbide mixture. The product gas was dried with calcium chloride and condensed with liquid air. The condensate was refluxed under a liquid-air dephlegmator to remove acetylene, and finally distilled into cylinders. No record was available of the temperatures observed during this distillation operation, nor the quality of the product. Apparently, sufficient methyl acetylene was prepared by this method to supply Ludwigshafen's experimental needs, but no records of commercial manufacture at Griesheim could be found.

Work on the production of Mg_2C_3 was apparently stopped; this may have been due to the unfavorable economics of the above-disclosed process, to the pressure of other work during the war period, or to the possibility of obtaining methyl acetylene as a by-product from arc acetylene manufacture at Huls.

Acetylene Homologs and Diacetylene from Arc Acetylene

Introduction. With the introduction at Huls in 1940 of the large-scale production of acetylene by the electric arc process,* it became necessary

* See page 3 for a brief description of the arc process.

for the first time to remove as impurities in the acetylene gas significant quantities of methyl, ethyl, phenyl, and vinyl acetylenes, and diacetylene. The pilot plants at Baton Rouge and at Leuna, which provided the experimental background for the installation at Huls, were operated so that the dilute acetylene from the arc was worked up in a single pass through the appropriate reactor. The residual gases were vented, or utilized for heating, or operation of gas motors. However, when acetaldehyde production from the concentrated arc acetylene by the customary Knapsack process was undertaken at Huls, all impurities and by-products became enriched in this continuous process, diacetylene was particularly troublesome because it inactivated the contact acid. The separation of pure acetylene from the arc gas thus became necessary for the first time. Many setbacks were apparently experienced by the Germans in overcoming the difficulties in the purification of the arc acetylene.[4]

Preliminary Gas Purification. The crude arc gas containing approximately 16 per cent of acetylene is quenched to 150°C and sent to two cyclones in series in which 60 to 70 per cent of the total carbon black is knocked down The gas is sprayed with water in a wash tower, and the residual carbon black is separated by bag filters which are heated to prevent condensation. Most of the water in the gas is removed by spray cooling to 20 to 25°C. Naphthalene, other aromatics and traces of high-boiling highly unsaturated hydrocarbons are removed by a low-pressure, counter-current oil scrubbing unit. Hydrogen cyanide is removed by water scrubbing, and finally hydrogen sulfide is removed by passing through iron oxide boxes.

This partially purified gas now goes to a pressure scrubber in which the gas is compressed to about 18 to 19 atm and is dissolved in water in a perforated plate column The insoluble gas consisting primarily of methane, ethane, ethylene and hydrogen is withdrawn to a Linde plant where ethylene and hydrogen are separated, and the paraffins recycled to the arc. The acetylene is degassed from the water and is now about 95 to 98 per cent pure. Normally, it is free from the customary impurities present in carbide acetylene; however, if the gas feed to the arc contains much hydrogen sulfide, then organic sulfur compounds, mainly carbon oxysulfide, which have a deleterious influence on the acetaldehyde process may be present. On the other hand, derivatives of acetylene are invariably present which, while chemically similar to acetylene, act as contact poisons in the acetaldehyde synthesis.

Composition of the 95 to 98 Per Cent Acetylene. The separation and characterization of the multiple components present in the 95 per cent arc acetylene after preliminary purification necessitated the development of completely new methods, although sufficiently sensitive detections were possible by ultraviolet absorption spectra measurements. The impurities

[4] *PB* 878, *PB* 879, *PB* 81826 (*FIAT* 929).

detected up to now, their concentration and physical properties are shown in Table VII-1.

Removal of Acetylenic Homologs. *Oil Scrubbing* In the first years of operation, these acetylenic derivatives, particularly diacetylene, were removed by oil scrubbing. However, the acetylene was still not pure enough for acetaldehyde synthesis but had to be aftertreated with concentrated sulfuric acid. Apparently, the sulfuric acid treatment removes by polymerization most of the C_6 acetylenes (in part of unknown structure). Purification with sulfuric acid without previous oil scrubbing is impossible because of tremendous acid consumption, and high heats of reaction

This method of removing diacetylene gave considerable trouble because of the difficulty of removing the diacetylene from the oil. Degassing by heating, or by reducing the pressure had to be abandoned because of the strong tendency of the diacetylene to polymerize and plug up the apparatus. The best method was to blow out the dissolved diacetylene at ordi-

Table VII-1. Impurities in Arc Acetylene

	B P	M P	Vapor Pressure (at −80°C in mm Hg)	Alpha (at 25° in oil)	Conc (g/m³)
Methyl acetylene	−27 5	−104 7	40	15	20
Ethyl acetylene	+8.5	−137	1	55	10
Vinyl acetylene	+5 8	—	1	47	30
Diacetylene	+9 5	−36	1 3	82	70
Methyl diacetylene	+55	<−80	0 5	1000	(2)
Ethyl diacetylene	+87	<−80	<0 1	2000	(5)
Benzol	+80	+5 5	0 03	2000	30–50
Phenyl acetylene	+143	−46	<0 01	—	1 5

nary temperatures with the recycle hydrocarbons from the Linde plant and to return the diacetylene to the arc.

Furthermore, the methyl acetylene which was not removed either in the oil scrubbing or sulfuric acid wash likewise caused trouble. Originally, it was thought that the methyl acetylene could be recovered from the acetaldehyde plant as its hydration product, acetone. This separation, however, ran into difficulty because the small amount of diacetylene which was not removed was hydrated to acetylacetylene (1-butyne-3-one) and was obtained along with the acetone. Rapid polymerization of the acetyl acetylene often blocked up the side-stream column.

Low-Temperature Cooling Process. The low-temperature cooling apparatus which operates at −80°C removes almost completely all impurities in the acetylene except methyl acetylene. Warm, crude acetylene is diluted with cold acetylene in a counter-flow unit and cooled to about 0°C, and predried in a second unit. In the next stage, the gas is cooled to

−35°C and then passes to the low-temperature cooler which it leaves at a temperature of nearly −80°C. The impurities separate out in the various stages according to their melting and boiling points.

The operation of the separate cooling stages must be carried out in such manner that a gas phase with more than 12 per cent diacetylene content does not form at any point. Acetylene-diacetylene mixtures containing more than 12 per cent diacetylene at atmospheric pressure may be decomposed by any spark or shock whatever, for example, even by a small piece of polymerizate falling down. Operation of the unit requires trained and circumspect personnel.

As compared to the scrubbing process which is foolproof and safe to operate, the low-temperature cooling process has the advantage that it furnishes higher purity acetylene (98 per cent as against 95 per cent), and more important, it provides a means of obtaining the higher acetylenes in concentrated form Both processes normally yield an acetylene with a diacetylene content of approximately 1 g/m³. Acetylene from either process appears to work as well in the acetaldehyde process as does the most highly purified carbide acetylene, but yields, of course, an acetaldehyde containing approximately 0 01 per cent diacetylene. The latter, even in percentages hardly detectable by analytical means, can lead to difficulties in the hydrogenation of the aldol prepared from such acetaldehyde, apparently because it inactivates the active centers of the copper-chromium-silica gel catalyst. In order to avoid enrichment, a part of the acetaldehyde normally recycled in the aldol plant is returned to the acetaldehyde distillation column.

Separation of the Higher Acetylenes from the Low Temperature Cooling Units. *From the 0°C Unit* The condensate obtained at approximately 0°C polymerized spontaneously upon standing with liberation of sparks. It contains, besides higher acetylenic hydrocarbons (C_6) of unknown nature, benzol, toluol, phenyl acetylene and styrene. It is believed that the C_6 acetylenes very rapidly form unstable peroxides which are responsible for this spontaneous polymerization. Ordinary stabilizers of the oxygen acceptor type as, for example, hydroquinone are ineffective here. Stabilization can be accomplished by adding benzol or by treatment with aqueous alkali at 90°C, whereby the easily polymerized substances are transformed to a harmless brown powder. Afterwards, the benzol, styrene, and phenyl acetylene can be recovered.

From the −35°C and −80°C Units. The separation (into pure components) of the higher acetylenes from the low temperature cooling units by distillation is extremely difficult since methyl acetylene boils at −23°C, vinyl acetylene at +4.5°C and diacetylene at +9.5°C. Furthermore, diacetylene can decompose explosively in the gas phase at temperatures over −20°C. Purified diacetylene or mixtures rich in diacetylene are a source

of great danger when the gases are worked up on a commercial scale at normal temperature. The condensates which accumulate at −35 and −80°C are diluted by the addition of an equal weight of methanol or ethanol and are thereby stabilized.

Originally, these condensates were disposed of either by recycling to the arc, or by reaction with carbonyl compounds in the presence of strong aqueous caustic. Later, the vinyl acetylene became highly desirable for transformation into either chloroprene, or methyl vinyl ketone For these syntheses, it must be free of diacetylene. Since diacetylene is the most

Table VII-2 By-Products of the Electric Arc Process (June 1944)

Basis 7500 cbm/h Crude Acetylene = 7 25 t/hr − 63000 t/year Purified Acetylene

	t/year
(1) L-carbon black f	6000
L-carbon black N	2400
(2) HCN	960
(3) Polymerizate of the low pressure gas purification from the filter presses	360
(4) Higher acetylenes from the low temperature cooling purification	
Diacetylene	4000
Vinyl acetylene	1500
Methyl acetylene	1000
(5) Aromatics	
From the low-temperature purification	
benzol	300
toluol	100
phenylacetylene + styrol	100
From the low-pressure gas purification of first runnings oil	800
Consisting of	
20% benzol	
8% toluol	
10–15% phenylacetylene	
7% naphthalene + indene	
10% higher acetylene	
Balance kogasin	
(6) Hydrogen sulfide from Bentheimer natural gas	600

reactive component, two processes for its removal based on the selective conversion were developed.

The simplest method for removal of diacetylene involves the addition of one mole of alcohol at 75°C in the presence of about one per cent of alkali (see page 305). Vinyl acetylene undergoes this same reaction, but only at a temperature of 100 to 108°C. The second process is based on reaction with methylol amines. Here again, diacetylene reacts at 60 to 70°C at atmospheric pressure, whereas the vinyl acetylene does not react until a temperature of 100 to 105°C is reached (see page 306).

After removal of the diacetylene from the low temperature condensate by either of these methods, the residual gas consists of about 15 per cent methyl acetylene, 80 per cent vinyl acetylene and 5 per cent hydrocarbons.

This gas may now be hydrated with an acid mercury catalyst to acetone and methyl vinyl ketone

By-Products of the Electric Arc Process. Although it is apparent from the description of the purification process that a great number of acetylenic and other by-products are available from arc acetylene, it may be somewhat surprising to see the figures in Table VII-2 relating to the tonnage of these products formed in the course of a year's operation.

The potential availability of these by-products was of great interest to the German chemical industry However, up until the end of 1945, their removal from the arc acetylene had been a continual source of trouble and danger. The separation of the individual components and subsequent utilization in chemical syntheses apparently had not been carried out on a plant scale

Chemical Reactions of Diacetylene

Reactions with Alcohols and Mercaptans. Diacetylene adds one mole of an alcohol at 75°C in the presence of about 1 per cent of sodium or potassium hydroxide[5]:

$$ROH + HC{\equiv}C{-}C{\equiv}CH \xrightarrow{OH^-} ROCH{=}CHC{\equiv}CH$$

Apparently, addition takes place as formulated to produce alpha-alkoxyvinyl acetylenes, since on reduction *n*-butyl alkyl ethers are produced.

Vinyl acetylene will, of course, undergo the same type reaction but only at 100 to 105°C[6]:

$$ROH + H_2C{=}CHC{\equiv}CH \rightarrow ROCH_2CH{=}C{=}CH_2 \rightarrow ROCH_2C{\equiv}C{-}CH_3$$

As previously indicated, this difference in temperature at which reaction with alcohols occurs is the basis of one method of removing diacetylene from vinyl acetylene.

Methoxyvinyl acetylene cannot be prepared by this procedure without pressure, since the reflux temperature is below the 75°C minimum required. However, by diluting the methanol with approximately twice the quantity of dioxane, a temperature of 75°C can be reached, and the methoxyvinyl acetylene is thus obtained

The alkoxyvinyl acetylenes, $ROCH{=}CHC{\equiv}CH$, prepared to date and their boiling points are shown below:

Alkyl Group R	B P	Pressure (mm)
CH_3	116–120	760
C_2H_5	136–137	760
C_4H_9	176–178	760
$HOCH_2CH_2$	80–90	2
$CH_3OCH_2CH_2$	183–186	760

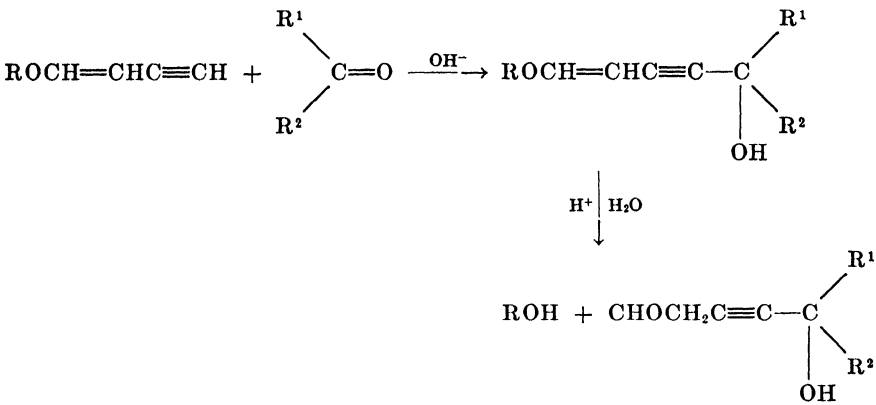
[5] *D R Pat 601,822, Fr Pat. 765,741*, I. G Farbenindustrie patent proposal *O.Z.-1,935*; *D.R Pat. Anmeldung I-4,602.*

[6] *U S Pat 2,103,725*; *J. Am. Chem. Soc* , 56, 1169 (1934)

The alkoxyvinyl acetylenes are vinyl ethers and, as such, are easily hydrolyzed to the corresponding alcohol and the acetylenic aldehyde, ethinyl acetaldehyde, which is unstable:

$$ROCH{=}CHC{\equiv}CH \xrightarrow[H^+]{H_2O} ROH + OCHCH_2C{\equiv}CH$$

However, if the alkoxyvinyl acetylene is condensed with a carbonyl compound in the presence of an alkali, unsaturated hydroxy ethers are formed. On hydrolysis, a stable acetylenic hydroxy aldehyde results[7]:



At higher temperatures and increased alkali concentrations, the alkoxyvinyl acetylenes add a mole of alcohol yielding butynol acetals which may, under more drastic conditions, add a second mole of alcohol to the triple bond to give beta-alkoxycrotonaldehyde acetals[8].

$$ROCH{=}CHC{\equiv}CH + ROH \rightarrow (RO)_2CHC{\equiv}C{-}CH_3 \xrightarrow{ROH} (RO)_2CHCH{=}\underset{\displaystyle OR}{\underset{|}{C}}{-}CH_3$$

Mercaptans apparently react very similarly with diacetylene, leading to a series of compounds analogous to those described above.

