THE CHEMISTRY OF PERCHLOROCYCLOPENTENES AND CYCLOPENTADIENES

H. E. UNGNADE

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

AND

E. T. McBEE

Department of Chemistry, Purdue University, West Lafayette, Indiana

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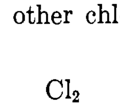
I. INTRODUCTION

The thermal chlorination of paraffin hydrocarbons having five or more carbon atoms yields, among other products, three cyclopentane derivatives: viz., hexachlorocyclopentadiene (I), octachlorocyclopentene (II), and 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)cyclopentene (III). These compounds are distinguished from other chlorination and chlorinolysis products, such as carbon tetrachloride, tetrachloroethylene, and hexachlorobenzene, by their unusual chemical reactivity, which permits their conversion to a variety of new and interesting compounds.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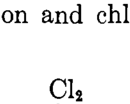
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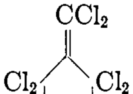
III

Octachlorocyclopentene (II) and hexachlorocyclopentadiene (I) are conveniently taken up together, since they are interconvertible and can be prepared by the same process. Hexachlorocyclopentadiene (I) is manufactured commercially, and octachlorocyclopentene (II) can be made available economically in large amounts.

Octachlorocyclopentene (II) has been known since 1877, when Krafft obtained it among other products by the chlorination of hexyl iodide at 240°C. (112). In the older literature the compound is referred to as "perchlormesol," a name introduced by Krafft. Hexachlorocyclopentadiene (I) does not appear in the literature until 1930 (239). It is possible, however, that the compound was known before this time (40).

Commercial methods for the preparation of these chlorocarbons and uses for them have been developed much more recently. The details of preparing Diels–Alder adducts of hexachlorocyclopentadiene (I) and fungicides, insecticides, plant-growth regulators, and flame-retardant resins derived from them have been published only in the last few years. The extraordinary interest in these compounds is reflected in the large number of derivatives which have been prepared in a short period of time.

1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene (III) was first described in 1912 (189). Its structure, however, remained in doubt for some time and was not fully established until recently (159, 222). Unlike the preceding chlorocarbons, it is not available commercially and is of interest primarily for its properties and chemical reactions.

This review covers the literature through June, 1957, and is limited to a survey of the chemistry of the chlorocarbons indicated in formulas I, II, and III.

II. HEXACHLOROCYCLOPENTADIENE

A. Methods of preparation

Hexachlorocyclopentadiene (I) is best prepared by a two-stage process from pentane, isopentane, or mixtures of the two (68, 132, 133, 134, 164). The hydrocarbons are chlorinated photochemically in the liquid phase at 80–90°C. (133, 134) until they have an average composition of approximately $C_5H_5Cl_7$ and a density of 1.63–1.70 (132). The resulting polychloropentanes are then vaporized and passed together with an excess of chlorine over a porous surface-active solid such as fuller's earth maintained at 300–430°C. and through an unpacked section of tube held at 450–525°C. (68, 164). Depending on the conditions of the thermal chlorination step and the final temperature, the intermediate octachlorocyclopentadiene (II) can be isolated (137).[1] At 500°C. it is completely dechlorinated (113, 115) and hexachlorocyclopentadiene (I) is obtained in 90 per cent yield.

The conversion of pentanes and hexanes to hexachlorocyclopentadiene (I) has been studied in detail (132, 137). Chlorine is usually introduced into these hydrocarbons by a continuous liquid-phase photochemical process (134). The subsequent thermal chlorination step has been examined for pentanes containing two to seven atoms of chlorine per mole. If hydrocarbons with a relatively small

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[1] The compound designated as hexachlorobutadiene in this paper was actually octachlorocyclopentene (38).

chlorine content, such as the dichloropentanes, are thermally chlorinated, the molar ratio of chlorine to starting material must be confined between the relatively narrow upper and lower explosive limits of 6 to 9 moles (137). Similar difficulties are encountered in the vapor-phase chlorination of paraffin hydrocarbons. Most suitable for the thermal chlorination are polychloropentanes or cyclopentanes with approximately seven chlorine atoms per mole. The optimum temperature of the thermal chlorination step in the absence of a catalyst lies between 450° and 500°C. at short contact times. At temperatures below 450°C. some octachlorocyclopentene (II) is produced (132). At higher temperatures, under pressure, or with longer contact times, extensive chlorinolysis occurs and the main products are carbon tetrachloride and hexachloroethane (137). The molar ratio of chlorine to polychloropentanes and hexanes must be above 4.7:1 in order to obtain good yields of hexachlorocyclopentadiene (I), the optimum ratio being 5.7:1 (132). Under comparable conditions polychloropentane, isopentane, and cyclopentane give 54.6–55.3, 54–57, and 74.5 per cent yields of hexachlorocyclopentadiene, whereas polychloroneopentane gives only carbon tetrachloride and tetrachloroethylene. Polychlorinated hexanes, including neohexane, under the same conditions can furnish hexachlorocyclopentadiene (I) but in yields of only around 20 per cent (132, 133). The yields in the thermal chlorination step can be considerably improved by the use of a porous surface-active catalyst such as alumina, silica gel, fuller's earth, activated carbon, floridin, or bauxite, impregnated with chlorides of iron, nickel, or cobalt (68, 164, 165); the optimum temperature is lowered to 280–450°C. and the ratio of chlorine to polychloropentanes can be made somewhat smaller (165). The product of this step is octachlorocyclopentene (II), which can be isolated at this point or dechlorinated to I (165, 166). The thermal dechlorination of octachlorocyclopentene at 450–500°C. is substantially quantitative but rather slow. It can be rendered rapid and complete by the use of catalytic surfaces of nickel or cobalt or their chlorides, e.g., an unpacked section of nickel pipe (166).

It is claimed that the thermal chlorination of pentane or pentene can be accomplished also in one stage at 500°C., either without a catalyst (28) or with barium sulfate (251), to give hexachlorocyclopentadiene (I) directly.

The third process for preparing hexachlorocyclopentadiene (I) involves the liquid-phase chlorination of cyclopentadiene below 50°C. The resulting tetrachlorocyclopentane is converted to octachlorocyclopentene (II) in 97.5 per cent yield by catalytic chlorination over arsenious oxide or phosphorus pentachloride at 175–250°C. (121, 181). Octachlorocyclopentene (II) is then dechlorinated thermally in yields of 85–97 per cent (113, 121, 166).

Cyclopentadiene can be converted to hexachlorocyclopentadiene (I) in 44–85 per cent yield by chlorination with 6 to 11 moles of aqueous sodium or potassium hypochlorite at −5° to +50°C. (31, 61, 98, 128, 203, 208, 210, 215, 239). The two-phase reaction mixture is vigorously stirred and undesirable side reactions are suppressed by addition of 1 mole per cent of sodium sulfamate (98). An emulsifying agent, such as sodium lauryl sulfate, may be added (128), and petroleum ether can be used as diluent (239). The chief by-product in this process is a pentachlorocyclopentadiene which dimerizes on standing to a solid, m.p. 214°C. (215). It probably contains 1,2,3,4,5-pentachlorocyclopentadiene (210) and other isomers. Its formation is favored by smaller mole ratios of hypochlorite to cyclopentadiene (203). The method of halogenation in aqueous bases also has been used for the preparation of pentachloromethylcyclopentadiene (245) and hexabromocyclopentadiene (203).

The cyclopentane ring can be built up by condensing trichloroethylene with carbon tetrachloride and $\frac{1}{15}$ mole of aluminum chloride at 100°C. and pyrolyzing the resulting mixture of chlorinated hydrocarbons at 500°C. The product contains 75 per cent of hexachlorocyclopentadiene (I) (173) and small amounts of carbon tetrachloride, tetrachloroethylene, and hexachlorobenzene. The intermediate chlorinated hydrocarbons consist largely of C_5 and C_7 compounds, among which the following have been identified: octachlorocyclopentene (173), isolated in 74 per cent yield (198); 1,1,2,3,3,4,5,5,5-nonachloro-1-pentene (IV); dodecachloro-3-ethyl-1-pentene, $C_7H_2Cl_{12}$; and the unsaturated ethylcyclopentane derivatives C_7Cl_{10} and C_7HCl_{11} (173). The aluminum chloride-catalyzed condensation of trichloroethylene and carbon tetrachloride can be carried out stepwise. Intermediate compounds have been isolated and further condensed with the original starting materials (194, 198). The following steps in the reaction are based on this evidence:

$$CHCl{=}CCl_2 + CCl_4 + AlCl_3 \rightarrow CCl_3CHClCCl_3$$

$$CCl_3CHClCCl_3 + AlCl_3 \rightarrow CCl_3CCl{=}CCl_2$$

$$CCl_3CCl{=}CCl_2 + CHCl{=}CCl_2 + AlCl_3 \rightarrow \underset{\text{IV}}{CCl_3CHClCCl_2CCl{=}CCl_2}$$

$$CCl_3CHClCCl_2CCl{=}CCl_2 + AlCl_3 \rightarrow \underset{\text{II}}{C_5Cl_8} \quad \text{(nearly quantitative) (194)}$$

The intermediate nonachloropentene (IV) also can be dehydrohalogenated with aqueous or alcoholic potassium hydroxide (194) to give octachloro-1,3-pentadiene in overall yields of 67–73 per cent (113).

$$CCl_3CHClCCl_2CCl{=}CCl_2 + KOH \rightarrow CCl_2{=}CClCCl{=}CClCCl_3$$

The latter is converted to octachlorocyclopentene in 96 per cent yield by warming with aluminum chloride in methylene chloride (194). An alternate preparation for hexachloropropene, which is normally preferred in the stepwise process, utilizes the condensation of tetrachloroethylene with chloroform and aluminum chloride and dehydrochlorination of the formed *unsym*-heptachloropropane (113, 190).

Among the preceding methods of preparation for hexachlorocyclopentadiene (I), the chlorination of cyclopentadiene with sodium hypochlorite has been used as a laboratory method (203). Other methods which belong to this category are the dechlorination of octachlorocyclopentene (II) by heat (166) or with hydrogen and platinum (156) and the synthesis used by Prins for the preparation of the compound by condensation of dichloroethylene and hexachloropropene with aluminum chloride (40, 192).

$$CCl_2{=}CClCCl_3 + CHCl{=}CHCl + AlCl_3 \rightarrow CCl_2{=}CClCCl_2CHClCHCl_2$$
$$\text{(84\% yield)}$$

$$CCl_2{=}CClCCl_2CHClCHCl_2 + AlCl_3 \rightarrow C_5Cl_6$$
$$\text{(70\% yield)}$$

Hexachlorocyclopentadiene has been prepared in small yield from trichloroethylene and chloroform by stepwise condensation and dehydrochlorination with aluminum chloride. The isolated intermediates in the reaction are hexachloropropane and pentachloropropylene (194).

$$CHCl{=}CCl_2 + CHCl_3 \rightarrow CHCl_2CHClCCl_3$$

$$CHCl_2CHClCCl_3 + AlCl_3 + CCl_4 \rightarrow CCl_2{=}CClCHCl_2$$
$$\text{(93\% yield)}$$

$$CCl_2{=}CClCHCl_2 + CHCl_3 + CHCl{=}CCl_2 \xrightarrow{AlCl_3} C_5Cl_6 + C_6HCl_9 + C_{10}Cl_{12}$$
$$\text{(28\% yield)}$$

B. Physical properties and absorption spectra

Hexachlorocyclopentadiene (I) has been reported as being a pale yellow (113) or greenish yellow (194) liquid with a harsh pungent odor (113). Its viscosity η^{20} = 37.5 dynes/cm. (36). Other physical constants are given below:

Boiling Point	References	Refractive Index	References	Density	References
°*C.*					
45–45.5/0.06 mm.	(194)	$n_D^{20} = 1.5647$	(114, 115)	$d_{15.5}^{15.5} = 1.717$	(70)
72/0.68 mm.	(115)				
78–79/1 mm.	(239)	$n_D^{20} = 1.5652$	(132)	$d_4^{20} = 1.7119$	(132)
83–84/4 mm.	(132)				
94/5 mm.	(113, 115)	$n_D^{25} = 1.5614$	(40, 194)	$d_4^{25} = 1.7019$	(40, 194)
104-105/1 mm.	(196)				
108/10 mm.	(113, 115)	$n_D^{25} = 1.5625$	(70)	$d_4^{25} = 1.7020$	(115)
163.6–163.8/100 mm.	(114, 115)				
228–229/740 mm.	(173)				
234/atm.	(194)	$n_D^{25} = 1.5629$	(113, 115)	$d_{15}^{25} = 1.7035$	(113)
236–238/760 mm.	(132)				
239/753 mm.	(113, 115)				
239/760 mm.	(70)				

On cooling hexachlorocyclopentadiene (I) crystallizes to a solid, whose melting point has been reported as −77°C. (40), 7.8–8.2°C. (132), 9–10°C. (115), 9.6°C. (70), and 10–10.8°C. (114, 115). A crystalline form, melting at −0.8° to −0.2°C., can be converted to the more stable form, melting at 10–10.8°C., by strong cooling or seeding (114, 115). The freezing-point depression for the compound is 16.1°C./mole and the latent heat of fusion is 10.0 cal./gram (70).

Hexachlorocyclopentadiene (I) has an absorption band in the ultraviolet at 322 mμ (82) and 323 mμ (log ϵ = 3.17) in ethanol (138, 156, 159). When the allylic chlorine atoms are replaced successively by hydrogen atoms, this maximum is shifted to shorter wavelengths but the molar absorptivity is increased (156). The infrared spectrum of the diene has two bands in the double-bond stretching region at 6.24 and 6.36 μ (1603 and 1572 cm.$^{-1}$) (159), 6.22 (s) and 6.35 (m) μ (1606 and 1575 cm.$^{-1}$), and three bands in the C—Cl stretching region at 12.45 (s) μ, 14.21 (s) μ, and 14.75 (s) μ (803, 704, and 678 cm.$^{-1}$) (243). The Raman spectrum shows two lines in the double-bond region at 1606 and 1572 cm.$^{-1}$ (40).

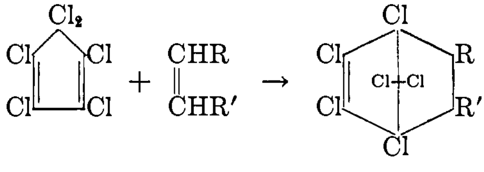
C. Biological properties and uses

Hexachlorocyclopentadiene (I) is toxic to mice and was shown to be responsible for the toxicity of early preparations of chlordan (83). The liquid can be absorbed through the skin, and its vapor is toxic. The physiological effects of the vapor are believed to be similar to those of carbon tetrachloride vapor, and the material should therefore be handled with caution (70). The LD-50 value in rats is 300 mg./kg. of body weight (70). Hexachlorocyclopentadiene is claimed to be a fungicide (253). It is used as a dust absorbed on powdered clay or as an emulsion mixed with dispersing agents. It has a relatively high bactericidal activity but is apparently not injurious to plants (253). It has been used as a vulcanizing agent for *Hevea* rubber and diene elastomers (118).

D. Reactions

Hexachlorocyclopentadiene (I) shows an unexpected tendency to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20° and 200°C. It condenses even with simple olefins, which normally do not react with dienes, and with polynuclear aromatic hydrocarbons, such as naphthalene and anthracene. The condensation is probably the most extensively investigated reaction of the diene and has furnished a variety of new compounds which are not accessible by other methods (see table 1).

Open-chain and cyclic olefins of the types RCH=CH$_2$ and RCH=CHR′ containing from four to eighteen carbon atoms have been successfully condensed with hexachlorocyclopentadiene (10, 33, 206, 215). Halogenated olefins do not react with the diene I if they have two chlorine atoms or one chlorine atom and one alkyl group on a double-bonded carbon. It appears therefore that the reaction requires that halogen-containing olefinic dienophiles contain at least one hydrogen on each of the double-bonded carbon atoms (150). The products of the reaction are 1:1 adducts which are assigned a [2.2.1]bicycloheptene structure (V), largely by analogy with the structures of nonchlorinated compounds.



