THE CHEMISTRY AND UTILIZATION OF CYCLOPENTADIENE

PHILIP J. WILSON, JR., AND JOSEPH H. WELLS

Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania[1]

Received September 27, 1943

Cyclopentadiene is a low-boiling cyclic diolefin which has been found among the products resulting from the pyrolysis of organic compounds. Commercially important quantities can be recovered from the distillates produced in carbonization of coal, particularly the forerunnings from coke-oven light oil. The chemistry of cyclopentadiene is reviewed with particular reference to its industrial application. Not only is this substance of interest for the production of resins, but it can also be the starting point for the synthesis of a large number of other organic products, some of which should find use in a variety of fields. On standing, cyclopentadiene spontaneously polymerizes to dicyclopentadiene, a compound solid at ordinary temperatures. Because the latter is readily reconverted to the monomer, it forms a more convenient form in which to handle cyclopentadiene. The properties of dicyclopentadiene are likewise reviewed.

I. INTRODUCTION

Dienes are vitally important to our national life at present, because they can be utilized to produce synthetic products which may replace natural rubber. This family of compounds is consequently receiving much attention in order to find members which will improve the properties of the new rubbers and will be useful in the synthesis of resins. A very interesting diene is cyclopentadiene, which not only possesses the reactive, conjugated, double-bond structure, but also contains an active methylene group. Already from cyclopentadiene a large number of polymers and derivatives have been prepared, some of which are proving of commercial value in the field of synthetic resins. A few of the more significant reactions will be emphasized at this point.

Cyclopentadiene can be polymerized in the presence of catalysts to produce rubber-like compounds. The reaction is analogous to the production of synthetic rubbers from other conjugated dienes. The present sources of cyclopentadiene are not sufficiently productive at this time to furnish any appreciable volume of synthetic rubbers for use in tires. Cyclopentadiene, however, may find application in the rubber program as a copolymer which will modify the properties of other rubbers.

By the heat polymerization of cyclopentadiene there are produced structures which are characterized by a chain of hexagonal carbon rings, each containing a bridging methylene group and terminated at one end by a pentagonal ring. Dicyclopentadiene, which forms spontaneously in cyclopentadiene at ordinary temperatures, is the simplest member of the series. Its structure is similar to that of indene except for the methylene bridge and two extra hydrogens. The

---

[1] Multiple Industrial Fellowship sustained by the Carnegie-Illinois Steel Corporation, Pittsburgh, Pennsylvania.

highest polymers are waxy solids, the application of which—to replace natural waxes, for instance—has not as yet been explored.

The preparation of a very large number of derivatives by the addition of cyclopentadiene and an olefin by the Diels–Alder reaction is possible. This synthesis enables the preparation of such important compounds as terpene, camphor, and partially hydrogenated benzene derivatives. Thus, norcamphor has been produced from cyclopentadiene and acrolein. The compounds formed by the heat polymerization of cyclopentadiene are also examples of Diels–Alder reaction products. Another is the addition of maleic anhydride to cyclopentadiene. The product, *cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride, is similar in structure to phthalic anhydride, except for the addition of a methylene bridge and two extra hydrogens. It can be used to produce alkyd resins. High-boiling esters of the acid have been recommended as plasticizers. The complex quinones produced by the addition of cyclopentadiene to quinones may prove of interest in the dye industry.

By the condensation of cyclopentadiene with aldehydes and ketones highly colored fulvenes are produced. These may find application in pharmaceuticals. Barbiturates prepared from cyclopentadiene and malonates already have important pharmaceutical applications. Derivatives, such as alcohols, amines, and halogenated compounds, can be readily synthesized from cyclopentadiene.

These reactions render cyclopentadiene of especial interest as a raw material in the resin, pharmaceutical, and synthetic organic chemical fields. The surface has scarcely been scratched; further study of the diene and of its derivatives will doubtless extend the number and the importance of the industrial applications. Supplies of the compound can be made available as the needs arise.

II. Source and Production

A. PYROLYSIS OF HYDROCARBONS

Cyclopentadiene is one of the many compounds formed during the pyrolysis of hydrocarbons at high temperatures, and both it and its dimers have been separated from the volatile products of such reactions. In the carbonization of coal, the tar, the light oil, and the coke-oven gas have yielded these two compounds. Kraemer and Spilker (140) in 1896 first reported the presence of cyclopentadiene in coal-tar fractions.

1. Benzol forerunnings

The presence of cyclopentadiene in the forerunnings fraction produced during the distillation of coke-oven light oil has been frequently reported (50, 56, 107, 108, 143, 188, 230, 239). A forerunnings fraction completely resinified by sulfuric acid was found by Kruber (142) to consist mostly of cyclopentadiene; the residue appeared to be dicyclopentadiene. In some crude light oils Gillies (93) found as much as 1.2 per cent of cyclopentadiene. At present benzol forerunnings is probably the largest potential source of cyclopentadiene which is receiving attention. From the experience of the authors it is estimated that the concentrations in light oil will be between 0.5 and 1 per cent by volume, equivalent to between 0.1 and 0.2 pound of cyclopentadiene per ton of coal carbonized. Although such a yield appears small, the potential volume available from the coal coked annually in the United States would represent many thousand gallons of cyclopentadiene; its recovery, particularly in the larger plants, would frequently prove practical.

Because cyclopentadiene spontaneously polymerizes at ordinary temperatures to dicyclopentadiene, which boils at approximately 170°C., the latter will be present in the higher-boiling fractions of the light oil, particularly after standing, or in coal-tar fractions. No steps appear to have been taken as yet towards the recovery of dicyclopentadiene from these higher-boiling fractions, but Carmody and coworkers (49, 50, 51, 52) have produced resins by polymerizing the dicyclopentadiene with other compounds present in the fractions. The solvent-naphtha fraction of the light oil thus represents another potential source of cyclopentadiene, provided recovery methods can be developed.

2. Coke-oven gas

Ross and Race (188) found cyclopentadiene in both coal gas and water gas. They separated cyclopentadiene derivatives from the oils produced by brominating the gases, and identified cyclopentadiene in the forerunnings from the anthracene oil which had been used to wash naphthalene from the gas. In France the Bethune Company recovered 35–45 pounds of cyclopentadiene per 1000 tons of coal by liquefaction and fractional distillation of coke-oven gas, according to Horclois (111). Fractional distillation of the gas does not appear to be a very efficient method for separating such a small fraction, but as yet no better method has been disclosed.

3. Carburetted water gas

When petroleum oil is cracked to carburetted water gas, cyclopentadiene is found among the products and may be recovered from the tar, drip oil, or condensates produced by refrigeration of the gas, according to Ward (230). A fraction which he distilled from water-gas condensates contained 18 per cent of cyclopentadiene, as well as isoprene, piperylene, pentenes, and other hydrocarbons. Such condensates can apparently become another useful source of cyclopentadiene.

4. Hydrocarbon cracking

Cyclopentadiene has been found in many products obtained by the pyrolysis of natural gas, petroleum, and its fractions. It was first isolated in 1891 by Étard and Lambert (81) from oil gas. Cyclopentadiene was identified in the products from the cracking of Persian natural gas by Birch and Hague (39). Volzhinskiĭ and Shcheglova (228) reported that 30–35 per cent of the 28–50°C. fraction which they obtained in the vacuum cracking of kerosene consisted of dienes, and that the greater part was cyclopentadiene. Small amounts of cyclopentadiene were produced during the cracking of a Pennsylvania gas oil at 950°C. and 175 mm. pressure, according to Tropsch and coworkers (224). Potolovskiĭ and Vimberg (177) found that a low-boiling fraction obtained during the pyrolysis of a Russian gas oil contained 5.5–6.0 per cent cyclopentadiene, as well as some isoprene. The fraction boiling between 27° and 50°C. produced by the pyrolysis of another gas oil was reported by Dedusenko (60) to contain 3.5–3.7 per cent of cyclopentadiene. In the fraction boiling at 30–45°C. obtained from a gasoline produced by vapor-phase cracking at 570°C., Moor and Katzman (157) found 6–8 per cent of cyclopentadiene.

When Frey and Hepp (90) cracked the lower paraffins, other than methane, at 850°C., cyclopentadiene was one of the principal products. Cyclopentadiene was present in the oil fraction boiling below 200°C. which Cambron and Bayley (47) produced by cracking propane at 800–810°C. in alloy-steel tubes under conditions of turbulent flow. Kazanskiĭ and Plate (121) separated a little cyclopentadiene from the products obtained by pyrolyzing cyclopentane at 650°C. In the treatment of ethylene hydrocarbons at elevated pressures and temperatures Dunstan and coworkers (73) produced some cyclopentadiene.

5. *Pyrolysis of phenol*

When Ruhemann (189) heated phenols at 750°C. in contact with quartz, glass, or pumice, carbon monoxide split off and the nucleus rearranged to form cyclopentadiene. In 1886 Roscoe (187) first found dicyclopentadiene in the products obtained by the pyrolysis of phenol.

B. RECOVERY FROM OILS

The dimerization of cyclopentadiene was utilized by Ward (230) for its recovery from oil fractions containing other polymerizable dienes. By heating the mixture to a temperature in the neighborhood at 100°C., under a pressure sufficient to maintain the larger part of the reaction mixture in the liquid phase, dicyclopentadiene was produced. Dimerization takes an appreciable time, and in one example Ward heated the oil at 92°C. for 24 hr. The dicyclopentadiene was separated from the product by fractional distillation under vacuum, using a pressure of 25 mm. of mercury absolute. A product containing 95–97 per cent of dicyclopentadiene was obtained.

In the Annual Report of the Mellon Institute for 1941–42 (238) there is mentioned a process, developed by the authors, for the recovery of cyclopentadiene from benzol forerunnings, which also depends on the formation and recovery of dicyclopentadiene.

Dicyclopentadiene is readily reconverted to the monomer by distilling the former under atmospheric pressure. By maintaining the top temperature of the fractionating column of their still at 40–41°C., Kistiakowsky and coworkers (131) obtained a distillate of cyclopentadiene alone. As dicyclopentadiene boils at approximately 170°C., it was refluxed to the still kettle. Dicyclopentadiene thus represents a convenient form in which to handle and store cyclopentadiene. Ward (230) recommended that it be stored in an atmosphere free from oxygen, such as nitrogen, to avoid the formation of peroxides. A number of investigators have used the depolymerization of dicyclopentadiene to cyclopentadiene as a means for obtaining a high-grade material for use in experimental work (131, 159).

The Diels–Alder reaction of cyclopentadiene with maleic anhydride has been utilized for separating cyclopentadiene from coke-oven light oil. The crystalline *cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride was separated from the unreacted oil, according to the patent of the I. G. Farbenindustrie (114). Morrell and coworkers (156) used the reaction for removing cyclopentadiene from gasoline.

Tyutyunnikov (226) used maleic anhydride, benzoquinone, α-naphthaquinone, or a similar substance for separating the cyclopentadiene from light-oil fractions. Because indene, coumarone, and related substances react with the same reagents, the cyclopentadiene adduct was recovered with them as a high-melting resin. Potolovskiĭ and Vimberg (177) also employed benzoquinone for removing cyclopentadiene from a light-oil fraction. Cyclopentadiene cannot be recovered directly from the maleic anhydride adduct, but it may prove practicable to decompose the quinone derivatives with recovery of the reagents.

C. SYNTHESIS OF CYCLOPENTADIENE

Cyclopentadiene has been synthesized by the dehydrogenation of cyclopentane, according to Morrell (155). A 9 per cent yield was obtained by Grosse and coworkers (98, 99) by passing cyclopentane, at 500–600°C. and 0.25–1 atmosphere pressure, over dehydrogenating catalysts such as Al_2O_3 impregnated with oxides of chromium, molybdenum, and vanadium. The time of contact was 0.5–6 sec. Frey (89) found 2.7 per cent of cyclopentadiene in the products of the dehydrogenation of cyclopentane at 575°C. in a silica tube.

Cyclopentadiene has been prepared by boiling 1,2-dibromocyclopentane at 110°C. for several days with ethylene glycol and potassium (159). The same investigators, Mousseron and Granger (160), also obtained it by heating either 2-methoxy- or 2-ethoxy-cyclopentanol with sulfuric acid.

Cyclopentadiene was synthesized by Zelinskiĭ and Levina (245) from cyclopentanone. The latter was reduced, using hydrogen and an osmium catalyst, to cyclopentanol, which in turn was dehydrated to cyclopentene by heating with anhydrous oxalic acid. The dibromide produced from the cyclopentene in a chloroform solution was finally converted to cyclopentadiene by heating at 180°C. with an acetic acid–sodium acetate mixture.

III. PHYSICAL PROPERTIES

A. PHYSICAL CONSTANTS

Values for the melting and boiling points, the density, and the refractive index of cyclopentadiene are collected in table 1.

The following densities for cyclopentadiene at different temperatures are given by Raistrick and coworkers (178):

TEMPERATURE	d^4
°C.	
0	0.8235
10	0.8131
20	0.8021
25	0.7966
30	0.7914

Barrett and Burrage (32) have determined the vapor pressures of cyclopentadiene at different temperatures. When the reciprocal of the absolute temperature was plotted against $\log_{10} P$, a straight line was obtained in the range 0–15°C. From this curve, the following two values have been read: a pressure of 250 mm. of mercury at 12°C., and 44.7 mm. at −22.9°C.

TABLE 1

Physical constants of cyclopentadiene

MELTING POINT °C.	BOILING POINT °C.	BOILING POINT At mm. of mercury absolute	DENSITY	INDEX OF REFRACTION
−85 (202a)	40	760 (202a)	0.8026 d_4^{20} (231)	1.4429 n_D^{20} (231)
	41	760 (140)	0.803 d_4^{20} (81)	1.4398 $n_D^{19.5}$ (245)
	41.5–42	760 (209)	0.7983 $d_4^{19.5}$ (245)	1.4446 $n_D^{18.6}$ (140)
	41.5	760 (77)	0.80475 $d_4^{18.6}$ (140)	1.44627 $n_D^{16.1}$ (31)
	42.5	760 (81)	0.8070 $d_4^{16.1}$ (31)	1.44632 $n_D^{16.1}$ (31)
	41	757 (245)	0.8085 $d_4^{16.1}$ (31)	
	40.2–40.8	757 (31)	0.8071 $d_4^{15.7}$ (77)	
	40–41	755 (103)	0.81500 d_{15}^{15} (140)	
	40	715 (220)	0.8083 $d_4^{14.1}$ (77)	
	40.83	772 (131)	0.8228 d_4^{0} (30)	

Additional physical constants are as follows:

Dispersion $\times 10^4$ $(n_F - n_C)$	132 (231)
Specific dispersion $\left(\frac{n_F - n_C}{d}\right)$	164 (100, 231)
Heat of vaporization per gram mole	7 kg.-cal. (234)
Heat of combustion per gram mole	
of cyclopentadiene	847.8 kg.-cal. (127)
of gaseous cyclopentadiene	707 ± 7 kg.-cal. (234)
Heat of formation from carbon and hydrogen per gram mole:	
Calculated from heat of combustion	1153 ± 7 kg.-cal. (234)
Calculated from bond energies	1152 ± 7 kg.-cal. (234)

Cyclopentadiene in benzene gives an abnormal depression of the freezing point, according to Garelli (91), probably owing to the formation of a tightly bound solution, but dicyclopentadiene, its dimer, affords normal values.

The spontaneous ignition point of cyclopentadiene in oxygen was found to be 510°C., and in air, 640°C. by Zerbe and Eckert (246), using the drop method. Although in agreement on the value in air, Tausz and Schulte (211) obtained 414°C. in oxygen.

The octane number, as reported by Lovell and coworkers (148), was greater than 100; the aniline equivalent, 34; and the critical compression ratio, 10.9. Addition of tetraethyllead to cyclopentadiene was shown by Campbell and coworkers (48) to have a negative effect on the critical compression ratio.

B. SPECTRA

1. Infrared

The absorption spectra of fresh and polymerized cyclopentadiene have been studied in the infrared range by Lambert and Lecompte (144). In particular in the region of 700 cm.$^{-1}$ the polymer shows a plurality of strong absorption bands. The strong band at 961 cm.$^{-1}$ in the fresh material is displaced to 930 in the polymerized cyclopentadiene, and strong bands at 1237 and 1310 cm.$^{-1}$ in the former have disappeared in the dimer.

2. Ultraviolet absorption

Pickett and coworkers (172) have found that in the ultraviolet range between 32,000 cm.$^{-1}$ and 66,000 cm.$^{-1}$ the vapor shows an intense absorption band with a maximum at 43,000 cm.$^{-1}$, on which are superimposed narrow diffuse bands with maxima at 38,800 cm.$^{-1}$, 39,650 cm.$^{-1}$, 40,400 cm.$^{-1}$, and 41,170 cm.$^{-1}$, and a group of sharply defined bands beginning at 40,000 cm.$^{-1}$ In hexane solution, the cyclopentadiene absorption maximum has approximately the same intensity as for the vapor but is shifted to 41,800 cm.$^{-1}$ and has but two narrow strong bands. The presence of such an intense absorption band with characteristic, superimposed, narrow bands makes it possible to identify cyclopentadiene in minute traces and to estimate its concentration in mixtures of other hydrocarbons.