Reactions with Methylolamines. Diacetylene reacts readily at 60 to 70°C at atmospheric pressure with methylolamines with elimination of water and formation of unilaterally- or bilaterally-substituted products[9]:

$$R_2NCH_2OH + HC{\equiv}C{-}C{\equiv}CH \rightarrow R_2NCH_2C{\equiv}C{-}C{\equiv}CH \xrightarrow{R_2NCH_2OH} R_2NCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2NR_2$$

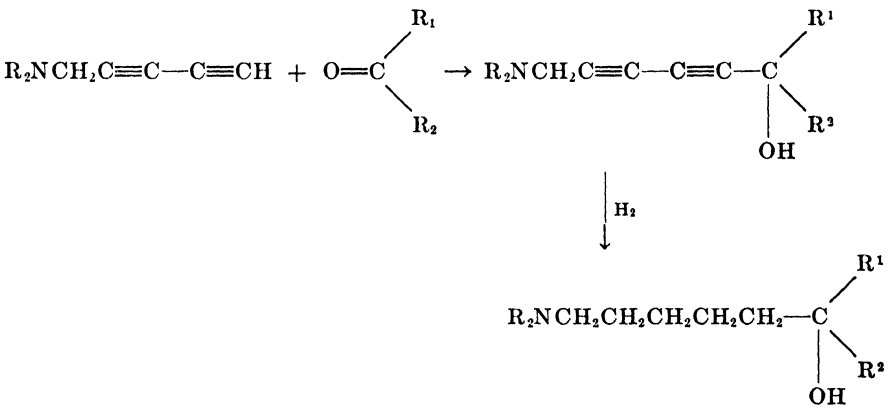
[7] I G Farbenindustrie patent proposal *O.Z.-13,896*, *D R.Pat. Anmeldung J-74,019* IVd/12o

[8] I G Farbenindustrie patent proposal *O Z.-13,586*; *D.R.Pat Anmeldung J-72,881* IVd, 12o

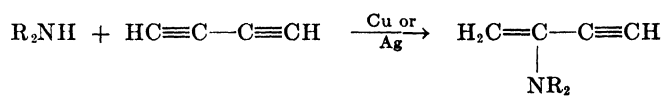
[9] I G Farbenindustrie patent proposal *O.Z.-13,430*; *D.R.Pat. Anmeldung J-72,303* IVd/120o.

Vinyl acetylene reacts only when the temperature is raised to 100 to 105°C, and this difference in reaction temperature has been utilized in the previously described process for the removal of diacetylene from vinyl acetylene.

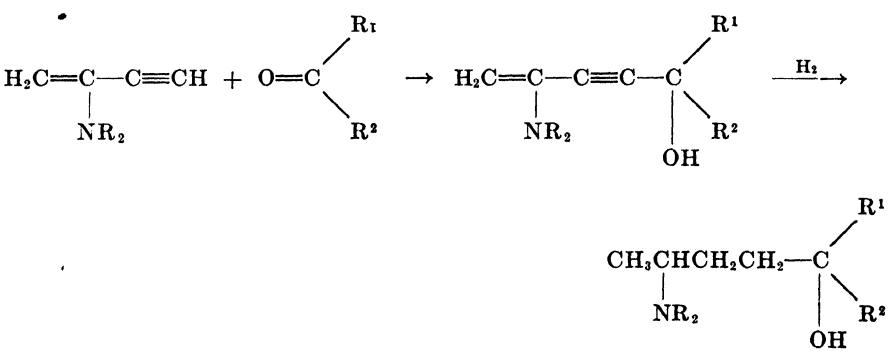
The monoamino diacetylene product could be condensed with carbonyl compounds in the presence of alkali and the resultant hydroxyamino diacetylene derivative reduced to branched-chain amino alcohols[10]:



Reactions with Dialkylamines. Diacetylene reacts with dialkylamines at 45 to 50°C in the presence of copper or silver salts (acetylides) to produce aminovinyl acetylenes



which by further reaction with carbonyl compounds and reduction yielded amino alcohols:



[10] I G. Farbenindustrie patent proposal *O.Z.-18,217*; *D R.Pat. Anmeldung J-71,403* IVd/12o.

Reactions with Carbonyl Compounds. Diacetylene may be converted to hexadiynediol by reaction with formaldehyde at 95°C in the presence of a silver catalyst (silver acetylide or silver salt of diacetylene)[11]. Reduction over Raney nickel gave hexanediol-1,6.[12] Oxidation of the hexanediol-1,6 gave adipic acid in 80 per cent or better yield[13]:

$$2CH_2O + HC{\equiv}C{-}C{\equiv}CH \xrightarrow{Ag} HOCH_2C{\equiv}C{-}C{\equiv}C{-}CH_2OH$$

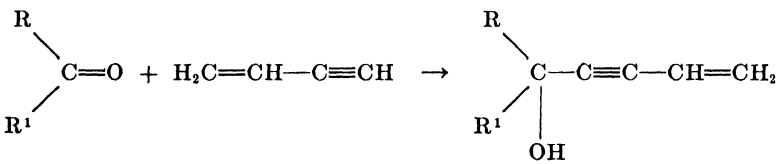
$$\downarrow$$

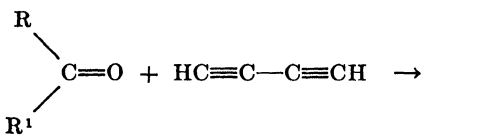
$$HOCH_2(CH_2)_4CH_2OH \rightarrow HOC{-}(CH_2)_4COH \quad (\text{O} \quad \text{O})$$

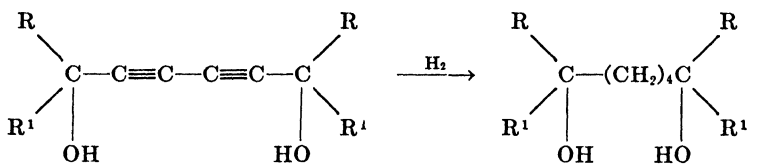
However, diacetylene could not be made to react with other carbonyl compounds by this technique.

At a later date, it was found that diacetylene would react with formaldehyde in the presence of potassium hydroxide as a catalyst in a solvent such as ether or tetrahydrofuran. Further development led to the condensation of diacetylene with carbonyl compounds in the presence of 30 to 50 per cent of aqueous potassium hydroxide Vinyl acetylene, if present, reacts simultaneously, but acetylene does not under these conditions. Apparently, equilibrium is reached at atmospheric pressure when 90 per cent of the diacetylene is reacted, so that this method cannot be used to remove diacetylene from acetylene completely

The separation of the vinyl acetylenic alcohols from the 1,6-diacetylene glycols was not difficult, and as a result, the substituted secondary 1,6-diacetylenic glycols were easily and cheaply available by this process:







Hydrogenation of the 1,6-diacetylenic glycols gave the saturated 1,6-glycols which were of interest in polyurethane syntheses.

[11] *D.R.Pat. Anmeldung J-72,678* IVd/12o.
[12] *D.R.Pat. Anmeldung J-72,176* IVd/12o.
[13] *D.R Pat Anmeldung J-72,458* IVd/12o.

The rate of reaction of both vinyl acetylene and diacetylene with carbonyl compounds is so rapid that even aldehydes can be used in the presence of the strongly alkaline catalyst with the formation of less than 2 per cent of aldols.

As indicated earlier in discussing removal of acetylenic homologs from arc acetylene, the condensate from the low-temperature cooling unit was disposed of by reaction with carbonyl compounds. This is apparently the only development in the diacetylene field which has yet attained pilot-plant scale operation.

Vinyl Acetylene[14]

In addition to the vinyl acetylene available from the arc process, a small pilot plant (2 tons/month) for its synthesis from the dimerization of acetylene was operated. The process used appeared to be very similar to the well-known process originally used by Nieuwland and later exploited by DuPont in their manufacture of 2-chlorobutadiene and its polymers:

$$2HC{\equiv}CH \xrightarrow[HCl]{CuCl} HC{\equiv}C{-}CH{=}CH_2$$

The reactor consists of an unpacked mild steel tube of 40-foot height, water-jacketed for most of its length. The tube at the start of a run is half-filled with a catalyst solution containing 660 pounds of cuprous chloride, 10 pounds of copper powder, 480 pounds of ammonium chloride, 15 pounds of 36 per cent hydrochloric acid and 830 pounds of water. The liquid level is maintained by adding 0.1 to 0 2 per cent of hydrochloric acid The acidity of the catalyst is maintained as near as possible to 0 5 per cent hydrochloric acid. Lower acidities result in low rates of reaction, while higher acidities favor the formation of 2-chlorobutadiene.

The temperature is maintained at 60°C, a higher temperature promoting acetaldehyde formation. Acetylene is introduced at the bottom of the tower at a rate of 35 to 40 volumes per hour per volume of catalyst solution. Conversion is only about 10 to 12 per cent per pass The gases leaving the reactor pass to a series of coolers to knock down the condensable products while the uncondensed gases are recycled to the base of the reactor.

The liquid condensate passes to a still which separates the vinyl acetylene from the divinyl acetylene and other higher-boiling impurities. The vinyl acetylene contains about one per cent of acetaldehyde which is removed by washing with a 20 per cent solution of sodium bisulfite.

Pressures throughout the reactor and purification system are atmospheric, pressures above atmospheric leading to detonation of the vinyl acetylene if ignition should occur. The yield of vinyl acetylene is 80 per cent based on the acetylene fed; 15 per cent of divinyl acetylene is formed, while 5 per cent of the acetylene is lost as vent gas, acetaldehyde, cuprene, etc. The life of a catalyst charge is about five months.

[14] *PB* 49198 (*BIOS* 751).

Chapter VIII

Explosive Decompositions of Acetylene—Technique and Equipment for Handling Acetylene Under Pressure

Decomposition of Acetylene

Introduction

Thermodynamically,[1] acetylene is unstable with respect to its elements at room temperature and when decomposed to its elements at 18°C liberates 53,500 calories per gram mole. The pressure rise accompanying this decomposition is due primarily to an increase in temperature since the decomposition products are mainly carbon and hydrogen. Assuming no heat loss, the temperature should increase from 18 to around 3100°C, with an accompanying increase in pressure of some twelvefold. This calculated value for the pressure increase is in good agreement with experimental results obtained for the thermal decomposition of acetylene; however, the decomposition in many cases has been observed to proceed so rapidly that the result is a detonation with instantaneous pressures up to 200 times the initial pressure or 20 times the calculated pressure.

It has long been known that acetylene may decompose violently at certain concentrations, temperatures and pressures. Enthusiasm for the use of acetylene commercially has been dampened considerably owing to its unstable nature; in fact, in several countries legislation prohibiting the use of acetylene under pressure has been enacted. Thus, in Germany the official maximum pressure for acetylene was set at 1.5 atm gauge, at least up until the early war years, while England changed the limiting-pressure specifications from 0 75 atm gauge to 1.5 atm gauge only shortly before the war.[2] Obviously, such legislation should have prevented Reppe's original work on reactions of acetylene under pressure, however, he apparently ignored the legal restrictions and did not disclose the nature of his acetylene work to the Reichswirtschafts Ministerium until such time as the safe application of acetylene under pressure had been demonstrated by actual plant operations.

As Reppe's work with acetylene under pressure developed, particularly in the ethinylation reaction leading to his synthesis of butadiene, it became evident that exhaustive studies of the decomposition of acetylene should

[1] *Ind. Eng. Chem.*, **40**: 1177 (1948).
[2] *PB* 91664 (*BIOS* 1162).

be made if the projected large-scale plants employing acetylene pressures of 5 atmospheres or higher were to operate safely.

Rimarski,[3] president of the Chemische Technische Reichanstalt (C.T.R.) at Berlin, as early as 1925 had contributed to the large amount of information available relative to the explosive characteristics of acetylene; based on this work, the C.T.R. had set the official maximum pressure for acetylene at 1 5 atm gauge. Boesler and Weissweiler of the I. G. Farbenindustrie have since carried out an intensive investigation of the explosive characteristics of acetylene; most of this work has not been published and has remained as reports in the I. G. files. It was hoped that these studies would supply information concerning the nature of the pressure impacts resulting from decomposition of acetylene and the velocity of the explosion waves, which would ultimately lead to methods of preventing the decomposition, or at least of preventing it from becoming a detonation.

Decomposition of Acetylene by Initial Ignition

Boesler[4] conducted experiments to determine the decomposition pressure of pure acetylene as a function of (1) vessel diameter, (2) moisture content, (3) temperature, and (4) the composition of the igniting wire; he also determined the decomposition pressure of acetylene gas mixtures as a function of the gas added, *viz.*, nitrogen, hydrogen, methane, ethylene, etc., and as a function of temperature.

Apparatus. The experiments were carried out in a bomb (Figure VIII-1) of a diameter and height of 270 mm. In order to determine the effect of different vessel diameters on the resulting decomposition pressure, cylindrical liners (A) of 100-, 150-, and 200-mm diameter were used, also for preliminary experiments a smaller bomb having a diameter of only 50 mm was used. The gas inlet and outlet were located in the cover as was the igniting apparatus (B). In the bottom were openings (C) for a sight glass for observation of the igniting process, and two openings for a thermocouple (D) and the electric leads (E) of the electric heater (F). This heater consisted of resistance wire wrapped around an insulator and covered on the inner side with asbestos to eliminate the effect of radiation on the thermocouple. Manometers were provided in the inlet and outlet gas lines for determination of the pressure in the bomb. These manometers were always calibrated after the completion of a series of experiments.

All gases were dried by passing through calcium chloride towers in the gas supply line. In preliminary experiments in which this procedure was not followed, especially with a mixture of hydrogen, an appreciable scattering of data occurred.

[3] *Autogene Metallbearbeitung*, **18:** 311 (1925)

[4] From a report by Boesler, 1930. A complete translation of this report also appears in *PB* 20078 (*FIAT* 720) by N. A. Copeland and M. A. Youker.

In the case where acetylene saturated with water vapor was being investigated, the gas passed through towers containing water instead of calcium chloride. In order to make certain that saturation had been reached, a certain amount of water was sprayed into the bomb, and the gas was allowed to stand for some time before ignition.