I V

Hexachlorocyclopentadiene

TABLE 1

Diels–Alder reactions with hexachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
C_2:				
Acetylene	180		332–334	(73, 80)
1,2-Dibromoethylene	200	16	210	(150)
cis-1,2-Dichloroethylene	180, 200	27, 38	170–190	(150, 184)
trans-1,2-Dichloroethylene	200	26		(150)
Vinyl chloride	120–200	24	125–136	(12, 96, 97, 103, 124)
Vinyltrichlorosilane	190–200	78	Liquid	(99)
C_3:				
Propargyl bromide	85–150	95	Liquid	(33)
Acrylonitrile	100	33	143	(188)
1,3-Dichloropropene	130	15	78–80	(150)
Acrolein	Refluxed	84	145-148	(236, 237, 238)
Acrylic acid	120		181-182.5	(238)
3-Bromopropene	85–95	12, 87	79–80	(33, 150)
	85–150		77	
1-Chloropropene	150–160	8	197–198	(150)
3-Chloropropene	125	90, 68	54–55	(10, 33, 150)
	85-155	43	Liquid	
Allyl alcohol	85-150*	53, 98	164–165	(33, 150)
			165	
C_4:				
Chloromaleic anhydride	178–180	40	240–247	(217, 219)
Fumaroyl chloride			134–136	(217)
Maleic anhydride	100–170	83, 85, 89	232‡, 238, 235–237, 231–233, 240-241	(61, 95, 100, 108, 188, 209, 215, 217, 244, 247)
Acetylenedicarboxylic acid	150	45	162–163	(139)
Furan	70		285–286†	(79)
	130–135	16	277–280	(184)
Butynediol			49–51	(217)
Thiophene			†	(172)
Allyl cyanide				(238)
Allyl isothiocyanate	*	46	114-115	(169)
Butadiene	150		Liquid	(61, 244)
	150		230–233†	(61, 244)
Butadiene monoxide	25–150	97	101–104, 87-89	(33, 116)
Dihydrofuran	135	76	219-226	(15)
Divinyl ether	120		Liquid	(46)
Methyl vinyl ketone	80–125	41, 76	70, 74–74.5	(30, 188)
Crotonic acid			171–172	(238)
Methyl acrylate			176–178	(238)
Vinylacetate	150	89	44	(34)
Vinylacetic acid			119–123	(238)
Dichloromethylallylsilane	100–120	57	Liquid	(48)
C_4:				
Citraconic anhydride	166–188	20	243.5	(217)
			236.5–240.5	(219)
Itaconic anhydride	195		131–134.6	(217, 218)
Cyclopentadiene	70–120	70, 94, 97	154, 155, 170–180	(5, 14, 61, 67, 110, 171, 184, 207, 208, 209, 210, 215, 244)
	175, 280–320	11	306†	(202, 207, 209, 215, 216)
2-Methylfuran	65–75		42–42.5, 175–176	(79, 249)
Isoprene	150		Liquid	(61, 244)
Cyclopentene	100–150	50, 84	160, 162–165, 165–170	(215, 216, 249, 254)
4-Chloro-1-pentene	100–155	72	Liquid	(10)
1-Pentene	100–155	21	Liquid	(10)
2-Pentene	100–155	33	Liquid	(10)
3-Methyl-1-butene	100–155	32	Liquid	(10)

TABLE 1—*Continued*

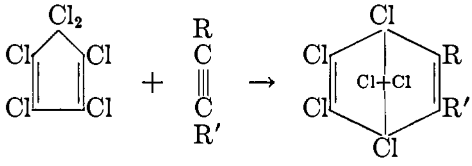
Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
C_6:				
p-Benzoquinone	100–160	53	184, 188, 183-186	(128, 188)
Methylcyclopentadiene	100–150	74	Liquid	(215)
Methyl maleate	§		80–81	(184)
Cyclohexene	85–150	85, 88, 90, 93	73–74, 76.7, 75, 77, 78	(10, 33, 215, 216, 249, 254)
1-Methylcyclopentene	120–125		51–53	(249)
1-Hexyne	150	26	Liquid	(139)
Diallyl sulfide	130		Liquid	(252)
1-Hexene	85-155	55, 60, 65	Liquid	(10, 33, 215, 216)
2-Hexene	100–155	44	Liquid	(10)
4-Methyl-2-pentene	100–155	17	Liquid	(10)
3,3-Dimethyl-1-butene	100–155	31	25	(10)
Diethyl vinylphosphonate	140–150	80	Liquid	(117)
C_7:				
Heptafluorobutyl acrylate	120	57	Liquid	(243)
Toluquinone	130	56, 86	168-170	(128)
Bicycloheptadiene	85–90, 100, 105	71, 93	104–104.5, 93–95	(122, 249)
	Refluxed	100	Infusible†	(122)
5-Chlorobicyclo[2.2.1]-2-heptene			92–94	(184)
5,5-Dichlorobicyclo[2.2.1]-2-heptene	200		119-121	(123)
Bicycloheptene	115, 150	Good	76.5–77, 77-78	(123, 249)
Cycloheptene			73-74	(254)
1-Heptyne	150	18	Liquid	(139)
4-Methylcyclohexene	85–155	75, 90, 97	Liquid	(10, 33, 215, 216)
3-Cyclohexene-1-methanol	130	67	Liquid	(34)
Allyl butyrate	85–150	80	Liquid	(33)
1-Heptene	100–155	50, 54	Liquid	(10, 215, 216)
3-Heptene	100–155	45	Liquid	(10)
Diethoxymethylvinylsilane	135–150	79	Liquid	(48)
Diethyl propenephosphonate	100		Liquid	(117)
C_8:				
Phenylacetylene	115-150	21	Liquid	(61, 139, 244)
3,6-Epoxy-4-cyclohexenedicarboxylic anhydride	55	62	282–283	(125)
m-Nitrostyrene	125–130	83	111.5–112	(186)
Styrene	140–170	78	73-74, 73-76, 73.7-74.5	(61, 186, 244, 249)
5-Methylbicyclo[2.2.1]-2-heptene	150	Good	55–58	(249)
1,5-Cycloöctadiene			>300†	(254)
Ethyl maleate	100	12	67	(188)
Cycloöctene			82–84	(254)
4-Ethylcyclohexene	100–155	80, 82	Liquid	(10, 215, 216)
3-Cyclohexene-1,1-dimethanol	130	91	133	(34)
1-Octene	85–150	35, 86	Liquid	(33, 215, 216)
Vinyltriethoxysilane	180-190		Liquid	(99)
C_9:				
Indene	95–100		152-156	(61, 244)
Allyl phenyl ether	175–185	55	Liquid	(232)
5-Acetoxybicyclo[2.2.1]-2-heptene	95, 150		170–172, 172–173	(123, 249)
5-Ethylbicyclo[2.2.1]-2-heptene	150		56–58	(249)
Cyclononene			43–44	(254)
4-Propylcyclohexene	100–155	75	42	(10)
C_{10}:				
1,4-Naphthoquinone	130	53	118–120	(128)
Naphthalene	150–160, 155, 157	<1	163-164, 160	(22, 78, 79, 179, 215)
		19, 30, 44, 20	216†, 211.5–213.5†, 210–211†, 214–215†	(22, 78, 79, 81, 179, 215, 216)

TABLE 1—*Concluded*

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
C_{10}—*Continued:*				
Dicyclopentadiene	140–170		152, 152–155	(61, 207, 244)
	150–170		252–256[†]	(61, 244)
Dihydrodicyclopentadiene	120		100–101	(214)
Diisopropyl maleate	[§]	73	96–97	(184)
Ethyl propargylmalonate				(238)
Cyclodecene			Liquid	(254)
C_{11}:				
10-Undecenoic acid			Liquid	(238)
C_{12}:				
Phenylbenzoquinone	130		167–169	(128)
Tetracyclododecene	160		173–175	(123)
5-Amylbicyclo[2.2.1]-2-heptene	150		Liquid	(249)
C_{13}:				
2,3-Dicarbethoxybicyclo[2.2.1]-2,5-heptadiene	140–150	93	119	(122)
5-Phenylbicyclo[2.2.1]-2-heptene	135–140		91–92.5	(123)
C_{14}:				
Anthracene	150–160	11, 35	233–234[†], 240[†], 240–241[†]	(22, 78, 79, 179, 215, 216)
		<1	Above 300[¶]	(22, 215)
C_{18}:				
1-Octadecene	85–150	97	Liquid	(33)
C_{19}:				
Methyl oleate	175		Liquid	(11)

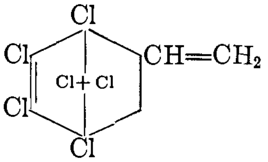
[*] In boiling xylene.
[†] Bis adduct.
[‡] Isolated as acid.
[§] In boiling toluene.
[¶] Tetrakis adduct.

Acetylene and substituted acetylenes react to give [2.2.1]bicycloheptadienes (VI). The product from the first member of the series, however, is probably a polymeric adduct (73, 80).

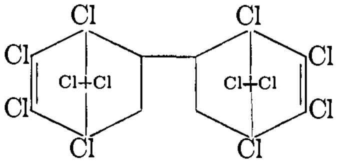

I VI

Bicycloheptadienes such as VI have a reactive CCl_2 bridge which can be hydrolyzed and eliminated by heating with sodium methoxide in methanol (139).

If the dienophile contains multiple unsaturation, the condensation reaction often can be controlled by varying the molar proportions of the reactants to give either 1:1 or 1:2 adducts, as is the case with butadiene, which yields a vinylbicycloheptene (VII) or an octahydrodimethanobiphenyl derivative (VIII).

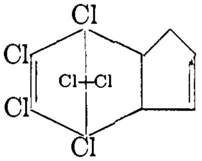


VII

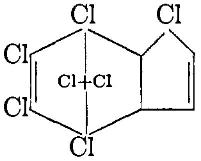


VIII

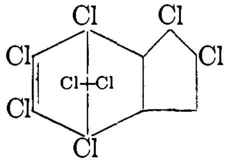
The 1:1 adduct derived from cyclopentadiene, 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (chlordene or hexachlor) (IX), is of special importance because it is the starting material for the preparation of the commercial insecticides chlordan and heptachlor. Chlordan is an oily liquid which is obtained by the chlorination of chlordene (IX) with chlorine in boiling carbon tetrachloride or with sulfuryl chloride and Friedel-Crafts catalysts until a composition of $C_{10}H_6Cl_8$ is reached (74, 75, 77, 86, 94, 204, 205). The commercial product is a mixture of compounds varying in insecticidal activity, which has been separated by chromatographic adsorption (163, 248). In addition to chlordene (IX) it contains heptachlor (X), *cis*- and *trans*-octachlor (XI), nonachlor (XII), and possibly isomers of these substances (19, 167, 171, 209, 212).



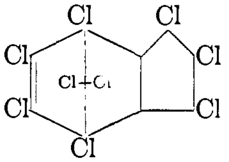
IX
Chlordene



X
Heptachlor



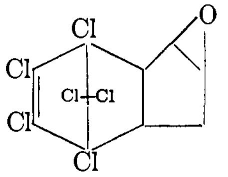
XI
Octachlor



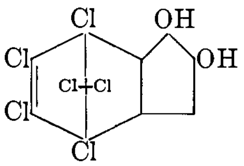
XII
Nonachlor

The commercial insecticide heptachlor, a low-melting solid, contains 1,4,5,-6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (heptachlor) (X) besides smaller amounts of octachlor (XI) and related compounds. It can be prepared (*1*) by the chlorination of chlordene (IX) with chlorine in carbon tetrachloride at 15–45°C. in the presence of porous catalysts such as alumina, silica gel, or fuller's earth (1, 2, 90, 104, 105, 106) or in boiling benzene in the presence of fuller's earth (14), (*2*) by chlorination with sulfuryl chloride and benzoyl peroxide in carbon tetrachloride (74, 77), or (*3*) indirectly by peroxide-catalyzed bromination at 50–55°C. to the liquid 1-bromo derivative (56, 62, 63, 64, 77) and replacement of the bromine by chlorine. Direct exchange of bromine by chlorine can be accomplished in good yield (85 per cent) by treating the bromo derivative with hydrogen chloride and aluminum chloride or ferric chloride in nitroethane (162), or by stirring with silver chloride in ethanol (77). The bromo derivative can be hydrolyzed to the alcohol by the use of potassium carbonate in dioxane (62, 64) or by way of the acetate and subsequent hydrolysis (63, 64). The replacement of the hydroxyl group with chlorine is brought about by heating with thionyl chloride (62, 109). Chlordene also can be oxidized to the alcohol in one step by refluxing with moist selenium dioxide in dibutyl ether, *n*-butyl acetate, ethylene glycol, diethyl ether, or dioxane (109) or to the acetate by selenium dioxide in acetic acid at 120–130°C. The acetate is then converted to heptachlor by heating with hydrochloric acid and zinc chloride (overall yield = 85–90 per cent) (110). 1-Bromochlordene reacts with benzene in the presence of mercuric fluoride to give the insecticidal 1-phenyl derivative (45). The analogous condensation with naphthalene is catalyzed by ferric chloride (45). 1-Thiocyanochlordene is formed from the bromo compound on heating with potassium thiocyanate in acetone (56).

The oxidation of chlordene (IX) with peracetic acid yields the corresponding epoxide (XIII), m.p. 231–232°C. (57, 60, 184). When this oxidation is carried out in the presence of acetic anhydride at 45°C. a diacetate is formed which can be hydrolyzed to the insecticidal glycol XIV, m.p. 139–140°C. by methanolic hydrogen chloride (58, 59).



XIII

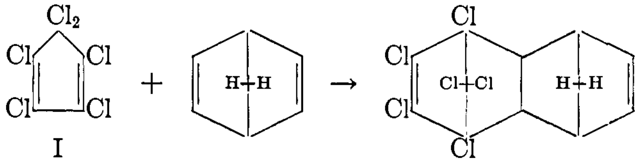


XIV

The insecticides heptachlor (X), octachlor (XI), and nonachlor (XII) are degraded biologically by rats and dogs to the heptachlor epoxide, m.p. 159–160°C., which is stored in the lipide tissues (24). Analogous oxidative degradation occurs in the cow, since the same epoxide can be demonstrated in the butterfat of the milk after feeding heptachlor (25). Heptachlor (X) and octachlor (XI) give pink to violet colors with ethanolamine and diethanolamine, respectively, in basic solution. These colors are used in sensitive spectrophotometric methods for the quantitative determination of the compounds (23, 183, 187).

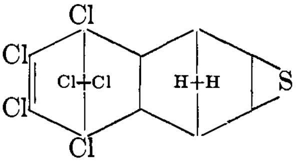
Both chlordene (IX) and the 1-halochlordenes can be converted to chlorohydrins by reaction with *tert*-butyl hypochlorite in acetic acid and transesterification of the resultant acetates with methanolic hydrogen chloride. The chlorohydrins are accessible also from the corresponding epoxides or glycols (5, 32, 47). In the case of chlordene (IX), the reaction with hypochlorites yields one geometric isomer, while the other is obtained from the action of thionyl chloride on chlordene glycol (32). The chlorohydrins derived from the chlordenes as well as the epoxides are said to be potent insecticides (47).

Equimolar proportions of hexachlorocyclopentadiene and [2.2.1]bicycloheptadiene react to give a hexachlorotetracyclododecadiene (XV), m.p. 104–104.5°C., which is the parent compound of another series of insecticides (87, 122, 131, 171) and is sold commercially under the name of aldrin. The compound has one unreactive chlorinated double bond and one unsubstituted double bond which undergoes addition reactions with halogens, halogen acids, alcohols, and carboxylic acids (127, 130). The dibromo derivative gives the episulfido compound (XVI) when refluxed with alcohol and sodium sulfide hydrate (234). Both this compound and the episulfoxy derivative that it yields on oxidation with per acids (235) are insect toxicants. On mild oxidation with peracetic or perbenzoic acid or hydrogen peroxide in aqueous *tert*-butyl alcohol, aldrin is converted to the epoxy compound dieldrin (XVII), m.p. 176–177°C. (7, 87, 131, 171, 178, 234). Under more rigorous conditions, e.g., with potassium permanganate, aldrin is oxidized to a dicarboxylic acid (XVIII). It reacts with phenyl azide to give a triazole derivative (XIX), which forms a colored derivative when coupled with diazotized 2,4-dinitroaniline (127). A sensitive quantitative method for the analysis of the compound is based on the spectrophotometric determination of the color produced (20, 21, 39).

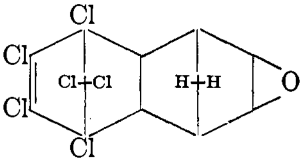


I

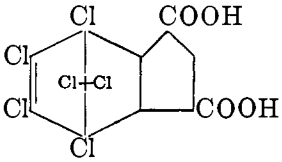
XV
Aldrin



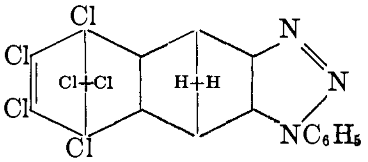
XVI



XVII
Dieldrin

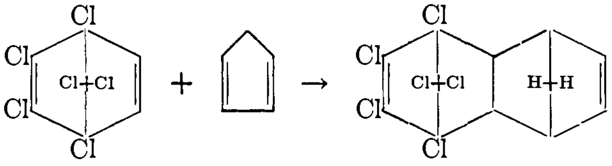


XVIII



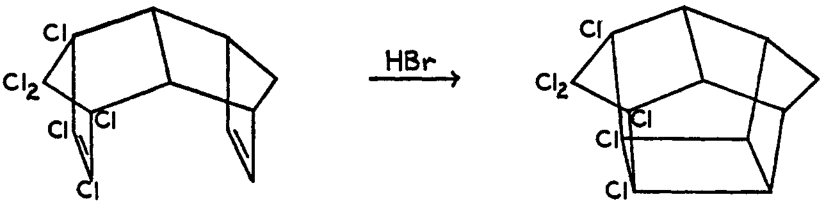
XIX

An isomer of aldrin is produced when hexachloro[2.2.1]bicycloheptadiene (XX) is condensed with cyclopentadiene (4, 12, 124). The required chlorinated diene is prepared by condensation of hexachlorocyclopentadiene with vinyl chloride and dehydrochlorination of the adduct with alcoholic bases (12, 103, 124). The new isomer, isodrin (XXI), m.p. 240–242°C., can be epoxidized with peracetic acid to give endrin, m.p. 245°C., an isomer of dieldrin (XVII) (4, 8, 12, 180). Similarly, isodrin yields addition compounds with hydrogen, chlorine, bromine, hydrogen bromide, and acetic acid involving the unchlorinated double bond (4, 124). These compounds are designated as the β series, as distinguished from the addition compounds of aldrin (XV) (α series). The structural configuration in the β series is established as endo-endo because isodrin (XXI), which belongs to this series, can be isomerized to a cage compound, 2,2a,3,3,4,8-hexachloroperhydro-1,5:2,4-ethanediylidenecyclopenta[*c*, *d*]pentalene (XXII) by treatment with hydrogen bromide in ether (126). The configuration of aldrin (XV) (α series) has been written as both exo-exo (XVa) and endo-exo (XVb), and there is at present no definite proof for either form (12). The insecticidal activities of the compounds vary considerably in the two series (167). The epoxy compound endrin is also an effective rodenticide (71).