In the Schumann region there is a prominent group of narrow sharp bands between 50,350 cm.$^{-1}$ and 54,000 cm.$^{-1}$ Pickett and coworkers reported twenty-six bands in this region. Nine of the stronger bands have been recorded by Scheibe and Grieneisen (193). The band maxima agree within experimental error.

The measured frequencies of Price and Walsh (177a) are less by about 50 cm.$^{-1}$ than those of Pickett. Two main frequency differences are involved,—one about 1450 cm.$^{-1}$ and the other about 480 cm.$^{-1}$ Price and Walsh ascribed the first to a valence vibration in the C=C bonds and the second to a twisting of the methylene group.

3. Raman spectra

Cyclopentadiene was among the five-membered rings the Raman spectra of which were studied by Reitz (184) by means of models. Calculated frequencies were compared with the experimental ones and with the frequency charges as a function of symmetry properties. He found no evidence of an abnormal behavior of the C=C bond. A number of lines, most of which were depolarized, have been recorded by Reitz (183, 185). The results are in modest agreement with those of Truchet and Chapron (225), Lambert and Lecompte (144), and Kohlrausch and Seka (135, 136). The particular feature in connection with cyclopentadiene is the shift $\Delta\bar{\nu}1500$ attributable to the ethylenic linkage. While this large decrease is not analogous to that observed with the allenes, it is much lower than that seen in other unsaturated cyclic hydrocarbons (106).

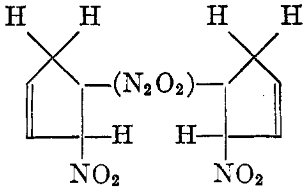
The molecular spectrum of cyclopentadiene has been studied by Mulliken (161, 162, 163), and an electron-diffraction investigation has been made by Schomaker and Pauling (194).

IV. CHEMICAL PROPERTIES

A. REACTIONS WITH MINERAL ACIDS AND ALKALIS

Cyclopentadiene reacts explosively with charring with concentrated sulfuric (140, 195, 237) and fuming nitric acids (140). Dilute acids resinify it, and soluble alkalis have a similar effect (140, 237). Potassium hydroxide in alcohol resinifies cyclopentadiene with vigorous evolution of heat (140). Kraemer and Spilker (140) isolated a compound, $C_{10}H_{12}(SO_3H)_2$, which was produced by the action of sulfuric acid on cyclopentadiene. Deep blue, high-molecular-weight products were prepared by treating cyclopentadiene with concentrated sulfuric acid at −80°C., according to Staudinger and Bruson (204). By addition of nitric acid to cyclopentadiene in chloroform Weger (237) obtained a nitrosate.

When Wieland and Stenzl (242) passed a current of nitric oxide gases through cyclopentadiene dissolved in ethyl ether, finely crystalline, pale yellow flocks were formed. They changed into a sticky brown mass, without loss in weight, when separated from the solution and allowed to stand for about three-quarters of an hour. It was concluded that the final product was cyclopentadiene pseudonitrosite:



B. HALOGEN DERIVATIVES

1. Addition of halogens

Halogens and halogen acids add readily at the unsaturated carbon linkages of the cyclopentadiene molecule. By such additions a series of halogenated derivatives have been prepared which range, in the case of chlorine, from monochlorocyclopentene to tetrachlorocyclopentane. Addition of a halogen takes place in two steps: first, the union of one molecule to each molecule of cyclopentadiene, to form $C_5H_6X_2$; then addition of the second halogen molecule. The reactions, which are vigorous, should be performed at a low temperature and in an inert solvent (140). According to Grosse and Wacker (100), the theoretical bromine number of cyclopentadiene is 485.

Thiele (220) added bromine slowly to cyclopentadiene dissolved in chloroform to produce *trans*-1,4-dibromocyclopentene-2. Farmer and Scott (85) prepared both the *cis*- and the *trans*-isomers by brominating at -15°C. in *n*-hexane solution. In one experiment the yield of the solid *trans*-isomer amounted to 40 per cent, but it could be varied by changing the proportion of hexane. The colorless liquid left after removal of the crystals contained 1,2-dibromocyclopentene-3 and a small amount of *cis*-1,4-dibromocyclopentene-2. By treatment with potassium permanganate, the bromopentenes were oxidized to the corresponding dibromoglycols, which in turn were oxidized with dilute chromic acid to dibromoglutaric acid.

Rapid addition of the bromine favored formation of *cis*-1,4-dibromocyclopentene-2, according to Mayes (151), who brominated cyclopentadiene at -25°C. in chloroform. At the same time a considerable quantity of tetrabromocyclopentane was formed. Solid *trans*-1,4-dibromocyclopentene-2 was precipitated slowly from the liquid *cis*-isomers on standing, but on slow distillation the crystals reverted to the *cis*-form. The corresponding cyclopentadienediols were formed by heating the dibromo compounds with potassium acetate and acetic acid to produce the diacetates, and saponifying the latter with alcoholic hydroxides.

Schultze (195) observed that the difficulties he encountered in brominating both double bonds of cyclopentadiene were due to a rapid autoöxidation prior to the reaction with bromine. Minute traces of the oxidation product had an enormous influence, and he concluded that bromination was a chain reaction. He described procedures for the quantitative bromination of the two double bonds in both cyclopentadiene and dicyclopentadiene either by titrating *in vacuo* or by introducing the cyclopentadiene into an excess of free bromine.

On addition of bromine in acetic acid to cyclopentadiene Staudinger and Bruson (204) obtained a deep blue, insoluble compound corresponding to the formula $C_{10}H_{11}CH_2COBr$; when heated it decomposed without melting with evolution of hydrogen bromide. Pauly and coworkers (169) reported that cyclopentadiene would slowly add close to two atoms of iodine from a tenth-normal iodine solution.

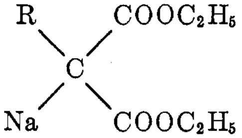
2. Addition of hydrogen halides

Dry hydrogen chloride, passed into a solution of cyclopentadiene in an inert solvent, such as toluene and chloroform, at low temperatures (-15°C. to -40°C.), added with the production of cyclopentenyl chloride (95, 140, 170). This compound decomposed on standing, with resinification and evolution of hydrogen chloride. It should be stored in the dark at low temperatures or, better, used at once (95, 140, 165, 170).

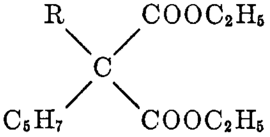
The halogenated derivatives of cyclopentadiene are interesting starting points for the synthesis of a large number of organic derivatives, including amines, alcohols, and thiocyanates. The preparation and application of these derivatives have so far received only limited attention. Ammonium hydroxide reacted with cyclopentenyl chloride to produce cyclopentenylamine and small amounts of an alcohol, and all primary and secondary bases react in a similar manner (140); e.g., by the addition of aniline at a temperature below 10°C., Noeldechen (165) obtained anilidocyclopentene. By the addition of chlorine to cyclopentenyl chloride at low temperatures Kraemer and Spilker (140) produced trichlorocyclopentane, which in the cold was resistant to concentrated sulfuric or nitric acid. Bases reacted with it slowly, while chlorine or hydrogen chloride split off.

3. Preparation of barbiturates

An application for the cyclopentenyl halides, which is suggestive to the pharmaceutical industry, is the preparation of barbiturates,—compounds with important sedative, analgesic, and hypnotic properties. Some of the barbiturates have also been used in the preparation of perfumes. The cyclopentenyl chloride is combined with the sodium compound of a malonic ester,



where R can be either hydrogen, an aryl group, or an aliphatic group, to produce the corresponding cyclopentenylmalonic ester:

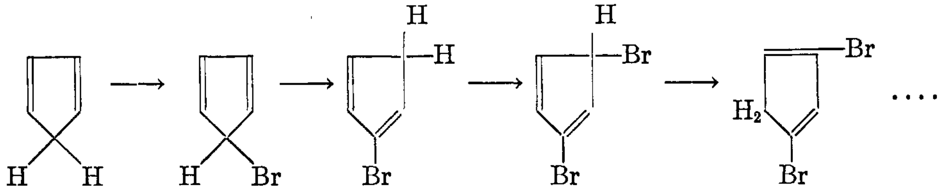


The preparation and properties of a number of barbiturates from these derivatives have been described by Chaux (54, 55) and by Horclois (111).

Noller and Adams (166) reacted a malonic ester and sodium alcoholate at 45–50°C., and then slowly added the cyclopentenyl chloride to the product at about 5°C. The cyclopentenylmalonic ester was saponified to form the acid and then decomposed by heating to produce the Δ^2-cyclopentenylacetic acid, a homolog of chaulmoogric acid which is of interest in the treatment of leprosy, according to Perkins and Cruz (170). Amides and ureides, as well as esters of cyclopentenylmalonic acid, have been prepared by the same reaction (181).

4. Action of hypohalites

The active hydrogen of cyclopentadiene has been replaced by treating the compound with an aqueous alkaline solution of a hypohalite. Strauss and coworkers (210) observed that the replacement progressed until all six hydrogens were eliminated. When a solution of cyclopentadiene in petroleum ether was shaken with hypobromite, crystals of hexabromocyclopentadiene began to separate in 10 min. The yield exceeded 50 per cent. The course of the reaction was represented as follows:



By treatment with hypochlorous acid, the cyclopentadiene in a light-oil fraction produced in the cracking of a gas oil was separated as the chlorohydrin. Dedusenko (60) then distilled the aqueous solution of the chlorohydrins with potassium hydroxide and from the alkaline residue separated *cis*-cyclopentadiol by extraction with ether.

C. REDUCTION

Cyclopentadiene reduces an ammoniacal silver solution with production of a silver mirror (188). Low yields of cyclopentene or cyclopentane were obtained by the action of zinc and hydrochloric acid on cyclopentadiene in alcoholic solution (140).

Because dilute acids and alkalis resinify cyclopentadiene, Weger (237) has recommended its reduction by the use of finely divided nickel, and with this catalyst Eijkman (78) has obtained cyclopentane. Its solvent properties have attracted some industrial attention. Kazanskiĭ and Glushnev (120) have produced cyclopentene by reducing cyclopentadiene with calcium ammonia, $Ca(NH_3)_6$. By passing the diene with hydrogen over platinum–charcoal at 160°C., Zelinskiĭ and Levina (245) have prepared cyclopentane and tricyclodecane.

Foresti (88) determined an activity curve for the rates of hydrogenation of cyclopentadiene in the presence of platinum as a function of the apparent pH of the medium in which the reaction was carried out. The form of the curve was typical of that for monoölefins. It showed a slight rise with increase in the apparent pH in acid and a sharp drop in alkaline media.

The following heats of hydrogenation for cyclopentadiene at 82°C. were reported by Kistiakowsky and coworkers (131):

$C_5H_6 + H_2$	-22.200 kg.-cal. per mole
$C_5H_6 + 2H_2$	-50.865 ± 0.047 kg.-cal. per mole

The heats of hydrogenation permit an estimation of the resonance energy of double-bond conjugation in the molecule. The expected value for the heat of hydrogenation if the double bonds did not interact would be twice the heat of hydrogenation of cyclopentene, i.e., 53.840 kg.-cal. per mole. The observed value is about 3.0 kg.-cal. per mole less. This can be ascribed to double-bond interaction. It is equal to the difference between the second and first heats of hydrogenation in the stepwise reduction of cyclopentadiene to cyclopentane. This resonance energy is somewhat smaller than that usually associated with such conjugated systems.

D. OXIDATION

Cyclopentadiene reacts spontaneously with the oxygen of the air to form brown gummy products. Because the oxidation products may contain cyclopentadiene peroxide, they should be handled with great caution until more experience has been gained with their properties. Engler and Frankstein (80) found that, after a week's standing, 2 g. of cyclopentadiene had absorbed only 30 per cent of the oxygen theoretically required for formation of the diperoxide. They accounted for the low absorption by the formation of dicyclopentadiene and of a resinous coating which prevented contact between the oxygen and the inner layers of cyclopentadiene.

The properties of cyclopentadiene peroxides have received little attention. The results of some further studies made by Engler and Frankstein (80) on the oxidation products of dimethylfulvenes prepared by condensation of acetone and cyclopentadiene are suggestive of what might be expected. A 5–7 per cent solution of the fulvene in benzene treated with oxygen became turbid, owing to formation of an insoluble diperoxide. The accelerating effects produced by light and by an increase in temperature are presented as follows:

At 6°C. in the dark	Precipitation started after 21 days
At 6°C. in dispersed daylight	Precipitation started after 14 days
At 19°C. in dispersed daylight	Precipitation started after 4 days
At 35°C. in dispersed daylight	Precipitation started after 30 hr.
At 42°C. in dispersed daylight	Precipitation started after 20 hr.

The primary product at the higher temperatures was the insoluble diperoxide, but a soluble form was a secondary product. The insoluble diperoxide exploded if heated to 130°C. or if ground with ether in a mortar.

The reaction of cyclopentadiene and oxygen was found by Stobbe and Dümhaupt (208) to be unaffected by light. Large amounts of gum were formed when a gasoline containing 10 per cent of cyclopentadiene was exposed to oxygen at 100°C. and 100 pounds pressure by Flood and coworkers (87). Gum formation was inhibited by the addition of 0.1 g. of α-naphthol per liter of oil.

In contact with catalysts cyclopentadiene has been almost completely oxidized. At 250–300°C. in the presence of manganese vanadate oxidation proceeded in 23 to 26 sec. with formation of carbon dioxide and a little carbon monoxide, according to Wilken-Jordan (243). The cyclopentadiene–air ratios varied from 1:0.86 to 1:1.10.

A 32.4 per cent yield of maleic acid was secured by Milas and Walsh (154) when cyclopentadiene was oxidized with air at 410°C. in contact with a vanadium pentoxide catalyst. Formaldehyde and carbon dioxide were identified in the exit gases. Conover (57) patented the production of maleic acid by oxidizing cyclopentadiene with at least twenty times its weight of air at 400–525°C. in contact with a vanadium oxide catalyst. No advantage of cyclopentadiene over benzene for producing maleic anhydride has been indicated and the potential supply of the former is much smaller.

Cyclopentadiene reacted rapidly with perbenzoic acid to produce a dark brown, oily mass, according to Bauer and Bahr (33). Criegee (58) reported that lead tetraacetate oxidized cyclopentadiene with the production of 3-cyclopentene-1,2-diol diacetate and the monoacetate monoacetylglycolate of 3-cyclopentene.

E. POLYMERIZATION

1. *Formation of dicyclopentadiene*

Cyclopentadiene is readily polymerized and a variety of products can be obtained by the use of appropriate conditions. The spontaneous dimerization of two molecules of cyclopentadiene to form one of dicyclopentadiene, $C_{10}H_{12}$, has already been mentioned. The dimer occurs in the form of colorless crystals which melt at 32–32.5°C. and possess a camphor-like odor; the boiling point of the dimer is approximately 170°C.

Dicyclopentadiene was first identified by Roscoe (187) in 1886 in the products from the pyrolysis of phenol. He observed that the crystals decomposed to form a low-boiling compound when heated at atmospheric pressure, but distilled unchanged under vacuum.

2. *Rate of polymerization and depolymerization*

In their early work with cyclopentadiene Étard and Lambert (81) observed its spontaneous dimerization and measured the change in rate by the increase in density at intervals of time.

In experiments using the change in the refractive index as a measure of the dimerization rate, Stobbe and Reuss (209) found the temperature to be a vital factor. At -80°C. no polymerization occurred; at -15°C. a slow conversion was apparent; and at 20°C. cyclopentadiene was completely transformed to the dimer in 30 days. At 100°C. the reaction was still faster. Light had little effect on the rate of polymerization.

The rates of polymerization as measured by the refractive index were found by Terent'ev and Solokhin (217) to be in error by about 1.5 to 2.0 per cent, owing to the formation of higher polymers. This conclusion was reached by comparing the rates secured by refractive-index measurements with those obtained by a diazo method. The latter, which involved reaction of cyclopentadiene with *p*-nitrobenzenediazonium chloride in acetic acid, were followed by the change in color of the solution.

The magnetic susceptibility was used by Farquharson (86) to follow the rate of dimerization. The susceptibility of cyclopentadiene, -0.717×10^6, decreased as the reaction proceeded.

Barrett and Burrage (32) prepared vapor pressure–composition curves from known mixtures of cyclopentadiene and its dimer, and used them to determine the rate of polymerization. After 93 days at 12°C. the mixture contained only 0.73 per cent of the monomer, and the transformation was apparently complete after a year.