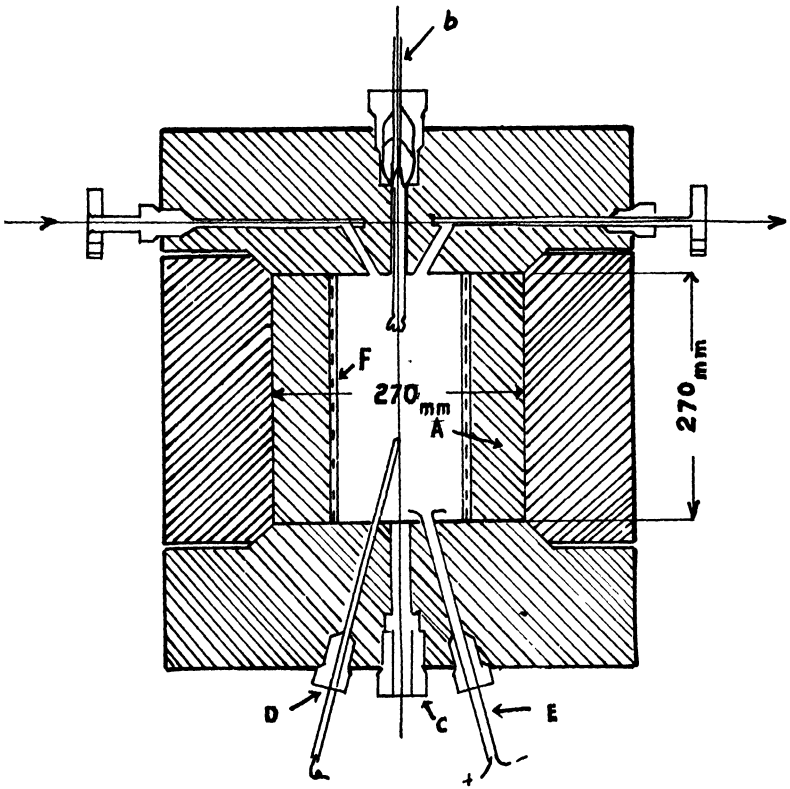


FIGURE VIII-1 Bomb for laboratory experiments on acetylene decomposition.

Experimental Procedure. After being well swept with 99 per cent acetylene taken from a cylinder, the bomb was filled with gas to a pressure approximating the decomposition pressure expected and the ignition brought about by fusion of a metal wire. If decomposition did not occur, the pressure would be raised 0.1 to 0.2 ata* for another trial at the same temperature until decomposition took place. In order to ascertain the point accurately, two additional experiments were always carried out at a slightly higher and lower pressure.

The decomposition pressure was measured by manometers. It would have been very interesting to have measured the actual pressure rise during

*ata equals 1 kg/cm² equals 0.968 atm. Unfortunately, the terms ata and atm are often used interchangeably.

decomposition, which might be done by means of an optical indicator. In the absence of such equipment only relative values were observed. The highest pressure reached could not be determined accurately in this way, since in the comparatively long and narrow lines to the manometers a certain amount of throttling occurs which distorts the readings. Also, the manometers probably register high because of inertia. As a comparison, the final pressure developed was determined by calculation from the heat released and the specific heat of the gases. Furthermore, the nature of the decomposition was observed through the sight glass This could be done better than had been expected.

The construction of the igniting apparatus and the investigation of the influence of ignition were the subject of special experiments. Rimarski originally used a platinum wire 0.15 mm in diameter, which could be brought to different temperatures or to fusion by proper regulation of the current. He also made use of a Bosch spark plug, but this latter method was rejected after some experiments which showed it to be unsuitable.

The difference between an incandescent and a fusing wire already observed by Rimarski was substantiated by Boesler. It was shown that with a fusing wire decomposition occurs at a lower pressure than with an incandescent wire. For example, with pure acetylene decomposition was observed at 1.40 ata with the former and at 1 60 ata with the latter. For this reason, a series of experiments were carried out with different wire temperatures. Of course, it is obvious that if trends are to be determined, a definite type of ignition must be used throughout. Also, according to the experiments performed thus far, the speed of ignition was also important; quick fusion of the igniting wire proved to be a reliable method and gave results which could always be reproduced.

The material of the igniting wire is extremely important, and it was therefore especially investigated for pure acetylene.

Dependence of Decomposition Pressure on Igniter Temperature (Composition of the Igniting Wire). Sufficient electrical energy was used on the wires of various materials (molybdenum, platinum, iron, copper, aluminum and lead) to cause instantaneous fusion. With the exception of the lead wire, which had a diameter of 1 mm, only wires of 0.5-mm diameters were used.

For the different materials the following decomposition pressures were obtained for pure, dry acetylene:

	Melting Point (°C)	Decomposition Pressure (ata)
Mo	2550	1.40
Pt	1760	1.40
Fe	1530	1.71
Cu	1080	1.84
Al	660	2.65
Pb	330	7.50

The results are shown graphically in Figure VIII-2. Particularly noteworthy is the sharp rise of decomposition pressure in the low-temperature region.

Although the melting points of the materials cannot be regarded as a direct measure of ignition temperature, one sees a definite relationship

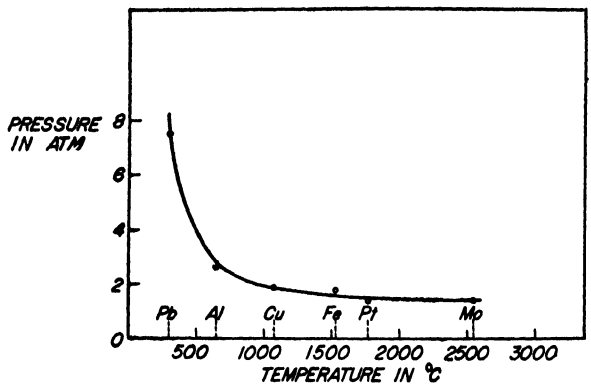


FIGURE VIII-2 Decomposition of pure dry acetylene
Effect of ignition temperature

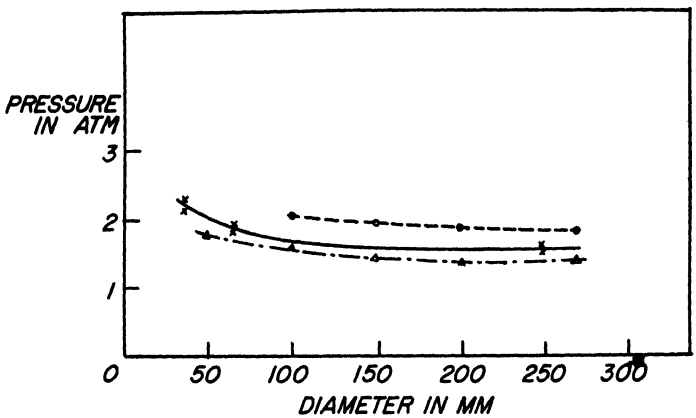


FIGURE VIII-3 Limiting pressure for decomposition of wet and dry acetylene as a function of diameter of vessel

——x—— Rimarski's experiments with 0 15-mm Pt wire igniter
-.-.△.-- Boesler's experiments with 0 5 mm Pt wire igniter
-- O -- Boesler's experiments with acetylene saturated with water

between the melting points of the material and the decomposition pressure. It can be assumed from this, that to bring about decomposition, certain energy is necessary. Since this energy is small with a lead wire, the corresponding decomposition pressure is very high and for platinum and molybdenum, is very low.

In order to carry out all other experiments under constant conditions, the following variables were held fixed:

(1) The igniting apparatus was always in the cover of the vessel.

(2) The igniting wire was of platinum of 0.5-mm diameter.

(3) The wire length was 10 mm.

(4) The igniting current was such as to cause an instantaneous fusion of the wire.

The following experimental results are valid only for the above conditions.

Relationship Between Limiting Decomposition Pressure and Vessel Diameter-Magnitude of Explosion Pressure. First of all, the decomposition pressure of pure, dry acetylene at various vessel diameters was determined at a gas temperature of 15 to 17°C. The experimental results of Rimarski served as a starting point for this work, although his values throughout lay somewhat higher than Boesler's, as already mentioned above. This discrepancy is probably due to the unavoidable differences in igniting methods. The curves (Figure VIII-3) which show the decomposition pressure as a function of vessel diameter are exactly similar in the two cases.

The following table shows values determined:

Vessel Diameter (mm)	Decomposition Pressure (ata) *Boesler Experiments*	Vessel Diameter (mm)	Decomposition Pressure (ata) *Rimarski Experiments*
50	1 80	38	2 1 to 2 3
100	1 60	66	1 80 to 1 85
150	1.45		
200	1 40		
270	1 40	250	1 50 to 1 55

The three points determined by Rimarski are not sufficient to give a good picture of the dependence of decomposition pressure on vessel diameter. However, the intermediate values determined at 150- and 200-mm diameter show that the decomposition pressure approaches the value 1.40 ata asymptotically, and as a matter of fact, reaches this value at a diameter of only 200 mm. It was concluded, therefore, that the critical pressure of decomposition of pure, dry acetylene is independent of the diameter for vessels greater than 200 mm in diameter, but is a function of diameter for smaller vessels. The cause of the different pressures with different diameters is explained by the so-called "wall effect." It is probable that dissipation of heat through the wall at ignition has an influence on the progress of the decomposition. This theory is supported by the fact that with dilute acetylene no dependence of decomposition pressure on vessel diameter could be observed, because the dissipation of heat through the walls of the bomb is small compared to the heat taken up by the gas mixture.

The pressure rise caused by the decomposition of pure acetylene takes place very rapidly, and at a vessel diameter of 270 mm and an initial ace-

tylene pressure of 1.40 ata, the final pressure amounts to 13 ata, *i.e.*, approximately 9.5 times the initial pressure. Rimarski obtained 15 ata final pressure with an initial pressure of 1.80 ata. From the heat of decomposition of acetylene (53,500 cal/mole) and the specific heat of carbon and hydrogen, a final temperature of 3100°C would be obtained, neglecting heat transmitted by the walls. This corresponds to a pressure rise of 12 times. This value checks satisfactorily with the measured value. [With a bomb diameter of 50 mm, a final pressure of only 6 ata was observed in spite of the higher initial pressure (1.80 ata) because of the larger rate of heat transfer to the walls.]

Relationship Between Decomposition Pressure and Gas Temperatures. The dependence of limiting decomposition pressure on the gas temperature was determined for pure dry acetylene in a bomb of 270-mm diameter. The ignition was by means of the instantaneous fusion of a platinum wire of 0.5 mm-diameter. The following table shows the results:

Temperature (°C)	Decomposition Pressure (ata) *Boesler Observations*
15	1 40
100	1 25
150	1 13
180	1 06

Temperature (°C)	Decomposition Pressure (ata) *Rimarski*
15	1 60 (1 45)*
50	1 48 (1 40)*
100	1 33
140	1 10

* The values shown in parentheses were determined by means of an incandescent wire.

The results are shown graphically in Figure VIII-4. There are some differences between Boesler's values and those of Rimarski, which can only be explained by the fact that Rimarski used an incandescent platinum wire.

Acetylene Saturated with Water. The determination of the decomposition pressure of acetylene saturated with water vapor lay beyond the scope of this investigation as originally visualized. However, individual values were determined in order to make a further comparison with Rimarski's results. With acetylene saturated with water vapor at 15°C, a curve of decomposition pressure *vs* vessel diameter was obtained which was parallel to that for dry acetylene; the decomposition pressures for moist acetylene are about 25 per cent higher than those for dry acetylene, as shown in Figure VIII-3.

For moist acetylene, the curve of pressure *vs* temperature is the reverse of that for dry gas (Figure VIII-5). The reason for this is that with in-

creasing temperature the water content of the gas increases appreciably so that the acetylene is diluted. The same phenomenon appears here as was noted later in experiments with mixtures with other gases. Also, the

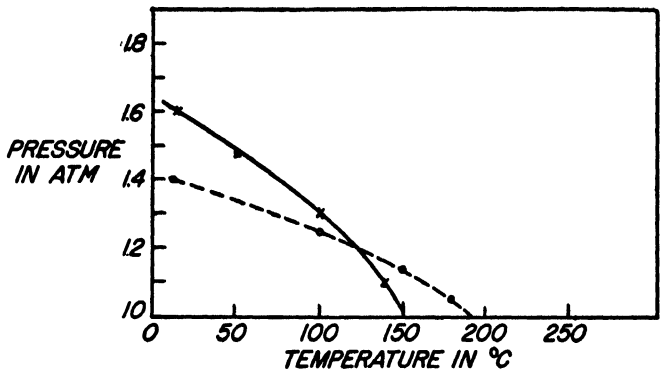


FIGURE VIII-4 Limiting decomposition pressure of acetylene as a function of temperature

—x— Rimarski's data
- - O - - Boesler's data

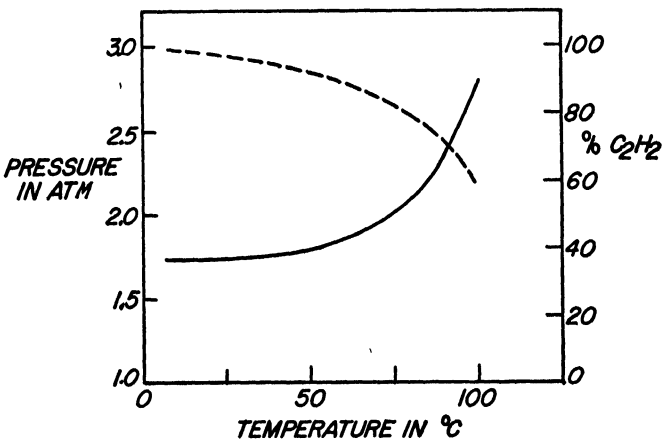


FIGURE VIII-5. Effect of temperature on the decomposition of acetylene saturated with water vapor Solid line is pressure; dotted line represents percentage of acetylene in mixture Curves are based on Weissweiler's data which are not in agreement with observations made by Rimarski

presence of water vapor has some effect on the type of decomposition. The relatively high specific heat doubtless serves to hinder the progress of the decomposition. Boesler's experiments do not indicate that after dissociation of the water vapor, some sort of reaction with decomposition products takes place, which as reported by Rimarski causes an especially powerful

decomposition. Even if the measured values of the decomposition pressures had checked those of Rimarski's, Boesler could detect only a decrease in the power of the explosion. This decrease became greater with increasing temperature (and consequently water content) The values observed are as follows:

Temperature (°C)	Decomposition Pressure (ata)	
	Boesler	*Rimarski*
15	1.75	—
50	1.80	1 70
80	2.10	2 40
100	2.80 (uncertain)	—

Decomposition of Pure Acetylene as Effected by Pressure and Temperature without Ignition

Decomposition will not take place when pure acetylene, either dried or saturated with water vapor, is compressed to 60 ata at 18°C or to 50 ata at 97°C.