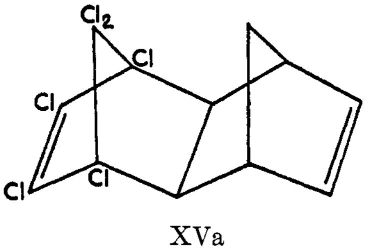
XX

XXI
Isodrin

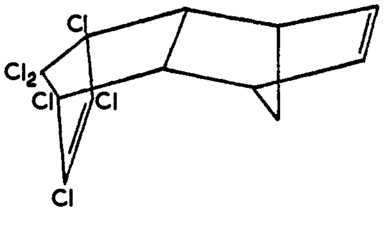


XXI

XXII



XVa



XVb

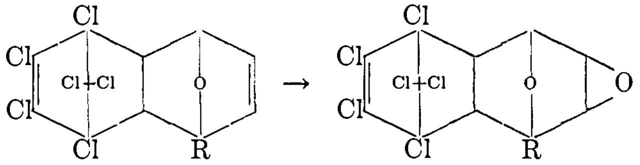
Other adducts of hexachloro[2.2.1]bicycloheptadiene (XX), derived from α-substituted furans (XXIII) (91, 96, 97, 101), can be epoxidized with per acids

TABLE 2

Diels-Alder reactions with hexachlorobicyclo[2.2.1]heptadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
Furan	165		138.7-139.6	(6, 96, 97)
Cyclopentadiene	65-100	58+	240-242	(4, 12, 124)
2-Methylfuran	155		Solid	(6, 96, 97)
Furfuryl alcohol	122-150		162-163	(91, 101)
Furfuryl methyl ether	122-175		93-95	(91, 101)
Furfuryl acetate	122-180		88-90	(91, 101)
Furfural diacetate	122-175		218.5-221	(91, 101)

at 75°C. to give active insecticides (XXIV) (92, 97, 101, 102). The reaction conditions and the properties of the adducts are listed in table 2.

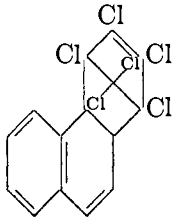


XXIII XXIV

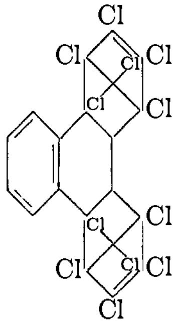
The reactive unsubstituted double bond in hexachloro[2.2.1]bicycloheptadiene (XX) also can be epoxidized with per acids. The crystalline insecticidal epoxide, m.p. 111-112°C., is hydrolyzed and acetylated by heating it with a mixture of sulfuric acid, acetic acid, and acetic anhydride. Ester interchange with methanolic hydrogen chloride yields the corresponding glycol, which can be converted to fire-resistant polymers by heating with dibasic acid anhydrides (103).

Pyrolysis of hexachloro[2.2.1]bicycloheptadiene (XX) at 190°C. initiates an exothermic reaction which leads to complete isomerization to 2,3,4-trichlorobenzotrichloride (246). The pyrolysis product may be further converted to 2,3,4-trichlorobenzoic acid by hydrolysis (246).

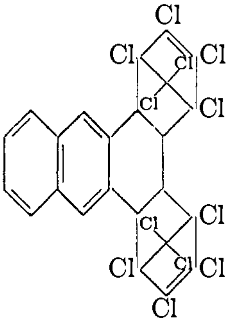
When the dienophile has multiple double bonds belonging to an aromatic system such as naphthalene, it becomes difficult to isolate a 1:1 adduct with hexachlorocyclopentadiene, because the remaining unsaturation in the reacting nucleus is activated and reacts with greater ease with a second molecule of the diene to give a bis adduct (XXVI) (22, 78, 79, 81, 179). A trace of the 1:1 adduct (XXV), which has been isolated in the case of naphthalene, probably arises from a partial reversal of the Diels-Alder reaction. Anthracene yields a bis adduct (XXVII) accompanied by a trace of tetrakis adduct (XXVIII) and 9,10-endo[hexachlorocyclopentadiene]dihydroanthracene (22, 78, 79). The presence of benzene or naphthalene structures in these adducts has been established by means of ultraviolet spectra. The aromatic portion of the addition compounds is capable of undergoing substitution reactions.



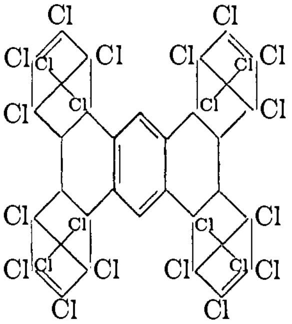
XXV



XXVI

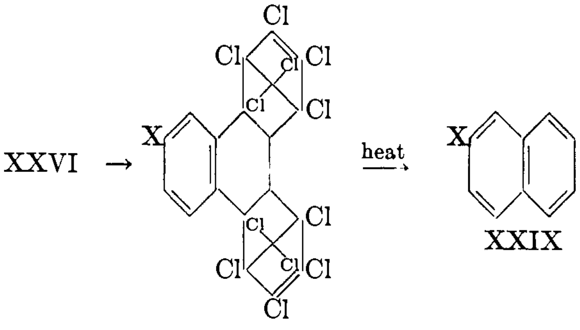


XXVII



XXVIII

Since the Diels–Alder addition reaction is reversible above 165°C., β-substituted naphthalenes (XXIX) can be prepared (in yields of 80–95 per cent) from the bis adduct of naphthalene (XXVI) (22, 81) by substitution and pyrolysis of the substituted intermediate (XXX), e.g.,



XXX

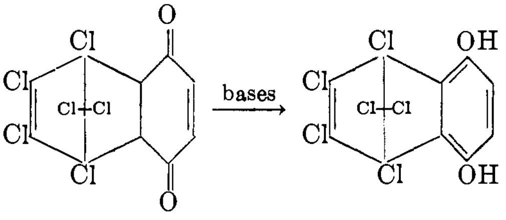
$X = NO_2, Br, SO_2Cl.$

Other compounds which have been prepared in this way are 1,2,3,4-tetrachloronaphthalene and 2,3-dibromonaphthalene (22, 81).

Hexachlorocyclopentadiene can be condensed in good yields with allylic compounds. It yields substituted [2.2.1]bicycloheptenes with allyl halides and esters, allyl alcohol, allyl sulfide, allyl isothiocyanate, and allyl phenyl ether. The adducts are given in table 1.

Compounds with activated double bonds undergo the Diels-Alder reaction with hexachlorocyclopentadiene (I) quite easily. The adducts with styrene and substituted styrenes are useful as fungicides (186) (see table 3). Butadiene monoxide gives an adduct which is a flame-proofing agent and a stabilizer for vinyl chloride (33, 116). Addition reactions occur readily with hexachlorocyclopentadiene (I) and dihydrofuran, vinyl acetate, vinyl and propenyl phosphonates, vinylsilanes, and acrylonitrile. The products are listed in table 1. Divinyl ether and 2-substituted furans yield 1:1 adducts with hexachlorocyclopentadiene (I), but furan and thiophene give only 1:2 adducts (79). The addition compound from divinyl ether reacts with boron trifluoride and other Friedel-Crafts type catalysts to give a polymer with excellent adhesive properties (46). Unsaturated aldehydes, ketones, acids, and esters add to hexachlorocyclopentadiene (I) at temperatures at or below 100°C. Some of the adducts, like those from acrylic and vinylacetic acids, are plant-growth regulators which can cause defoliation in deciduous plants, regulate flowering and shoot development, and in general act as antagonists to indoleacetic acid (236, 237, 238). Other biologically active substances in this group are prepared by condensing the acrolein adducts of chlorinated cyclopentadienes with active methylene compounds (236). The active substances are summarized in table 4.

p-Quinones react with hexachlorocyclopentadiene at 100–170°C. to give the expected addition compounds (XXXI) (128, 188), which can be isomerized to hydroquinones (XXXII) under the influence of bases at 60–120°C. (233).



XXXI XXXII

One of the more important adducts in this group, 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid or chlorendic acid (XXXIII),[2] is obtained by heating hexachlorocyclopentadiene with maleic anhydride and hydrolyzing the product. The same acid (XXXIII) has been reported as the product from the oxidation of chlordene (IX) with chromic acid (67). Later attempts to repeat the oxidation have been unsuccessful (211). It is possible, however, to convert IX to XXXIII by degradation with nitric acid (202). Therefore, while the spatial configuration of these products is unknown, chlorendic acid

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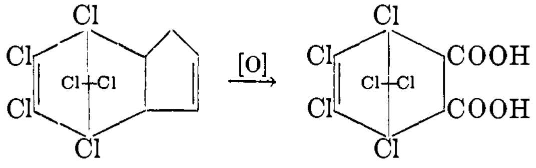
[2] The simple name "chlorendic anhydride" for 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride conforms to the International System of Nomenclature and to the system of Patterson and Capell in *The Ring Index* [Chem. Eng. News **32**, 873 (1954)].

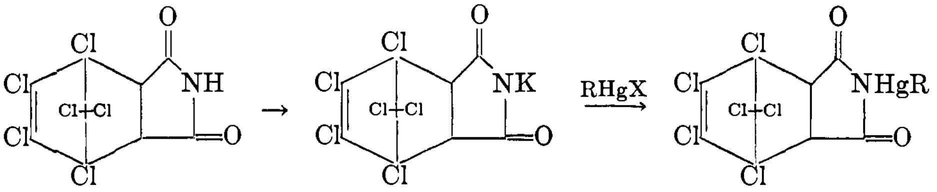


IX XXXIII
Chlorendic acid

and its derivatives probably belong to the same stereochemical series as the chlordan insecticides.

Chlorendic acid (XXXIII) and the corresponding anhydride (XXXIV) are commercial products (217, 247). The acid is remarkably stable to alkali, since the chlorine atoms are not appreciably affected even by prolonged refluxing with aqueous or alcoholic bases (188, 247).

Chlorendic anhydride (XXXIV) reacts with dry ammonia in aromatic solvents at 100–140°C. (247), with ammonium carbonate on heating (95, 100), or with aqueous ammonia at room temperature (135) to give chlorendic imide (XXXV) and with primary amines to give *N*-substituted imides (XXXVI) (see table 5) (13, 247). The latter also can be prepared by alkylating an alkali salt of the imide (XXXVII) (3, 13, 247). The second method is used for preparing the mercurated fungicidal compounds (XXXVIII) which are listed in table 3.



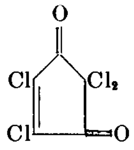
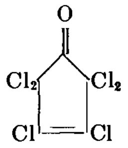
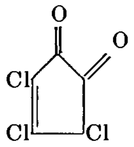
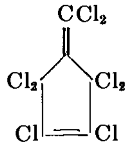
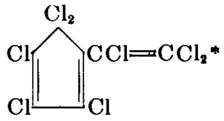
XXXV XXXVII XXXVIII
Chlorendic imide

Chlorendic acid (XXXIII) or its anhydride (XXXIV) can be converted to the corresponding diesters (XXXIX) by heating with simple alcohols and acidic catalysts (247), or the esters may be prepared from hexachlorocyclopentadiene (I) by Diels–Alder reaction with alkyl maleates (188). Monoesters, on the other hand, are prepared from chlorendic anhydride (XXXIV) and simple monohydric alcohols at room temperature without a catalyst. Examples of mono- and diesters of chlorendic acid are given in table 6. The butyl ester of chlorendic acid is recommended as a lubricant at extreme pressures (29), as are the dithiophosphoric acids and dithiophosphates derived from adducts of hexachlorocyclopentadiene (I) and unsaturated alcohols (34). A number of these and related extreme-pressure additives for lubricating oils appear in table 7.

Unusually flame-resistant alkyd-type resins are formed from chlorendic anhydride (XXXIV) and polyhydric alcohols (217). Dihydric alcohols yield

TABLE 3

Fungicides derived from hexachlorocyclopentadiene

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
Tetrachloro-4-cyclopentene-1,3-dione	$C_5Cl_4O_2$		51–51.2	(175)
Hexachloro-3-cyclopenten-1-one	C_5Cl_6O		88	(170, 175)
3,4,5-Trichloro-3-cyclopentene-1,2-dione	$C_5HCl_3O_2$		68.3–68.6	(175, 194)
1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene	C_6Cl_8		183	(174)
Pentachloro-1-trichlorovinyl-1,3-cyclopentadiene	C_7Cl_8		Liquid	(174)

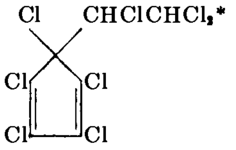
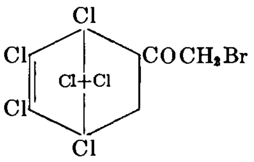
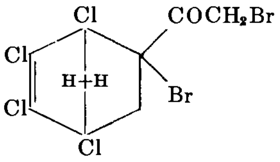
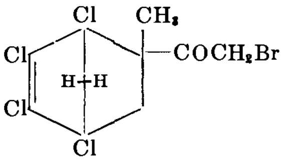
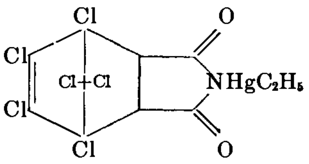
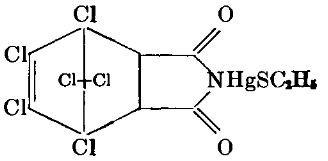
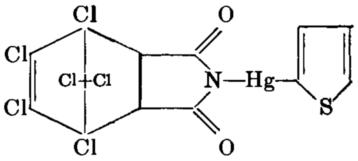
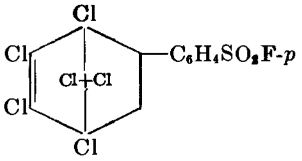
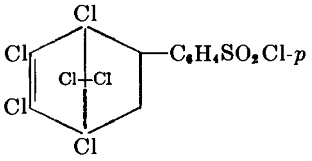
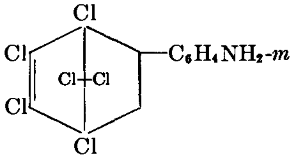
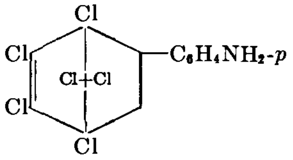
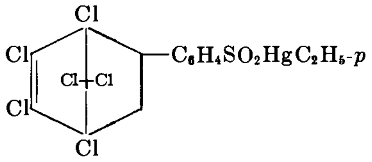
Pentachloro-5-(α,β,β-trichloroethyl)-1,3-cyclopentadiene	$C_7H_2Cl_8$			(174)
Bromomethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-hepten-2-yl ketone	$C_9H_5BrCl_6O$		92.5–93	(30)
Bromomethyl 2-bromo-1,4,5,6-tetrachlorobicyclo[2.2.1]-5-hepten-2-yl ketone	$C_9H_6Br_2Cl_4O$		118.5–119	(30)
Bromomethyl 2-methyl-1,4,5,6-tetrachlorobicyclo[2.2.1]-5-hepten-2-yl ketone	$C_{10}H_9BrCl_4O$		111–112 126–127	(30)
N-Ethylmercuri-3,4,5,6,7,7-hexachloro-3,6-methano-1,2,3,6-tetrahydrophthalimide	$C_{11}H_7Cl_6HgNO_2$		140–141	(3, 95)

TABLE 3—*Concluded*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
N-Ethylthiomercuri-3,4,5,6,7,7-hexachloro-3,6-methano-1,2,3,6-tetrahydrophthalimide	$C_{11}H_7Cl_6HgNO_2S$		Solid	(108)
N-(α-Thienylmercuri)-3,4,5,6,7,7-hexachloro-3,6-methano-1,2,3,6-tetrahydrophthalimide	$C_{13}H_5Cl_6HgNO_2S$		216–217	(100)
5-(*p*-Fluorosulfonylphenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{13}H_7Cl_6FO_2S$		161.5–163	(185)
5-(*p*-Chlorosulfonylphenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{13}H_7Cl_7O_2S$		163.5–165	(185)

5-(*m*-Aminophenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{13}H_9Cl_6N$		97.5–98.5	(186)
5-(*p*-Aminophenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{13}H_9Cl_6N$		105–106	(186)
5-(*p*-Ethylmercurisulfonylphenyl)-1,2,-3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{15}H_{12}Cl_6HgO_2S$		226–227	(201)

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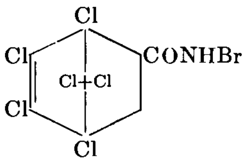
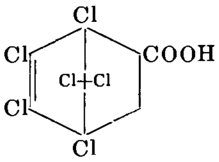
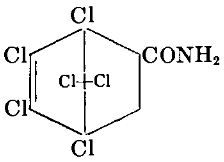
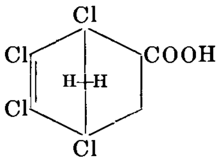
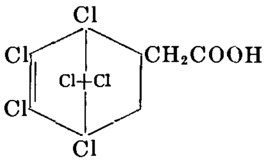
* In view of recent work (226), these structures are now uncertain.

TABLE 4

Plant-growth regulators derived from hexachlorocyclopentadiene

Name	Molecular Formula	Structure	Melting Point °C.	Reference
N-Bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2-carboxamide	$C_8H_4BrCl_6NO$			(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-carboxylic acid	$C_8H_4Cl_6O_2$		181–182.5	(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-carboxamide	$C_8H_5Cl_6NO$		161–162	(238)
1,4,5,6-Tetrachlorobicyclo[2.2.1]-5-heptene-2-carboxylic acid	$C_8H_6Cl_4O_2$		138–140 157–158	(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-acetic acid*	$C_9H_6Cl_6O_2$		119–123	(238)

* The salts of this acid are biologically active.