The kinetics of the dimerization of cyclopentadiene in both the gaseous and the liquid states were extensively studied by Wassermann and his associates (32, 37, 82, 119, 125, 126, 127, 164, 235). In the gaseous state at constant volume the decrease in pressure was used to measure the rate at temperatures between 79° and 150°C. and pressures between 154 and 735 mm. The results were expressed by the equation

$$k = 1.2 \times 10^{6} e^{\frac{-16.7}{RT}}$$

in liters per gram mole per second. The reaction was bimolecular and no indication of a chain mechanism was observed. Dissociation of the dicyclopentadiene into a monomer was a monomolecular reaction and in the pure liquid state the rate was expressed by the equation:

$$k = 6 \times 10^{12} e^{\frac{-34}{RT}} \text{ per second}$$

The parameters in the Arrhenius equation, $Ae^{\frac{-E}{RT}}$, for the association of cyclopentadiene when dissolved in both polar and non-polar solvents were similar to those for the reaction in the gas phase. The solvents included benzene, paraffin (125, 126), ethanol, acetic acid, carbon disulfide, and aniline (119). The solvent effects were not large enough to produce changes of A and E exceeding the experimental errors.

The rate constants obtained by Kistiakowsky and coworkers (104, 130) for the dimerization of cyclopentadiene and decomposition of the dicyclopentadiene were of the same order of magnitude as those calculated by Wassermann. The reaction rate in the gas phase was followed by the change in pressure, and in the liquid phase by the refractive index. In the latter case the rate started off as that of a second-order reaction and then changed to that of a first order, owing, it was concluded, to the formation of higher polymers.

Rate constants obtained by Schultze (196) for the dimerization of gaseous cyclopentadiene at temperatures between 132°C. and 182°C. and initial pressures between 180 and 510 mm. were similar to the values obtained by Wassermann.

Baur and Frater (34) followed the dimerization of cyclopentadiene and the dissociation of dicyclopentadiene at 149–194°C. and pressures of 109–638 mm. of mercury by measurements with glass-spiral manometers. The values of

$$K = \frac{(\text{cyclopentadiene})^2}{\text{dicyclopentadiene}}$$

were 277, 591, 742, 1177, and 2200 at 149°, 165.5°, 170°, 180°, and 195°C., respectively. At equal distances from equilibrium these investigators found depolymerization more rapid than polymerization. The heat of reaction was 12.3 kg.-cal. up to 185°C.; above that temperature polymerization was relatively more rapid. The energy of activation for polymerization was 5.4 kg.-cal.

The rate of dimerization was increased at 80°C. in the presence of oxygen, benzoyl peroxide, and diphenylethylene peroxide. Staudinger and Lautenschlager (206) attributed the increase to autoöxidation and concluded that self-formed peroxides were more active catalysts than was benzoyl peroxide. No increase was observed at 45°C.

Hammick and Langrish (103) reported that the presence of peroxide is necessary for the dimerization of liquid cyclopentadiene in carbon tetrachloride solution at 25°C. Peroxides formed when the solution was exposed to the air for any length of time (according to the Kharasch ferrous thiocyanate test). Addition of 1 per cent of acetonitrile as an antioxidant reduced the rate of polymerization, and polymerization did not occur at all in acetonitrile solution. The rate of polymerization was calculated from bromine absorption tests which were run periodically on dilute solutions of the hydrocarbons in carbon tetrachloride under standardized conditions.

On the other hand, in the researches of Stobbe and Reuss (209), Schultze (195), Harkness and coworkers (104), and Benford and coworkers (37) on the rate of dimerization, this reaction was not influenced by the presence of oxygen peroxides even in relatively high concentrations. The various experiments were carried out between 14°C. and 177°C. and at pressures between 1 and 4000 atmospheres. The presence of acetonitrile did not affect the rate in the work of Benford and his associates (37). The conclusion was reached that peroxidic intermediates did not play a part in the reaction. Schultze (196) reported that gum formation in motor spirits proceeded in the absence of air. The presence of nitrogen or water did not affect polymerization.

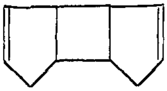
More information is obviously needed on the factors which affect dimerization; in particular, the differences in the effect of peroxides should be reconciled. The catalytic influence of other compounds, on which data are still meager, should be thoroughly explored. To be able to speed up the rate of dimerization would be especially advantageous in processes for the recovery of cyclopentadiene from oils.

Trichloroacetic acid was observed to be catalytically active in accelerating the rate of dimerization of cyclopentadiene in a benzene or a paraffin solution, and acetic acid was found to have an accelerating action in the gas phase, according to Wassermann (235a).

Ingold and Wassermann (116) found that the dimerization of cyclopentadiene in paraffin solution at 155°C. became heterogeneous in the presence of certain heavy-metal sulfides. The majority of the black sulfides were catalytically active, but the white and yellow ones were inefficient under the test conditions. The activity of a sulfide depended markedly on the method of preparation, possibly owing to the effect of impurities. They suggest that a periodic intermediate compound takes part in the reaction.

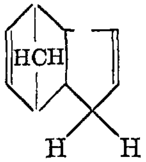
3. Structure of dicyclopentadiene

The structure of dicyclopentadiene was first represented by Kraemer and Spilker (140) with a cyclobutane ring between two cyclopentene rings:

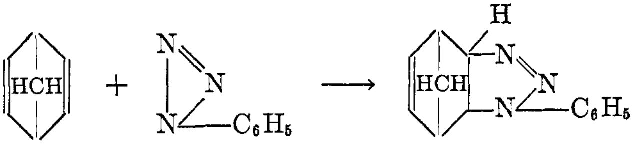


and for many years the work of other investigators supported this conclusion (203, 204, 207).

In 1933 Alder and Stein (15, 16, 20, 24) established that dicyclopentadiene had the structure



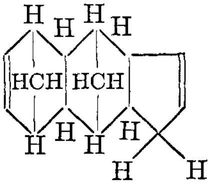
which corresponds to that of a partially hydrogenated indene containing a bridged methylene group. Thus, they found that dicyclopentadiene would add one molecule of phenyl azide, which is a characteristic reaction for bicycloheptene:



This reaction, however, would not occur with the double bond of a cyclopentene ring.

Pirsch (18, 174) supported the bicycloheptene structure with his work on the melting points of acenaphthene and a number of other aromatic compounds dissolved in dicyclopentadiene, dihydrodicyclopentadiene, and tetrahydrocyclopentadiene. The molecular depressions were high in all cases, averaging 46.2, 45.4, and 35, respectively.

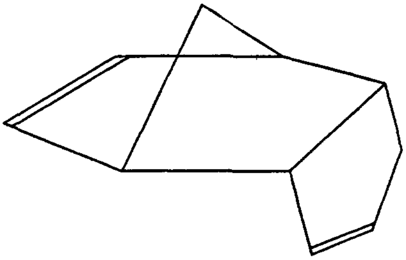
The constitution of dicyclopentadiene indicates that polymerization has taken place by the Diels-Alder mechanism. The formation of higher polymers follows the same course; thus tricyclopentadiene has the structure:



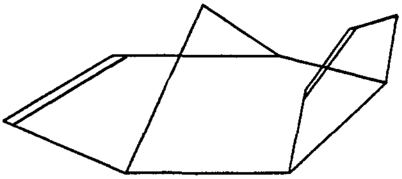
Each polymer is capable of adding another molecule in the same way. The formation of a continuous series of homologs is limited only by the physical properties. The solubility of the higher polymers decreases so rapidly, however, that polymerization practically ceased with the formation of pentacyclopentadiene (20).

4. Steroisomers

The polymers of cyclopentadiene with the bicycloheptene structure are three-dimensional. Two stereoisomers of dicyclopentadiene are possible:



Endo-form



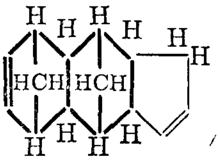
Exo-form

The former is produced, according to Alder and coworkers (20, 22), during polymerization at ordinary temperatures; the exo-form can probably be produced only at higher temperatures. When solid dicyclopentadiene was heated for several hours at 100°C., the product consisted of a mixture of the endo- and exo-forms. Derivatives of dicyclopentadiene possess corresponding endo and exo stereoisomeric forms.

Staudinger and Rheiner (207) separated endo- and exo-dicyclopentadienes by filtration of commercial dicyclopentadiene in a stream of carbon dioxide, followed by vacuum distillation. The distillate was crystallized and redistilled. The endodicyclopentadiene had a melting point of 32.5°C., but that of the exo-form was only 19.5°C. The boiling point of the latter was the higher of the two.

Waring and coworkers (232) obtained an isomer of dicyclopentadiene, which melted at 27.8°C., by allowing freshly distilled cyclopentadiene to stand at 15°C. After recrystallization, the melting point increased to 31.5°C. The refractive indices of both sets of crystals were the same,—1.5120 at 20°C. The lower-melting isomer had only a slight odor, but the dimer melting at 31.5°C. had the typical camphor-like odor.

Eight stereoisomeric forms are possible for tricyclopentadiene, but it occurs in only two forms. Alder and coworkers (18, 20, 24) have shown that the spatial configuration of that position of the carbon skeleton represented by thick lines in the formula



is exactly the same in each case, and that the isomerism is to be attributed to the alternative spatial arrangements that can be assumed by the cyclopentene ring with respect to the plane of the adjoining ring. It is probable that the two forms of the trimer arise by addition to the two known forms of the dimer, respectively.

Endo- and exo-tricyclopentadienes were separated by recrystallizing from alcohol. The endo-form, melting at 57–63°C., was filtered off. The studies of Alder and Stein (19) indicated that the endo-form had the higher energy content.

5. Formation of higher polymers

Higher polymers of cyclopentadiene were obtained by Staudinger and Rheiner (204, 207) by heating dicyclopentadiene in sealed tubes.

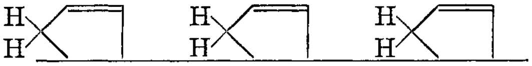
Time of heating, hours	14	22	90
Temperature, °C.	150–60	170–80	200
Tricyclopentadiene	40	50	25
Tetracyclopentadiene	10	30	45
Pentacyclopentadiene	2	5	10
Unchanged	50	10	5

The trimer and tetramer were crystalline solids and gave normal values for the molecular weight by the freezing-point method in benzene. The pentamer was an amorphous solid which formed colloidal dispersions and gave abnormally high values for the molecular weight by the cryoscopic method.

These polymers were separated by fractional vacuum distillation and by selective solvents, and were identified by molecular-weight determinations. An insoluble solid was obtained which probably consisted of the hexamer and higher polymers. When heated to 500°C., again under low vacuum, the polycyclopentadiene depolymerized with the formation of cyclopentadiene (204). Kronstein (141) obtained polymers with similar properties by heating cyclopentadiene to 160°C. in sealed tubes for 5 hr. and dicyclopentadiene to 180°C. for 3 hr. Industrial applications for the wax-like polymers which can be produced by the above methods have not been described, but they appear deserving of attention.

Polymerization of cyclopentadiene in the liquid phase at temperatures of 0° to 40°C. and under pressures up to 5000 atmospheres proceeded in three stages, according to Raistrick and coworkers (178). The first was dimerization to endodicyclopentadiene, and then association to higher polymers occurred, but finally an explosive decomposition produced a highly carbonized residue, usually enclosed in a thin envelope of horny insoluble material. The gaseous products were 92 per cent methane and 8 per cent hydrogen. The decomposition was accompanied by a sudden pressure rise which amounted to 2000 atmospheres or more, depending on the experimental conditions and the volume of reactant used. The decomposition was very sensitive to such conditions as temperature, pressure, the diameter of the reaction tube, and the material from which the tube was made. The explosive decomposition occurred within definite pressure limits at each temperature. Thus, at 13°C. it occurred at 6100 atmospheres; at 20°C., at 4900 atmospheres; at 30°C., at 3700 atmospheres; and at 40°C., at 3100 atmospheres.

Commercial resins have been produced by heat polymerization of cyclopentadiene and dicyclopentadiene without the use of catalysts. Carmody and coworkers (52) found that polymerization proceeded actively above 200°C. but that depolymerization might occur when the substances were heated above 260°C. A resin was produced from a close-cut coal-tar fraction containing dicyclopentadiene as the chief component by heating gradually to 200°C., but at no time to a temperature over 250°C., in the absence of air and catalysts (49). The product was of low molecular weight, heat-stable, color-stable below 225°C., resistant to oxygen and corrosive fumes, odorless, tasteless, and non-toxic. The average molecular weight indicated the presence of octamers, but a chain theory of polymerization,



was favored (52).

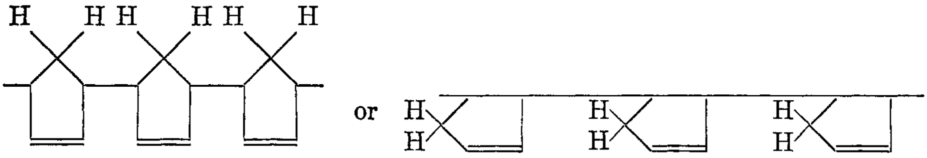
6. *Polymerization with catalysts*

The influence of catalysts on the formation of higher polymers of cyclopentadiene has been studied by only a few investigators. Their results, however, fully justify a comprehensive investigation of the subject and examination of the products.

Bruson and Staudinger (44, 45, 205) produced high polymers by treating cyclopentadiene with many compounds, principally metallic halides. In many cases polymerization was rapid and proceeded at low temperatures. Thus, to 100 parts of cyclopentadiene dissolved in chloroform at a temperature of 0°C. or less was added 1 part of anhydrous stannic chloride dissolved in chloroform. Polymerization took place with evolution of heat; the solution became viscous and turned a deep orange color. After the solution had stood for 5 min., the polymer was precipitated as a white rubbery mass by the addition of an excess of absolute alcohol. The yield was quantitative. The stannic chloride combined with the alcohol to form a soluble compound which did not contaminate the rubber substance.

The polymer had the appearance of rubber. It could be vulcanized with sulfur chloride in chloroform and dispersed in rubber solvents, and was insoluble in ether, acetone, and ethanol. On standing in the air it absorbed oxygen and became insoluble in all known solvents, the final oxidation product having the formula $(C_5H_6O)_x$. The film formed by painting a benzene solution of the rubber on a surface became hard and insoluble on exposure to the air. The use of the polymer as a lacquer was suggested.

The polymers produced by Staudinger and Bruson (205) had the general formula $(C_5H_6)_x$, and molecular weights between 1260 and 6670. The polymers added 1 mole equivalent of bromine per mole of cyclopentadiene. The following structures for the resin were suggested:

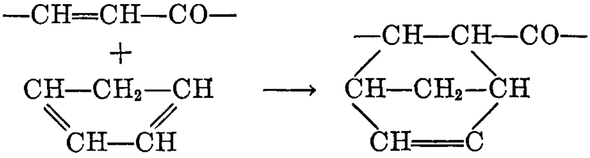


The use of phenyldiazonium fluoborate for polymerizing cyclopentadiene was patented by Bruson (43). Boron trifluoride, when mixed with another gas, such as nitrogen, and passed into cyclopentadiene produced a solid polymer, according to Chaney (53).

Soday (200a) and Trepp (223a) found that the cyclopentadiene polymers produced by certain metallic chloride catalysts were of two broad types, one of which is characterized by being soluble in solvents such as benzene, toluene, chloroform, carbon tetrachloride, and high-flash naphtha, while the other is insoluble in these solvents. The proportion of soluble polymer is influenced by four factors: temperature, concentration of cyclopentadiene, proportion of uniformly distributed catalyst, and time. The soluble polymer may be used for metal coatings. The catalysts were zinc chloride (200a), aluminum chloride (200a), ferric chloride (223a), aluminum bromide (223a), and titanium tetrachloride (223a).

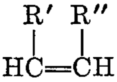
F. DIELS–ALDER REACTION

Cyclopentadiene can act as the diene in the Diels–Alder reaction with α,β-unsaturated carbonyl compounds. The products are cyclohexene derivatives having a bridged or endomethylene group:



The reaction is obviously similar to the dimerization of cyclopentadiene, except for the replacement of 1 mole of cyclopentadiene by an unsaturated carbonyl molecule.

Many Diels–Alder reactions of cyclopentadiene have been investigated by Diels, Alder, and their coworkers. The added reagents include maleic anhydride, maleic acid, acrolein, acrylic acid, itaconic anhydride, citraconic anhydride, quinones and other unsaturated compounds with the general formula

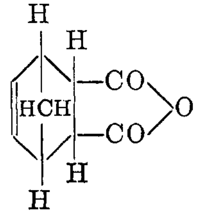


$$\overset{R'}{HC}=\overset{R''}{CH}$$

wherein R′ and R″ stand not only for —CHO, —COOH, or —CO—alkyl groups, but also for hydrogen or alkyl. In Norton's (167) thorough review of the Diels–Alder reaction these reactions have been included. The Diels–Alder reaction, therefore, presents a most fertile field for synthesizing from cyclopentadiene a wide range of compounds,—sesquiterpenes, alkaloids, camphors, and similar hydrogenated cyclic compounds which are of interest to the resin, pharmaceutical, organic chemical, and other industries. McCrone (151a), for instance, has pointed out the structural similarity between pyrethrum and products obtained by the addition of cyclopentadiene to various unsaturated acids. He considers it possible that effective insecticides can be produced by the reaction.