Decomposition of Acetylene Mixed with Other Gases

The determination of the decomposition pressures of acetylene in gas mixtures was the chief object of this work and mixtures occurring in industry were used, such as acetylene admixed with varying amounts of hydrogen, nitrogen, carbon monoxide, methane and ethylene All tests were carried out in the 270-mm bomb. The results of these tests may be summarized briefly. The limiting pressure for decomposition varies with the amount and kind of diluent added and with the temperature. The addition of small percentages of diluents has a small but limited effect upon the decomposition pressure; as the amount of diluent is increased and the partial pressure of acetylene is decreased, the limiting pressure for decomposition is greatly increased. Of the gases tested as diluents, methane was most effective and hydrogen least effective in increasing the limiting decomposition pressure.[5] The limiting pressures for decomposition of the various mixtures decreased as the temperature of the gas was increased. Figures VIII-6 and VIII-7 show the results of these tests. The areas below the curves represent safe operating conditions; those above the curve represent unsafe ones.

Explosive Decompositions of Acetylene in Pipes

Although the tests described above were highly informative and in large part the basis on which Reppe operated in his early work, the investigation

[5] The U. S. Bureau of Mines has also investigated the effect of dilutents upon the explosibility of acetylene. The results are described in *Bureau of Mines, R.I.-4196* (Jan, 1948). "The Effect of Hydrocarbons and Other Gases upon The Explosibility of Acetylene".

of the decomposition of acetylene was intensified in 1940 to 1941 at Ludwigshafen and Griesheim. Two problems of great importance had increased the need for additional information concerning the explosive characteristics of acetylene under pressure. One was the necessity for determining the maximum pressure to which acetylene or acetylene mixed with inert gases can be compressed for long-distance transmission without danger

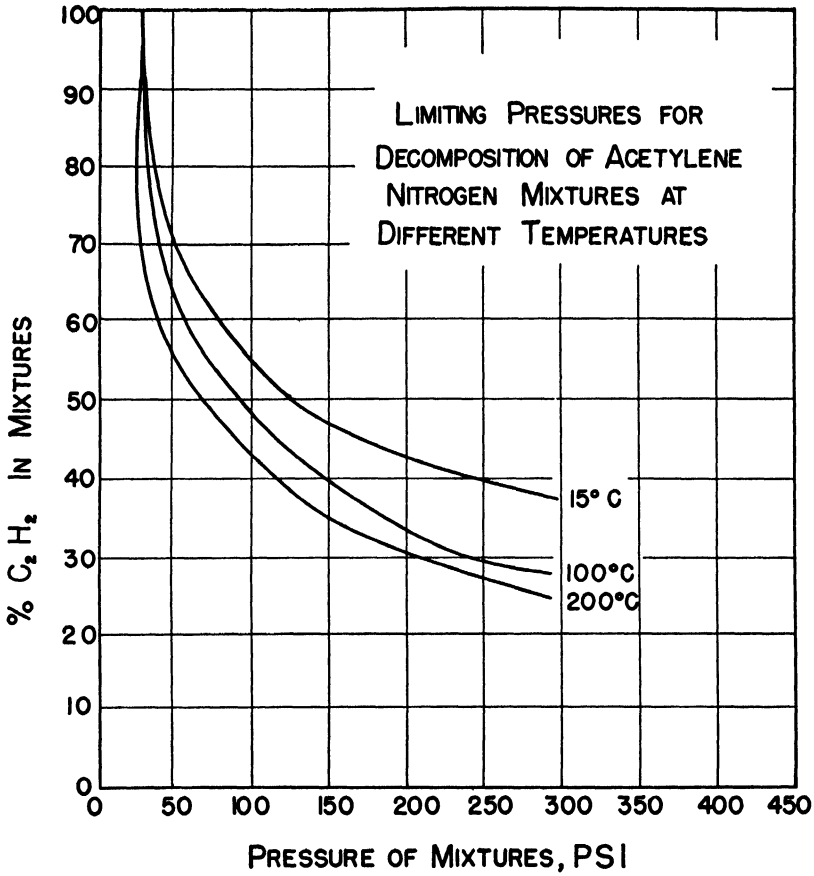


FIGURE VIII-6 Limiting pressures (psi) for decomposition of acetylene nitrogen mixtures at different temperatures

of detonations. This was necessitated by the projected long-distance acetylene transmission line from Gogolin to Radwitz, a distance of 83 kilometers. The second problem was how to prevent explosive decompositions and the possibility of detonations when working with acetylene under several atmospheres pressure in large technical equipment, particularly in the presence of large masses of copper acetylide catalyst as required in the butynediol process.

A study was made of the decomposition of acetylene in long high-pressure pipes. The purpose of using pipes was to determine at what pressures acetylene could be pumped through piping without decomposing, as it was only in piping acetylene to the reactors that acetylene existed in a pure state and with little opportunity for dilution with other gases. It was found that pipes 5.5 meters long were too short to obtain data from which sound conclusions could be drawn. The longer pipes were required to obtain data on the type of wave front formed when explosion or decomposition took place. In very long pipes there is also a chance that the explosion will turn into a detonation. For acetylene this means that the velocity of

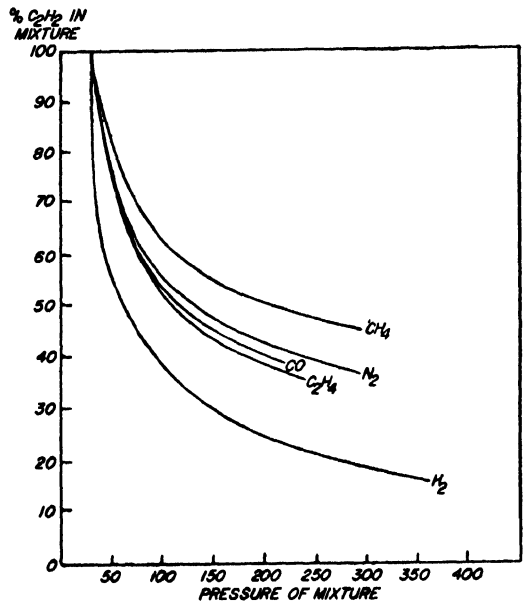


FIGURE VIII-7. Limiting pressure (psi) for decomposition of mixtures of acetylene and other gases at 15° C

decomposition increases to that of detonation—that is, to 1,000 to 2,000 meters per second.

Dr. Rimarski of the C.T.R believed that a 30-meter length pipe was sufficient to allow an explosion and decomposition wave to become a detonation wave. Experiments proved this assumption. In the first tests with a pipe 120 mm in diameter and 5.5 meters long, no detonations were observed even at 7 atm acetylene pressure; detonations occurred, however, in the 30-meter pipes of the same diameter even at very low initial pressures (less than 1 atm).

Details of the experiments are given herewith. Six 30-meter long pipes, having diameters of 25, 50, 100, 200, 300 and 400 mm, were buried hori-

zontally in the ground and 99.2 per cent pure acetylene stored in steel cylinders pumped into the test pipes. An igniting device consisting of three parallel platinum wires 0.15 mm in diameter was fitted into the end of the pipes, and a current density of 15 amperes applied when ignition was desired. Pressure devices of various sorts were attached to the ends of the pipes. These devices consisted of expandable copper cylinders, ball pressure gauges, and piezo-electric quartz indicators.

It was found that acetylene at a pressure of 2 atm was safe in 50-mm diameter pipes and that no detonation would occur. In pipes 100 mm in diameter or above, the explosions became a detonation at 0.4 to 0.6 atm initial pressure. In these experiments, the term "detonation" refers to a velocity of decomposition which is above 1,000 meters per second, causing explosion pressures of more than 12 times the initial pressure. These tests show that for practical purposes long pipes containing acetylene under pressure are very dangerous, particularly as the diameter of the pipe increases, and that special precautions must be provided to protect them.

The representatives of the C.T.R. concluded that in the projected long-distance line which would require a pipe 430 to 450 mm in diameter for the desired capacity, the pressure could not exceed 0.3 atm gauge. However, admixed with 50 per cent nitrogen, the initial pressure could be raised to 3.0 atm gauge Plans for the long-distance line were eventually dropped.

Prevention of Explosive Decompositions of Acetylene

Experiments were then carried out to investigate the possibility of preventing explosive decompositions of acetylene with particular reference to the conditions present in the butynediol plant.

Experiments in 1-Meter Pipes. The pipes (90 mm diameter, nominal pressure 325 atm) were arranged horizontally. Ignition was by fusion of a platinum wire 0.3 mm in diameter; the pressure was measured by piezo-quartz. Initial acetylene pressures of 4 to 9 atm at temperatures of 30, 40, 100, 110 and 130°C were used. The gas was dry in most experiments, but in some it was saturated with water vapor according to the vapor pressure at the experimenting temperature. In other experiments aqueous solutions of formaldehyde and butynediol were used together with varying quantities of catalysts (copper acetylide on siliceous support), dry or wet, fresh and aged. The following results were obtained:

With dry gas the maximum pressure due to decomposition was 10 to 12 times the initial pressure and was reached 0.2 to 0.3 second after ignition. In the presence of dry catalysts and at a low initial temperature (30 to 40°C), 14 times the initial pressure resulted upon ignition. Results became more favorable when wet catalysts were used; the checking effect of humidity (1 atm partial pressure) was evident. Final pressures now were only 3 to 6 times the initial pressure. (The vapor pressure of water

is 0.043 atm at 30°C, 1.46 atm at 110°C and 2.75 atm at 130°C.) For 6 atm of total pressure in butynediol reactors at 130°C, 2.75 atm are attributed to water and only 3.25 atm to acetylene. It is assumed that for constant initial pressure the partial pressure of acetylene will decrease proportionally to the quotient of the absolute temperature, that is, for 30 and 130°C in the relation 303/403, or 25 per cent.

All experiments proved that the maximum pressure is not substantially increased by the presence of wet or even of dry catalyst. (The catalyst did not fill the whole space of the testing unit.) The time required to develop maximum pressure is somewhat decreased. These results are very reassuring in case acetylene decomposition should occur for any reason. The catalyst is comparatively harmless and cannot be compared with the well-known primers, such as mercury fulminate, since in decomposition of the catalyst its heat of formation is released but no gases are liberated.

A few experiments were made in the 1-meter pipe with acetylene-nitrogen and acetylene-carbon dioxide mixtures. It was found that a small amount of an inert gas had no substantial influence upon the maximum decomposition pressure but larger amounts prevented decomposition. The following table gives final pressures for mixtures of nitrogen and acetylene, starting with 6 atm initial pressure at 25°:

Per Cent of Nitrogen	Maximum Decomposition Pressure (atm)
0	62
10	61
20	58
30	53
47	49
48	43
49	no decomposition

Dilution with carbon dioxide is also beneficial because 42 per cent of carbon dioxide is sufficient to prevent decomposition. A mixture of 50 per cent of acetylene and 50 per cent of carbon monoxide which could be ignited at 7 atm initial pressure was investigated. Rise of pressure was very slow, taking approximately 0.9 to 1.3 seconds Tests in which ethyl alcohol vapor was added to acetylene exhibited the same stopping effect as nitrogen, carbon dioxide, carbon monoxide and water.

Experiments in 5.5-Meter Pipe. All the experiments which had been done in the 1-meter pipe were repeated with a 5.5-meter pipe, 120 mm in diameter, with practically the same results. This pipe was also filled with 50 liters of copper acetylide catalyst; 6 atm of acetylene were pumped in, and the mixture ignited. Decomposition stopped 10 cm deep in the catalyst bed. The catalyst, which filled the whole tube space, had a decidedly checking action. One test where the catalyst was spread over the whole bottom of the pipe so that it filled just one-quarter of the cross-sectional

area gave 128 atm maximum decomposition pressure in 0.01 second at 6 atm initial pressure.

Several safety devices were tried with this 5.5-meter pipe. The aim was to find one which would check decomposition under all circumstances Hence, severe experimental conditions were chosen: dry, pure acetylene under 6 atm at room temperature with the starting space of the explosion (that is, distance between igniting wire and safety device) 0.5, 2.5, and 5 meters. All explosions could be stopped by filters made of sand, gravel and porous quartz plates. Naturally, these safety devices introduced a considerable pressure drop, which is out of the question for the manufacture of butynediol. In the search for a more efficient safety device with little resistance, sponges made of metal threads were tried. For some time it was believed that these gave a satisfactory answer, as may be seen from the following table:

(1) *Starting distance of explosion wave*	*0.5 m*
5 sponges, 376 g each	no breaking through
5 sponges, 115 g each.	no breaking through
(2) *Starting distance of explosion wave*	*2 5 m*
5 sponges, 334 g each	no breaking through
5 sponges, 283 g each	no breaking through
(3) *Starting distance of explosion wave*	*5 m*
8 sponges, 350 g each	no breaking through
5 sponges, 350 g each	breaking through slightly
5 sponges, 210 g each	breaking through strongly

As a result of these experiments, sponges were tried at Griesheim in a 30-meter pipe, 200 mm in diameter. An exceedingly dangerous property of the sponges was discovered; they had successfully stopped explosions in two experiments, but suddenly 20 minutes later a vigorous detonation occurred, completely destroying the end of the wire sponges; the zone of decomposition spread slowly through the sponges until it finally caused the whole quantity of acetylene to explode. The use of metal sponges as a safety precaution was therefore dropped.

A very suitable safety device which prevents with certainty any explosion of acetylene from becoming a detonation was finally found by filling the pipes with bundles of narrow tubes. This brought about only a small pressure drop in the gas cycle. The first experiments of C.T.R. at Griesheim showed that decomposition of acetylene never becomes a detonation if the tubes are narrow and less than 1 inch in diameter. It has been known for many years that it is very difficult to explode gas-air mixtures in narrow tubes and that the limits of explosion are lowered considerably. The reason for this is the rapid dissipation of the heat by the tube walls and by the column of undecomposed gas. Theoretical calculation shows

that the wall thickness of such narrow tubes may be very small without interfering with their efficiency.

In Griesheim a pipe 30 meters long and 100 mm in diameter was filled with thirteen 12.5-mm and six 10-mm tubes, a space of 30 cm on each side being left unfilled as an ignition area. In these pipes detonation properties at various initial pressures were studied. At a low initial acetylene pressure of 3.4 atm, the tube filling not only prevented detonation but was also able to check explosions. The decomposition of acetylene did not proceed to the end of the tube but stopped half way. At higher initial pressures (4, 5, 6 atm) there was a breaking through, and final pressures of 120 atm maximum were recorded by the piezo-quartz. The end of the pipe was only moderately warm.