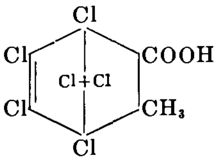
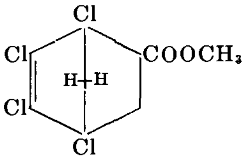
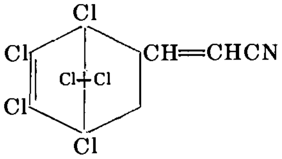
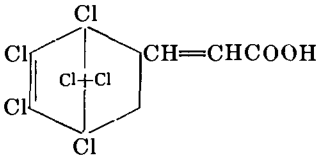
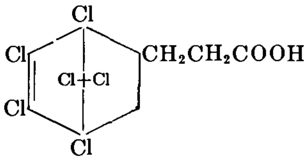
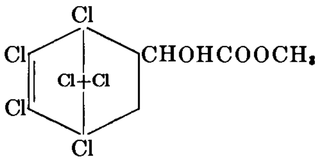
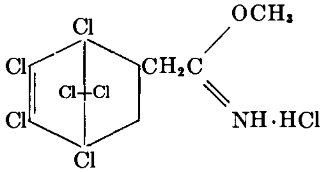
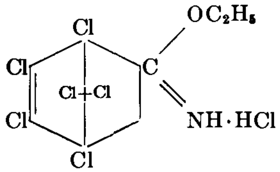
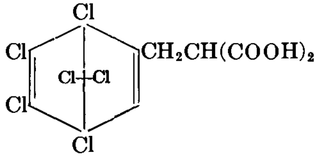
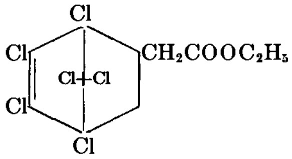
1,4,5,6,7,7-Hexachloro-3-methylbicyclo[2.2.1]-5-heptene-2-carboxylic acid	$C_9H_6Cl_6O_2$		171–172	(238)
Methyl 1,4,5,6-tetrachlorobicyclo-[2.2.1]-5-heptene-2-carboxylate	$C_9H_8Cl_4O_2$		62–63 86.5–87	(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-acrylonitrile	$C_{10}H_5Cl_6N$		122–122.5	(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-acrylic acid	$C_{10}H_6Cl_6O_2$		120.5–121.5	(238)
1,4,5,6,7,7-Hexachlorobicyclo[2 .2.1]-5-heptene-2-propionic acid	$C_{10}H_8Cl_6O_2$		84–84.5	(238)

TABLE 4—*Continued*

Name	Molecular Formula	Structure	Melting Point	Reference
			°C.	
Methyl 1,4,5,6,7,7-hexachloro-α-hydroxybicyclo[2.2.1]-5-heptene-2-acetate	$C_{10}H_8Cl_6O_3$			(238)
Methyl 1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]-5-heptene-2-acetimidate hydrochloride	$C_{10}H_9Cl_6NO \cdot HCl$		123–125	(238)
Ethyl 1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]-5-heptene-2-carboximidate hydrochloride	$C_{10}H_9Cl_6NO \cdot HCl$			(238)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-2,5-heptadienyl-2-methylmalonic acid	$C_{11}H_6Cl_6O_4$		163–165	(238)
Ethyl 1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]-5-heptene-2-acetate	$C_{11}H_{10}Cl_6O_2$		Liquid	(238)

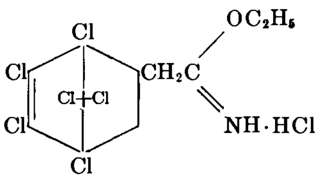
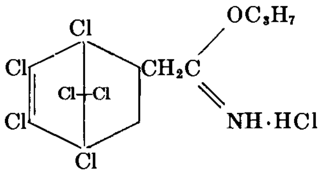
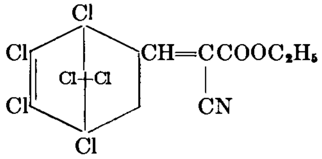
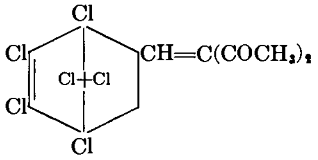
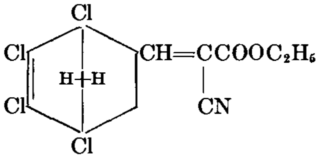
Ethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2-acetimidate hydrochloride	$C_{11}H_{11}Cl_6NO \cdot HCl$		140 (d.)	(238)
Isopropyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2-acetimidate hydrochloride	$C_{12}H_{13}Cl_6NO \cdot HCl$		150–151 (d.)	(238)
Ethyl 1,4,5,6,7,7-hexachloro-α-cyanobicyclo[2.2.1]-5-heptene-2-acrylate	$C_{13}H_9Cl_6NO_2$			(238)
3-(1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-hepten-2-ylmethylene)-2,4-pentanedione	$C_{13}H_{10}Cl_6O_2$		97–99	(236)
Ethyl 1,4,5,6-tetrachloro-α-cyanobicyclo[2.2.1]-5-heptene-2-acrylate	$C_{13}H_{11}Cl_4NO_2$			(236)

TABLE 4—*Concluded*

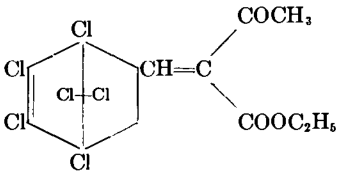
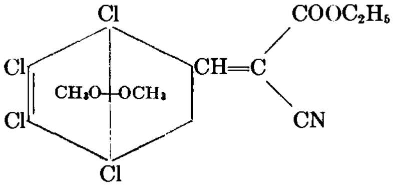
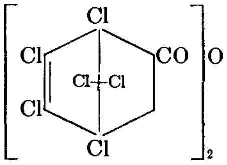
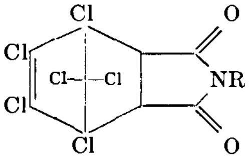
Name	Molecular Formula	Structure	Melting Point	Reference
			°C.	
Ethyl 1,4,5,6,7,7-hexachloro-α-acetylbicyclo[2.2.1]-5-heptene-2-acrylate	$C_{14}H_{12}Cl_6O_3$			(236)
Ethyl 1,4,5,6-tetrachloro-α-cyano-7,7-dimethoxybicyclo[2.2.1]-5-heptene-2-acrylate	$C_{15}H_{15}Cl_4NO_4$			(236)
1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]-5-heptene-2-carboxylic anhydride	$C_{16}H_6Cl_{12}O_3$		190–192	(238)

TABLE 5

Chlorendic imides

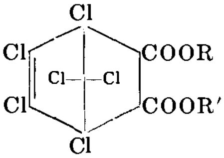


XXXVI

R	Yield	Melting Point	References
	per cent	°C.	
H	95, 80	276, 272-274, 279-280. 274, 277	(13, 95, 100, 135, 184, 247)
Ethylmercuri		140-141	(3, 95)
Ethylthiomercuri		Solid	(108)
Allyl		116, 115-116	(13, 247)
α-Thienylmercuri		216-217	(100)
Butyl	85	105	(13, 247)
Pentyl		112, 100-102	(13, 247)
p-Chlorophenyl		264, 263-264	(13, 247)
p-Sulfamidophenyl		325-327	(13)
Phenyl		231, 229-230	(13, 247)
Cyclohexyl			(13)
Heptyl		75, 73.5-74	(13, 247)
Octyl		59, 58.5-59	(13, 247)
2-Ethylhexyl		95, 90-91	(13, 247)
Nonyl		92, 88-90	(13, 247)
1-Naphthyl		Solid	(13)
Decyl		35, 32	(13, 247)
Dodecyl		45, 46.5-47.5	(13, 247)
Hexadecyl		63, 65-66	(13, 247)
Octadecyl		72, 73-79	(13, 247)

TABLE 6

Esters of chlorendic acid

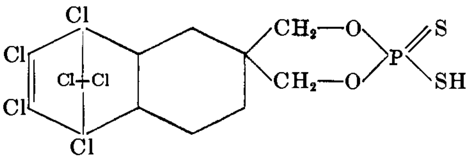
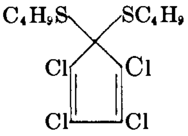
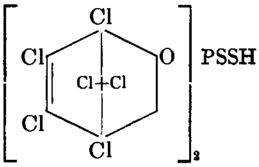
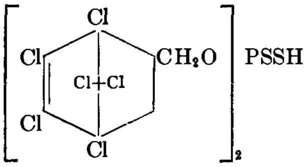
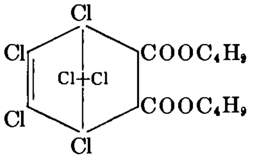
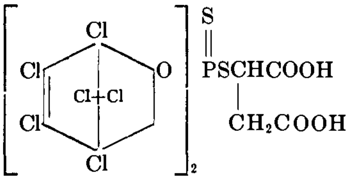
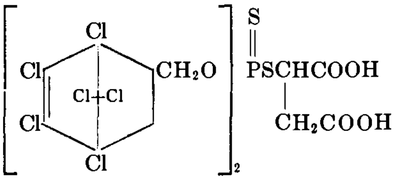
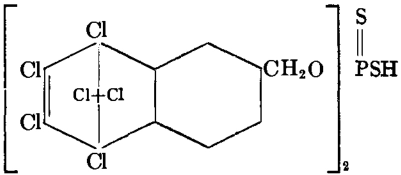


XXXIX

R	R′	Melting Point	References
		°C.	
CH_3	H	122	(247)
C_2H_5	H	125	(247)
CH_2CH_2Cl	H	156	(247)
CH_3	CH_3	78, 80-81	(184, 247)
C_2H_5	C_2H_5	67	(188, 247)
CH_2CH_2Cl	CH_2CH_2Cl	97	(247)
$CH(CH_3)_2$	$CH(CH_3)_2$	96-97	(184)
n-C_4H_9	n-C_4H_9	Liquid	(247)
$CH_2CH(C_2H_5)C_4H_9$	$CH_2CH(C_2H_5)C_4H_9$	Liquid	(247)

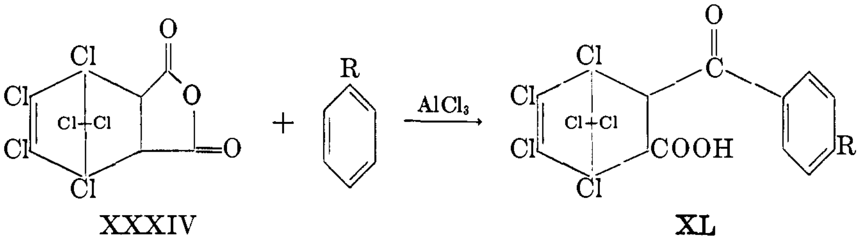
TABLE 7

Extreme-pressure additives for lubricating oils derived from hexachlorocyclopentadiene

Molecular Formula	Structure	Melting Point °C.	Reference
$C_{13}H_{13}Cl_6O_2PS_2$		206–207	(34)
$C_{13}H_{18}Cl_4S_2$		Liquid	(35)
$C_{14}H_7Cl_{12}O_2PS_2$		Liquid	(34)
$C_{16}H_{11}Cl_{12}O_2PS_2$		Liquid	(34)
$C_{17}H_{20}Cl_6O_4$		Liquid	(29)
$C_{18}H_{11}Cl_{12}O_6PS_2$		143	(34)
$C_{20}H_{15}Cl_{12}O_6PS_2$		Liquid	(34)
$C_{24}H_{23}Cl_{12}O_2PS_2$		Liquid	(34)

linear polyesters which are soluble thermoplastic resins, while polyhydric alcohols give thermosetting resins (247).

Chlorendic anhydride (XXXIV) can be used to acylate benzene and toluene in the presence of aluminum chloride (135). It has not been possible, however, to cyclize the products (XL) to analogs of anthraquinone.

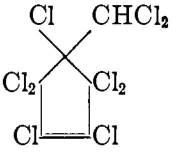


XXXIV XL

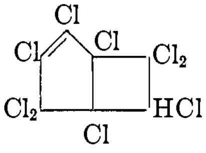
R = H, CH_3.

Chloromaleic, itaconic, and citraconic anhydrides undergo the Diels–Alder reaction with hexachlorocyclopentadiene (I) at elevated temperatures (160–195°C.). The adducts produce flame-resistant resins with glycols and peroxides (218, 219).

Hexachlorocyclopentadiene (I) can be chlorinated photochemically (194) or even better in the presence of aluminum chloride (176) to give octachlorocyclopentene (II). When heated with aluminum chloride at 90–95°C. without a solvent, with methylene chloride, carbon tetrachloride, tetrachloroethylene, or hexachlorobutadiene, it is dimerized to a chlorocarbon, $C_{10}Cl_{12}$, m.p. 485°C. (42, 85, 155, 194). Aluminum chloride catalyzes the addition of chloroform and trichloroethylene to hexachlorocyclopentadiene (I); these addition reactions give C_6HCl_9 and C_7HCl_9, originally regarded as nonachloromethylcyclopentene (XLI) (194) and 5-(1,2,2,2-tetrachloroethyl)pentachlorocyclopentadiene (177), respectively. More recently the structure of the trichloroethylene adduct has been established as nonachlorobicyclo[3.2.0]-2-heptene (XLII) (226).



XLI



XLII

The enhanced reactivity of hexachlorocyclopentadiene (I) in the presence of aluminum chloride has been ascribed to the pentachlorocyclopentadienyl cation $C_5Cl_5^+$ (177).

The catalytic hydrogenation of hexachlorocyclopentadiene (I) with a platinum catalyst proceeds stepwise. When the hydrogen uptake is limited to one molar equivalent, the product is the liquid 1,2,3,4,5-pentachlorocyclopentadiene. Further catalytic hydrogenation converts this diene to 1,2,3,4-tetrachlorocyclopentadiene (XLIII), m.p. 62–63°C. (156). The structure of the

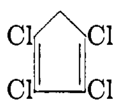
TABLE 8

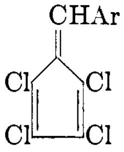
*6-Aryl-1,2,3,4-tetrachlorofulvenes**

Aryl	Yield	Melting Point	Reference
	per cent	°C.	
Phenyl	48	81-82	(141)
4-Chlorophenyl	57	143–144	(141)
4-Hydroxyphenyl	16	163–167	(141)
4-Dimethylaminophenyl	51	126–127	(141)
4-Methoxyphenyl	50	127–128	(141)
3-Nitrophenyl	24	144	(141)
4-Hydroxy-3-methoxyphenyl	32	178-179	(141)
3,4-Methylenedioxyphenyl	45	153–154	(141)
3,4-Dimethoxyphenyl	47	138–139	(141)
Styryl	41	144–145	(141)
Furyl	50	109–110	(141)

* The fulvenes were prepared by refluxing equimolar quantities of aldehyde and 1,2,3,4-tetrachlorocyclopentadiene in ethanol.

latter has been established by the preparation of a series of highly colored fulvenes (XLIV) (141) (see table 8). 1,2,3,4-Tetrachlorocyclopentadiene (XLIII) on further hydrogenation gives only cyclopentane (156).


XLIII


XLIV

1,2,3,4,5-Pentachlorocyclopentadiene is obtained also by the reduction of hexachlorocyclopentadiene (I) with stannous chloride in acetone (9, 156) and with lithium aluminum hydride at −50°C. (156). The pentachloro compound is not further reduced with lithium aluminum hydride. It reacts with this reagent with liberation of 1 mole of hydrogen and can be recovered by hydrolysis of the reaction mixture. It is postulated that the colored compound produced with lithium aluminum hydride is a carbanion (156).

Other pentachlorocyclopentadienes have been obtained as by-products from the chlorination of cyclopentadiene with hypochlorites (203, 210, 213, 215). That they contain 1,2,3,4,5-pentachlorocyclopentadiene is quite certain, since they can be reduced to XLIII by the action of zinc and hydrochloric acid (213) and condense at least in part to a crystalline dimer, m.p. 214°C. (215). The presence of other isomers has not been rigorously excluded.

The reduction of hexachlorocyclopentadiene (I) with zinc and hydrochloric acid (9, 141, 210, 213), zinc and acetic acid (22, 227), or zinc-copper and hydrochloric acid gives a good yield of XLIII in one step (141, 210). Both 1,2,3,4-tetrachloro- and 1,2,3,4,5-pentachlorocyclopentadiene undergo self-condensation to Diels–Alder dimers at room temperature or on warming. They can be recovered from the dimers by heating. Both react readily with common dienophiles to give the expected Diels–Alder adducts (see tables 9 and 10). In the case

TABLE 9

Diels–Alder reactions with 1,2,3,4-tetrachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
Acrylonitrile	90–95	31	94	(227)
Acrolein	*	Good	Liquid	(237)
Acrylic acid			138–140‡, 157–158‡	(238)
Maleic anhydride	80, 100†	94	198–200§, 185–190	(9, 141, 227)
Methyl vinyl ketone	115	53, 56	51-51.5 (exo)	(30)
	30–40		67.5–68.5 (endo)	
Methyl acrylate			62–63‡, 86.5-87‡	(238)
Tetrachlorocyclopentadiene	*†	45, 61	190–192, 193, 192–193	(141, 213, 227)
Cyclopentadiene	80*	47, 76	Liquid	(141, 213, 227)
Methyl isopropenyl ketone			55-57‡, 106–107‡	(30)
p-Benzoquinone	140	54, 60, 66	167–168, 171, 168–173 (d.)	(141, 213, 227)
			221–222¶	(227)
3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride	55		285–286	(125)
1,4-Naphthoquinone	130–135	68	186–189 (d.)	(227)

* The reactants were refluxed.

† The reactants were refluxed in benzene.

‡ Stereoisomers.

§ Isolated as acid.

¶ Bis adduct.

TABLE 10

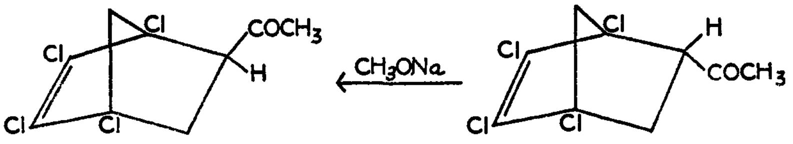
Diels–Alder reactions with 1,2,3,4,5-pentachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
Maleic anhydride	120–200	69	183-184.5†	(156)
1,2,3,4,5-Pentachlorocyclopentadiene	25	*	217-218, 215	(9, 156)
Cyclopentadiene	65	57.5	100–101	(156)

* The dimerization reaction occurs on standing at room temperature and is essentially quantitative. It is reversed at 340°C.

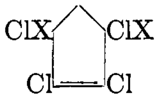
† Isolated as acid.

of the tetrachlorocyclopentadiene adduct with methyl vinyl ketone, it has been possible to isolate exo (XLV) and endo (XLVI) forms. The endo form (XLVI) can be converted to the exo form (XLV) by warming with sodium methoxide, but the latter is unchanged by this reagent (30). The bromination products of these and related ketones are effective fungicides (see table 3) (30). Other stereoisomers have been isolated from the adducts of XLIII with methyl isopropenyl ketone (30) and with acrylic acid and acrylic ester (238).