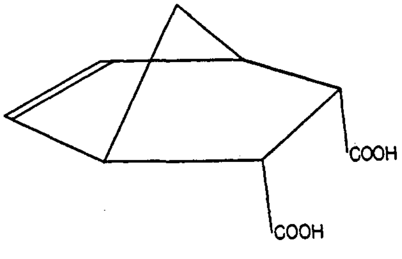
1. *Maleic anhydride and derivatives*

An important example is the reaction between cyclopentadiene and maleic anhydride to form *cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride (65, 69):

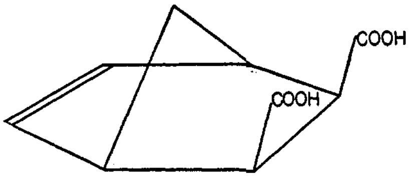


It occurs spontaneously with evolution of heat when cyclopentadiene is added to a suspension of maleic anhydride in benzene. The new anhydride is precipitated in the form of brilliant snow-white crystals, and the yield is quantitative. By catalytic hydrogenation or reduction with zinc and acetic acid the acid can be transformed into the fully hydrogenated system containing the methylene bridge (17). The endomethylene structure was established by Alder and Schneider (13). Thus, they obtained cyclopentane-1,2,3,4-tetracarboxylic acid by oxidation with alkaline permanganate.

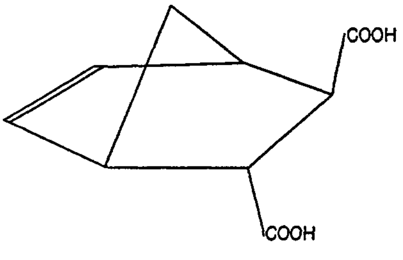
The 3,6-endomethylene-Δ^4-tetrahydrophthalic acid occurs in the following three forms:



Endo-cis



Exo-cis

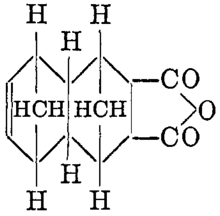


Trans

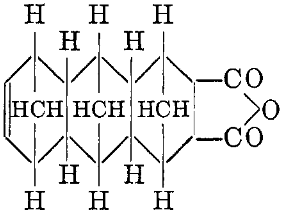
Only the endo-*cis*-form is produced from the reaction of cyclopentadiene and maleic anhydride (22). Alder and coworkers (23) produced the *trans*-form by the reaction of fumaryl chloride in ether with cyclopentadiene. The *trans*-acid has also been produced by heating the methyl ester of the endo-*cis*-acid with sodium in absolute alcohol. After removal of the alcohol and acidification the *trans*-acid was crystallized from solution (22). On distilling the *trans*-acid under vacuum some decomposition occurred; fumaric acid and the endo-*cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic acid were found in the products. No exo-*cis*-acid was found (22).

The endo-*cis*-acid could not be converted to the exo-*cis*-form until the double bond in the dicycloheptene ring was saturated. When the dibromoendo-*cis*-acid was heated to 210–220°C., the dibromoexo-*cis*-anhydride was formed. The exo-*cis*-tetrahydrophthalic acid resulted on removal of the bromine with zinc dust and acetic acid (22).

Alder and coworkers (24) found that the double bond in the endomethylene anhydride was susceptible to further 1,4-additions with diene compounds. One or 2 moles of cyclopentadiene with 1 mole of the anhydride reacted to form



and



respectively. Similarly, butadiene, isoprene, diphenylbutadiene, or anthracene have been added to these compounds and to tetrahydrophthalic anhydride by Alder and his associates (24).

Morgan (158) has studied the reactions involving the dicarboxylic anhydride group of both the anhydride and the hydrogenated anhydride. The reactions were based on the corresponding reactions of phthalic anhydride, but in many respects the derivatives of the new anhydrides differed materially in behavior. The differences necessitated modifications in the modes of preparation and isolation of the derivatives. The investigation should be continued and the substitution of the endomethylenetetrahydrophthalic anhydride for phthalic anhydride in commercial applications for the latter should be tried.

Alder and coworkers (13, 21, 27) have described the preparation of lactones, hydroxy acids, and other derivatives by treatment of the endomethylenetetrahydrophthalic acid with reagents such as diluted sulfuric acid or with oxidizing agents. By the addition of cyclopentadiene to maleic ester (27), maleic amide (110), dimethylmaleic anhydride (65), dibromomaleic anhydride (62), citraconic acid (61), or pyrocinchoninic acid anhydride (63), the corresponding derivatives of the endomethylenetetrahydrophthalic acid anhydride were produced.

The endomethylenetetrahydrophthalic anhydride can be used in place of phthalic anhydride for the production of alkyd resins, but nothing has been reported as yet on its use for this purpose. Hopff and Rapp (110) have made copolymers with styrene, acrylic ester, vinyl compounds, and other materials. The products varied from solids to rubber-like materials, depending on their composition.

Esters of endomethylenetetrahydrophthalic acid are high-boiling liquids. The methyl ester produced by the addition of cyclopentadiene to methyl maleate boils at 145–147°C. under 18 mm. pressure (22). The esters have been used by Jordan and Krzikalla (117) as plasticizers in nitrocellulose lacquers.

Diels and Friedrichson (71) showed that the same type of addition occurred when cyclopentadiene and acetylenedicarboxylic anhydride were mixed.

2. Additions with aldehydes, quinones, and acids

The formation of dicyclopentadiene is an example of a reversible association of the type $a + b = K_f/K_d$. Other examples are the addition reactions of cyclopentadiene with benzoquinone, acrolein, naphthaquinone, and other compounds.

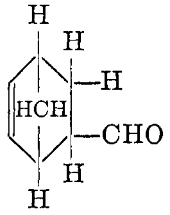
The equilibrium constant

$$K = \frac{K_f}{K_d} = B^{\frac{HR}{T}}$$

has been measured and B and H evaluated for the additions of cyclopentadiene to acrolein, benzoquinone, and naphthoquinone, respectively, in both the gaseous state and in solution, by Benford and coworkers (36). The heat of reaction (H) was approximately 17 kg.-cal. per gram mole in these cases.

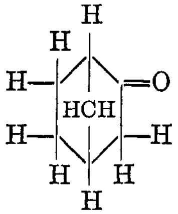
Rate constants for the reactions have been determined by Kistiakowsky and Lacher (129) and by Wassermann (124, 233, 235). The forward reaction was homogeneous and of the second order; the decomposition was of the first order.

(*a*) *Aldehydes:* The compound produced by the addition reaction of cyclopentadiene with acrolein had the typical endomethylene structural formula:

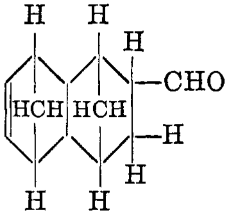


A 95 per cent yield of this endomethylene-3,6-tetrahydro-Δ^4-benzaldehyde was obtained by Diels and Alder (65). Decomposition of the aldehyde into the reactants was appreciable when heated to 150°C., and was rapid at 200°C., according to Kistiakowsky and Lacher (129).

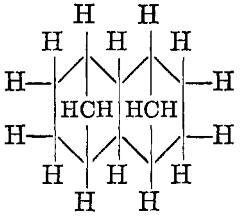
Compounds related to the terpenes have been synthesized from the addition products of cyclopentadiene and acrolein. Diels and coworkers (66, 68) hydrogenated the double bond in the endomethylenetetrahydrobenzaldehyde and eliminated the aldehyde group to produce norcamphor:



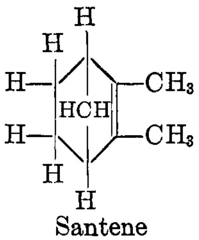
By addition of 2 moles of cyclopentadiene to 1 mole of acrolein, Alder and Windemuth (27) obtained the compound:



Subsequently, by reduction and elimination of the aldehyde group, they produced 1,4,5,8-bis(endomethylene)decalin:



Addition of cyclopentadiene and crotonaldehyde took place in the 1,4-manner when the two were heated at 100°C. for 4 hr. From the 2,5-endomethylene-6-methyl-Δ^3-tetrahydrobenzaldehyde Diels and coworkers (68) prepared santene.



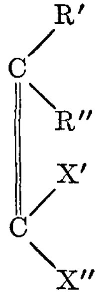
Santene

The addition products of cyclopentadiene and unsaturated aldehydes were used by Diels and Alder (64) to prepare products with flower-like odors. As condensing agents they used sodium or potassium methoxide or barium hydroxide.

(*b*) *Acids:* The addition product of acrylic acid and cyclopentadiene was obtained as an oil with an intense valerian odor (65). Komppa and Beckman (137) obtained the same product by the addition of cyclopentadiene to crotonic acid, and by heating dicyclopentadiene with crotonic acid to about 170°C.

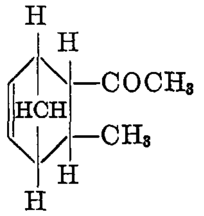
The addition of dimethylacrylic acid $(CH_3)_2C{=}CHCOOH$, to cyclopentadiene was observed by Komppa and Komppa (138) to proceed with considerable difficulty because of steric hindrance on the part of the methyl groups.

Alder and Rickert (11) added cyclopentadiene to a number of substituted, unsaturated malonic esters and to other derivatives of malonic acid having the general structure,



where R′ and R″ included aliphatic groups, and X′ and X″ included —COOR, —CN, or $—COCH_3$ groups.

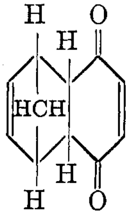
(*c*) *Ketones:* Heating at 150°C. for 5 hr. was necessary for the reaction of ethylideneacetone and cyclopentadiene to form the compound



according to Diels and Alder (65). The reaction of cyclopentadiene with vinyl phenyl ketone, $CH_2{=}CHCOC_6H_5$, was studied by Allen and coworkers (29), and with the compound $(p\text{-}ClC_6H_4COCH{=})_2$ by Adams and Wearn (2). When cyclopentadiene was added to *trans*-dibenzylethylene, *trans*-2,3-dibenzoyl-1,4-endomethylene-1,2,3,4-tetrahydrobenzene was produced.

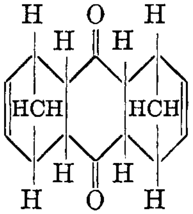
The enols of β-diketo compounds contain double bonds in conjugation with a carbonyl group, i.e., an active double bond which should add to dienes. However, all such compounds investigated by Nylén and Olsen (168) were incapable of undergoing the diene synthesis. The following keto–enol compounds were reacted with cyclopentadiene without results: acetoacetic ester (7.4 per cent), acetylacetone (76 per cent), benzoylacetone (94 per cent), dibenzoylmethane (96 per cent), ethyl benzoylacetate (29 per cent), ethyl oxalacetate (80 per cent), and oxalacetone. The percentages in parentheses represent the enol fraction in each case. To test the effect of the chelate structure on the above reactions, derivatives were chosen in which the hydrogen of the hydroxyl group was covered. Of the three investigated, only acetoxymaleic anhydride formed an addition product with cyclopentadiene. The investigators concluded that the oxygen at the active double bond did not in itself prevent the addition of the diene.

(*d*) *Quinones:* The reactions between cyclopentadiene and several quinones,—benzoquinone, α-naphthaquinone, and chloranil,—were described by Albrecht (5) in 1906. The additions are of the characteristic 1,4-type (36, 129, 235) and take place readily on mixing the reagents. Thus the compound



was produced from cyclopentadiene and benzoquinone.

When cyclopentadiene was added to cyclopentadienequinone, dicyclopentadienequinone

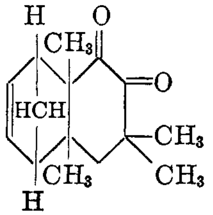


was formed (5), according to Diels and Alder (61).

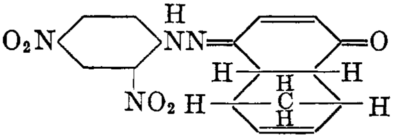
The addition products of cyclopentadiene and quinones are highly colored compounds, and the changes in color of the solutions were used by Wassermann (233) to measure the rate of the additions. In benzene at 25°C., the rate constant for the formation of cyclopentadienequinone was about twenty-five times that for the dicyclopentadienequinone. Fairclough and Hinshelwood (83) found the formation of cyclopentadienequinone to be about five times as fast in polar as in non-polar solvents. The effects of catalysis on the rates of diene synthesis for cyclopentadiene with benzoquinone, α-naphthaquinone, and tetrachlorobenzoquinone have been studied by Wassermann (235a, 235b, 236). The experiments with sulfuric, phosphoric, and hydrochloric acids and with certain organic bases did not lead to conclusive results. Iodoacetic acid, *p*-toluenesulfonic acid, pyridine, 2,2′-dipyridyl, three salts of heavy metals, iodine, *trans*-stilbene, oxygen, peroxides, acetonitrile, and ethyl trichloroacetate were ineffective, but phenol, bromoacetic acid, chloroacetic acid, trichloroacetic acid, α-naphthaquinone, acetic acid, and trimethylamine were catalytically active. The last tests were made in both polar and non-polar solvents. An investigation of the kinetics of a selected list of catalytic processes showed that the primary step is of the third order and that the activation energy is near to zero. More information is needed on the effects of catalysts on the reactions.

In a study of the stereoisomeric forms of the quinones Alder and Stein (16) showed that the adduct of cyclopentadiene and benzoquinone can occur in an endo- and an exo-form. Although with two cyclic dienes attached to the quinones six forms are possible, only a single form resulted.

When Smith and Hac (199) added cyclopentadiene to tetramethyl-*o*-benzoquinone (prehnitenequinone), they obtained a 63 per cent yield of cyclopentadiene-prehnitenequinone:



Bergmann and Bergmann reported (38) that cyclopentadiene and *p*-phenylquinone will add. The addition reaction of cyclopentadiene and certain hydroxyazo compounds was used by Lauer and Miller (145) to show their tautomeric quinoid structure. Thus, with 2,3-dinitroazophenol the compound



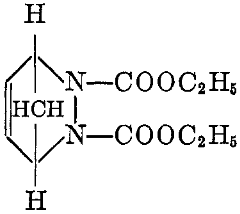
was produced.

No attempts to utilize the complex quinones in dyestuffs have been described, but they appear to merit some attention from this industry.

3. Reaction of cyanides and other nitrogen compounds

Cyclopentadiene has reacted with compounds in which the —CO— group has been replaced by the —CN group by means of the Diels–Alder method. By heating crotononitrile with cyclopentadiene under pressure 3,6-endomethylene-Δ^4-tetrahydro-1-methyl-2-cyanobenzene has been prepared. A similar reaction with the nitrile of sorbic acid has been patented (112, 113).

1,4-Addition occurred when an azo ester and cyclopentadiene were combined. The cyclopentadieneazo ester,

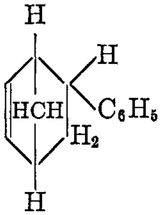


was hydrogenated to form endomethylenepiperidazine, according to Diels and coworkers (70).

4. Other Diels–Alder reactions

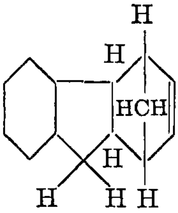
Cyclopentadiene and the methyl ester of acetylenedicarboxylic acid with cooling gave dimethyl 3,6-endomethylene-3,6-dihydro-*o*-phthalate. Diels and Alder (67) found that the ester decomposed into the original material on heating. By catalytic reduction the dimethyl ester of 3,6-endomethylene-Δ^1-tetrahydro-*o*-phthalic acid was produced.

From styrene and cyclopentadiene the compound 2,5-endomethylene-1,2,5,6-tetrahydrodiphenyl,



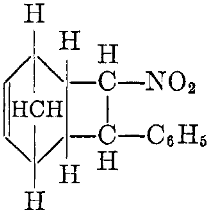
was formed. Alder and Rickert (9) noted that, like all bicycloheptene compounds, the product could be catalytically hydrogenated with unusual ease, to the hexahydro derivative. The double bond in the bridged ring underwent further diene syntheses with relative ease. The diphenyl, therefore, was always accompanied by a compound consisting of two molecules of cyclopentadiene and one of styrene.

The same investigators (10) found that fluorene derivatives could be produced by the addition of indene to cyclopentadiene. The product was largely 1,4-endomethylenetetrahydrofluorene,



together with a hydrocarbon in which two molecules of cyclopentadiene were combined, as in the case of styrene.