The efficiency of bundles of tubes for checking explosions decreases with increasing depositions of soot. If an acetylene decomposition has occurred, soot must be removed from all parts of the system. Even with sooty bundles, decomposition was so slow that the final pressures could not be measured. The process was similar to slow burning and the efficiency was restored fully after cleaning

After the experiments with the tube bundles, some tests were made with two tubes 60 meters long, 12 5 mm in diameter, and 10 mm in diameter. Pressures were 5.1 to 8 atm and 8.5 to 10 atm. It was found that in a 12.5-mm tube no decomposition occurs up to 5 to 6 atm initial pressure, and that in both tubes final pressure of the explosion was less than ten times the initial pressure. With these 60-meter tubes it was also found that many bends and elbows in the lines do not stop the propagation of the decomposition. It was also surprising that strong cooling of the tube, which was coiled and immersed in water, had no effect at all upon the spread of the explosion wave.

Other experiments involving safety devices were carried out in November and December, 1941, at Griesheim and Ludwigshafen, with results as indicated below.

Discussion of the Results

First Series of Experiments. A length of horizontal pipe 30 m long, 120-mm diameter, was packed with 50 tubes of 10-mm diameter and 2 tubes of 8-mm diameter. The ends of these tubes were welded together and to the inner surface of the 120-mm pipe. At each end a section 30 cm deep was filled with iron Raschig rings 35 x 35 mm. At an initial acetylene pressure of 9 atm, the decomposition pressure was 250 atm. In the later experiments this section was decreased from 30- to 6-cm depth; the maximum decomposition pressure was lower and it was concluded that large free spaces must be avoided.

Second Series of Experiments. A 30-meter length of horizontal pipe 120

mm in diameter was packed with Raschig rings of 35-mm diameter and 35-mm length, made of 0.5-mm thick iron sheets. Previous experiments of the C.T.R. in 100-mm diameter tubes gave detonations with an initial pressure of 0.6 to 1.0 atm; hence, these tests were started with an initial pressure of 0.8 atm and did not exceed 6 atm The Raschig rings definitely checked spreading of the decomposition wave. No breaking through was obtained at 1.4 atm, at 2 atm there was a slight break through; at 3 atm again there was no break through; and at 4 and 6 atm there was a break through, but no detonation. At 6 atm initial pressure, the copper cylinder compression device recorded 320 atm; ball impression gave 303, 81 and 85 atm. The pipe was cut after these tests, and it was found that the Raschig rings were partly pushed together, causing formation of hollow spaces more than 1 meter long. The deposit of soot in the pipe was surprisingly small. The comparatively large rings checked spreading of the decomposition wave to such an extent that even at 6 atm initial pressure no damage was done to the pipe. If the resistance of Raschig ring packings in long tubes does not cause any difficulties, it is permissible to use ring packing as a safety precaution against detonation.

A 120-mm diameter tube was filled with Raschig rings made of clay with exterior dimensions of 25 x 25 mm No breaking through occurred in the first tests at 3 5 and 6 atm initial pressure. When the pipe was opened, it was found that the Raschig rings had been hurled away from the ignition end some 6 meters and had been crushed to powder. The tube was refilled and the initial pressure raised to 8 atm. Breaking through became evident, the flange becoming leaky, but the pipe itself remained intact. The copper cylinders at the end recorded 268, 230, and 275 atm pressure, but it is believed that these figures were high.

The experiments with Raschig rings show that these rings are suitable for protecting against detonations. They can be used for packing large irregularly-shaped spaces, curves and elbows It is believed that metal rings are preferable to ceramic rings, because they are not crushed by the impact of the explosion wave.

Third Series of Experiments. A 30-meter vertical pipe, with an inside diameter of 10 mm, capable of withstanding 325 atm pressure was arranged with an ignition chamber at the lower end. Pressures were recorded by piezo-quartz oscillographs. At an initial acetylene pressure of 5 and 6 atm, no penetration occurred, from 7 atm up, penetration occurred and at an initial pressure of 14 atm, a final pressure of 278 atm was recorded. It is believed that these pressures are higher than was actually obtained.

A 30-meter vertical tube 12.5 mm in diameter, nominal pressure 64 atm, with ignition at the lower end and pressures recorded by piezo-quartz, was used. There was a breaking through at 5 atm pressure. The pressure increase was recorded as 81 atm for 6 atm initial pressure and 199 atm for an

initial pressure of 10 atm. Ball pressure indicating equipment was also used; but the figures obtained, namely 200 and 300 atm for initial pressures of 5 and 10 atm, were considered in error and too high.

A 30-meter vertical pipe, 16 mm in diameter, nominal pressure 325 atm, was used with ignition taking place at the bottom. Failure occurred at a pressure of 5 atm. The initial pressure was raised to 12 atm, and a pressure rise of 315 atm was recorded by means of piezo-quartz. The pressure rise was very rapid. Because of the short time during which the quartz is loaded (0.01 to 0.001 second), the values are probably too high.

Experiments were conducted with an entrance chamber connected to the bottom of a 30-meter pipe, 10 mm in diameter. This chamber measured 500 mm long by 70 mm diameter and had a volume of 1.9 liters. Ignition was made at the bottom end of the chamber. In these experiments, the pressure rises were naturally very rapid. Whereas the same pipe without an entrance chamber, with an initial pressure of 10 atm gave a pressure rise of 160 atm, the same experiment with an entrance chamber yielded a rise of 275 atm. At 5 and 6 atm initial pressures, which previously had not given penetration without the pre-chamber, the final pressures were 144 and 185 atms These experiments demonstrated, as was expected, that no unprotected large empty spaces can be tolerated

Techniques for the Safe Handling of Acetylene under Pressure

It is evident now that the German scientists were not successful in their endeavor to develop a technique which would prevent acetylene decompositions under all process conditions; however, they were reasonably successful in developing techniques which would confine such decompositions and prevent them from becoming detonations. The safety devices and operational procedure for all German acetylene processes were therefore based on the realization that acetylene was inherently an unstable gas at any pressure. Decomposition of acetylene cannot be prevented entirely, but by suitable devices it is possible to prevent detonations and to confine such decompositions so that the pressure increase does not exceed ten- to twelvefold, an increase which can be easily taken care of by the design of the equipment.

Two general methods have been developed to minimize the danger of explosive decompositions of acetylene under pressure: (1) by diluting the acetylene with a gaseous diluent such as nitrogen, carbon dioxide, or methane; (2) by keeping every acetylene molecule within a certain maximum distance of a solid, such as a wall, by limiting the amount of free space in the system to a minimum, *i.e.* by using small bore lines for carrying acetylene feeds and by subdividing all large voids into smaller spaces by filling them with bunches of small tubes less than 0.5 inch in diameter, or with steel, or porcelain Raschig rings.

The first method is generally used for batch operations in an autoclave. For continuous operations, particularly with a fixed bed catalyst, the second method is generally used. If high partial pressures of acetylene are not required, the acetylene stream generally is diluted with a gaseous diluent, usually nitrogen.

Based on the experiments described above and the conclusions drawn therefrom, the first butynediol plant in Schkopau was constructed with regard for the following facts:

(1) All pipe lines with a diameter of 1 inch and above, which are to carry acetylene under pressure, should be filled with bundles of tubes or their equivalent.

(2) The interior diameter of the filling tubes should be 0 5 inch or less, if possible.

(3) Soot decreases the efficiency of these narrow tubes, hence, the surfaces must be smooth and must be kept clean

(4) Bends do not check explosion and must also be filled with narrow tubes If a larger pressure drop can be tolerated, Raschig rings or other packings may serve the purpose

(5) Dead spaces must be subdivided into many small spaces by Raschig rings or other fillers

As an additional safety precaution, the pressure gauges must be damped and designed so as to bear a multiple of their nominal indications Ring balances for volume control should be of the Oppau high-pressure type.

In carrying out vinylation reactions under pressure, acetylene should not be allowed to come in contact with dry caustic alkali. One explosion occurring in the vinyl ether plant was traced to the fact that the liquid level in the vinylation tower had fallen during the run, thus allowing deposition of dry potassium hydroxide on the walls above the liquid level. Contact of this alkali with the acetylene under pressure was sufficient to initiate an explosion

Warning. Despite all knowledge of the fundamental principles of the explosive characteristics of acetylene under pressure and despite all precautions taken to prevent them, explosive decompositions nevertheless have occurred during the operation of both the vinyl ether and butynediol processes. Therefore, before running any reaction involving acetylene under pressure, it is advisable to determine whether the reaction mixture is safe or whether it can decompose under the reaction conditions. Hanford and Fuller[6] have described how such a test may be carried out in a simple practical manner by loading a 1200-ml Aminco hydrogenation bomb with the desired mixture and attempting to decompose it by fusing on iron wire in the gas phase. If no decomposition occurred, the acetylene pressure was increased and the operation repeated until sufficient data were available to permit a decision as to whether or not the desired experiment was safe.

[6] *Ind. Eng. Chem.*, **40**: 1171 (1948).

It should be remembered as Hanford and Fuller point out that "the characteristics of acetylene have not changed as the result of any research. What has changed is a better understanding of the factors that enter into the control of the tremendous force that can be developed during its decomposition."

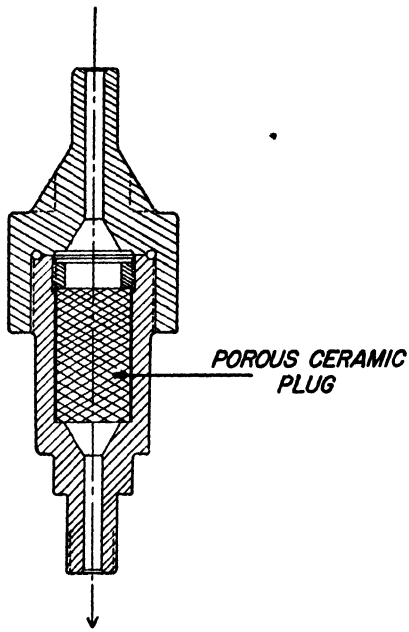


FIGURE VIII-8 Ceramic safety check valve

EQUIPMENT AND MATERIALS OF CONSTRUCTION

Safety Equipment

Reppe and his co-workers designed most of their equipment which involved the pumping of acetylene gas so that check valves would prevent a flash back through the pumps or other equipment in the event of ignition of the acetylene.

The porous stone filter shown in Figure VIII-8 proved successful in many installations. Where acetylene was being pumped under relative low pressures such as in the pipe lines of Reppe's laboratories, a check valve was used which operated much after the fashion of a Schraeder air valve found in automobile tubes. (Such a valve is shown in Figure VIII-9.)

In processing equipment where large volumes of flammable gases were encountered, checks against flash backs were usually steel towers filled with sand.

Pumps

In many of the acetylene processes, it became necessary to pump acetylene or gases containing acetylene at pressures above atmospheric. Reppe claims the invention of a pump, known as the water-ring pump, which works much like our common laboratory pressure and vacuum pumps. The essential difference is that Reppe designed the pumps to use water as the sealant and, of course, had them constructed in sizes capable of handling large volumes of gas. The water-ring pump is illustrated in Figures VIII-10 and VIII-11.

In addition to the water-ring pump, Reppe made considerable use of what might be described as a water-leg pump. While it is questionable whether Reppe was the first to construct this type pump, since it has been in use in this country for oil pumping, he at least put it to excellent use. This pump is illustrated in Figure VIII-12. The main advantage of this pump is that during the pumping operation no heat is added to the reaction, and since the gas or fluid being pumped actually serves as the piston, no contaminants can enter the system.

Autoclaves

During his many years of work on the reactions of acetylene and other organic compounds under pressure, Reppe was naturally concerned with the development of equipment which would facilitate the carrying out of general exploratory laboratory investigations of this type in a safe and practical manner. He was confident that he had achieved this objective as is shown by describing briefly the small autoclaves which he used for preliminary investigations of new acetylene reactions under pressure, and the arrangements used for mounting and servicing these autoclaves.

Small Experimental Shaking Autoclaves. The smallest autoclaves had a capacity of 180 ml and were usually fabricated of an alloy steel (V_2A or V_4A) and lined if desired with copper, copper alloys, or even with precious metals such as platinum or silver. The overall dimensions were 3.5 cm I.D., 5.0 cm O.D. with an internal length of 20 cm. The maximum working pressure was 300 atm at a maximum temperature of 300°C.

A drawing of one of these small shaking autoclaves is shown in Figure VIII-13. The various parts are:

(*A*) Inlet and outlet for reaction gases
(*B*) Thermocouple well
(*C*) Hexagonal cap
(*D*) Hexagonal body
(*E*) Lenticular sealing plug, ground fit

The autoclaves were constructed so that they could easily be opened and closed. This was accomplished by using a hexagonal closing cap and having the shoulder of the autoclave shaped hexagonally.