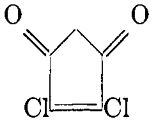


XLV XLVI

The methylene group in 1,2,3,4-tetrachlorocyclopentadiene (XLIII) is remarkably reactive. Besides forming fulvenes with aromatic aldehydes (141), it couples readily with diazonium salts and forms a crystalline oxime with ethyl nitrite and hydrogen chloride (227). The conjugated system in XLIII has a strong tendency for addition reactions. The crystalline addition compounds with chlorine or bromine are given structure XLVII, because they can be hydrolyzed with sulfuric acid to the known 4,5-dichloro-4-cyclopentene-1,3-dione (XLVIII) (169, 213, 227).



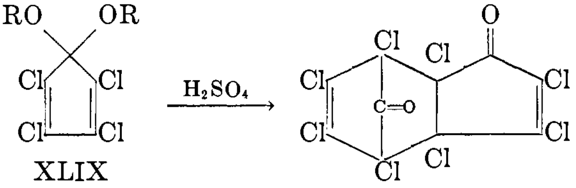
XLVII



XLVIII

Hexachlorocyclopentadiene (I) can be dechlorinated to cyclopentadiene by heating with zinc dust and ethanol (141), a reaction which has been used successfully for structural elucidation in similar compounds (38, 230).

Both hexachlorocyclopentadiene (I) and some of its reduction products are decomposed by alkali. In the case of pentachloro- and tetrachlorocyclopentadienes no definite products have been isolated from such reactions. With hexachlorocyclopentadiene (I) it is possible to avoid extensive decomposition by adding sodium ethoxide (113) or potassium hydroxide in methanol, ethanol, butanol, octanol, or ethylene glycol at temperatures of 20–60°C. at such a rate that a low momentary concentration of alkali is present (26, 176, 182). Under these conditions the dialkoxy ketals (XLIX) can be isolated in good yield. Analogous thioketals are formed by the reaction of hexachlorocyclopentadiene (I) with sodium alkyl mercaptides in alcohols or benzene (35, 182). The dihexyl thioketal is an extreme-pressure additive for lubricating oil (35), and its maleic acid adduct is said to have excellent rust-inhibiting properties when added to mineral oils (35). The ketals (XLIX) are yellow liquids which give Diels–Alder adducts with many dienophiles, the ease of reaction indicating a greater reactivity than in hexachlorocyclopentadiene (I) (26, 136, 146, 176, 182, 184). The addition products are listed in tables 11 and 12. The ketal bridge in the dienes or their adducts is readily hydrolyzed with acid; thus, tetrachloro-5,5-diethoxycyclopentadiene reacts with concentrated sulfuric acid at 0–5°C. to give the dimer (L), m.p. 166–170°C., of the intermediate cyclopentadienone (176), which also is obtained by the reaction of hexachlorocyclopentadiene (I) with fluosulfonic acid at 80–120°C. (147, 176).



XLIX

L

TABLE 11

Diels–Alder reactions with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	per cent	°C.	
Acrylonitrile	*	70	88–89	(136)
Acrolein	*	65	Liquid	(136)
Acrylic acid	*	76	163–164	(136)
Allyl bromide	*	90	63–64	(136)
Allyl alcohol	*	71	83.5–84.5	(136)
Maleic anhydride	‡	81	196–197, 192¶	(146, 176, 184)
Furan	130–135	55	243	(184)
Thiophene	140		310–311	(184)
Butadiene	140	16	206–207	(184)
Methyl vinyl ketone	*	38	86–87	(136)
Cyclopentadiene	†	76	Liquid	(26, 184)
p-Benzoquinone	*	82	162–164	(136)
Methyl maleate	†	44	103–104	(184)
5-Chlorobicyclo[2.2.1]-2-heptene	125–130	64	113–114	(184)
Phenylacetylene	§	17	89–90	(136)
p-Chlorostyrene	*	92	101–102	(136)
Styrene	*	94	82–83	(136)
Ethyl maleate	†	36	81	(184)
Indene	*	52	120–121	(136)
Isopropyl maleate	†	56	124–125	(184)

* The reactants were refluxed for 48 hr. without solvent.

† Refluxed in toluene.

‡ Refluxed in xylene.

§ 2,3,4,5-Tetrachlorobiphenyl was formed when the compounds were refluxed with benzene.

¶ Isolated as acid.

TABLE 12

Diels–Alder reactions with 5,5-diethoxy-1,2,3,4-tetrachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	per cent	°C.	
Maleic anhydride	125–145*	85, 88	213–215	(146, 182)
			219–220	(184)
Furan	130–135	36	141–143‡	(184)
Thiophene	135–140	8	177–179‡	(184)
Butadiene	140	25	235–237‡	(184)
Cyclopentadiene	Room temperature†	63	49–50	(182, 184)
Methyl maleate	†	55	80	(184)
5-Chlorobicyclo[2.2.1]-2-heptene	125–130		110–111	(184)
Ethyl maleate	†		71	(184)
Isopropyl maleate	†		94–96	(184)

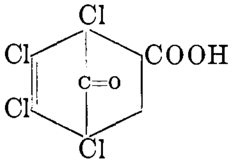
* Refluxed in xylene.

† Refluxed in toluene.

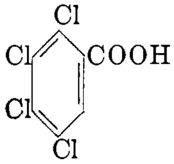
‡ Bis adduct.

The structure of the diketone (L) is based on its method of formation, the conversion to hexachloroindone by boiling water, and its thermal degradation to octachlorodihydroindone by loss of carbon monoxide and further isomerization by heat to octachlorohydrindone (256, 262, 263). The structure of L is further confirmed by infrared and ultraviolet absorption measurements. Two carbonyl bands at 5.53 and 5.81 μ (1809 and 1721 cm.$^{-1}$) correspond to strained-ring and conjugated keto groups (158). The ultraviolet absorption spectrum in hexane shows high- and low-intensity bands characteristic of conjugated carbonyl compounds with increased absorptivities and superimposed fine structure attributable to the strained-ring carbonyl group and the isolated double bond (158). From aqueous solutions the diketone L is obtained as a hydrate (147), a property observed with other chlorinated strained-ring carbonyl compounds.

The Diels–Alder adducts of the ketals XLIX can be hydrolyzed to bridge carbonyl compounds, pyrolyzed, and dehydrogenated to aromatic systems. As an example, the adduct of tetrachloro-5,5-dimethoxycyclopentadiene with acrylic acid has been hydrolyzed to 7-keto-1,4,5,6-tetrachlorobicyclo[2.2.1]-5-heptene-2-carboxylic acid (LI). The carbonyl bridge is eliminated on refluxing with nitrobenzene, and the 1,6-dihydrotetrachlorobenzoic acid is converted to 2,3,4,5-tetrachlorobenzoic acid (LII) by oxidation with potassium permanganate in acetone (136). 5-Phenyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-hepten-7-one is obtained from the hydrolysis of the styrene adduct of tetrachloro-5,5-dimethoxycyclopentadiene and 5-bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-hepten-7-one from the analogous hydrolysis of the allyl bromide adduct of the same ketal (136). The carbonyl bridge in these compounds is readily eliminated by heating. Hydrolysis by sulfuric acid of the corresponding maleic anhydride adduct at 90°C., for instance, yields 4,5-dichlorobenzene-1,2,3-tricarboxylic anhydride directly (176). The bridge carbonyl is reactive toward carbonyl reagents, such as dinitrophenylhydrazine (136) and Grignard reagents (136), and is very likely strained in view of the high frequency of its infrared absorption band (5.56 μ, 1798 cm.$^{-1}$, for 5-bromomethyl-1,2,3,4-tetrachlorobicyclo[2.2.1]-2-hepten-7-one) (158).



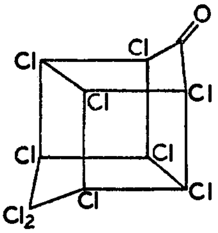
LI



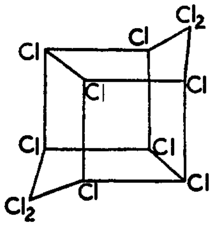
LII

Tetrachloro-5,5-dimethoxycyclopentadiene reacts with excess bromine in carbon tetrachloride, and the product can be hydrolyzed to 2,3,4,5-tetrachloro-4,5-dibromo-2-cyclopentenone by stirring with concentrated sulfuric acid at 35°C. and pouring the mixture on ice. Alkaline hydrolysis of the dibromoketone gives the crystalline 5-bromo-2,3,4,5-tetrachloropentadienoic acid (145).

Sulfur trioxide, chlorosulfonic acid, sulfuryl chloride, or fuming sulfuric acid (41, 44, 144) reacts with hexachlorocyclopentadiene (I) at 35–80°C. with the formation of sulfur-containing compounds which on hydrolysis give an insecticidal monoketone hydrate in yields of 70–72 per cent. The anhydrous ketone, $C_{10}Cl_{10}O$, forms solvates with water, acids, alcohols, amines, and thiols, has a strained-ring carbonyl band at 5.6 μ (1786 cm.$^{-1}$) (44), and absorbs like a saturated monoketone in the ultraviolet (155). On being heated with phosphorus pentachloride at 125–150°C. it is converted to a chlorocarbon, $C_{10}Cl_{12}$, m.p. 485°C., identical with the product of the self-condensation of hexachlorocyclopentadiene (I) with aluminum chloride (41, 42, 43, 44, 85, 155, 194). According to more recent work the pure chlorocarbon $C_{10}Cl_{12}$ (m.p. 485°C.) is unaffected by sulfuric acid, nitric acid, sulfur trioxide, and zinc dust and hydrochloric acid (155). In view of the reported reactions, physical properties, and absorption spectra, the originally proposed structure of dodecachlorotetrahydro-4,7-methanoindenone (41, 42, 43, 44) for the ketone and the Diels–Alder dimer structure for the chlorocarbon $C_{10}Cl_{12}$ are no longer tenable and the compounds are best represented by the caged structures shown in formulas LIII and LIV (155).

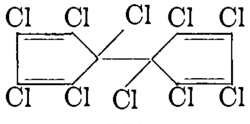


LIII

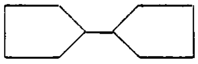


LIV

When hexachlorocyclopentadiene (I) is dechlorinated with hydrogen and palladium on carbon at atmospheric pressure (138, 231), it is converted in part (20 per cent) to $C_{10}Cl_{10}$, m.p. 123–124°C., which also can be prepared in 73 per cent yield by coupling I with cuprous chloride or powdered copper in 80 per cent methanol or ethanol at 25°C. (or below) (138, 225), or by refluxing with copper in toluene (119), or with copper bronze in petroleum ether (b.p. 90–100°C.). The structure of the compound has been established as bis(pentachlorocyclopentadienyl) (LV) by catalytic reduction to bicyclopentyl (LVI) and by its absorption spectra (138, 153).

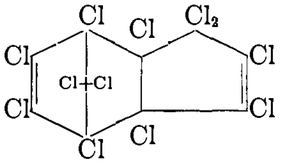


LV

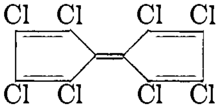


LVI

Photochemical chlorination of LV at 15°C. gives a 65 per cent yield of a $C_{10}Cl_{12}$ isomer, m.p. 220–221°C. This compound can be isomerized to LIV by aluminum chloride in boiling methylene chloride (138) or by heating with antimony trifluoride and pentachloride at 150°C. Since it cannot be reduced to bicyclopentyl and possesses isolated double bonds, it has been assigned the Diels–Alder dimer structure shown in formula LVII. Pyrolysis of LV at 250°C. gives an 85 per cent yield of perchlorofulvalene (LVIII), m.p. 347°C., which on chlorination also furnishes LVII (138, 153). The structure of perchlorofulvalene (LVIII) is based on its reduction product, bicyclopentyl (LVI), and its absorption spectra (153). The bicyclopentyl series is also accessible by thermal chlorination of the dimer of 1,2,3,4,5-pentachlorocyclopentadiene. The product, a bis(perchlorocyclopentenyl), is identical with the product obtained from the exhaustive chlorination of bicyclopentyl (154).



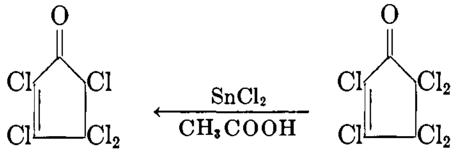
LVII



LVIII

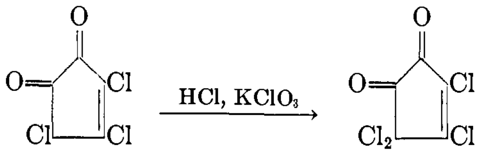
Molecular oxygen acts on hexachlorocyclopentadiene (I) at 90–150°C. with formation of a mixture of hexachlorocyclopentenones (170).

Hexachlorocyclopentadiene (I) is hydrolyzed by stirring with excess concentrated sulfuric acid at 80–90°C. (142, 176). The resulting 2,3,4,4,5-pentachloro-2-cyclopentenone (LIX), m.p. 82–83°C., is identical with the compound of Zincke and Meyer (194, 262), which was prepared by reduction of hexachloro-2-cyclopentenone (LX) with stannous chloride in acetic acid. It absorbs 1 mole of bromine at 25°C., and the bromoketone formed is cleaved by 10 per cent aqueous potassium hydroxide to give 5-bromotetrachloropentadienoic acid (142, 145, 176). 2,3,4,4,5-Pentachloro-2-cyclopentenone (LIX) is dehydrochlorinated with great ease. The reaction is brought about by stirring with potassium iodide in acetone (142, 176), sodium acetate in water, and very likely by dissolving in 95 per cent ethanol (158). The product in the first two cases is the dimer of the unstable tetrachlorocyclopentadienone (L); in the last one it is probably a halochromic salt of the diketone (L), since the ultraviolet spectrum of the alcoholic solution of LIX is identical with that of the solution of the diketone (L) in alcoholic hydrochloric acid (142, 158). The structures of these ketones are confirmed by their absorption spectra (158).



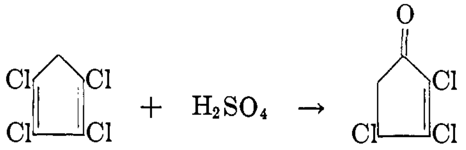
LIX LX

At higher temperatures (100–120°C.) the reaction of hexachlorocyclopentadiene (I) with sulfuric acid goes further, and the predominant product from the hydrolysis is 1,2,5-trichlorocyclopentene-3,4-dione (LXI), m.p. 68.3–68.6°C. (194). The dione (LXI) can be perchlorinated to tetrachlorocyclopentene-3,4-dione (LXII), m.p. 51–51.2°C. (194), by treating with hydrochloric acid and potassium chlorate. Both diketones are claimed to possess fungicidal activity (175).



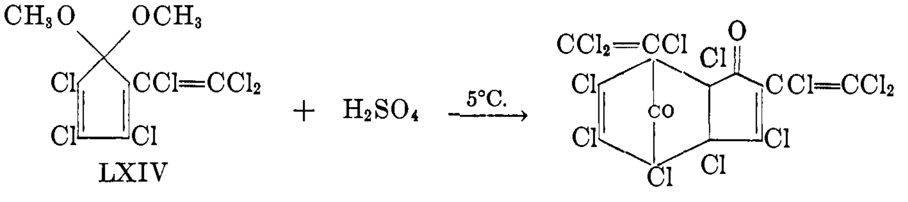
LXI LXII

The action of concentrated sulfuric acid on 1,2,3,4-tetrachlorocyclopentadiene (XLIII) at room temperature gives an 80–82 per cent yield of 2,3,4-trichloro-2-cyclopentenone (LXIII), m.p. 27–28°C. (140, 227). On bromination, LXIII absorbs first 1 mole of bromine, and then more slowly a second, with elimination of hydrogen bromide. Both LXIII and its monobromo derivative are dehydrohalogenated to dienone dimers by the action of sodium acetate (140).



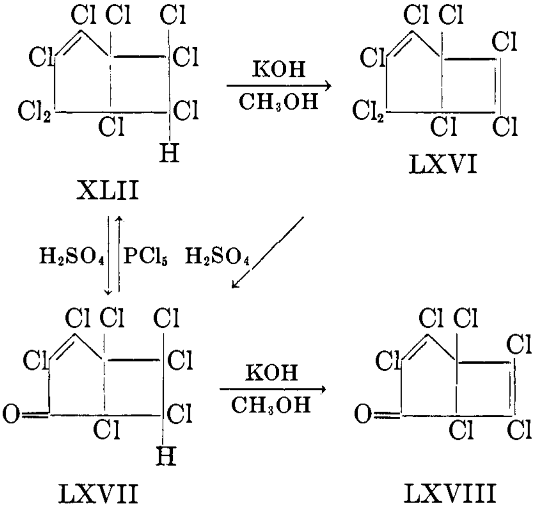
XLIII LXIII

Hexachlorocyclopentadiene (I) can be condensed with trichloroethylene and aluminum chloride (113, 148, 177). At 80°C. the product is C_7HCl_9 (XLII), which can be dehydrochlorinated to isomeric chlorocarbons, C_7Cl_8. The liquid chlorocarbon C_7Cl_8, originally believed to be octachloro-1- or 2-vinylcyclopentadiene, is obtained by heating C_7HCl_9 (XLII) with aluminum chloride at 110°C. (148, 177). It reacts with methanolic potassium hydroxide at 40–45°C. to give a ketal (LXIV), m.p. 39°C., which is hydrolyzed by sulfuric acid at 5°C. to an unstable red oily dienone, isolated usually as the dimer (LXV), m.p. 207°C. The position of the trichlorovinyl group in these compounds was regarded as uncertain, and the hydrolysis step was written tentatively as follows (148, 177):

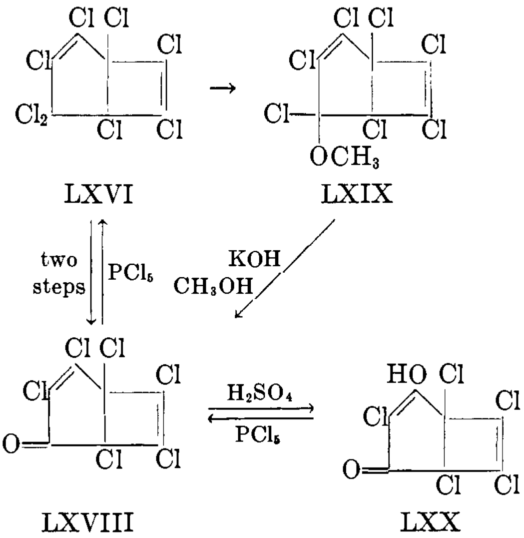


LXIV LXV

When the compound C_7HCl_9 (XLII) is dehydrochlorinated with potassium hydroxide in methanol at 42–45°C., the C_7Cl_8 isomer (LXVI), m.p. 53°C., is formed (113); it can be hydrolyzed to an α,β-unsaturated ketone, C_7HCl_7O (LXVII), by concentrated sulfuric acid at 90–95°C. (177). These and other reactions and the absorption spectra of the compounds can be explained by assuming that a bicyclo[3.2.0]heptane ring system is formed in the aluminum chloride-catalyzed reaction of hexachlorocyclopentadiene (I) with trichloroethylene (226). The subsequent reactions are then formulated by the following equations:



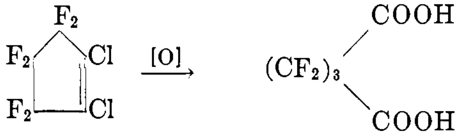
Further degradation with methanolic base converts the chlorocarbon C_7Cl_8 (LXVI) to a methoxy compound (LXIX), the structure of which is established by its facile hydrolysis to the unsaturated ketone LXVIII. The latter in turn has been further hydrolyzed to a diketone (LXX) by the action of sulfuric acid at 125°C.