Cyclopentadiene and β-nitrostyrene reacted to give a 95 per cent yield of a compound which was apparently

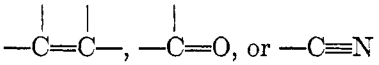


according to Allen and Bell (28).

The I. G. Farbenindustrie (115) has patented a process for the copolymerization of cyclopentadiene with styrene and other olefin compounds at temperatures below 0°C. in the presence of inorganic halides of an acid character, such as aluminum chloride, zinc chloride, or boron trifluoride. The polymerization was effected in the presence of an inert solvent, such as chloroform or carbon tetrachloride.

5. *Reactions with nitro and sulfone compounds*

In most of the previous additions of $—\overset{|}{C}{=}\overset{|}{C}R$ to cyclopentadiene, the R belonged to one of the groups

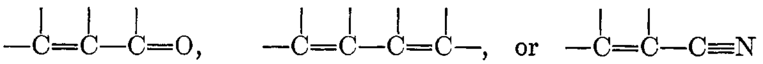


$$—\overset{|}{C}{=}\overset{|}{C}—,\ —\overset{|}{C}{=}O,\ \text{or}\ —C{\equiv}N$$

and conjugation of an unsaturated substituent to the double bond which was added was considered an essential prerequisite. Alder, Rickert, and Windemuth (12) have shown that this is by no means necessary. Cyclopentadiene has been reacted with α,β-unsaturated nitro compounds, $—\overset{|}{C}{=}\overset{|}{C}NO_2$, and with sulfones, $—\overset{|}{C}{=}CHSO_2R$, according to 1,4-addition. Nitroethylene and several of its homologs added cyclopentadiene easily at 100–110°C. On catalytic hydrogenation the adducts took up 1 mole of hydrogen with ease, and the resulting saturated nitro compounds were reduced to the corresponding amines with zinc dust and acetic acid. The 2-nitro-5-norbornylene obtained from nitroethylene and cyclopentadiene was sterically homogeneous. The adduct of cyclopentadiene and the cyclic sulfone butene-1-sulfone-1,4, $\underline{CH_2CH_2CH{=}CHSO_2}$, resembled dicyclopentadiene in external appearance and reacted very easily with phenyl azide.

6. Reactions with vinyl compounds

Vinyl compounds have been added to cyclopentadiene by reactions of the Diels–Alder type. The reactions are examples of a type of synthesis in which a double bond not belonging to the



$$—\overset{|}{C}=\overset{|}{C}—\overset{|}{C}=O, \quad —\overset{|}{C}=\overset{|}{C}—\overset{|}{C}=\overset{|}{C}—, \text{ or } —\overset{|}{C}=\overset{|}{C}—C\equiv N$$

types, and free from special constitutional influences of other kinds, proved capable of adding a diene. The reaction of vinyl compounds widens greatly the field for synthesis of new organic derivatives, particularly of the terpene family.

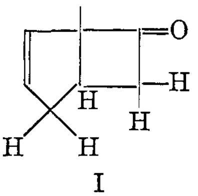
By heating cyclopentadiene and ethylene at 190–200°C. for 23 hr. at a maximum pressure of 5800 pounds, Joshel and Butz (118) produced bicyclo[2,2,1]-2-heptene

in almost quantitative yield.

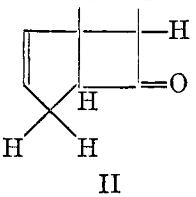
Alder and Rickert (8) obtained addition products by prolonged heating of cyclopentadiene and a number of vinyl compounds, including vinyl acetate, vinyl formate, vinyl chlorate, 1,2-dichloroethene, and trichloroethene. Alder and Windemuth (26) showed that addition with allyl compounds, including the alcohol, esters such as the salicylate or phthalate, the chloride, bromide, and iodide, and the amine, takes place smoothly at temperatures varying in the individual cases from 100°C. up to 180°C. Vinylacetic acid and vinylacetonitrile added more slowly than acrylic acid or acrylonitrile, but the reaction nevertheless took place at temperatures of 170–180°C. An adduct of cyclopentadiene and allyl isothiocyanate had an intense dill odor (26). Cyclopentadiene added Δ^3-vinylcyclohexene to give the product 2,5-endomethylene-$\Delta^{3,3}$-octahydrodiphenyl, according to Alder and Rickert (9).

G. ADDITIONS WITH KETENES

The reaction of cyclopentadiene with ketene to form an unsaturated ketone has been reported by Brooks and Wilbert (42). The product had either structure I or structure II.



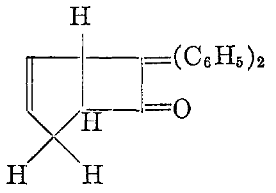
I



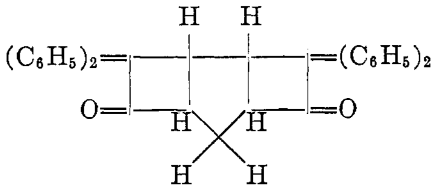
II

The reactants were heated in toluene for an hour at 100°C.

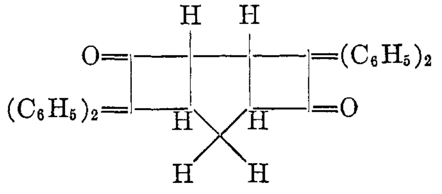
The reaction of diphenylketene and cyclopentadiene has been studied by several investigators. The structure of the product,



has been confirmed by the work of Smith and coworkers (198). Staudinger (201, 202) found that the white crystalline product could be decomposed into the original components by heating at 160–180°C. When the crystals were heated with more diphenylketene at 110°C. for 9 days, Smith and coworkers (198) were able to obtain a compound with structure I or structure II.

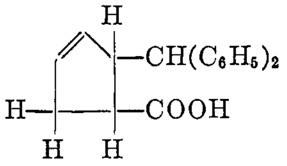


I



II

Farmer and Farooq (84) obtained an 85 per cent yield of the adduct of cyclopentadiene and diphenylketene. By alkali fission two isomeric forms of 2-benzohydrylcyclopentene-1-carboxylic acid,



were produced. Dimethylketene and cyclopentadiene have been combined by Lewis and coworkers (147).

H. OTHER POLYMERS OF CYCLOPENTADIENE

Synthetic resins which are copolymers of cyclopentadiene with indene, styrene, coumarone, and other unsaturated compounds have been produced from benzene forerunnings and polymerizable constituents of crude solvent naphtha or a polymer of these constituents. Carmody (50) agitated the mixture at a temperature of not over 20°C., while slowly adding aluminum chloride.

From coke-oven light-oil fractions which had been refined with sulfuric acid, Carmody and Kelly (51) recovered new aromatic compounds which they believe were formed by union of the unsaturated compounds, including cyclopentadiene, with the aromatics, such as benzene and toluene. The new compounds were high-boiling oils and were produced by steam distilling the residues from the distillation of the acid-refined light oil at 200–270°C.

The Friedel–Crafts reaction has been used for the preparation of resins from cyclopentadiene and acid chlorides, such as stearyl, lauryl, oleyl, or linoleyl chlorides. Acylation and polymerization of the cyclopentadiene proceeded simultaneously. The inventors, Ralston and coworkers (179, 180), used as a starting material crude solvent naphtha containing dicyclopentadiene as a major constituent, together with lesser quantities of coumarone and indene. The products of the reaction between the cyclopentadiene and the chloride were usually changed to hard resins by heating to 100°C. for a number of hours.

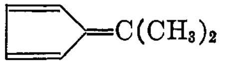
A composition resistant to corrosive influences was produced by mixing a dicyclopentadiene resin with a halogenated rubber and a styrene resin, according to Kodak, Ltd. (132).

I. CONDENSATIONS

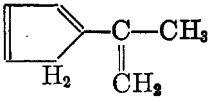
The methylene group (—CH_2—) is active, so that cyclopentadiene has been used in a number of condensations. This reaction also affords an excellent method for the preparation of a large number of new derivatives.

With aldehydes and ketones in the presence of alkaline condensing agents cyclopentadiene condenses easily to produce fulvenes in which the R and R′ may be hydrogen, alkyl, or aryl groups. The color of the fulvenes increases with the size of the R and R′, becoming blood-red with aromatic substitution. Condensations of cyclopentadiene with acetone, acetophenone, benzophenone, and other ketones were first carried out by Thiele (221). The colors of the products increased progressively from an intense orange to a blood-red. The aldehyde condensation products were also strongly colored, but resinified so easily that they could not be separated in the pure form. The condensation product from formaldehyde was a yellow oil of peculiar odor which changed very easily into yellow flakes, and absorbed oxygen rapidly.

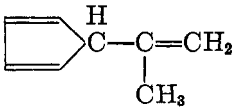
Ziegler and Crössman (247) pointed out the possibility that methylated fulvenes exist in several tautomeric forms, shown by structures I to IV.



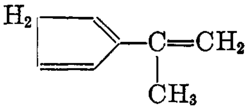
I



II

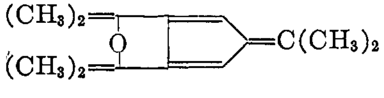


III

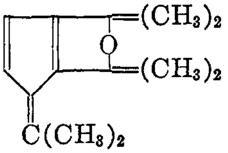


IV

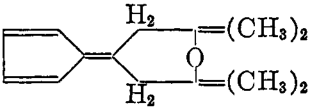
The methylene group in these fulvenes condensed further in certain instances. They suggested that the condensation product of dimethylfulvene with two molecules of acetone, which was prepared by Thiele and Balhorn (223), had the structure:



or

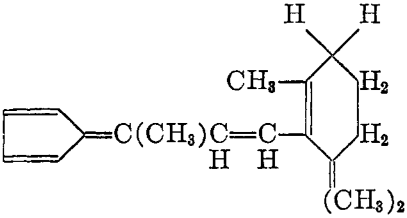


rather than



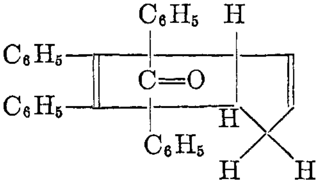
Kohler and Kable (134) condensed cyclopentadiene with cyclohexanone and cyclopentanone and isolated the corresponding fulvenes, which also were highly colored compounds and combined vigorously with maleic anhydride by the Diels–Alder reaction. The products were stable in the solid state, but when dissolved in indifferent solvents, such as ethyl acetate or benzene, dissociated into the original components. Dissociation was evidenced by the gradual disappearance of the fulvene color.

Basic fulvene derivatives were prepared by condensing cyclopentadiene with oxo-amino compounds or their *N*-monoallyl or *N*,*N*-dialkyl derivatives in the presence of an alkaline condensing agent. Diethylaminodimethylfulvene was produced, for instance, from $(C_2H_5)_2NCH_2COCH_3$ (4). An orange fulvene containing the β-ionone carbon ring,



was prepared by Willstaedt (244) by the condensation of β-ionone and cyclopentadiene. Kohler and Kable (133) obtained an 85 per cent yield of this product.

Tetraphenylcyclopentadienone and cyclopentadiene did not give the fulvene reaction. Grummitt and coworkers (101) refluxed the reagents in benzene solution for 4 hr. to produce a 75 per cent yield of 4,5,6,7-tetraphenyl-4,7-endocarboxyl-8,9-dihydroindene:

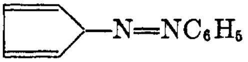


By hydrogenation of the fulvenes at 40°C. and 50 atmospheres pressure in contact with nickel on kieselguhr, Pines and Ipatieff (173) prepared alkylated cyclopentanes.

Reactions somewhat analogous to the formation of fulvenes have been reported by Thiele (221). Isonitrosocyclopentadiene, $C_5H_4{=}NOH$, was produced by the addition of ethyl nitrite, drop by drop, to a solution of cyclopentadiene in sodium ethylate and absolute ethanol. When ethyl nitrate was substituted for the nitrite, nitrocyclopentadiene, $C_5H_5NO_2$, was produced. The product was isolated as the sodium or silver salt, both of which were highly colored. With an oxalic ester the cyclopentadieneoxalic ester was produced. Both the nitro and oxalic ester compounds coupled with diazo compounds.

J. REACTIONS WITH DIAZONIUM COMPOUNDS

Cyclopentadiene and benzenediazonium chloride reacted in the presence of sodium acetate to produce brown crystals of cyclopentadieneazobenzene,



according to Eibner (75, 76). Guha and Hazra (102) could not induce cyclopentadiene to react with diazomethane in dry ether at 0°C., at room temperature, or in the presence of methanol as a catalyst, but found that cyclopentadiene would react with diazoacetic ester, $N_2CHCOOC_2H_5$, at 0°C. The product exploded when warmed to room temperature. Cyclopentadiene coupled easily with both diazotized *p*-nitroaniline and 2,3-dinitroaniline, according to Terent'ev and Gomberg (214). Thiele (221) reported that cyclopentadiene reacted with diazobenzene chloride in alcoholic solution to produce intensely colored compounds which resinified easily.

K. OTHER REACTIONS OF CYCLOPENTADIENE

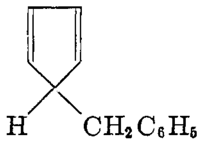
1. Cracking

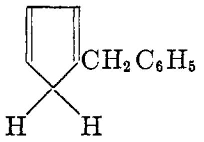
When cyclopentadiene or dicyclopentadiene was passed through a tube heated to dull redness, a good yield of naphthalene, together with some benzene and anthracene, was obtained by Weger (237). Meyer and Hofmann (152) produced naphthalene by heating a coil of platinum wire to a dull red in an atmosphere of cyclopentadiene. In their opinion the five-membered rings were not converted to the hexagonal form directly, but were decomposed first to ethylene and acetylene. The latter then reacted to form naphthalene.

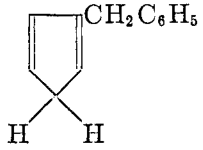
2. Reactions with metals and salts

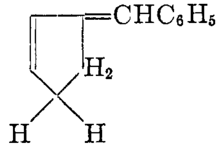
Potassium reacted with cyclopentadiene in benzene solution to produce cyclopentadiene potassium, according to Thiele (222). Hydrogen was evolved and the reaction was strongly exothermic. Carbon dioxide was readily absorbed with production of the potassium salt of cyclopentadienecarbonic acid. By addition of dilute sulfuric acid the free acid was formed.

Cyclopentadiene potassium has been used by Alder and Holzrichter (6) to produce arylated derivatives of cyclopentadiene. By heating a mixture of the cyclopentadiene potassium with benzyl chloride, a mixture of 1- and 2-benzylcyclopentadienes and a little dibenzylcyclopentadiene were produced. The products were separated by vacuum distillation. Four isomeric benzylcyclopentadienes are possible:









These derivatives formed dimers which could be decomposed, like dicyclopentadiene, by distillation at a controlled temperature. They all added maleic anhydride by the Diels–Alder reaction.

Gilliland and coworkers (94) were unable to obtain a reaction between cyclopentadiene and solid cuprous chloride, although other conjugated dienes, such as isoprene or butadiene, would react with the salt. Solutions containing cuprous chloride and ammonium chloride, however, were used for absorption of cyclopentadiene from gases by Luré and coworkers (149). Other dienes, such as piperylene, were also absorbed and a mixture of complex copper compounds was precipitated.

Mercuric chloride reacted with cyclopentadiene dissolved in methanol to produce a white precipitate which appeared to be a high-molecular-weight polymerization product, according to Hofmann and Seiler (109). The formula, $C_5H_4(HgCl)_2$, represents the proportions in which the reagents combined. The precipitate turned violet-brown in light and air.

Both halogen-substituted and addition derivatives of cyclopentadiene were produced by Grignard and Courtot (97) by use of the Grignard reaction. The reagent was prepared by the reaction of cyclopentadiene with the methyl Grignard reagent:

$$C_5H_6 + CH_3MgBr \rightarrow C_5H_4MgBr + CH_4$$

On addition of four atoms of bromine, tribromocyclopentene was formed. It would polymerize to the dimer, a brown powder. By decomposing the Grignard compound with cyanogen chloride the same investigators (97) obtained cyclopentadiene cyanide. After it had polymerized, the dimer was converted into dicyclopentadienedicarbonic acid. Horclois (111) reported the production of cyclopentadienecarbonic acid by treating the Grignard compound with carbon dioxide.

Cuprocyclopentadiene-tripropylphosphine, $CuC_5H_5 \cdot 2C_3H_7P$ was produced by van Peski and van Melsen (171) by the reaction between cyclopentadiene, cuprous oxide, and propylphosphine. It was suitable for use as an antiknock agent with gasoline.

3. Formation of alcohols

By reaction with hydrogen peroxide in contact with osmium tetroxide as a catalyst, cyclopentadiene in tertiary butyl alcohol solution was hydroxylated to 2-cyclopentene-1,4-diol, according to Milas and Maloney (153). By further oxidation under similar conditions, a 61 per cent yield of cyclopentane-1,2,3,4-tetrol was obtained. It was amorphous and extremely hygroscopic and turned black at 200°C. The alcohols from cyclopentadiene should prove interesting additions to this important family.