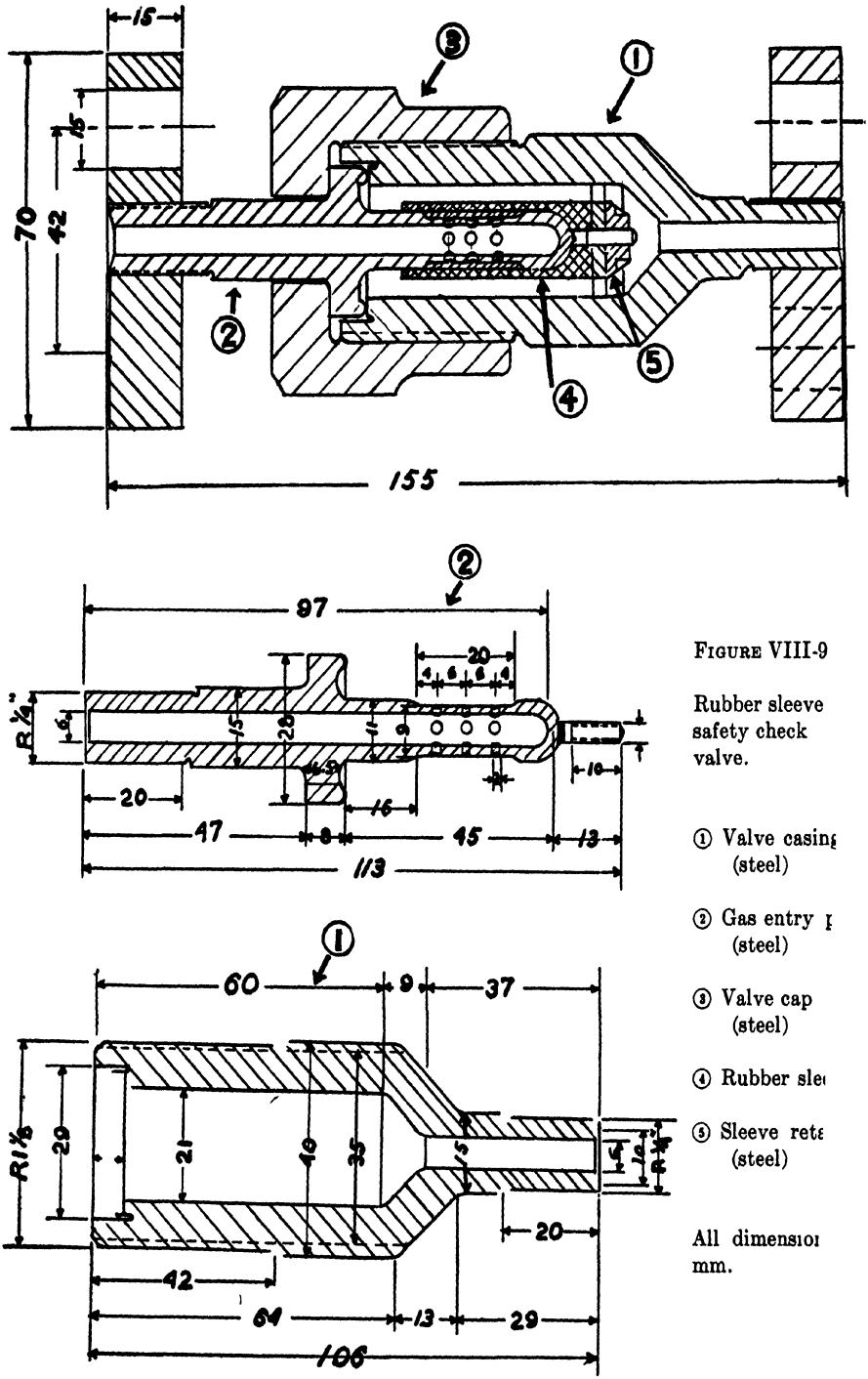


FIGURE VIII-9

Rubber sleeve safety check valve.

① Valve casing (steel)

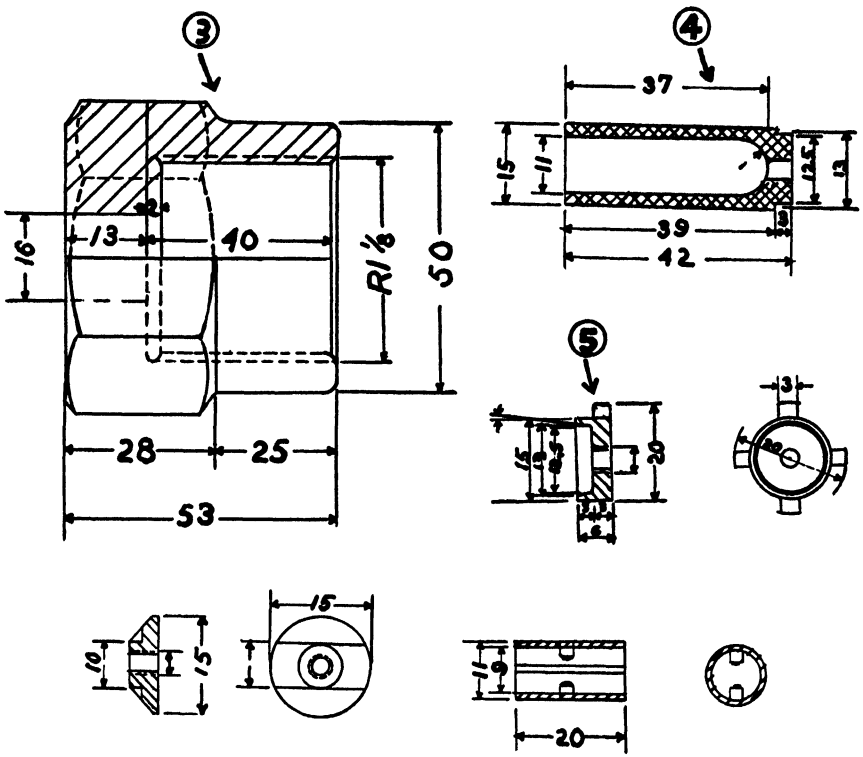
② Gas entry p (steel)

③ Valve cap (steel)

④ Rubber sle

⑤ Sleeve rete (steel)

All dimensio mm.



The autoclaves were connected to high pressure cylinders by means of spirals of high-pressure steel tubing, or in some cases copper alloy tubing. The reacting materials were charged into the autoclave through this tubing. Heating of the autoclaves was usually accomplished electrically by slipping the autoclave into a jacket wound with nichrome wire. Each autoclave was equipped with a thermocouple which was connected to a common millivoltmeter through a selector switch.

The use of stirrers was objectionable; agitation was accomplished by a shaking device. This shaking mechanism consisted of two parallel metal bars (Figure VIII-14) supported on a framework. The letters indicate the following parts:

(*A*) Pivoted fork which fits around upper neck of autoclave
(*B*) Stationary supporting rod
(*C*) Ball joint fitting in socket (*D*)
(*D*) Socket
(*E*) Oscillating rod

As many as 60 of the autoclaves were mounted on one rack, placed in an open room, without barricades or shields of any kind. Acetylene was

piped directly to these units under 30 atm pressure through small bore lines. Other gases such as carbon monoxide, hydrogen, etc. were also available.

5-Liter Experimental Stirred Autoclaves. For larger-scale work Reppe favored a 5-liter stirred autoclave which was a modification of those made

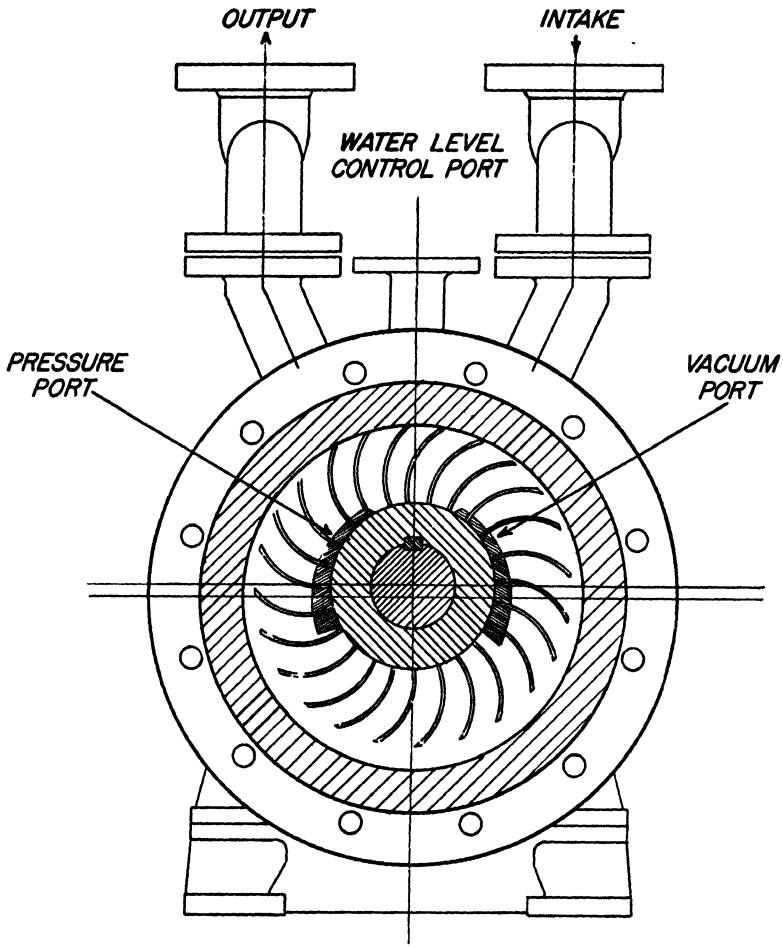


FIGURE VIII-10. Water ring pump.

by Andreas Hofer. The modified autoclaves were constructed to meet the following specifications:

(a) Provide a 5-liter reaction space, yet be light in weight and capable of withstanding high pressures and temperatures.

(b) Be capable of being opened and closed quickly.

(c) Be easy to fill and drain.

(d) Provide thorough agitation.

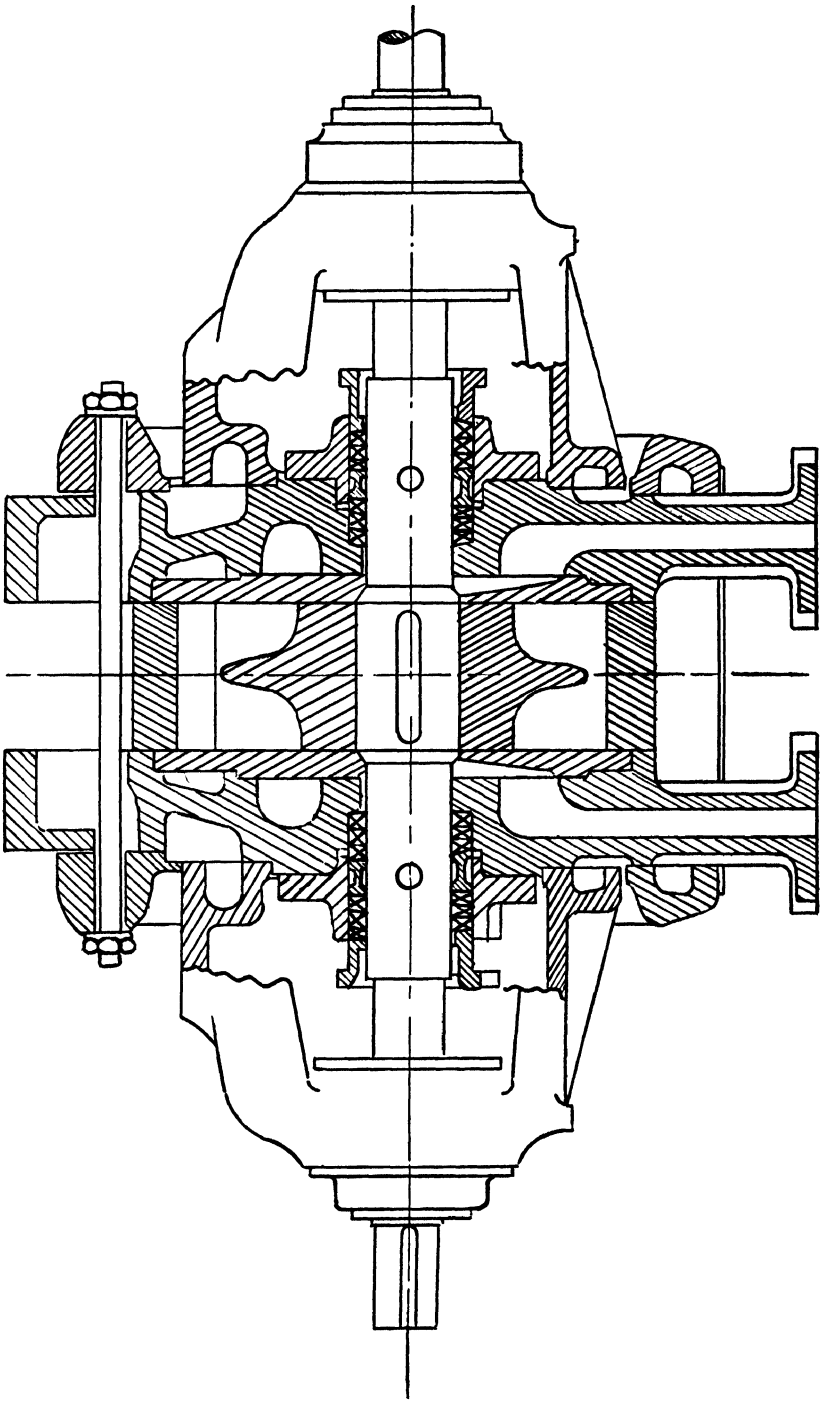


FIGURE VIII-11. Water ring compression pump

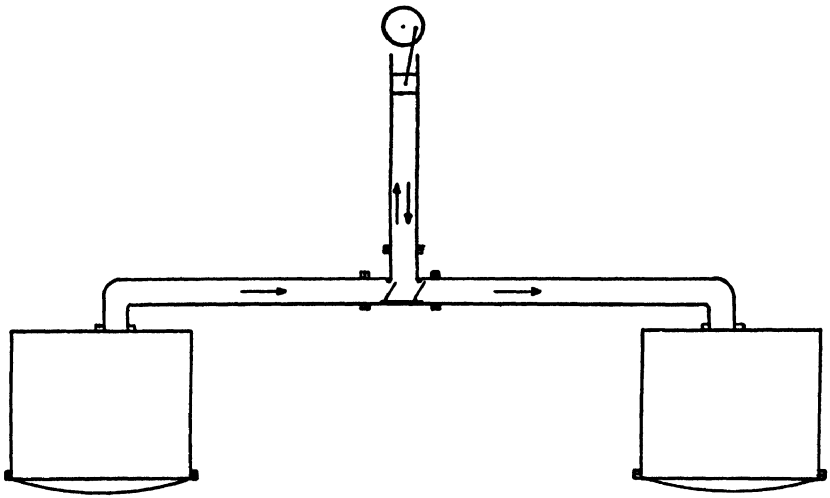


FIGURE VIII-12 Water-leg pump.

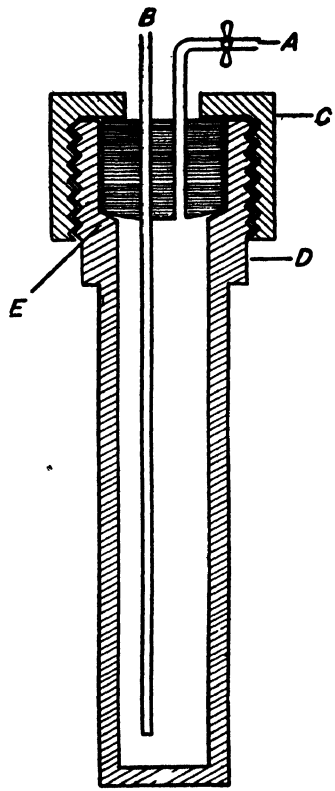


FIGURE VIII-13. Small experimental shaking autoclave.