The reconversion of LXX to LXVIII with phosphorus pentachloride, the oxidation of LXX to chloroacetic acid, and the absorption spectra of the ketones are in agreement with the assigned structures (226).

On heating with hexachloropropene at 218°C., hexachlorocyclopentadiene is converted in 51 per cent yield to 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene (III) (159).

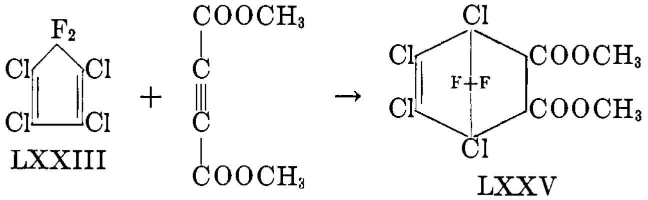
The fluorination of hexachlorocyclopentadiene (I) with antimony fluorides and fluorochlorides at 50–100°C. yields 1,2-dichlorohexafluorocyclopentene (LXXI) plus $C_5F_5Cl_3$ and smaller amounts of other halogenated 1,2-dichlorocyclopentenes of unknown structure, which arise from the addition of fluorine and the replacement of chlorine atoms (88, 157, 160, 161). Since 1,2-dichlorohexafluorocyclopentene can be oxidized to hexafluoroglutaric acid with potassium permanganate (52, 55, 88, 161), its structure is certain.



LXXI

LXXII
Hexafluoroglutaric acid

Fluorine-containing cyclopentadienes have been prepared only by the dehalogenation of fluorination products of octachlorocyclopentene (II) (157, 215). In this fashion $C_5Cl_6F_2$ yields $C_5Cl_4F_2$ (LXXIII) by treatment with zinc and sulfuric acid (215), zinc dust and hydrochloric acid (157), platinum-catalyzed hydrogenation, or pyrolysis above 480°C. (157). The structure of this compound has been established by pyrolyzing its Diels–Alder adduct (LXXV) with acetylenedicarboxylic ester (LXXIV). Both fluorine atoms are eliminated and the end-product is tetrachlorophthalic ester. The adduct, therefore, possesses a CF_2 bridge, and the diene a CF_2 group (157).



LXXIII

LXXIV

LXXV

The liquid diene LXXIII dimerizes so readily at room temperature to a colorless solid, m.p. 280–281°C., that this dimer always is a by-product in the preparation of the diene. The latter is regenerated from the dimer by pyrolysis at 480°C. (157). The tendency of 1,2,3,4-tetrachlorocyclopentadienes to react with dienophiles appears to be parallel to the ease of dimerization and depends largely on the type of CX_2 group in the diene. Dimerization of such dienes occurs in the order $CF_2 > CH_2 > CHCl$, while a CCl_2 group inhibits the reversible dimerization and Diels–Alder additions with $CCl{=}CCl$ compounds. The difluorodiene LXXIII is extraordinarily active in the Diels–Alder reaction, giving some adducts at room temperature within a few minutes. The properties of the

TABLE 13

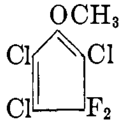
Diels-Alder reactions with 5,5-difluoro-1,2,3,4-tetrachlorocyclopentadiene

Dienophile	Reaction Temperature	Yield	Melting Point	References
	°C.	*per cent*	°C.	
Acrylic acid	70	72	116-116.5	(157)
Maleic acid	90, 100	88, 55	179-180, 182	(157, 202, 215)
5,5-Difluoro-1,2,3,4-tetrachlorocyclopentadiene	25	*	280-281, 274	(157, 215)
Cyclopentadiene	65, 35	74, 80	39-40, 37	(157, 215)
p-Benzoquinone	65, 45	56, 40	125-126, 123-124	(157, 215, 216)
Methylcyclopentadiene	35	75	Liquid†	(215)
Dimethyl acetylenedicarboxylate	120-175	46	71-72	(157)
p-Chlorostyrene	25	75	90-91	(157)
Styrene	25	95	45-46	(157)

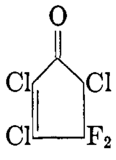
* The dimerization is essentially quantitative.

† Boiling point = 109-114°C./0.3 mm.

adducts are listed in table 13. Although the stereochemistry of the adducts is still unknown, it is assumed that the cyclopentadiene and maleic anhydride adducts belong to the same series, because the former can be degraded with nitric acid to the same dicarboxylic acid which results from the hydrolysis of the anhydride (202). 5,5-Difluoro-1,2,3,4-tetrachlorocyclopentadiene (LXXIII) reacts with potassium hydroxide in methanol to give a methoxy diene which has been assigned the structure LXXVI, based on the hydrolysis product 4,4-difluoro-2,3,5-trichlorocyclopentenone (LXXVII) (157), arising also directly from the action of fluosulfonic acid on the diene LXXIII. The diene structure in LXXVI is further confirmed by the preparation of an adduct with maleic anhydride (157).

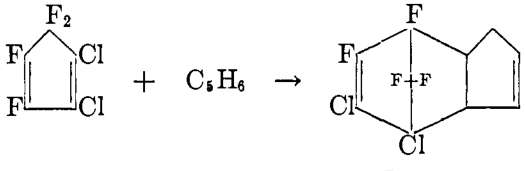


LXXVI



LXXVII

The analogous dechlorination of $C_6Cl_4F_4$ gives $C_5Cl_2F_4$ (LXXVIII), a liquid cyclopentadiene, which is further characterized only by its adduct with cyclopentadiene (LXXIX) and the chlorination product of the latter (M 344) (215). The assigned structures are presumably tentative.



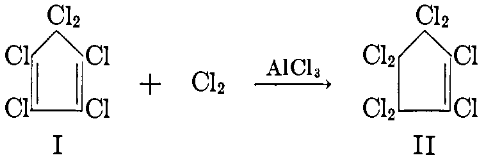
LXXVIII LXXIX

Many derivatives of hexachlorocyclopentadiene have been used as insecticides or have been claimed to possess insecticidal activity (37, 84, 167, 171, 240). The compounds appearing in table 14 are chosen from this group. Since many of these substances are toxic, threshold limit values have been published for the more common insecticides such as aldrin, dieldrin, and chlordan (241). Other insecticidally active compounds have been obtained by chlorinating Diels-Alder adducts of cyclopentadiene and various dienophiles which possess the same carbon skeleton as the active adducts of hexachlorocyclopentadiene. These chlorination products, however, do not necessarily have the same arrangement of the chlorine atoms and are therefore probably not related to hexachlorocyclopentadiene. A few examples of this kind are referred to here (18, 76, 89).

III. OCTACHLOROCYCLOPENTENE

A. Methods of preparation

Octachlorocyclopentene (II) has been prepared from cyclopentane derivatives, from open-chain paraffins or chloroparaffins with five or more carbon atoms, and from trichloroethylene and carbon tetrachloride. It can be prepared in nearly quantitative yield by the chlorination of hexachlorocyclopentadiene at 40–45°C. in the presence of aluminum chloride (176).



A two-stage synthesis from cyclopentadiene utilizes the photochemical liquid-phase chlorination to tetrachlorocyclopentadiene, which is then subjected to thermal chlorination over arsenious oxide or phosphorus pentachloride at 175–250°C. (121, 181).

A good commercial method for preparing octachlorocyclopentene (II) is the thermal chlorination of polychloropentane, isopentane, or mixtures of these chloroparaffins (137, 165). The remaining methods of preparation are suitable as laboratory methods.

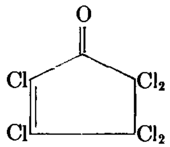
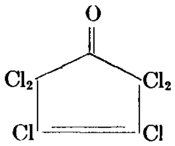
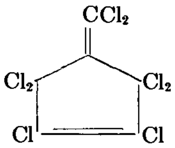
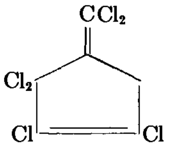
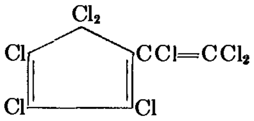
Highly chlorinated olefins, such as octachloro-1,3-pentadiene (113, 191, 193) and 1,1,2,3,3,4,5,5,5-nonachloro-1-pentene (IV) (194), are obtained from the condensation of trichloroethylene and carbon tetrachloride with aluminum chloride (173, 198) and can be cyclized to octachlorocyclopentene (II) by means of aluminum chloride in high yields. Since octachlorocyclopentene (II) is an intermediate in several methods for the preparation of hexachlorocyclopentadiene (I), a more detailed discussion of these methods is found in Section II,A.

Still other methods, which give octachlorocyclopentene (II) in smaller yields, have primarily historical value and are included for the sake of completeness. To this group belongs the exhaustive thermal chlorination of iodohexane, heptaldehyde, heptylic acid, 1,1-dichloroheptane (112), a mixture of octenes, diisoamyl, 1-iodohexadecane, Pennsylvania crude oil, and ozocerite (50).

Hexachloro-2-cyclopentenone (LX) (195, 260) and 2,3,4,4,5-pentachloro-2-

TABLE 14

Insecticidal compounds derived from hexachlorocyclopentadiene

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
2,3,4,4,5,5-Hexachloro-2-cyclopentenone	C_6Cl_6O		28	(242)
2,2,3,4,5,5-Hexachloro-3-cyclopentenone	C_5Cl_6O		87.5–88.5	(175)
1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene	C_6Cl_8		183	(174)
1,2,3,3-Tetrachloro-4-(dichloromethylene)cyclopentene	$C_6H_2Cl_6$			(174)
Pentachloro-1-trichlorovinyl-1,3-cyclopentadiene	C_7Cl_8		Liquid	(174)

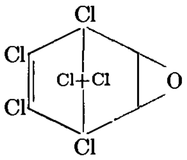
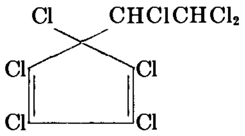
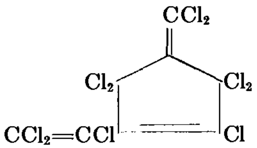
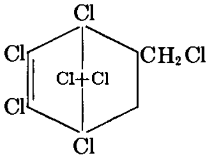
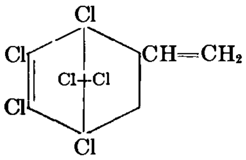
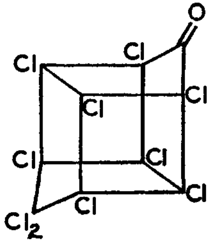
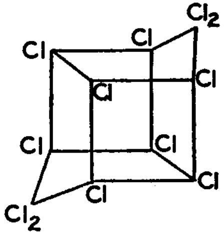
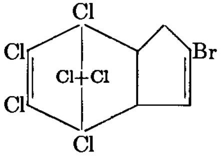
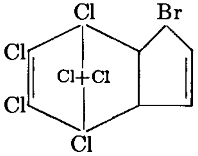
5,6-Epoxy-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_7H_2Cl_6O$		111–112	(103)
Pentachloro-5-(α,β,β-trichloroethyl)-1,3-cyclopentadiene	$C_7H_2Cl_8$			(174)
1,3,3,5,5-Pentachloro-2-trichlorovinyl-4-(dichloromethylene)-1-cyclopentene	C_8Cl_{10}			(174)
5-Chloromethyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_8H_5Cl_7$		Liquid, 54–55	(10, 33, 150)
5-Vinyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_9H_6Cl_6$		Liquid	(61, 244)

TABLE 14 -*Continued*

Name	Molecular Formula	Structure	Melting Point °C.	References
Decachlorooöctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]-pentalen-2-one	$C_{10}Cl_{10}O$		348–350, 349	(41, 42, 44, 155)
Dodecachlorooöctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]-pentalene	$C_{10}Cl_{12}$		485	(42, 43, 85, 155, 177, 194)
Unknown structure	$C_{10}H_2Cl_{12}O_3S$		146–147	(144, 176)
2-Bromo-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_5BrCl_6$		97–104	(74, 77)
1-Bromo-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_5BrCl_6$		Liquid	(5, 62, 63, 64, 74, 77)

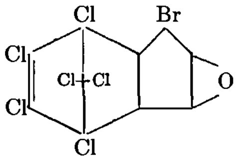
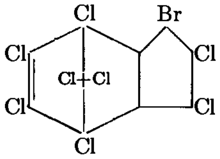
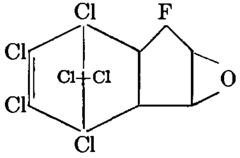
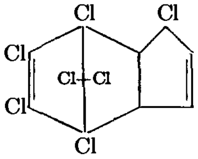
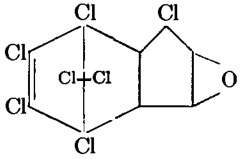
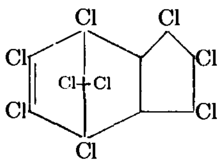
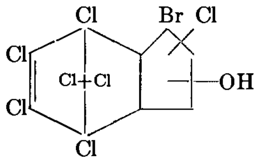
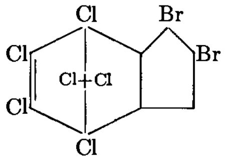
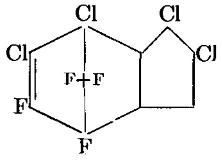
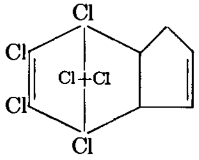
1-Bromo-2,3-epoxy-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_5BrCl_6O$			(5)
1-Bromo-2,3,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_5BrCl_8$		112–115	(74, 77)
1-Fluoro-2,3-epoxy-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_5Cl_6FO$		167–169	(5)
Heptachlor	$C_{10}H_5Cl_7$		95–96, 92–93, 92–94, 92.5–93, 92.5–92.8, liquid	(1, 2, 5, 14, 19, 62, 74, 77, 86, 87, 90, 104, 105, 106, 110, 162, 163, 167, 171)
2,3-Epoxy-1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_5Cl_7O$		83–85	(5)

TABLE 14—*Continued*

Name	Molecular Formula	Structure	Melting Point °C.	References
Nonachlor, enneachlor	$C_{10}H_5Cl_9$		122–123	(19, 167, 171)
2,3-Chlorohydrin of 1-bromo-4,5,-6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_6BrCl_7O$		147	(47)
1,2-Dibromo-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_6Br_2Cl_6$			(209)
M 344	$C_{10}H_6Cl_4F_4$		Liquid	(215)
4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene; chlordene; hexachlor; H-C-A	$C_{10}H_6Cl_6$		154, 155	(14, 61, 67, 110, 171, 207, 208, 209, 215, 244)

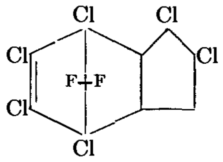
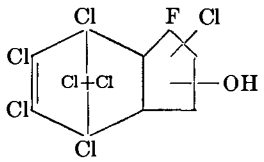
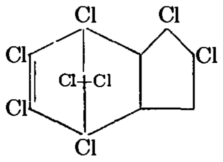
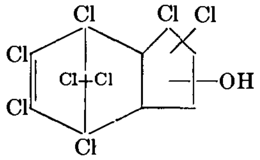
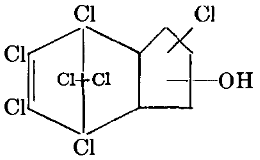
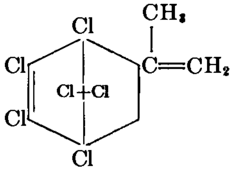
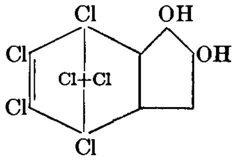
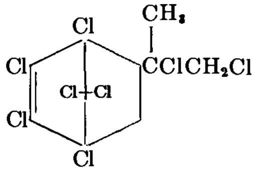
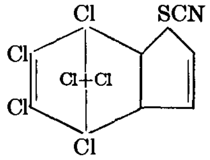
M 377	$C_{10}H_6Cl_6F_2$		Liquid	(157, 215)
2,3-Chlorohydrin of 1-fluoro-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_6Cl_7FO$		147–149	(47)
Octachlor, M 410, chlordan, compound 1068	$C_{10}H_6Cl_8$		β, cis: 102–104, 102–103.5, 101–104 α, trans: 104–106, 105.5–106.5, 106.5–108, 93–100	(19, 74, 75, 77, 86, 93, 94, 163, 171, 205, 209, 215, 240, 248)
2,3-Chlorohydrin of 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{10}H_6Cl_8O$		153.7–155	(47)
1,4,5,6,7,8,8-Heptachloro-2-hydroxy- and 1-hydroxy-2,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_7Cl_7O$		92–102, 135–135.5	(32)