4. Reactions with sulfur and sulfur compounds

Cyclopentadiene readily reacts with sulfur at approximately 120°C. to form products which are at first slightly elastic, but become hard and brittle on standing, according to Mayberry (150).

Kruber and Schade (143) reported that the ethyl mercaptans and cyclopentadiene in motor benzol added to produce non-volatile resins. Posner (176) concluded that the mercaptans added at both the double bonds of cyclopentadiene. When cyclopentadiene and thiophenol were left in contact for several weeks and the product oxidized, a small amount of colorless crystals, which he identified as diphenylsulfonecyclopentane, $C_5H_8(SO_2C_6H_5)_2$, were obtained.

The formation of dyes or dye intermediates by condensation of a hydrocarbon containing the cyclopentadiene ring with a quaternary salt of a heterocyclic nitrogen compound containing as a reactive group either a *thioether* or a *seleno ether* group was patented by Kendall (122).

L. EFFECTS OF CYCLOPENTADIENE ON OILS

Cyclopentadiene or dicyclopentadiene in an oil will form gum; Schultze (196) concluded that gum formation by polymerization can occur in motor fuel even in the absence of air. The production of non-volatile resins in motor benzol by the addition of mercaptans to cyclopentadiene has already been mentioned (143).

Cyclopentadiene can be removed from an oil by washing with concentrated sulfuric acid. Claxton and Hoffert (56) concluded that cyclopentadiene and dicyclopentadiene were the substances chiefly responsible for the formation of sulfur dioxide during distillation of a coke-oven light oil which had been washed with acid. They found that the quantity of sulfur dioxide evolved was proportional to the amount of cyclopentadiene in the oil, and recommended that in the distillation process for removing the crude light oil from the wash oil the cyclopentadiene should be removed in a forerunnings fraction. Once dicyclopentadiene had formed, formation of the sulfur dioxide during the subsequent refining was very difficult to avoid. Sulfur dioxide formation could be minimized by using the lowest strength acid that would effect the required sulfur reduction, and by distilling at as low a temperature as possible. Dilution of the acid with a spacing agent, such as phosphoric acid, effected some improvement, but could not be recommended because of the cost. Boes (41) also considered cyclopentadiene responsible for sulfur dioxide formation during acid washing.

Hoffert and coworkers (107, 108) pointed out that in the presence of a high concentration of unsaturated compounds, including cyclopentadiene, thiophene is removed from light oil with lower strengths and amounts of acids than would otherwise be the case. The loss of light oil will be correspondingly greater, owing to the concurrent destruction of the unsaturates by the acid. Kopelevitsch and coworkers (139) suggested the addition of a light oil containing cyclopentadiene to benzol before washing with acid in order to assist the removal of thiophene.

V. Physiological Properties

Only one study has been made of the toxicity of cyclopentadiene. Elfstrand (79, 229) reported that "the vapors cause narcosis of frogs in 10 minutes and it takes 70 minutes for the animals to recover. They show a primary motor unrest, the respiration becomes slow and intermittent and finally arrested. The animals finally develop flaccid paralysis and the reflexes are reduced, although not abolished. It causes a peculiar rigidity of the muscles which slowly disappears on recovery from the narcosis; with sufficient exposure, however, this may pass into rigor so that electric stimulation becomes ineffective. The rate and energy of the heartbeat are somewhat reduced and already at the beginning of narcosis cardiac peristalsis may set in. In rabbits the vapors already cause complete narcosis after 10 minutes, the respiration is markedly reduced, and the heart rate is increased; convulsions may develop during narcosis. The recovery is rather slow and only complete after 18 hours. In rabbits the subcutaneous injection of 0.5 to 1.0 cc. causes no narcosis, while 3 cc. causes narcosis with fatal convulsions. The material causes marked local irritation and autopsy exudates were found in the pleural and pericardial cavities, and the kidneys were hyperemic."

VI. Identification and Determination

Cyclopentadiene has been detected in oils by means of color reactions. The green color produced in an oil containing cyclopentadiene by the addition of hydroquinone in methanol was used by Claxton and coworkers (56) as a qualitative test.

Vansheĭdt (227) found that solutions of hydrocarbons containing the group $(C{=}C)_2CH$, such as cyclopentadiene, indene, fluorene, and their derivatives, in acetone, pyridine, or naphthalene become colored on addition of alcoholic potassium hydroxide. On shaking in air the solutions are oxidized with a complete decolorization or color change. Vansheĭdt's reagent and *p*-dinitrobenzene produced characteristic green or blue colors with cyclopentadiene in acetone or pyridine, according to Levy and Campbell (146).

In his work on the reactions of aromatic diazo compounds with unsaturated compounds, Terent'ev (212, 215) found that by diazotization of *p*-diaminobenzene in phosphoric acid at −10°C. with sodium nitrite in concentrated sulfuric acid, a reagent was obtained which gave a red to red-brown color with hydrocarbons containing double bonds. With cyclopentadiene the reaction was very sensitive.

Cyclopentadiene reacts mole for mole with *p*-nitrobenzenediazonium chloride.

By titrating the unreacted reagent with β-naphthol it was possible to determine the amount of the diene in a mixture (213, 219). The diazonium chloride also reacts with 1,3-diethylenic hydrocarbons, but not with aromatic hydrocarbons or compounds with conjugated hetero atoms. Terent'ev (217, 218) also stated that the reaction can be used for the determination of cyclopentadiene in a mixture with its polymer.

Two other qualitative reactions have been described by Terent'ev (216). When gas containing at least 0.25 mg. of cyclopentadiene was passed through an aqueous solution of mercuric nitrate slightly acidified with nitric acid, a white cloudiness appeared. Benzene, toluene, ethylene, bivinyl, and isoprene did not interfere, but butenes and acetylene also caused precipitates, although less rapidly.

When 12–15 cc. of gas containing 0.05 per cent of cyclopentadiene was passed into a 0.25 per cent solution of *p*-benzoquinone in ethanol, a deep blue color developed. Even butene and acetylene did not interfere (216).

Afanas'ev (3) described another color reaction for cyclopentadiene. One drop was mixed with 1 cc. each of chloroform and glacial acetic acid and the product treated cautiously with two or three drops of concentrated sulfuric acid. As little as 0.1 mg. gave a distinct violet coloration. Terent'ev reported that the test was not specific for cyclopentadiene (216).

Cyclopentadiene gave an intense red color and a red precipitate with sodium nitroprusside in methanol solution made slightly basic with sodium or potassium hydroxide. Indene gave the same test, according to Scagliarini and Lucchi (192).

The Diels–Alder reaction of cyclopentadiene with maleic anhydride is a useful method both for its identification and for its determination (7, 61). Birch and Scott (40) used it for identification of diolefins in a compression gasoline produced in a high-temperature cracking unit. Other conjugated dienes, such as butadiene and isoprene, however, add with maleic anhydride by the Diels–Alder method.

The conjugated dienes in the fraction boiling between 20° and 80°C. from coal-gas light oil were determined by Gooderham (96) by the maleic anhydride reaction, in which the fraction is vaporized in a constant-volume steam-jacketed buret. Absorption of the cyclopentadiene by the maleic anhydride was complete in a few minutes.

Precipitation of the maleic anhydride adduct is quantitative. Dedusenko (59) separated the crystals by filtration and used them in determining the cyclopentadiene content of an oil.

Kirsanov and coworkers (128) treated freshly distilled cyclopentadiene with maleic anhydride for an hour. An iodide–iodate solution was added to the product and the excess iodine was titrated with thiosulfate. They reported that the method was accurate to ±1 per cent. It was used for measuring the rate of dimerization of cyclopentadiene in a crude benzene. *p*-Benzoquinone could not be used for the addition with cyclopentadiene; after 3 hr. the reaction was only 85 per cent complete.

Cyclopentadiene and indene, Hammick and Langrish (103) found, can be estimated with an accuracy of 2–3 per cent by determining the amount of bromine which reacts with a dilute solution of the hydrocarbon in carbon tetrachloride. A 100 per cent excess of bromine was used, and the concentration of the cyclopentadiene solution was less than 0.05 *M*. Under these conditions the cyclopentadiene added four bromine atoms and dicyclopentadiene added two bromine atoms. Schultze (195) also described bromination methods for the analysis of cyclopentadiene and dicyclopentadiene. The dienes absorb oxygen from the air so rapidly that quantitative bromination is impossible, but when titrated in vacuum or in the presence of an excess of free bromine from the very beginning of the test, the formation of peroxides is prevented and the results are quantitative.

VII. PROPERTIES OF DICYCLOPENTADIENE AND HIGHER POLYMERS OF CYCLOPENTADIENE

A. SOURCE AND PRODUCTION

Dicyclopentadiene is always found in cyclopentadiene when the latter is allowed to stand. The formation of the dimer from cyclopentadiene, and of the higher polymers, has been discussed at an earlier point in this article.

B. PHYSICAL PROPERTIES

The stereoisomeric forms of di- and tri-cyclopentadienes have been discussed above. Endodicyclopentadiene, the form produced by ordinary polymerization, occurs as colorless crystals with a camphor-like odor. The tri and tetra polymers are also crystalline, but the higher ones are amorphous insoluble compounds. Pentacyclopentadiene was reported to sublime at high vacuum by Staudinger and Bruson (204) and to separate as a gel from very dilute solutions. By heating the polymers were depolymerized to cyclopentadiene. Thus, cyclopentadiene split off when polycyclopentadiene was decomposed by heating to 370°C.

The physical constants for the polymers of cyclopentadiene which are available are tabulated in table 2.

The following values are available for the heats of combustion, fusion, and vaporization of endodicyclopentadiene and higher polymers.

COMPOUND	HEAT OF COMBUSTION AT CONSTANT PRESSURE (35)	HEAT OF FUSION (19)	HEAT OF VAPORIZATION (19)
	kg.-cal. per mole	*kg.-cal. per mole*	*kg.-cal. per mole*
Endodicylopentadiene	1378.4	0.5	9.2
Endotricyclopentadiene	2055.8	5.1	11.1
Tetracyclopentadiene	2730.8		13.0

Alder and Stein (19) calculated the heat of fusion from cryoscopic data and the heat of vaporization according to Trouton's law.

Burchfield (46) has supplied the following constants for calculating the vapor

TABLE 2

Physical constants of cyclopentadiene polymers

POLYMER	MELTING POINT, °C.		BOILING POINT			DENSITY			INDEX OF REFRACTION		
			°C.	Pressure in mm.							
Endodicyclopentadiene.	31.5	(232)	163	766	(19)	1.012	$d_4^{17.5}$ (solid)	(187)	1.48031	$n_{H_\alpha}^{77.25}$	(77)
	32	(19, 32, 204, 209)	170	760	(140, 202a)	0.9302	$d_4^{77.25}$	(77)	1.51047	$n_{H_\alpha}^{20}$	(209)
	32.5	(240)	100	61.1	(140)	0.9756	d_4^{35}	(140)			
	32.9	(187)	90	41.3	(140)	0.9766	d_4^{33}	(140)			
	33.6	(131)	80	25.9	(140)	0.950	d_4^{57}	(37)			
			70	24	(209)	0.942	d_4^{66}	(37)			
			64–5	14	(135)	0.925	d_4^{78}	(37)			
			61	14	(35)	0.888	d_4^{100}	(37)			
			56	13	(240)						
			69	12	(204)						
			51	0.1	(178)						
Exodicyclopentadiene..	19.5	(207)									
Tricyclopentadiene.....	68	(15)	254	766	(15)						
			110	3	(202a)						
	60	(202a, 204, 207)	105	3	(204)						
	66	(24)	90–92	0.06	(207)						
Tetracyclopentadiene..	188–190	(202a)	344	766	(19)						
	190	(204)	160–5	1	(204)						
			160	1	(202a)						
Pentacyclopentadiene..	270	(202a, 204)									
Hexacyclopentadiene...	373	(202a)									

pressure of dicyclopentadiene between 40.1° and 90.8°C. by the Clausius–Clapeyron equation: $A = 7.925$; $B = -2218$.

Tetracyclopentadiene and lower polymers are easily soluble in many organic liquids at ordinary temperatures, but pentacyclopentadiene is soluble in benzene and similar solvents only when hot. On cooling it is deposited as gelatinous needles. Polycyclopentadiene is completely insoluble (204).

The ignition point of dicyclopentadiene by the drop method was found by Zerbe and Eckert (246) to be 510°C. in oxygen and 680°C. in air. The antiknock properties of the dimer are good; the octane number was reported by Lovell and coworkers (148) to be over 100, the aniline equivalent 65, and the critical compression ratio 11.0. The addition of tetraethyllead lowered the critical compression ratio, Campbell and coworkers (48) found.

The dielectric constant decreased from 2.43 at 40°C. to 2.31 at 100°C., according to Waring and coworkers (232).

Infrared absorption spectra for dicyclopentadiene have been determined by Lambert and Lecomte (144). The differences in the spectra between dicyclopentadiene and its monomer have been pointed out previously. Kettering and Sleator (123) determined the infrared absorption in the region 1–30 μ for gaseous dicyclopentadiene by means of prisms of sodium and potassium halides, and plotted the per cent absorption against the wave length. The resolution was insufficient to separate rotational bands in any of the lines.

Raman bands have been tabulated for dicyclopentadiene by Reitz (106, 183, 185). The results of Lambert and Lecomte (144) indicate the greater complexity of the dimer structure over that of cyclopentadiene.

An x-ray investigation of polymerized cyclopentadiene by Hengstenberg (105) showed that although the tri-, tetra-, and poly-cyclopentadienes had different lattices, the molecules were all of the same size, 2.8Å., in one direction.

C. CHEMICAL PROPERTIES

1. *Reactions with sulfuric acid*

Although dicyclopentadiene is somewhat less reactive than cyclopentadiene, its properties and those of the higher polymers render these substances of interest in a number of industrial fields. The structure of dicyclopentadiene is rather suggestive. It is similar to that of indene, except that the former possesses a methylene group bridging the hexagonal ring, and two extra hydrogens. The indene structure renders dicyclopentadiene of some importance to resin producers. A large number of derivatives can be prepared from dicyclopentadiene, and useful applications for some of them are to be anticipated.

With dicyclopentadiene concentrated sulfuric acid reacts with charring, Boes (41) reported. In the presence of syrupy phosphoric acid or 50 per cent sulfuric acid dicyclopentadiene polymerizes without evolution of cyclopentadiene (235a, 235b). The resinous products produced with dilute sulfuric acid contain a sulfone, $C_{20}H_{22}SO_2$, a hard brittle mass, the amount of which depends on the strength of the acid. No appreciable amount of cyclopentadiene was evolved by dry distillation of the sulfone. By the action of sulfuric acid diluted with acetic acid, deep blue derivatives have been obtained from poly- and di-cyclopentadienes (204).

2. Nitro compounds and reactions with nitric acid

The polymers of cyclopentadiene are oxidized by nitric acid, according to Staudinger and Bruson (204). The insoluble polycyclopentadiene is attacked with difficulty, but the lower polymers react more easily. Kraemer and Spilker (140) prepared the nitrosate by treating a solution of dicyclopentadiene in chloroform with nitric acid at −15°C. When dicyclopentadiene was mixed with amyl nitrite and acetic acid, the mixture cooled, and hydrochloric acid in 10 per cent alcoholic solution added, the nitrosochloride was produced. Dicyclopentadiene nitrosobromide was prepared by Rule (190) in similar manner. Wieland (239, 240) recommended the preparation of the nitrosochloride by heating dicyclopentadiene and bisnitrosochloride in amyl alcohol.

3. Halogen derivatives

Two molecules of a halogen will add to one of dicyclopentadiene, according to Kraemer and Spilker (140). Pauly and coworkers (169) found that dicyclopentadiene would add less than two atoms of iodine. The measurements of Ghosh and Bhattaryya (92) indicated that the photoiodination reaction was unimolecular with respect to dicyclopentadiene.

Polycyclopentadiene did not decolorize bromine in a carbon disulfide solution, Staudinger and Bruson (204) observed. Tricyclopentadiene added 2 moles of bromine from a solution in carbon disulfide and tetracyclopentadiene added 1 mole. Pentacyclopentadiene decolorized the bromine solution. Deep blue, high-molecular-weight products, whose constitution has not been determined, were obtained by the action of bromine in acetic acid on dicyclopentadiene.

4. Hydrogenation

Dicyclopentadiene has been progressively hydrogenated through the dihydro to the tetrahydro derivative (17, 175). Nickel was used as the catalyst by Eijkman (78). The double bond in the bicycloheptene ring was the more reactive, and the heat of hydrogenation amounted to 33.2 kg.-cal. per gram mole. That for the pentagonal ring was 26.2 kg.-cal., according to Alder and Stein (19).