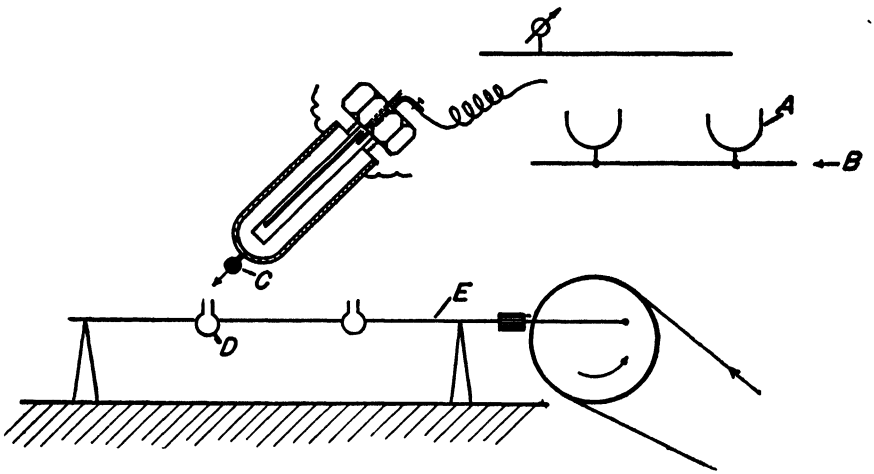


FIGURE VIII-14. Shaking assembly for small autoclaves.

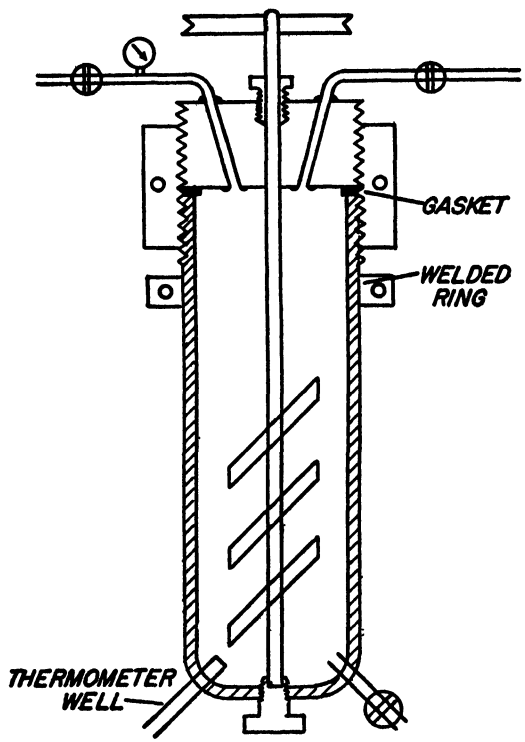


FIGURE VIII-15. Five-liter experimental autoclave.

The improved five-liter stirred autoclave consists of a chamber proper (approximately 10 cm x 70 cm) with a cap fitted to the body proper by

means of a union as shown in Figure VIII-15. The cap, union, and body were drilled or slotted to allow opening by means of spanner wrenches. A gas-tight seal is obtained by using metal packing rings, pressure being obtained by tightening the union. No other details are available.

Hofer Autoclaves. Several of the autoclaves manufactured by Andreas Hofer in various sizes and types are shown in Figures VIII-16 through VIII-20, together with the available information pertaining to them. Figure VIII-21 details the construction of one special type of autoclave stirrer shaft stuffing box.

Steels for High-Pressure Apparatus

Two wartime steels, designated as N-8 and N-10, were in use in Germany for high pressures and temperatures, particularly where hydrogen-resistant steels were necessary.

N-8 steel had the following percentage analysis: 0.20 to 0.25 carbon, 0.4 silicon, 0.50 to 0.6 manganese, 2.0 to 2.3 chromium, 0.2 to 0.3 vanadium, and less than 0.02 sulfur and phosphorus. This steel was suitable for pressures up to 200 atm at 600°C.

N-10 steel (FDKM-10) had the following percentage analysis: 0.19 to 0.24 carbon, 0.4 silicon, 0.30 to 0.45 manganese, 2.7 to 3.0 chromium, 0.35 to 0.45 molybdenum, 0.75 to 0.85 vanadium, 0.30 to 0 45 tungsten, and less than 0.02 each, sulfur and phosphorus. This steel withstands 2,000 atm at 600°C. However, 520°C was recommended as the maximum metal temperature, and when this steel was used in preheaters at 700 atm, flue-gas temperatures were restricted to 560°C maximum. N-10 tubing had an O D./I D. ratio of 1.7 to 1.8, which at 700 atm gave a stress of 11.3 tons/sq in or 8.2 tons/sq in, according to whether the stress calculation is based on the elastic or plastic theory.

Because of failures of N-10 in service, the method of testing steels for hydrogen resistance was changed during the war. The original testing period of 200 hours had been found too short, and tensile testing of test pieces had not given satisfactory results. It was considered that the normal methods were not satisfactory for the testing of a material to be used so near its limits, and that test conditions should approach more nearly the actual plant conditions. Life tests on tubes under working pressures and temperatures were therefore developed, the tubes themselves being scaled-down versions of plant tubes. In this way, it was hoped to obtain results which would be of more direct applicability.

N-10 tubing was delivered in 3- to 4-m lengths in rolled form, and 4- to 5-m lengths in the form of bored-out bars. The latter type was favored because with such thick-walled tubes the cost was very little greater than for rolled tubes, and there was no risk of trouble from the small faults that were always present in the bores of rolled tubes. The tubing was

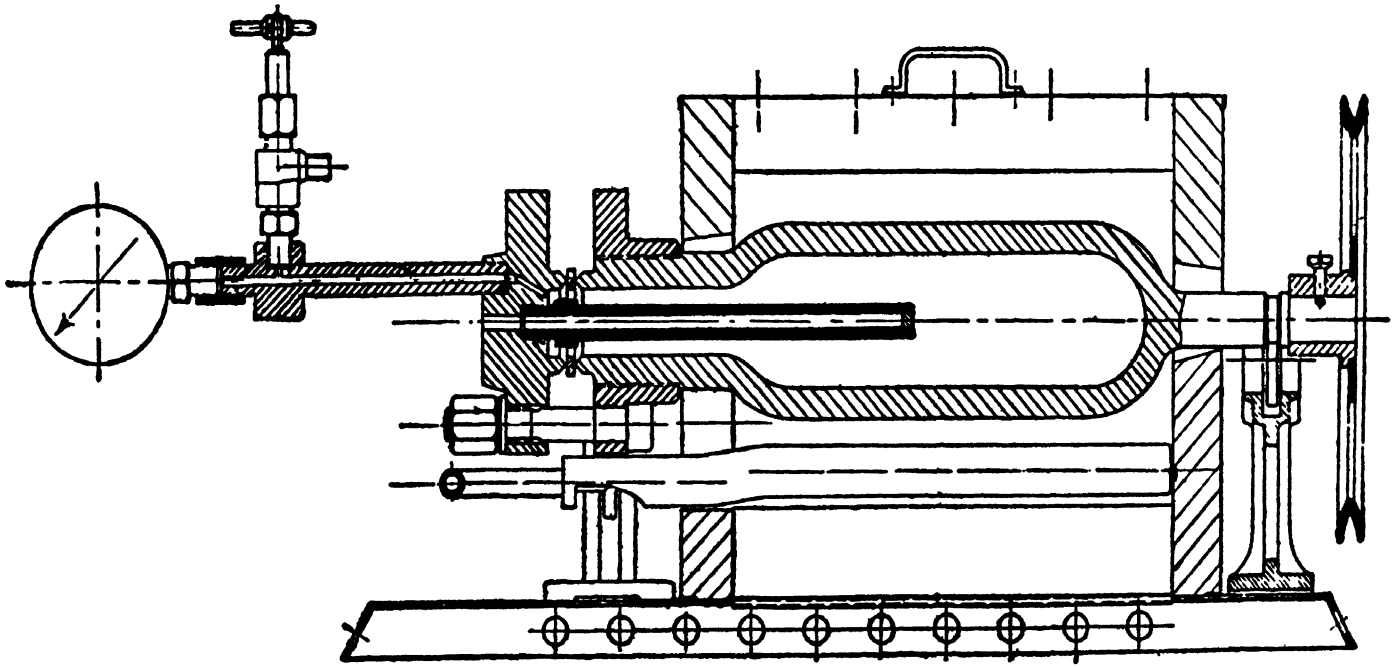


FIGURE VIII-16 Rotating autoclave designed by Andreas Hofer. Gas heated Speed of rotation 10 to 15 rpm. Capacities 1 5 to 20 liters Operating pressure 300 atm Maximum temperature 550° C. Cover sealed by the Ipatieff method.

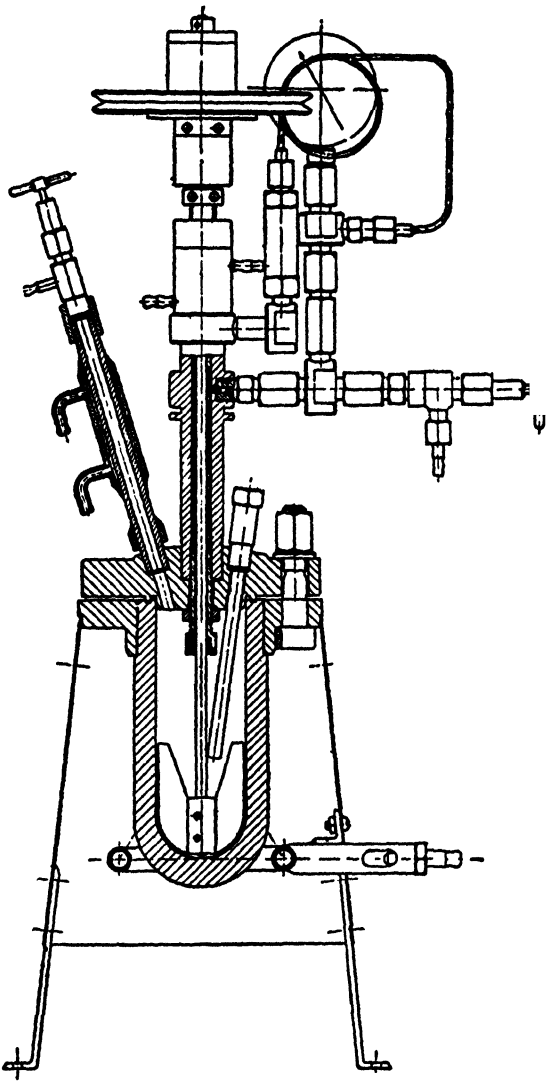


FIGURE VIII-17. Stationary vertical autoclave by Hofer. Capacities 0.5 to 100 liters. (Siemens-Martin Steel), 0.5 to 5 liters (Krupp's V2A and V4A steels). Operating pressure 300 atm at 550° C. Cover sealed by the spigot and recess method. Gas heated with reflux condenser attached. The stirrer shaft is sealed with a lantern ring stuffing box with oil fed from a bottle maintained at the autoclave operating pressure.

heat-treated according to a method developed at Leuna. After heating to 1050°C, the steel has a Brinell hardness of at least 350, which falls to 250 to 280 on annealing. Great difficulty was experienced in heat-treating

forged pieces of the alloy; therefore the use of N-10 for forgings was abandoned.

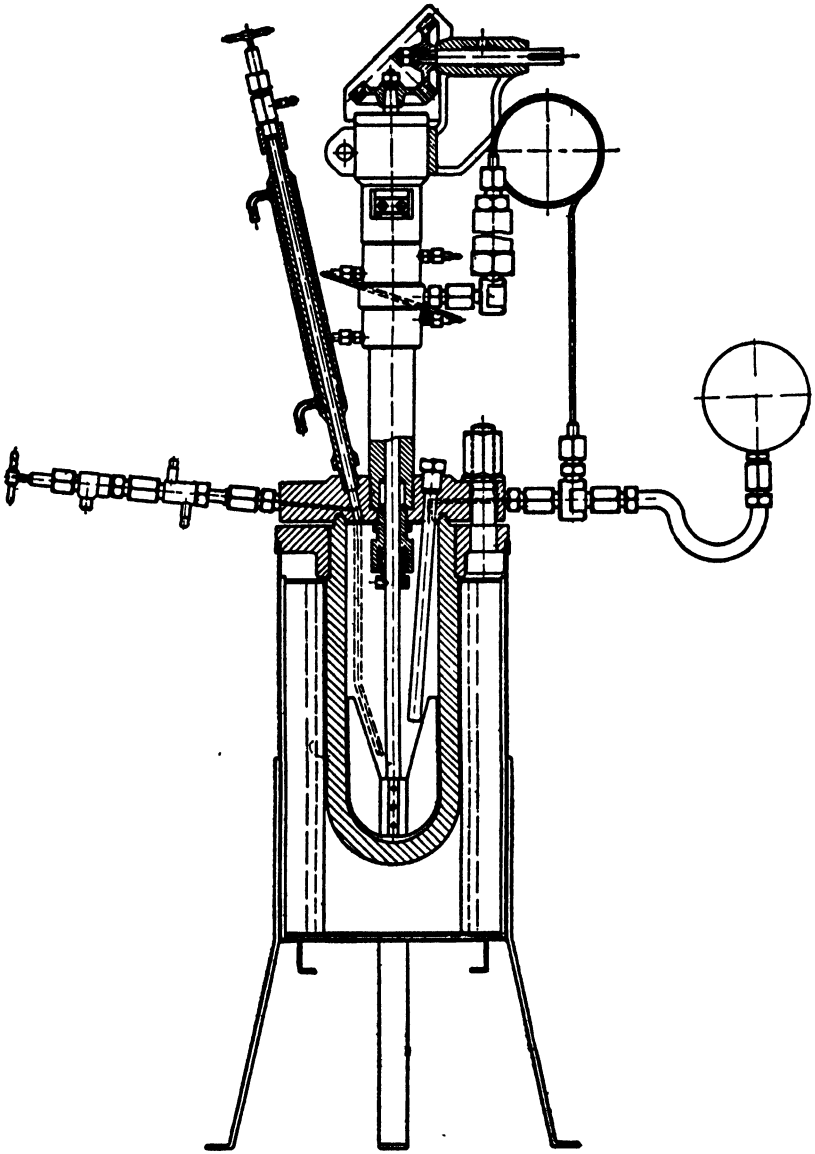


FIGURE VIII-18. Hofer vertical electrically heated autoclave.

It was disclosed that V2A was in use at Welheim for 700-atm preheaters and that no operating difficulties were experienced. It was stated that the I.G. would have used V2A for 700-atm preheaters if nickel had been

available, since the creep strength of V2A was superior to that of N-10 at high temperatures.