TABLE 14—*Continued*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
5-Isopropenyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{10}H_8Cl_6$		Liquid	(61, 244)
1,2-Dihydroxy-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{10}H_8Cl_6O_2$		139–140	(58, 59)
5-(1,2-Dichloro-2-propyl)-1,2,3,4,-7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{10}H_8Cl_8$		Liquid	(74, 77)
1-Thiocyano-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{11}H_5Cl_6NS$		85–87	(56)

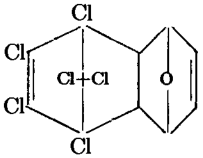
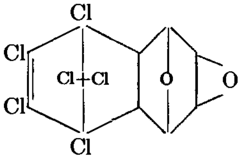
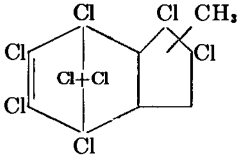
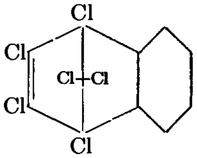
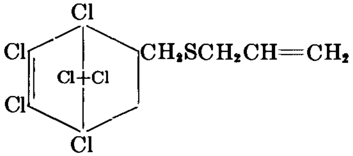
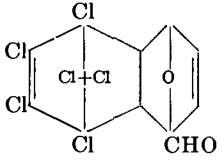
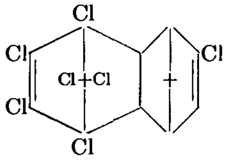
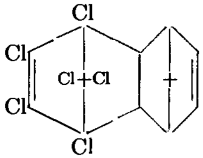
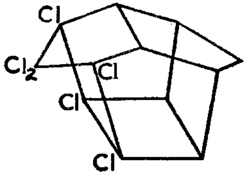
1,2,3,4,10,10-Hexachloro-5,8-oxa-1,4,4a,5,8,8a-hexahydro-1,4-methanonaphthalene	$C_{11}H_6Cl_6O$		138.7–139.6	(96, 97)
1,2,3,4,10,10-Hexachloro-5,8-oxa-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{11}H_6Cl_6O_2$		215–217	(97)
Chlorinated adduct of C_5Cl_6 and methylcyclopentadiene	$C_{11}H_8Cl_8$		Liquid	(77)
1,2,3,4,9,9-Hexachloro-1,4,4a,5,-6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{11}H_{10}Cl_6$		78	(10, 33, 215)
1,2,5,6-Tetrahydro-2,3,4,5,7,7-hexachloro-2,5-methanobenzyl allyl sulfide	$C_{11}H_{10}Cl_6S$		Liquid	(252)

TABLE 14—*Continued*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
1,2,3,4,10,10-Hexachloro-5,8-oxa-1,4,4a,5,8,8a-hexahydro-1,4-methano-5-naphthaldehyde	$C_{12}H_6Cl_6O_2$			(107)
1,2,3,4,6,10,10-Heptachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_7Cl_7$		55–57	(130, 234)
Aldrin (α series), compound 118	$C_{12}H_8Cl_6$		104–104.5, 100–103	(87, 122, 131, 171)
Isodrin (β series)			240–242, 240	(4, 12, 124)
2,2a,3,3,4,8-Hexachloroperhydro-1,5:2,4-ethanediylidenecyclopenta[*cd*]pentalene	$C_{12}H_8Cl_6$		288–289	(126)

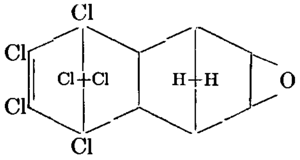
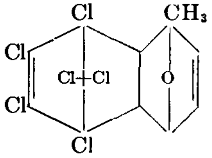
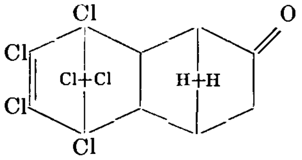
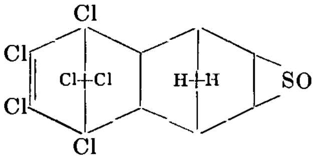
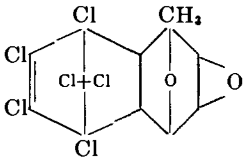
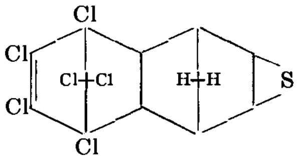
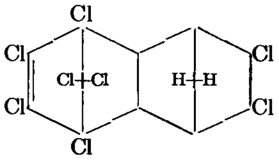
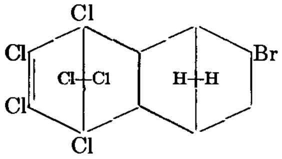
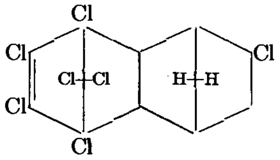
Dieldrin (α series)	$C_{12}H_8Cl_6O$		175–176, 176–177, 173, 162–177	(7, 87, 131, 171, 178, 234)
Endrin (β series)			245	(4, 8, 12, 178, 180)
1,2,3,4,10,10-Hexachloro-5-methyl-5,8-oxa-1,4,4a,5,8,8a-hexahydro-1,4-methanonaphthalene	$C_{12}H_8Cl_6O$		Solid	(96, 97)
6-Keto-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_8Cl_6O$		290–291	(4, 124)
1,2,3,4,10,10-Hexachloro-6,7-episulfoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_8Cl_6OS$		202 (d.)	(235)

TABLE 14—*Continued*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
1,2,3,4,10,10-Hexachloro-5-methyl-5,8-oxa-6,7-epoxy-1,4,-4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{12}H_8Cl_6O_2$			(97)
1,2,3,4,10,10-Hexachloro-6,7-episulfido-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_8Cl_6S$		199–202	(131, 234)
1,2,3,4,6,7,10,10-Octachloro-1,4,-4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_8Cl_8$		146 212–213 119–121 110–111	(130) (124) (129) (4)
6-Bromo-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,-4,5,8-dimethanonaphthalene	$C_{12}H_9BrCl_6$		110–111	(124)
1,2,3,4,6,10,10-Heptachloro-1,4,-4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_9Cl_7$		152–153	(123, 129)

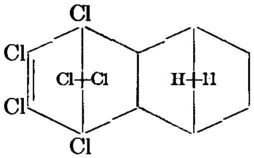
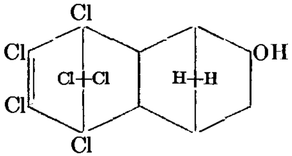
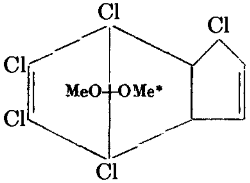
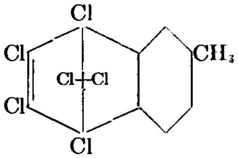
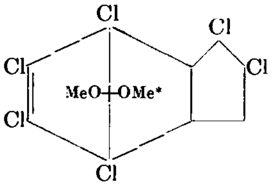
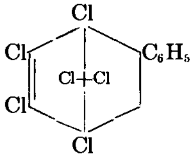
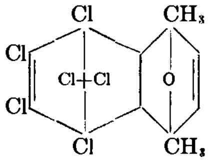
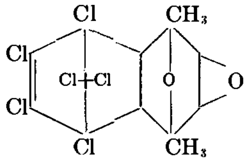
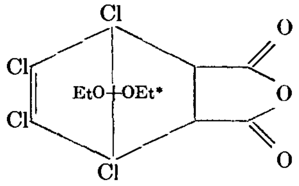
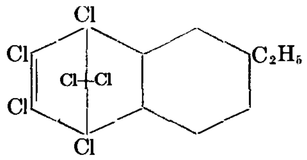
1,2,3,4,10,10-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_{10}Cl_6$		77–78 218–219	(123, 129) (124)
6-Hydroxy-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{12}H_{10}Cl_6O$		132–134 205	(123, 129) (4, 124)
1,4,5,6,7-Pentachloro-8,8-dimethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{12}H_{11}Cl_5O_2$		Liquid	(27)
1,2,3,4,9,9-Hexachloro-6-methyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{12}H_{12}Cl_6$		Liquid	(10, 33, 215)
1,2,4,5,6,7-Hexachloro-8,8-dimethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{12}H_{12}Cl_6O_2$		Liquid	(26)

TABLE 14—*Continued*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
5-Phenyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene	$C_{13}H_8Cl_6$		73-76	(61, 186, 244)
1,2,3,4,10,10-Hexachloro-5,8-dimethyl-5,8-oxa-1,4,4a,5,8,8a-hexahydro-1,4-methanonaphthalene	$C_{13}H_{10}Cl_6O$			(96)
1,2,3,4,10,10-Hexachloro-5,8-dimethyl-5,8-oxa-6,7-epoxy-1,4,-4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{13}H_{10}Cl_6O_2$			(97)
3,4,5,6-Tetrachloro-7,7-diethoxy-1,2,3,6-tetrahydro-3,6-methanophthalic anhydride	$C_{13}H_{12}Cl_4O_5$		213-215	(182)
1,2,3,4,9,9-Hexachloro-6-ethyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{13}H_{14}Cl_6$		Liquid	(10, 215)

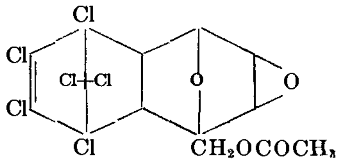
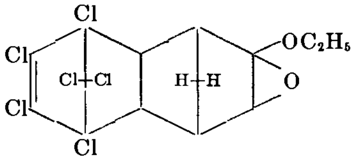
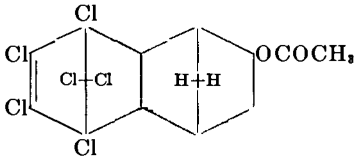
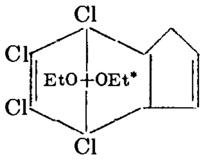
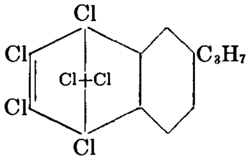
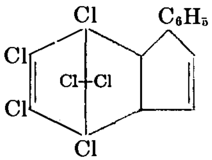
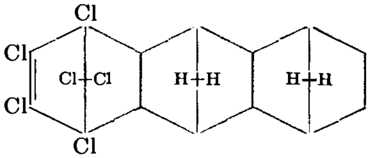
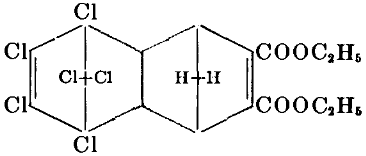
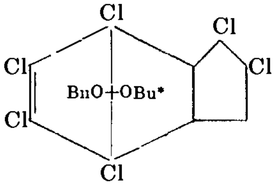
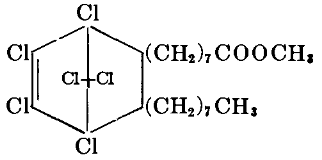
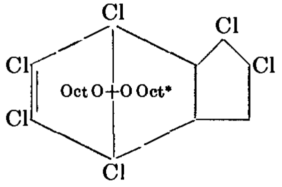
1,2,3,4,10,10-Hexachloro-5-acetoxymethyl-5,8-oxa-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{14}H_{10}Cl_6O_4$		Solid	(102)
1,2,3,4,10,10-Hexachloro-6-ethoxy-6,7-epoxy-1,4,4a,5,6,7,-8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{14}H_{12}Cl_6O_2$		112–113	(131, 234)
6-Acetoxy-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene	$C_{14}H_{12}Cl_6O_2$		170–172 204–208	(123, 129) (4, 124)
4,5,6,7-Tetrachloro-8,8-diethoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{14}H_{16}Cl_4O_2$		Solid	(182)
1,2,3,4,9,9-Hexachloro-6-propyl-1,4,4a,5,6,7,8,8a-octahydro-1,4-methanonaphthalene	$C_{14}H_{15}Cl_6$		42	(10)

TABLE 14—*Concluded*

Name	Molecular Formula	Structure	Melting Point	References
			°C.	
1-Phenyl-4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	$C_{16}H_{10}Cl_6$		77–78.5	(45)
1,2,3,4,13,13-Hexachloro-1,4,4a,-5,6,7,8,8a,9,9a,10,10a-dodecahydro-1,4,5,8,9,10-trimethanoanthracene	$C_{17}H_{16}Cl_6$		173–175	(123, 129)
6,7-Dicarbethoxy-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene	$C_{15}H_{16}Cl_6O_4$		119	(122)
1,2,4,5,6,7-Hexachloro-8,8-dibutoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{18}H_{24}Cl_6O_2$		Liquid	(26)

Methyl 1,4,5,6,7,7-hexachloro-3-octylbicyclo[2.2.1]-5-heptene-2-octanoate	$C_{24}H_{36}Cl_6O_2$		Liquid	(11)
1,2,4,5,6,7-Hexachloro-8,8-dioctyloxy-3a,4,7,7a-tetrahydro-4,7-methanoindane	$C_{26}H_{40}Cl_6O_2$		Liquid	(26)

* Me = CH_3; Et = C_2H_5; Bu = C_4H_9; Oct = C_8H_{17}.

cyclopentenone (LIX) (262), originally derived from the chlorination products of catechol, are converted to octachlorocyclopentene (II) by heating with phosphorus pentachloride at 250–280°C. Equally laborious and lengthy are the following methods of preparation, which involve the reaction with phosphorus pentachloride at 240–350°C. of (*1*) 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)cyclopentene (III) (230), derived from the thermal chlorination of paraffins with six or more carbon atoms, (*2*) tetrabromocyclopentenedione (xanthogallol) (49), a bromination product of catechol, (*3*) dibromodichlorocyclopentanetrione (51), and (*4*) 3-chloro-5,6-dihydroxy-2-(dichloromethyl)pyridine, which can be prepared from the products of the degradation of phenol with sodium hypochlorite (66).

B. Physical properties and structure

Octachlorocyclopentene (II) is occasionally confused with hexachlorobutadiene, particularly in the older literature (72). It is possible to distinguish between the substances when the melting points or boiling points are given (38). Hexachlorobutadiene is a liquid under ordinary conditions (m.p. −21°C.) and boils at 215°C., whereas octachlorocyclopentene, b.p. 283°C., has a melting point variously reported between 38° and 41°C. (72)[3] and is obtained without difficulty as colorless plates from 95 per cent ethanol (137) or ethanol containing 5 per cent tetrachloroethylene (38). The constants listed below have been reported for the olefin.

Boiling Point	References	Melting Point	References	Refractive Index	References	Density	Reference
°C.		*°C.*					
89/0.55 mm.	(115)	37.5	(198)	$n_D^{41} = 1.5689$	(194)	$d^{41} = 1.822$	(194)
107/1.6 mm.	(113, 115)	37–38	(158)	$n_D^{45} = 1.5683$	(113, 115)	$d_4^{45} = 1.814$	(115)
110–112/1.7 mm.	(198)	38	(137)*	$n_D^{50} = 1.5660$	(137)*	$d_4^{45} = 1.816$	(113)
123/3.8 mm.	(115)	38-38.2	(113, 115)	$n_D^{50} = 1.5662$	(38)	$d_4^{50} = 1.817$	(137)*
128–129/5 mm.	(173)	39	(38, 50, 112, 173, 176)				
134/6.0 mm.	(113, 115)						
140/10 mm.	(137)*	39–39.5	(115)				
142–143/12 mm.	(194)	39–40	(194, 199)				
183/20 mm.	(49)	40	(49, 230)				
283–284/733 mm.	(112)	40–41	(262)				
280 (d.)/751 mm.	(115)	41	(51, 260)				
283/atm.	(38, 260)						

* Octachlorocyclopentene was erroneously labelled hexachlorobutadiene by McBee, Hass, and Pierson (137).

The molecular refraction of octachlorocyclopentene (II) agrees closely with the values calculated from atomic refractions (38). Its Raman spectrum contains only one double-bond line at 1606 cm.$^{-1}$ (111) and is in agreement with the proposed structure (40). The chlorocarbon II has a broad absorption band in the ultraviolet in ethanol, $\lambda_{max} = 228$ mμ (log $\epsilon = 4.00$) (158, 159), $\lambda_{max} = 230$ mμ (log $\epsilon = 4.00$) (82, 138). The following bands have been assigned in

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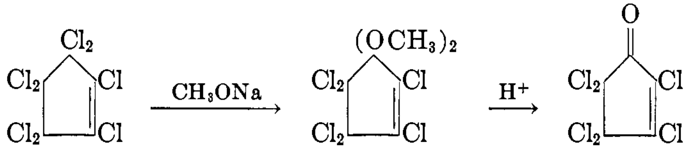
[3] The melting point given by Hoffmann (32°C.) (66) was probably obtained from rather impure material.

the infrared between 3 and 15 μ: 6.22 μ[4] (1607 cm.$^{-1}$) C═C stretching, 12.35 μ (810 cm.$^{-1}$) and 14.76 μ (677 cm.$^{-1}$) C—Cl stretching vibrations (158).