The higher polymers can also be hydrogenated. Alder and coworkers (24) dissolved tricyclopentadiene in methanol, added colloidal platinum, and agitated in an atmosphere of hydrogen. Data on the physical properties of the hydrogenated polymers of cyclopentadiene have been published by Alder and Stein (19) and Becker and Roth (69).

5. Oxidation

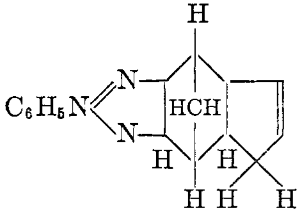
Dicyclopentadiene was oxidized easily by potassium permanganate in the cold, according to Kraemer and Spilker (140). In air dicyclopentadiene was resistant to oxidation below 300°C. and acted as an inhibitor for the combustion of more easily oxidizable hydrocarbons, such as decahydronaphthalene, Dumanois and coworkers (72) reported. Bauer and Bahr (33) found that when oxidized with perbenzoic acid dicyclopentadiene yielded a dioxide, which gave a mercuric chloride complex.

6. Reaction of sulfur and dicyclopentadiene

The reaction of dicyclopentadiene and sulfur has been studied over a wide range of concentration (150). At lower temperatures (below 105°C.) sulfur dissolved in dicyclopentadiene, the solubility ranging from about 1 per cent at 22°C. to 10 per cent at 100°C. Above 100°C. a reaction occurred with the evolution of hydrogen sulfide. This reaction increased in speed as the temperature was raised. Above 155°C. a vigorous exothermic reaction took place, accompanied by excessive foaming of the reaction mixture due to the rapid evolution of hydrogen sulfide. The characteristics of the products depended upon the composition of the mixture, the temperature, and the time of heating, and ranged from viscous oils to hard, brittle, non-crystalline solids. Mixtures containing up to 35 per cent of sulfur when heated less than 3 hr. below 155°C. yielded oils of varying viscosity. Plastic products were obtained when mixtures containing more than 50 per cent of sulfur were heated for 30 to 45 min. These products, although flexible and slightly elastic at first, slowly hardened and became brittle after standing for several days. Heating the reaction mixtures above 155°C. also produced hard brittle products. The solid products are only slightly soluble in most organic solvents. The resins may find application in the electrical industry or as a binder for the preparation of molding compositions.

7. Miscellaneous reactions

A characteristic reaction for the bicycloheptene ring structure is the coupling of phenyl azide, $C_6H_3N_3$, at the double bond in the endomethylene ring to give the addition compound (14):



The product is decomposed by mineral acids with liberation of nitrogen. Dihydrodicyclopentadiene will not react, according to Alder and Stein (15).

Komppa and Beckman (137) produced *trans*-3-methyl(exo)bicyclo[1,2,2]-heptene-2-carboxylic acid (endo) by the addition of crotonic acid to dicyclopentadiene. An iso-compound was also present in the products.

Wieland and Hasegawa (241) attempted to use the Friedel–Crafts reaction with acetyl chloride to synthesize unsaturated ketones. Dicyclopentadiene reacted vigorously but yielded no homogeneous product.

Mercuric chloride in methanol solution gave with dicyclopentadiene on 2 days' standing faint yellow needles of the compound $ClHg \cdot C_{10}H_{12}OCH_3$; in ethanol solution a similar compound, $ClHg \cdot C_{10}H_{12}OC_2H_5$, was produced, according to Hofmann and Seiler (109).

Sulfur chloride added to the polymers in chloroform solution, Staudinger and Bruson (204) reported, but the vulcanization product was impure and contained some acid.

8. Resin production

In addition to the previously mentioned dicyclopentadiene resins, the following have been described:

A coating for food containers has been prepared from solid polycyclopentadiene and styrene. Soday (200) copolymerized them by heating in a nitrogen atmosphere at 100–145°C. for 4–10 days. Methylstyrene yielded a similar product.

Dicyclopentadiene was one of the constituents in tar fractions which Rivkin and Sheehan (186) copolymerized with phenols to produce oily or resinous products; activated clay was used as a catalyst.

REFERENCES

(1) Adams, R., and Gold, M. H.: J. Am. Chem. Soc. **62,** 52–61 (1940).

(2) Adams, R., and Wearn, R. B.: J. Am. Chem. Soc. **62,** 1233–7 (1940); Chem. Abstracts **34,** 6270 (1940).

(3) Afanas'ev, B. N.: Ind. Eng. Chem., Anal. Ed. **8,** 15 (1936); Chem. Abstracts **30,** 1330 (1936).

(4) Akt.-Ges. vorm. B. Siegfried: German patent 657,416 (1938).

(5) Albrecht, W.: Ann. **348,** 31–49 (1906).

(6) Alder, K., and Holzrichter, H.: Ann. **524,** 145–80 (1936); Chem. Abstracts **30,** 8177 (1936).

(7) Alder, K., and Rickert, H. F.: Ann. **524,** 180–9 (1936); Chem. Abstracts **30,** 8178 (1936).

(8) Alder, K., and Rickert, H. F.: Ann. **543,** 1–27 (1939).

(9) Alder, K., and Rickert, H. F.: Ber. **71B,** 373–8 (1938).

(10) Alder, K., and Rickert, H. F.: Ber. **71B,** 379–86 (1938).

(11) Alder, K., and Rickert, H. F.: Ber. **72B,** 1983–92 (1939); Chem. Abstracts **34,** 729 (1940).

(12) Alder, K., Rickert, H. F., and Windemuth, E.: Ber. **71B,** 2451–61 (1938).

(13) Alder, K., and Schneider, S.: Ann. **524,** 189–202 (1936); Chem. Abstracts **30,** 8178 (1936).

(14) Alder, K., and Stein, G.: Ann. **485,** 211–22 (1931).

(15) Alder, K., and Stein, G.: Ann. **485,** 223–46 (1931); Chem. Abstracts **25,** 1806 (1931).

(16) Alder, K., and Stein, G.: Ann. **501,** 247–94 (1933).

(17) Alder, K., and Stein, G.: Ann. **504,** 205–15 (1933); Chem. Abstracts **27,** 5310 (1933).

(18) Alder, K., and Stein, G.: Ber. **67B,** 373–5 (1934).

(19) Alder, K., and Stein, G.: Ber. **67B,** 613–26 (1934); Chem. Abstracts **28,** 6114 (1934).

(20) Alder, K., and Stein, G.: Angew. Chem. **47,** 837–42 (1934); Chem. Abstracts **29,** 2516 (1935).

(21) Alder, K., Stein, G., Buddenbrock, F. v., Eckardt, W., Frercks, W., and Schneider, St.: Ann. **514,** 1–33 (1934); Chem. Abstracts **29,** 2157 (1935).

(22) Alder, K., Stein, G., Eckardt, W., Buddenbrock, R. v., and Schneider, J.: Ann. **504,** 216–57 (1933); Chem. Abstracts **27,** 5311 (1933).

(23) Alder, K., Stein, G., Liebmann, M., and Rolland, E.: Ann. **514**, 197–211 (1934); Chem. Abstracts **29**, 2158 (1935).

(24) Alder, K., Stein, G., Reese, J., and Grassmann, W.: Ann. **496**, 204–51 (1932).

(25) Alder, K., Stein, G., Schneider, S., Liebmann, M., Rolland, E., and Schulze, G.: Ann. **525**, 183–221 (1936).

(26) Alder, K., and Windemuth, E.: Ber. **71B**, 1939–57 (1938).

(27) Alder, K., and Windemuth, E.: Ber. **71B**, 2409–14 (1938).

(28) Allen, C. F. H., and Bell, A.: J. Am. Chem. Soc. **61**, 521–2 (1939); Chem. Abstracts **33**, 2112 (1939).

(29) Allen, C. F. H., Bell, A. C., Bell, A., and Van Allen, J.: J. Am. Chem. Soc. **62**, 656–64 (1940).

(30) Auwers, K. v.: Ber. **45**, 3077–80 (1912).

(31) Auwers, K. v., and Eisenlohr, F.: Ber. **43**, 806–26 (1910).

(32) Barrett, E. G. V., and Burrage, L. J.: J. Phys. Chem. **37**, 1029–35 (1933).

(33) Bauer, K. H., and Bahr, O.: J. prakt. Chem. **122**, 201–13 (1929); Chem. Abstracts **24**, 60 (1930).

(34) Baur, E., and Frater, S.: Helv. Chim. Acta. **24**, 768–82 (1941); Chem. Abstracts **35**, 6861 (1941).

(35) Becker, G., and Roth, W. A.: Ber. **67B**, 627–32 (1934).

(36) Benford, G. A., Khambata, B. S., and Wassermann, A.: Nature **139**, 669–70 (1937).

(37) Benford, G. A., and Wassermann, A.: J. Chem. Soc. **1939**, 362–88; Chem. Abstracts **33**, 4207 (1939).

(38) Bergmann, E., and Bergmann, F.: J. Org. Chem. **3**, 125–36 (1938); Chem. Abstracts **33**, 567 (1939).

(39) Birch, S. F., and Hague, E. N.: Ind. Eng. Chem. **26**, 1008–10 (1934); Chem. Abstracts **28**, 6982 (1934).

(40) Birch, S. F., and Scott, W. D.: Ind. Eng. Chem. **24**, 49–50 (1932).

(41) Boes, J.: Apoth.-Ztg., **17**, 340–1 (1902); Chem. Zentr. **1902**, II, 32.

(43) Bruson, H. A.: U. S. patent 1,892,101 (1933); Chem. Abstracts **27**, 1893 (1933).

(42) Brooks, B. T., and Wilbert, G.: J. Am. Chem. Soc. **63**, 870–1 (1941); Chem. Abstracts **35**, 2864 (1941).

(44) Bruson, H. A., and Staudinger, H.: Ind. Eng. Chem. **18**, 381 (1926); Chem. Abstracts **20**, 2091 (1926).

(45) Bruson, H. A., and Staudinger, H.: U. S. patent 1,720,729 (1929); Chem. Abstracts **23**, 4228 (1929).

(46) Burchfield, P. E.: J. Am. Chem. Soc. **64**, 2501 (1942); Chem. Abstracts **37**, 559 (1943).

(47) Cambron, A., and Bayley, C. H.: Can. J. Research **9**, 591–602 (1933); **10**, 145–63 (1934); U. S. patent 2,002,524–5 (1935); British patent 425,606 (1935).

(48) Campbell, J. M., Signaigo, F. K., Lovell, W. G., and Boyd, T. A.: Ind. Eng. Chem. **27**, 593–7 (1935); Chem. Abstracts **29**, 4560 (1935).

(49) Carmody, W. H.: U. S. patent 2,067,073 (1937); Chem. Abstracts **31**, 1519 (1937).

(50) Carmody, W. H.: U. S. patent 2,255,409 (1941); Chem. Abstracts **36**, 193 (1942).

(51) Carmody, W. H., and Kelly, H. E.: Ind. Eng. Chem. **32**, 954–7 (1940); Chem. Abstracts **34**, 5961 (1940).

(52) Carmody, W. H., Sheehan, W., and Kelly, H. E.: Ind. Eng. Chem. **30**, 245–51 (1938); Chem. Abstracts **32**, 3509 (1938).

(53) Chaney, N. K.: U. S. patent 2,220,211 (1940); Chem. Abstracts **35**, 1549 (1941).

(54) Chaux, R.: Compt. rend. **194**, 1193 (1932); Chem. Abstracts **26**, 3334 (1932).

(55) Chaux, R., and Dufraisse, C.: U. S. patent 1,869,666 (1932).

(56) Claxton, G., and Hoffert, W. H.: Gas World **113**, No. 2927, Coking Sect., 70–6 (1940); Chem. Abstracts **34**, 8221 (1940); Coke Oven Managers' Assoc. Yearbook 1941, 146–64; Chem. Abstracts **36**, 2706(1942).

(57) Conover, C.: U. S. patent 2,079,490 (1937).

(58) Criegee, R.: Ann. **481**, 263–302 (1930); Chem. Abstracts **24**, 5286 (1930).

(59) Dedusenko, L. S.: Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. Chim. **1936,** 59–64; Chem. Abstracts **31,** 1992 (1937).

(60) Dedusenko, L. S.: J. Gen. Chem. (U.S.S.R.) **9,** 1294–1302 (1939).

(61) Diels, O., and Alder, K.: Ann. **460,** 98–122 (1928).

(62) Diels, O., and Alder, K.: Ann. **478,** 137–154 (1930).

(63) Diels, O., and Alder, K.: Ber. **62B,** 554–62 (1929).

(64) Diels, O., and Alder, K.: U. S. patent 1,891,043 (1932).

(65) Diels, O., and Alder, K.: U. S. patent 1,944,731–2 (1934).

(66) Diels, O., Alder, K., Lubbert, W., Naujoka, E., Ouerberitz, F., Rohl, K., and Segeberg, H.: Ann. **470,** 62–103 (1929).

(67) Diels, O., Alder, K., and Nienburg, H.: Ann. **490,** 236–42 (1931).

(68) Diels, O., Alder, K., and Petersen, E.: Ann. **486,** 202–10 (1931).

(69) Diels, O., Alder, K., and Pries, P.: Ber. **62B,** 2081–7 (1929).

(70) Diels, O., Blom, J. H., and Koll, W.: Ann. **443,** 242–62 (1925).

(71) Diels, O., and Friedrichsen, W.: Ann. **513,** 145–55 (1934).

(72) Dumanois, P., Rentenauer, G., and Prettre, M.: Compt. rend. **208,** 1814–16 (1939).

(73) Dunstan, A. E., Hague, E. N., and Howes, D. A.: Chimie & industrie **34,** 273–5 (1935); Chem. Abstracts **29,** 7618 (1935).

(75) Eibner, A.: Ber. **36,** 2687–92 (1903).

(76) Eibner, A., and Laue, O.: Ber. **39,** 2022–7 (1906).

(77) Eijkman, J. F.: Chem. Zentr. **78,** II, 1206–11 (1907); Chem. Weekblad **4,** 41–52.

(78) Eijkman, J. F.: Chem. Weekblad **1,** 7–12 (1903); Chem. Zentr. **74,** II, 989.

(79) Elfstrand, M.: Arch. exptl. Path. Pharmakol **43,** 435 (1900).

(80) Engler, C., and Frankstein, W.: Ber. **34,** 2933–41 (1901).

(81) Étard, A., and Lambert, P.: Compt. rend. **112,** 945–7 (1891).

(82) Evans, M. G.: Trans. Faraday Soc. **35,** 824–34, 841–3 (1939).

(83) Fairclough, R. A., and Hinshelwood, C. N.: J. Chem. Soc. **1938,** 236–8.

(84) Farmer, E. H., and Farooq, M. O.: J. Chem. Soc. **1938,** 1925–30.

(85) Farmer, E. H., and Scott, W. D.: J. Chem. Soc. **1929,** 172–80.

(86) Farquharson, J.: Trans. Faraday Soc. **32,** 219–26 (1936).

(87) Flood, D. T., Hladkey, J. W., and Edgar, G.: Ind. Eng. Chem. **25,** 1234–9 (1933).

(88) Foresti, B.: Boll. soc., Eustachiana **38,** 19–27 (1940); Chem. Abstracts **36,** 6400 (1942).

(89) Frey, F. E.: Ind. Eng. Chem. **26,** 198–203 (1934).

(90) Frey, F. E., and Hepp, H. J.: Ind. Eng. Chem. **24,** 282–8 (1932).

(91) Garelli, F.: Chem. Zentr. **1896,** II, 883.

(92) Ghosh, J. C. and Bhattacharyya, S. K.: Science and Culture **3,** 120 (1937).

(93) Gillies, A.: Gas World **104,** No. 2700, Coking Sect. 52–5 (1936).

(94) Gilliland, E. R., Bliss, H. L., and Kip, C. E.: J. Am. Chem. Soc. **63,** 2088–90 (1941).

(95) Goheen, G. E.: J. Am. Chem. Soc. **63,** 744–9 (1941).

(96) Gooderham, W. J.: J. Soc. Chem. Ind. **56,** 26–36 (1937).

(97) Grignard, V., and Courtot, C.: Compt. rend. **158,** 1763–6 (1914).

(98) Grosse, A. V.: U. S. patent 2,157,202 (1939).

(99) Grosse, A. V., Morrell, J. C., and Mavity, J. M.: Ind. Eng. Chem. **32,** 309–11 (1940).

(100) Grosse, A. V., and Wackher, R. C.: Ind. Eng. Chem., Anal. Ed. **11,** 614–24 (1939).

(101) Grummitt, O., Klopper, R. S., and Blenkhorn, C. W.: J. Am. Chem. Soc. **64,** 604–7 (1942).

(102) Guha, P. C., and Hazra, G. D.: J. Indian Inst. Sci. **22A,** 263–74 (1939).

(103) Hammick, D. L., and Langrish, D.: J. Chem. Soc. **1937,** 797–801.