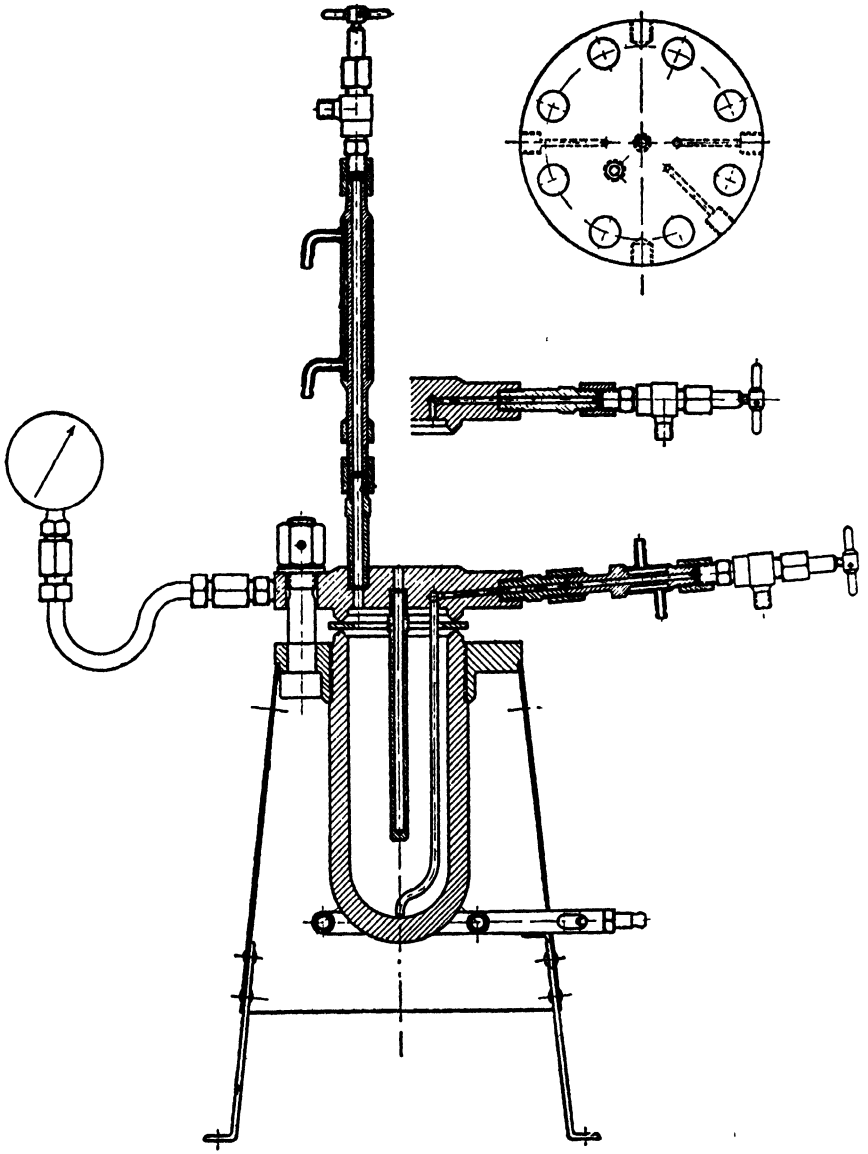


FIGURE VIII-19. Hofer vertical autoclave with Ipatieff joint.

Formerly, V2A steels were used for lining catalyst baskets in order to guard against attack by hydrogen and sulfur. When supplies of alloy steel became scarce, 15-mm thick ordinary steel shells were used with an

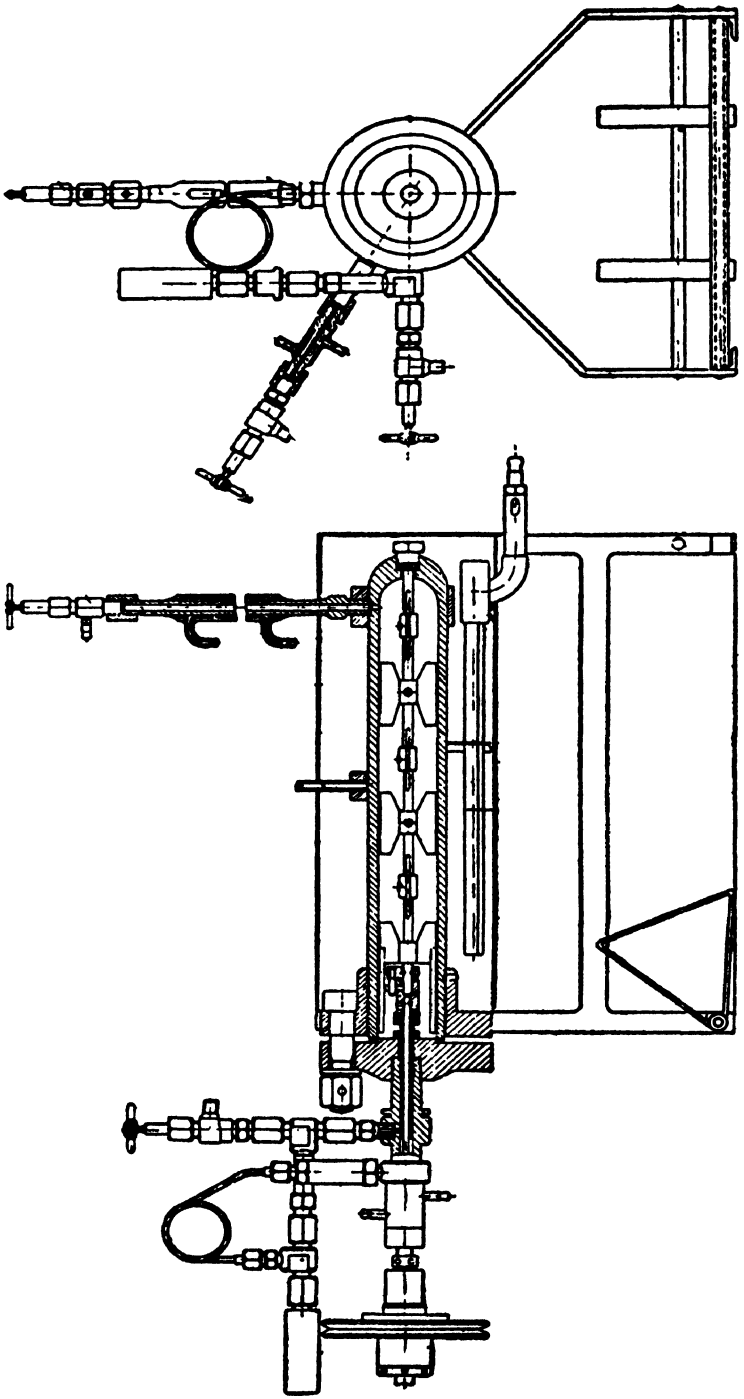


FIGURE VIII-20 Hofer horizontal autoclave with stirring gear.

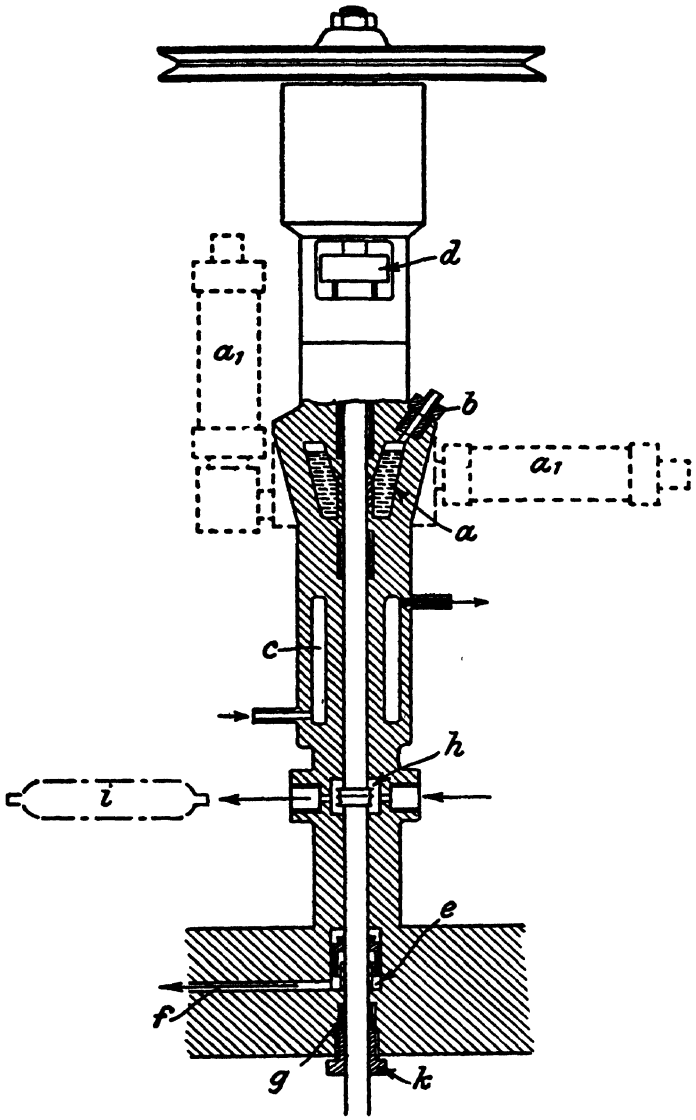


Figure VIII-21. Hofer stuffing box.

Chamber "a" is filled to 5 mm below the level of the filling plug "b" before starting operations Heavy cylinder oil or castor oil is used. Before heat is applied to the autoclave, water is circulated through the jacket "c" Gland nut "d" is tightened if oil seepage is noted An oil separating and collecting chamber "e" is installed to prevent the contents of the autoclave from being contaminated with oil. Hole "f" closed at one end with a valve enables checking the amount of oil leakage When the autoclave is charged with chemicals which may destroy the lubricant, a special gland "g" is installed. Fresh gas charged into the autoclave enters chamber "h", thus removing objectionable vapors. The contents of chamber "h" is collected in the bottle "i".

internal plating of V2A only 1 mm thick; at the same time, this gave a stronger basket which was not so likely to fail during a rapid blow-down.

Because of the shortage of chromium and molybdenum, manganese was used in flange steels; considerable difficulty was encountered in achieving the required tensile properties without getting a steel which was too brittle and susceptible to cracking. Because of its reduced ductility, the substitute steel was used only up to 350°C. This steel had the following percentage analysis: 1.1 to 1.4 manganese, 1.1 to 1.4 silicon, and 0.4 carbon. After water quenching, the tensile strength was 50 to 60 tons/sq in.

Corrosion-Resistant Alloys

In addition to a wide variety of stainless steels, the following alloys were stated to be highly resistant to corrosion. Unfortunately, no data are available to indicate the applications for which they were used.

Kurt's alloy[7]

75 to 90% molybdenum
6 to 15% nickel
4 to 13% iron
2 to 12% silicon

Field's alloy[8]

20% molybdenum
60% nickel
20% iron
0.3–3% manganese
0.5% silicon
0 2% carbon

These two alloys are claimed to be resistant to hydrochloric acid. Sheets immersed in a 37 per cent hydrochloric acid solution at 70°C showed a decrease in thickness of only 0.05 mm per month.

Powell's alloy[9] consisting of 25 per cent molybdenum, 65 per cent nickel, and 10 per cent copper, is equally resistant as is *Pfantsch's alloy* containing 90 per cent nickel, 7 per cent molybdenum, and 3 per cent silicon.

Corrosion-Resistant Linings or Coatings

In attempting to produce adipic acid by the Reppe process (carbon monoxide-tetrahydrofuran, see page 276), high-pressure vessels made of S and N steels were used, but the results were disappointing because the highly corrosive action of the reactants and products produced iron salts which acted as anti-catalysts. Super alloy steels of 18/8 extra type were

[7] *Aust. Pat. 106,973* (1927).
[8] *Chem. Met. Eng.*, **36**: 542 (1929).
[9] *Brass World*, **20**: 160 (1924).

somewhat better, but even with these alloys the results were such that the collaborators decided the process must be abandoned, or a corrosion-resistant material found.

It appeared that the best approach was through some sort of plating or lining. Tantalum was suggested but was discarded because of the scarcity of tantalum and the lack of knowledge of how to make foolproof weldings. It was known that tantalum could be soldered with niobium, but the latter material was also very scarce.

Tests indicated that lining the high-pressure vessels with molybdenum or tungsten or even vanadium and rhenium would give corrosion-resistant vessels. Molybdenum and tungsten can even be shaped if the metals are pure. In addition, these metals are capable of being welded electrically with an arc-atom burner. For lining purposes, the price of molybdenum is not exorbitant considering its low specific gravity (10 to 10.5); however, the Germans were unable to use molybdenum due to its scarcity.

The necessity of conserving scarce metals led the Germans to seek other methods for preventing corrosion. Coatings appeared to be more economical than linings; hence, efforts were made to find suitable means for applying thin continuous coatings. It was found that iron and steel vessels could be coated with tantalum by the tantalum chloride-iron exchange procedure. According to spectroscopic analysis, coatings containing 20 to 40 per cent tantalum were obtained. In some instances with tantalum chloride, coatings containing 60 to 70 per cent tantalum were formed. One drawback of the tantalum process is that large quantities of tantalum chloride are required at temperatures of 900 to 1000°C.

Nickel alloys containing 30 per cent tantalum were supposed to be resistant to hydrogen chloride, but this was found to be untrue. Such an alloy will resist dilute sulfuric acid at 60 to 70°C but dissolves in other mineral acids. Increasing the tantalum content to 65 to 70 per cent increased corrosion resistance materially.

An experimental autoclave of 250-cc capacity was built of steel to resist 250 atm pressure. The autoclave was lined with nickel and treated with tantalum chloride. A 30 to 40 per cent tantalum content was found on the nickel surface. This coating stood up against 200 atm of carbon monoxide.

Bismuth was tried but found unsatisfactory in a similar application; the nickel in the coating gradually formed nickel carbonyl. Later the experiments were extended, and a new process was discovered which utilized all metals whose alloys cannot be reduced by hydrogen and which form solutions or compounds with each other. Such metals are nickel, cobalt, antimony, bismuth, iron, gold, silver, and platinum. The procedure is to make a paste of the finely divided metals (less than 5 microns) with a suitable lacquer resin dissolved in xylene or toluene. The surfaces of the autoclave are given a thin coating of this paste together with a soldering flux of low volatility. The vessels are then heated to 900 to 1100°C in hydrogen.

Depending upon the condition of the surfaces of the autoclave, more or less smooth surfaces are obtained, which in any case are firmly linked to the base metal by diffusion. It remains to be determined whether this process can be simplified by the use of arc-atom burners and made similar to the lead lining of vessels. The addition of one to three per cent of manganese or manganese carbide to the metal powder paste improves the surface.

Toward the close of the war the Germans were actively engaged in trying to burn smooth coatings onto their reactors using the arc-atom burner.

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