C. Reactions

Attempts to convert octachlorocyclopentene (II) to perchlorocyclopentane have failed (223). It either resists addition of chlorine or under drastic conditions undergoes chlorinolysis to hexachloroethane (114, 115). Octachlorocyclopentene (II) loses 1 mole of chlorine on refluxing with aluminum chloride in methylene chloride (194) or when heated at 450–510°C. (113, 121, 173). The thermal dechlorination is catalyzed by nickel or cobalt or their chlorides (166). At its boiling point (280°C.), octachlorocyclopentene (II) is normally stable, but it can act as a chlorinating agent when it is boiled in the presence of a suitable acceptor such as a phthalocyanine (250). Prolonged heating at higher temperatures converts octachlorocyclopentene to hexachlorobenzene (112), which normally accompanies the thermal dechlorination product hexachlorocyclopentadiene (I) only in small amounts (113). On chlorinolysis with antimony pentachloride and iodine at 450°C., octachlorocyclopentene (II) is almost completely broken down to carbon tetrachloride (50). It is stable toward bromine in carbon tetrachloride and decolorizes permanganate in acetone or in aqueous alcohol only slowly (51). On stirring with concentrated sulfuric acid at 105°C., it is hydrolyzed to give hexachloro-2-cyclopentenone (LX), m.p. 28°C., in good yield (149, 158, 176, 194). The same ketone (LX) is formed by hydrolysis of the ketal LXXX, which is obtained by treating octachlorocyclopentene (II) with sodium methoxide (176). The structure of this ketone (LX) and that of the nonconjugated isomer, which is formed on heating hexachloro-2-cyclopentenone (LX), are based on extensive chemical and spectroscopic evidence (16, 158, 176, 195, 255, 257, 258, 259, 260, 261, 264). Pentachloropentadienoic acid, m.p. 124–125°C., is a by-product in the hydrolysis of II with sulfuric acid (194). It can be prepared by the cleavage of hexachloro-2-cyclopentenone (LX) with alkali (176). When heated at 150–300°C., pentachloropentadienoic acid loses hydrogen chloride and yields a solid, m.p. 78.5–80°C. ($C_5Cl_4O_2$), of unknown structure. This compound, possibly a lactone, is an effective insecticide (65).



II LXXX LX

Chemical reducing agents or catalytic reduction acts on octachlorocyclopentene (II) by removing chlorine. The catalytic hydrogenation with platinum oxide as catalyst can be stopped after 1 mole of chlorine is removed or it can be continued to give 1,2,3,4,5-pentachloro- or 1,2,3,4-tetrachlorocyclopentadiene (156). Lithium aluminum hydride in ether reduces octachlorocyclopentene (II)

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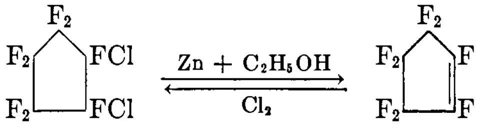
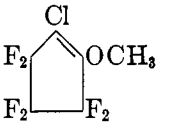
[4] The previous value (158) is in error.

to 1,2,3,4,5-pentachlorocyclopentadiene in 74 per cent yield (156), while zinc dust in acetic acid brings about its reduction to 1,2,3,4-tetrachlorocyclopentadiene (22).

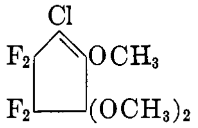
Octachlorocyclopentene (II) can be fluorinated with antimony trifluoride and antimony pentafluoride or the trifluorodichloride to give fluorine compounds from C_5Cl_7F to $C_5Cl_2F_6$ (55, 120, 157, 215). The structure of $C_5Cl_2F_6$ (LXXI) is derived from its oxidative degradation to hexafluoroglutaric acid (LXXII) (52, 55, 88, 161). Further fluorination of LXXI with antimony pentafluoride gives only very small amounts of fluorination products (55); cobalt trifluoride, on the other hand, reacts with LXXI at 90–200°C. to yield dichlorooctafluorocyclopentane (LXXXI). Perfluorocyclopentene (LXXXII) is formed when LXXXI is dechlorinated with zinc in ethanol (53). Both LXXI and LXXXII can be chlorinated photochemically to $C_5Cl_4F_6$ and $C_5Cl_2F_8$, respectively (53, 55), a reaction which is not possible in the case of octachlorocyclopentene (II). The halogens in 1,2-dichlorohexafluorocyclopentene (LXXI) are subject to displacement reactions with bases (54, 69). Methanolic potassium hydroxide, for instance, will displace either one chlorine atom or one chlorine atom plus two fluorine atoms with formation of the methoxy compounds LXXXIII and LXXXIV. One chlorine atom in LXXI can be replaced by hydrogen by heating LXXI with zinc in formamide (69). Heating of LXXI with aluminum chloride brings about an exchange of the allylic fluorine atoms with chlorine atoms (69).



LXXXI LXXXII

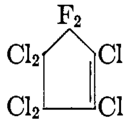


LXXXIII

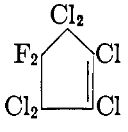


LXXXIV

Recent evidence for the dechlorination product of $C_5Cl_6F_2$ (157) permits the assignment of two alternative structures (LXXXVa and b) for this compound, but does not allow a choice between them.

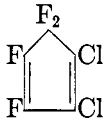


LXXXVa

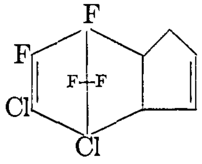


LXXXVb

The structures proposed for $C_5Cl_4F_4$ by different authors (120, 215) are in agreement. Unfortunately, however, the evidence for the structures of compounds LXXXVI and LXXXVII, which are derived from $C_5Cl_4F_4$ by dechlorination and Diels-Alder reactions (215), has not been published and the de-

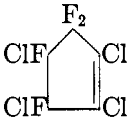


LXXXVI

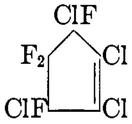


LXXXVII

chlorination reaction still allows two isomeric structures (LXXXVIIIa and b) for $C_5Cl_4F_4$ (120).



LXXXVIIIa



LXXXVIIIb

IV. 1,2,3,3,5,5-HEXACHLORO-4-(DICHLOROMETHYLENE)CYCLOPENTENE

1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene (III), m.p. 183°C., is one of the six isomers of C_6Cl_8 which have been described in the literature and the only one for which a five-membered ring structure has been established beyond doubt. The compound was first described by Prins in 1912 (189). It is related to hexachlorocyclopentadiene (I), from which it can be synthesized (194), and represents an end-product in the thermal chlorination of six-carbon-atom and higher paraffins (159).

A. Methods of preparation

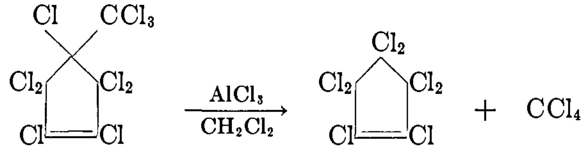
Unlike the preceding compounds, hexachloro-4-(dichloromethylene)cyclopentene (III) is not commercially available and the various methods of preparation are laboratory methods. The compound was first isolated (189, 190) from the dechlorination of hexachloropropene (LXXXIX) with copper bronze in methanol at 60–70°C. This reaction is still used for preparative purposes. It proceeds stepwise and the intermediates can be isolated if the reaction conditions are carefully controlled (230). The reaction sequence is written as follows:

$$\underset{\text{LXXXIX}}{CCl_2{=}CClCCl_3} \rightarrow \underset{\text{XC}}{CCl_2{=}CClCCl_2CCl_2CCl{=}CCl_2} \rightarrow$$

$$\underset{\text{XCI}}{CCl_2{=}CClCCl{=}CClCCl{=}CCl_2} \rightarrow \text{III}$$

The dechlorination of the intermediate decachloro-1,5-hexadiene (XC) can be carried out with alcoholic potassium hydroxide, which gives a 90 per cent yield of octachlorohexatriene (XCI). The latter is rearranged in nearly quantitative yield to C_6Cl_8, m.p. 72°C., by treatment with fuming nitric acid or to C_6Cl_8 (III), m.p. 183°C., by treatment with chlorine at 200°C. (230).

Decachloro-1,5-hexadiene (XC) is isomerized to decachloro-2,4-hexadiene by heating at 120°C. At higher temperatures either diene is dechlorinated and isomerized to C_6Cl_8, m.p. 183°C. (196). The aluminum chloride-catalyzed cyclization of the decachlorohexadienes leads to 1,2,3,3,4,5,5-heptachloro-4-(trichloromethyl)cyclopentene (XCII), m.p. 131–132°C. (196), which is cleaved to octachlorocyclopentene (II) by refluxing with aluminum chloride in methylene chloride. Prins regarded this reaction as evidence for a five-membered ring in the compound (196).



XCII II

1,2,3,3,4,5,5-Heptachloro-4-(trichloromethyl)cyclopentene (XCII) can be thermally dechlorinated to III, although in poor yield, and has been prepared from III by chlorination with liquid chlorine under pressure (221).

Hexachloropropene (LXXXIX) can be dechlorinated to C_6Cl_8 (III), m.p. 183°C., in good yield by cuprous chloride at 60°C. (143) and in poor yields by the use of aluminum in ether (221, 224) or granulated zinc (221). Aluminum in ether is a more vigorous dechlorinating agent and the reaction with hexachloropropene (LXXXIX) usually does not stop at the C_6Cl_8 stage, as it does with copper. The products contain C_6Cl_6 besides C_6Cl_8 compounds. Dechlorination with zinc gives not only C_6Cl_6 compounds but also trichloroacrylic acid as by-products (221).

Besides the octachlorohexatriene isomers C_6Cl_8, liquid (α), and C_6Cl_8, m.p. 72°C. (β) (230), a chlorocarbon C_6Cl_8, m.p. 94°C., is obtained by condensing dichloroethylene and carbon tetrachloride with aluminum chloride (199) and an isomer, m.p. 93°C., by the dehydrochlorination of 1,1,2,3,3-pentachloropropene with potassium hydroxide (197). All four of these isomers can be converted to C_6Cl_8 (III), m.p. 183°C., by thermal isomerization at temperatures of 200–280°C. (199, 221, 230). The C_6Cl_8 isomers melting at 93° and 94°C. are rearranged to C_6Cl_8 (III), m.p. 183°C., also by heating with aluminum chloride in carbon tetrachloride (199).

1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene (III) has been prepared in 64 per cent yield by heating a mixture of hexachloropropene (LXXXIX) and hexachlorocyclopentadiene (I) under reflux at 218–240°C. The reaction gives carbon tetrachloride and tetrachloroethylene as by-products. If these are allowed to accumulate in the reaction mixture, the temperature drops and the reaction stops. It can be pushed to completion by removing the low-boiling chlorocarbons as fast as they are formed (159). The chlorocarbon III can be prepared in good yield by condensing hexachlorocyclopentadiene (I) with chloroform and aluminum chloride and dehydrochlorinating the condensation product (C_6HCl_9) with ethanolic potassium hydroxide (194).

The thermal catalytic chlorination of hexane or higher open-chain paraffins or of methylcyclopentane yields the high-melting C_6Cl_8 isomer besides other products (159). In small amounts the chlorocarbon III has been isolated among other products from the reaction of trichloroethylene with aluminum (168), from the condensation of trichloroethylene with chloroform and aluminum chloride (189, 194), from the thermal dechlorination of octachloro-1,3-pentadiene (114, 115), and from the thermal chlorination of 1,1,2,5,6,6-hexachloro-1,3,5-hexatriene (228).

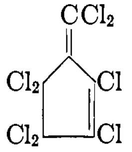
B. Properties

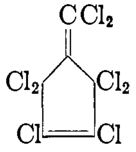
1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)cyclopentene (III) is a colorless crystalline solid for which the following melting points have been given: 179–180°C. (143, 222); 181–182°C. (222); 181–183°C. (222); 182°C. (222); 182–183°C. (114, 115, 159); 182.5–183.1°C. (199); 182.7–183.1°C. (199); 183°C. (168, 190, 194, 196, 197, 199, 220, 221, 224, 229, 230); 183–184°C. (17, 159, 189); 184–185°C. (189). It crystallizes in prisms from acetone (143), carbon tetrachloride (199), petroleum ether, ligroin, methanol, ethanol, chloroform, or benzene (159, 229), or from mixtures of these solvents (114, 199, 222). It is moderately soluble in carbon tetrachloride (9 g. per 100 g.) and carbon disulfide (17), difficultly soluble in ethanol and methanol (159, 222), and insoluble in water (159).

The compound absorbs in the ultraviolet [$\lambda_{max} = 223$ mμ, $\log \epsilon = 4.28$ in ethanol (159); $\lambda_{max} = 226$ mμ, $\log \epsilon = 4.28$ in ethanol (230)[5]; $\lambda_{max} = 224$ mμ, $\log \epsilon = 4.29$ in heptane (152)] and in the infrared [$\lambda(C{=}C) = 6.05$ and 6.20 μ (1610 and 1653 $cm.^{-1}$) (152, 159)]. It has two Raman lines in the C=C region at 1603 and 1640 $cm.^{-1}$ (17). On heating above 250°C. it starts to decompose to give hexachlorobenzene (159, 230). The decomposition is complete at 500°C. (114).

C. Structure

The structure of C_6Cl_8, m.p. 183–184°C., was written first as an eneyne (190) and later as an open-chain triene (191). A five-membered ring structure was established by a new synthesis from hexachlorocyclopentadiene (194) and by dechlorination to the red hexachlorofulvene (221). Additional data from Raman spectra (17) and from degradation products of the compound with acids led to a consideration of the structures IIIa and IIIb.


IIIa


IIIb

The conjugated structure IIIa could be eliminated by a study of the ultraviolet and infrared absorption spectra (159). The isomer melting at 72°C. and the

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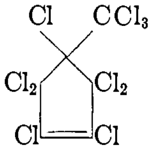
[5] Estimated from the curve.

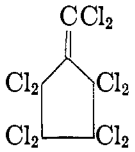
liquid isomer have been shown to be octachlorohexatrienes (220, 230). The structures of the other isomers, melting at 45°C., 93°C., and 94°C., remain uncertain.

D. Reactions

On dechlorination with aluminum (221) or with hydrogen and platinum (159) the colorless chlorocarbon C_6Cl_8 (III), m.p. 183–184°C., is converted to the red crystalline hexachlorofulvene, m.p. 153–154°C., from which it can be regenerated by direct chlorination (221). When it is chlorinated under pressure with liquid chlorine, a mixture of two decachloro compounds results. One of these, m.p. 131–132°C., is identical with the compound prepared by Prins by cyclization of the decachlorohexadienes with aluminum chloride (196) and regarded as a trichloromethylheptachlorocyclopentene (XCII). The isomer melting at 39°C. has been assigned the dichloromethyleneoctachlorocyclopentane structure (XCIII) (221).



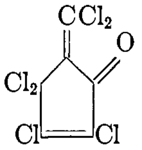
XCII



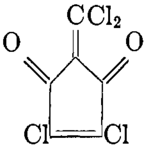
XCIII

The chlorocarbon III and its isomers, α-C_6Cl_8 (oil) and β-C_6Cl_8 (m.p. 72°C.), undergo chlorinolysis with phosphorus pentachloride at 300°C. to give carbon tetrachloride and octachlorocyclopentene (II) (230). Pyrolysis of the three isomers at 350°C. in a sealed tube yields chlorine and hexachlorobenzene (230).

Sulfuric acid, a mixture of sulfuric and nitric acids, or fuming nitric acid containing selenium (159) on heating converts III to a diketone $C_6Cl_4O_2$, m.p. 232–233°C. (159, 189, 200, 221), which is hydrolyzed by bases to chloroacetylene (159, 189, 190, 221) and dichloromaleic acid (159, 221). On being heated with phosphorus pentachloride at 250°C., the diketone gives back the starting material (III) (222). When the hydrolysis reaction of III is carried out with fuming nitric acid containing selenium, the same diketone is accompanied by a monoketone (XCIV), m.p. 84–85.5°C., which also can be reconverted to the chlorocarbon III by heating with phosphorus pentachloride (159, 221, 222) and is regarded as an intermediate in the reaction (221). On the basis of these transformations, the ketones have been assigned structures XCIV and XCV (222).



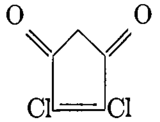
XCIV



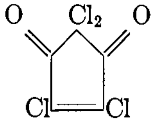
XCV

The diketone XCV possesses two active chlorine atoms (222). When it is boiled with methanol, ethanol, or dioxane and the mixture is poured into water, it is converted to 4,5-dichloro-4-cyclopentene-1,3-dione (XLVIII) (151, 159, 222).

Further chlorination of XLVIII yields tetrachlorocyclopentene-1,3-dione (XCVI); bromination yields the corresponding tetrabromodiketone (151). On



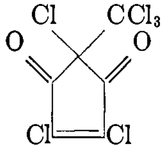
XLVIII



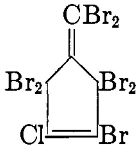
XCVI

chlorination, the diketone XCV absorbs only 1 mole of chlorine (222) and the resultant hexachlorodiketone contains one active chlorine atom (222), thus presumably retaining the endocyclic double bond (structure XCVII). The action of methanolic potassium hydroxide on III leads to products of unknown structure with the composition $C_{10}H_{13}Cl_3O_4$ and possibly $C_7H_6Cl_4O_2$. Both are converted to the dichlorodiketone XLVIII by acid hydrolysis (151).

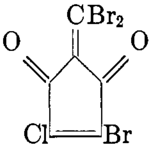
Hexachloro-4-(dichloromethylene)cyclopentene (III) undergoes halogen exchange with aluminum bromide which results in the introduction of four, six, or seven atoms of bromine without change of the carbon skeleton (152). The structures of the bromo compounds have been established by the oxidative degradation previously described for the chlorocarbon III (159, 222). As an example, 1-chloro-2,3,3,5,5-pentabromo-4-(dibromomethylene)cyclopentene (XCVIII) is converted to XCIX by oxidation with nitric acid and the diketone is cleaved to XCX by refluxing with ethanol (152).



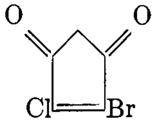
XCVII



XCVIII

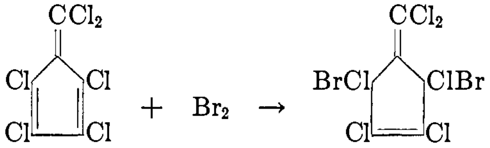


XCIX



XCX

A dibromo analog of III is obtained when hexachlorofulvene (XCXI) is brominated. The compound is presumably the 3,5-dibromo compound XCXII, since it gives the diketone XCV on hydrolysis with nitric acid, as does III (221).



XCXI XCXII

1,2,3,3,5,5-Hexachloro-4-dichloromethylenecyclopentene (III) reacts with trichloroethylene and aluminum chloride at 25°C. to give C_8HCl_{11}, m.p. 158–159°C., of unknown constitution (143).

The authors are indebted to Dr. Leonard T. Capell and to the late Dr. Austin M. Patterson for naming the three cage compounds which occur in Section II,D.

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