(104) Harkness, J. B., Kistiakowsky, G. B., and Mears, W. H.: J. Chem. Phys. **5,** 682–94 (1937).

(105) Hengstenberg, J.: Ann. **467,** 91–4 (1928).

(106) Hibben, J. H.: *The Raman Effect and Its Chemical Applications.* Reinhold Publishing Co., New York (1939).

(107) Hoffert, W. H.: *Motor Benzole.* National Benzole Association, London (1938).

(108) Hoffert, W. H., Claxton, G., and Hancock, E. G.: Gas J. **214,** 103–5, 167–71 (1936).

(109) Hofmann, K. A., and Seiler, E.: Ber. **39,** 3187–90 (1906).

(110) Hopff, H., and Rapp, W.: German patent 695,756 (1940).

(111) Horclois, R.: Chimie & industrie, Special No. 357–63 (April, 1934).

(112) I. G. Farbenind. A.-G.: British patent 341,047 (1928).

(113) I. G. Farbenind. A.-G.: French patent 37,498 (1929).

(114) I. G. Farbenind. A.-G.: British patent 352,164 (1933).
Krizikalla and Wolff: German patent 583,536 (1933).

(115) I. G. Farbenind. A.-G.: French patent 848,411 (1939).

(116) Ingold, E. H., and Wassermann, A.: Trans. Faraday Soc. **35,** 1022–4, 1052–3 (1939).

(117) Jordan, O., and Krzikalla, H.: German patent 543,825 (1930).

(118) Joshel, L. M., and Butz, L. W.: J. Am. Chem. Soc. **63,** 3350–1 (1941).

(119) Kaufmann, H., and Wassermann, A.: J. Chem. Soc. **1939,** 870–1.

(120) Kazanskiĭ, B. A., and Glushnev, N. F.: Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. Chim. **1938,** 1065–71; Chem. Abstracts **33,** 6233 (1939).

(121) Kazanskiĭ, B. A., and Plate, A. F.: Ber. **67B,** 1023–8 (1934).

(122) Kendall, J. D.: British patent 526,892 (1940).

(123) Kettering, C. F., and Sleator, W. W.: Physics **4,** 39–49 (1933).

(124) Khambata, A., and Wassermann, A.: J. Chem. Soc. **1939,** 375–81.

(125) Khambata, A., and Wassermann, A.: Nature **137,** 496–7 (1936).

(126) Khambata, A., and Wassermann, A.: Nature **138,** 368–9 (1936).

(127) Kharasch, M. S.: Bur. of Standards J. Research **2,** 359–430 (1929).
Doss, M. P.: *Physical Constants of the Principal Hydrocarbons,* 3rd edition, p. 159. The Texas Co., New York (1942).

(128) Kirsanov, A. V., Polyakova, I. M., and Kuznetsova, Z. I.: J. Applied Chem. (U.S.S.R.) **13,** 1406–13 (1940).

(129) Kistiakowsky, G. B., and Lacher, J. R.: J. Am. Chem. Soc. **58,** 123–33 (1936).

(130) Kistiakowsky, G. B., and Mears, W. H.: J. Am. Chem. Soc. **58,** 1060 (1936).

(131) Kistiakowsky, G. B., Ruhoff, J. R., Smith, H. A., and Vaughn, W. E.: J. Am. Chem. Soc. **58,** 146–53 (1936).

(132) Kodak, Ltd.: British patent 533,353 (1941).

(133) Kohler, E. P., and Kable, J.: J. Am. Chem. Soc. **56,** 2756–7 (1934).

(134) Kohler, E. P., and Kable, J.: J. Am. Chem. Soc. **57,** 917–18 (1935).

(135) Kohlrausch, K. W. F., and Seka, R.: Ber. **69,** 729–43 (1936).

(136) Kohlrausch, K. W. F., and Seka, R.: Ber. **71B,** 985–91 (1938).

(137) Komppa, G., and Beckmann, S.: Ann. **523,** 68–86 (1936).

(138) Komppa, G., and Komppa, O.: Ber. **69B,** 2606–10 (1936).

(139) Kopelevitsch, G. V., Brodovitsch, A. I., and Hecht, I. R.: Koks i. Khim. **1935,** No. 7, 19–22; Brit. Chem. Abstracts **1935B,** 1081.

(140) Kraemer, G., and Spilker, A.: Ber. **29,** 552–61 (1896).

(141) Kronstein, A.: Ber. **35,** 4150–3 (1902).

(142) Kruber, O.: Brennstoff-Chem. **13,** 187–90 (1932).

(143) Kruber, O., and Schade, W.: Brennstoff-Chem. **14,** 124–8 (1933).

(144) Lambert, P., and Lecomte, J.: Ann. phys. **10,** 503–82 (1938).

(145) Lauer, W. M., and Miller, S. E.: J. Am. Chem. Soc. **57,** 520–5 (1935).

(146) Levy, W. J., and Campbell, N.: J. Chem. Soc. **1939,** 1442–6.

(147) Lewis, J. R., Ramage, G. R., Simonsen, J. L., and Wainwright, W. G.: J. Chem. Soc. **1937,** 1837–41.

(148) Lovell, W. G., Campbell, J. M., and Boyd, T. A.: Ind. Eng. Chem. **26,** 1105–8 (1934).

(149) Luré, M. A., Marushkin, M. N., Chistov, V. O., Shlossberg, M. A.: Sintet. Kauchuk **3**, No. 6, 13–18 (1934); Chem. Abstracts **32**, 6098 (1938).

(150) Mayberry, M. G., Westlake, H. E., Jr., and Fanelli, R.: Unpublished data, 1942.

(151) Mayes, W. G.: Thesis, Cornell University, June, 1941.

(151a) McCrone, W. C.: Thesis, Cornell University, February, 1943.

(152) Meyer, H., and Hoffmann, A.: Monatsh. **37**, 681–722 (1916).

(153) Milas, N. A., and Maloney, L. S.: J. Am. Chem. Soc. **62**, 1841–3 (1940).

(154) Milas, N. A., and Walsh, W. L.: J. Am. Chem. Soc. **61**, 633–5 (1939).

(155) Morrell, J. C.: U. S. patent 2,157,939 (1939).

(156) Morrell, J. C., Dryer, C. G., Lowry, C. D., Jr., and Egloff, G.: Ind. Eng. Chem. **26**, 655–7 (1934).

(157) Moor, V. G., and Katzman, S. V.: Chem. Abstracts **29**, 2717 (1935).

(158) Morgan, M. S.: Thesis, University of Pittsburgh, January, 1943.

(159) Mousseron, M., and Granger, R.: Compt. rend. **205**, 327–9 (1937).

(160) Mousseron, M., and Granger, R.: Compt. rend. **206**, 922–4 (1938).

(161) Mulliken, R. S.: J. Chem. Phys. **7**, 121–35 (1939).

(162) Mulliken, R. S.: J. Chem. Phys. **7**, 339–52 (1939).

(163) Mulliken, R. S., Rieke, C. A., and Brown, W. G.: J. Am. Chem. Soc. **63**, 41–56 (1941).

(164) Newitt, D. M., and Wassermann, A.: J. Chem. Soc. **1940**, 735–7.

(165) Noeldechen, F.: Ber. **33**, 3348–54 (1900).

(166) Noller, C. R., and Adams, R.: J. Am. Chem. Soc. **48**, 2444–8 (1926).

(167) Norton, J. A.: Chem. Rev. **31**, 319–523 (1942).

(168) Nylén, P., and Olsen, A.: Kgl. Norske Videnskab. Selskabs, Forh. **11**, 229–32 (1938); Chem. Abstracts **33**, 5361 (1939).

(169) Pauly, H.: Ber. **67B**, 1177–99 (1934).

(170) Perkins, G. A., and Cruz, A. O.: J. Am. Chem. Soc. **49**, 517–22 (1927).

(171) Peski, A. J. van, and Melsen, J. A. van: U. S. patent 2,150,349 (1939).

(172) Pickett, L. W., Paddock, E., and Sackter, E.: J. Am. Chem. Soc. **63**, 1073–7 (1941).

(173) Pines, H., and Ipatieff, V. N.: J. Am. Chem. Soc. **61**, 1076–7 (1939).

(174) Pirsch, J.: Ber. **67B**, 101–4 (1934).

(175) Pirsch, J.: Ber. **67B**, 1115–19 (1934).

(176) Posner, T.: Ber. **38**, 646–57 (1905).

(177) Potolovskiĭ, L., and Vimberg, A.: Azerbaĭdzhanskoe Neftyanoe Khoz. **1936**, No. 2–3, 90–100; Chem. Abstracts **31**, 2797 (1937).

(177a) Price, W. C., and Walsh, A. D.: Proc. Roy. Soc. (London) **A179**, 201–14 (1941).

(178) Raistrick, B., Sapiro, R. H., and Newitt, D. M.: J. Chem. Soc. **1939**, 1761–73.

(179) Ralston, A. W., Vander Wal, R. J., Bauer, S. T., and Segebrecht, E. W.: Ind. Eng. Chem. **32**, 99–101 (1940).

(180) Ralston, A. W., Vander Wal, R. J., and Bauer, S. T.: U. S. patent 2,237,825 (1941); British patent 533,919.

(181) Rath, E.: British patent 400,452 (1933); French patent 747,207 (1933).

(183) Reitz, A. W.: Z. physik. Chem. **B33**, 179–95 (1936).

(184) Reitz, A. W.: Z. physik. Chem. **B35**, 363–81 (1937).

(185) Reitz, A. W.: Z. physik. Chem. **B38**, 275–91 (1937).

(186) Rivkin, J., and Sheehan, W. E.: Ind. Eng. Chem. **30**, 1228–32 (1938).

(187) Roscoe, H. E.: Ann. **232**, 348–52 (1886).

(188) Ross, R., and Race, J.: J. Soc. Chem. Ind. **29**, 604–8 (1910).

(189) Ruhemann, S.: Erdöl u. Teer **5**, 455–8 (1929).

(190) Rule, A.: J. Chem. Soc. **89**, 1339–45 (1906).

(191) Rule, A.: J. Chem. Soc. **93**, 1560–4 (1908).

(192) Scagliarini, G., and Lucchi, E.: Boll. sci. facolta chim. ind., Bologna **1940**, No. 1–2, 58–9; Chem. Abstracts **34**, 2287 (1940).

(193) Scheibe, G., and Grieneisen, H.: Z. physik. Chem. **B25**, 52–6 (1934).

(194) Schomaker, V., and Pauling, L.: J. Am. Chem. Soc. **61,** 1769–80 (1939).
(195) Schultze, G. R.: J. Am. Chem. Soc. **56,** 1552–6 (1934).
(196) Schultze, G. R.: Oel Kohle Erdoel Teer **14,** 113–17 (1938); Chem. Abstracts **32,** 8741 (1938).
(198) Smith, L. I., Agre, C. L., Leekley, R. M., and Prichard, W. W.: J. Am. Chem. Soc. **61,** 7–11 (1938).
(199) Smith, L. I., and Hac, L. R.: J. Am. Chem. Soc. **58,** 229–34 (1936).
(200) Soday, F. J.: U. S. patent 2,259,496 (1941).
(200a) Soday, F. J.: U. S. patent 2,314,904–5 (1943).
(201) Staudinger, H.: Ber. **40,** 1145–8 (1907).
(202) Staudinger, H.: Ber. **44,** 521–3 (1911).
(202a) Staudinger, H.: Ber. **59,** 3019–43 (1926).
(203) Staudinger, H.: Ann. **467,** 73–5 (1938).
(204) Staudinger, H., and Bruson, H. A.: Ann. **447,** 97–110 (1926); U. S. patent 1,720,929 (1929).
(205) Staudinger, H., and Bruson, H. A.: Ann. **447,** 110–22 (1926).
(206) Staudinger, H., and Lautenschlager, L.: Ann. **488,** 1–8 (1931).
(207) Staudinger, H., and Rheiner, A.: Helv. Chim. Acta **7,** 23–31 (1924).
(208) Stobbe, H., and Dümhaupt, F.: Ber. **52B,** 1436–42 (1919).
(209) Stobbe, H., and Reuss, F.: Ann. **391,** 151–68 (1912).
(210) Strauss, F., Kollek, L., and Heyn, W.: Ber. **63B,** 1868–85 (1930).
(211) Tausz, J., and Schulte, F.: Mitt. chem.-tech. Inst. tech. Hochschule Karlsruhe **2,** 1 (1924); Chem. Zentr. **95,** III, 905 (1924).
(212) Terent'ev, A. P.: J. Gen. Chem. (U.S.S.R.) **7,** 2026–7 (1937).
(213) Terent'ev, A. P.: Org. Chem. Ind. (U.S.S.R.) **4,** 535–42 (1937).
(214) Terent'ev, A. P., and Gomberg, L. L.: J. Gen. Chem. (U.S.S.R.) **8,** 662–8 (1938).
(215) Terent'ev, A. P., and Ivanova, E. M.: J. Gen. Chem. (U.S.S.R.) **7,** 2026–9 (1937).
(216) Terent'ev, A. P., and Ivanova, E. M. J. Gen. Chem. (U.S.S.R.) **7,** 2087–91 (1937).
(217) Terent'ev, A. P., and Solokhin, L. A.: Sintet. Kauchuk **1933,** No. 5, 9–12.
(218) Terent'ev, A. P., and Solokhin, L. A.: Sintet. Kauchuk **1933,** No. 5, 12–15.
(219) Terent'ev, A. P., Vinogradova, E. V. and Hal'pern, G. O.: Compt. rend. acad. sci. U.S.S.R. [N.S.] **4,** 267–72 (1935); Chem. Abstracts **30,** 3746 (1936).
(220) Thiele, J.: Ann. **314,** 300–2 (1900).
(221) Thiele, J.: Ber. **33,** 666–73 (1900).
(222) Thiele, J.: Ber. **34,** 68–71 (1901).
(223) Thiele, J., and Balhorn, H.: Ann. **348,** 1–15 (1906).
(223a) Trepp, S. G.: U. S. patent 2,314,908–9–10 (1943).
(224) Tropsch, H., Thomas, C. L., Egloff, G., and Morrell, J. C.: Ind. Eng. Chem. **30,** 169–72 (1938).
(225) Truchet, R., and Chapron, J.: Compt. rend. **198,** 1934–6 (1934).
(226) Tyutyunnikov, G. N.: Coke and Chem. (U.S.S.R.) **9,** No. 1, 31–2 (1939); Chimie & industrie **42,** 536 (1900).
(227) Vansheĭdt, A. A.: J. Gen. Chem. (U.S.S.R.) **4,** 875–84 (1934).
(228) Volzhinskiĭ, I. A., and Shcheglova, A. P.: Sintet. Kauchuk **1933,** No. 4, 31–5.
(229) Von Oettingen, W. F.: U. S. Pub. Health Bull. No. **255** (1940).
(230) Ward, A. L.: U. S. patent 2,211,038 (1940).
(231) Ward, A. L., and Kurtz, S. S., Jr.: Ind. Eng. Chem., Anal. Ed. **10,** 559–76 (1938).
(232) Waring, C. E., Kern, E. E., and Blann, W. A.: J. Am. Chem. Soc. **63,** 767 (1941).
(233) Wassermann, A.: Ber. **66B,** 1392–4 (1933).
(234) Wassermann, A.: J. Chem. Soc. **1935,** 828–39.
(235) Wassermann A.: J. Chem. Soc. **1936,** 1028–34.
(235a) Wassermann, A.: J. Chem. Soc. **1942,** 618–21.
(235b) Wassermann, A.: J. Chem. Soc. **1942,** 623–6.
(236) Wassermann, A.: French patent 838,454 (1939).

(237) WEGER, M.: Z. angew. Chem. **22,** 338–47, 391–5 (1909).
(238) WEIDLEIN, E. R.: Chem. Eng. News **20,** 443–61 (1942).
(239) WIELAND, H.: Ber. **39,** 1492–9 (1906).
(240) WIELAND, H., AND BERGEL, F.: Ann. **446,** 13–20, 31 (1926).
(241) WIELAND, H., AND HASEGAWA, C.: Ber. **64B,** 2516–22 (1931).
(242) WIELAND, H., AND STENZL, H.: Ann. **360,** 299–322 (1908).
(243) WILKEN-JORDAN, T. J.: J. Chem. Met. Mining Soc. S. Africa **32,** 283–95 (1932); Chem. Abstracts **26,** 5406 (1932).
(244) WILLSTAEDT, H.: Svensk Kem. Tid. **46,** 61–3 (1934).
(245) ZELINSKIĬ, N. D., AND LEVINA, R. J.: Ber. **66B,** 477–8 (1933).
(246) ZERBE, C., AND ECKERT, F.: Angew. Chem. **45,** 593–8 (1932); Oel Kohle **2,** 113 (1934).
(247) ZIEGLER, K., AND CRÖSSMANN, F.: Ann. **511,** 89–101 (1934).