

**Chromatographic Separation.**—The aromatic hydrocarbons were separated from the non-aromatic hydrocarbons by means of silica gel.<sup>22</sup> The aromatic portion was distilled and the composition of the various fractions determined by means of infrared spectral analysis and solid derivatives.

**Dehydrogenation.**—The non-geminal alkylcyclohexanes present in the saturated hydrocarbon portions were dehydrogenated at 280° to the corresponding aromatic hydrocarbons using platinum-alumina as a catalyst.<sup>15</sup> The aromatic hydrocarbons thus produced were separated chromatographically. The non-aromatic hydrocarbons remaining and containing geminal alkylcyclohexanes were dehydrogenated at 330°, and again chromatographed. The aromatic hydrocarbons separated from each of the dehydrogenation reactions were distilled separately on a spinning band column and each fraction analyzed by means of infrared spectrography.

**Identification of Aromatic Hydrocarbons.**—2,4,6-Trinitro-*m*-xylene,<sup>23a</sup> 1,2,4-trimethylbenzene-5-sulfonic acid<sup>23b</sup> and 1,2,3,5-tetramethyl-4,6-dibromobenzene were prepared by standard procedures.

*p*-Cymene was separated from the trimethylbenzenes by sulfonation using a similar procedure to that outlined by Smith and Cass.<sup>24</sup> *p*-Cymene under the conditions used did not undergo sulfonation, whereas the trimethylbenzenes

formed solid sulfonic acid derivatives. The *p*-cymene thus obtained was acetylated and converted to a solid 2,4-dinitrophenylhydrazone.<sup>25</sup>

**Materials.** *d*-Limonene.—It was separated by distillation from crude limonene, obtained from orange oil.<sup>26</sup> The *d*-limonene used for investigation distilled at 174–175°,  $n_D^{20}$  1.4722,  $\alpha_D^{20}$  +93.

**Mixture of Pyrenenes and Compound V.**—It was prepared by the pyrolysis of alloöcimene. The latter was obtained in 22% yield by the pyrolysis of pinene according to the method of Goldblatt and Palkin.<sup>27</sup> The alloöcimene fraction distilled at 63–68° at 7 mm.;  $n_D^{20}$  1.5440.

The pyrolysis of alloöcimene was made at 430°, according to the general procedure of Parker and Goldblatt.<sup>11</sup> The pyrolysate was distilled and a fraction boiling at 42–59° at 6 mm.,  $n_D^{20}$  1.4760 and representing 68% of the total was separated and used for the pyrolytic study. This fraction consisted according to the boiling point and physical constants of approximately 15%  $\alpha$ -pyronene, 15% compound V and 70%  $\beta$ -pyronene.

**Acknowledgment.**—The authors wish to acknowledge the many stimulating discussions with Professor R. L. Burwell, Jr., Robert H. Kozlowski and Victor Mark.

(22) B. J. Mair and A. F. Forziatti, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

(23) (a) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 522; (b) p. 527.

(24) L. I. Smith and O. W. Cass, *THIS JOURNAL*, **54**, 1606 (1932).

(25) H. Pines and A. W. Shaw, *J. Org. Chem.*, **20**, 373 (1955).

(26) Kindly supplied by Minute Maid Corporation, Plymouth, Florida.

(27) L. A. Goldblatt and S. Palkin, *THIS JOURNAL*, **63**, 3517 (1941).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## Chemistry of Hexachlorocyclopentadiene. III. Synthesis of Bis-(pentachlorocyclopentadienyl) and Related Compounds<sup>1,2</sup>

By E. T. McBEE, J. D. IDOL, JR., AND C. W. ROBERTS

RECEIVED MARCH 14, 1955

The reaction of hexachlorocyclopentadiene (I) with cuprous chloride in 80% ethanol at 25° gives bis-(pentachlorocyclopentadienyl) (IIa). The assignment of the structure of IIa is supported by its ultraviolet absorption spectrum and by reduction to bicyclopentyl. IIa fails to form Diels-Alder adducts, but adds one mole of chlorine giving a dimer of I assumed, on the basis of its pyrolysis to I, to be perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III). III is rearranged by aluminum chloride to the isomer, m.p. 485° (V). Exhaustive chlorination of bicyclopentyl gives a compound C<sub>10</sub>Cl<sub>14</sub> (IV), the carbon skeleton of which is established by reduction to bicyclopentyl.

### Discussion

The reductive coupling of compounds possessing allylic halogen atoms by copper powder, cuprous chloride and hydrogen over palladium has received the attention of previous investigators.<sup>3,4</sup>

Cuprous chloride in 80% ethanol at 25° with hexachlorocyclopentadiene (I) results in the formation of a solid compound, C<sub>10</sub>Cl<sub>10</sub> (II), in 73% yield. Compound II is also obtained both from I and copper-bronze powder in refluxing petroleum ether (b.p. 90–100°) and by passing hydrogen at atmospheric pressure into a solution of I in toluene in the presence of a palladium-on carbon catalyst.<sup>5</sup>

The infrared spectrum of II in carbon tetrachloride establishes the absence of hydrogen and shows

certain similarities to that of I (Table I), while molecular weight determination establishes that the material is dimeric in nature.

TABLE I

INFRARED ABSORPTION BANDS FOR HEXACHLOROCYCLOPENTADIENE AND BIS-(PENTACHLOROCYCLOPENTADIENYL) (II)

C <sub>6</sub> Cl <sub>6</sub> bands, $\mu$	C <sub>10</sub> Cl <sub>10</sub> bands, $\mu$
6.25	6.28
8.15	8.18
10.39	10.35
12.35–55	12.35

Classical zinc-acid and zinc-ethanol dehalogenation methods failed to give stable, easily isolable derivatives of II. However, low pressure hydrogenation using a platinum-iron catalyst resulted in the uptake of fourteen moles of hydrogen to give a compound C<sub>10</sub>H<sub>18</sub>. The use of iron as a cocatalyst halved the reaction time but did not otherwise influence the course of reaction or the nature of products. When glacial acetic acid was used as the hydrogenation solvent, only four moles of hydrogen

(1) Paper II. J. S. Newcomer and E. T. McBee, *THIS JOURNAL*, **71**, 952 (1949).

(2) Based on a thesis submitted by James D. Idol, Jr., to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented before the Organic Division at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 5, 1955.

(3) H. J. Prins, *Rec. trav. chim.*, **68**, 419 (1949).

(4) W. Borsche and G. Heimberger, *Ber.*, **48**, 458 (1915).

(5) D. K. Smith, Ph.D. Thesis, Purdue University, 1954.

was absorbed giving an unstable product. In ethanol, which is a more basic solvent, the reduction proceeded to give the completely dehalogenated, saturated product,  $C_{10}H_{18}$ . The compound  $C_{10}H_{18}$  was identified as bicyclopentyl by comparison of its physical constants and infrared spectrum (Table II) with those of an authentic specimen prepared by the reaction of cyclopentyl bromide with sodium.<sup>6</sup> This is conclusive evidence that the basic carbon skeleton of  $C_{10}Cl_{10}$  is identical with that of bicyclopentyl.

TABLE II  
INFRARED ABSORPTION BANDS FOR BICYCLOPENTYL AND HYDROCARBON FROM REDUCTION OF II

Bicyclopentyl bands, $\mu$	Hydrocarbon bands, $\mu$
3.61	3.65-3.75
3.68	
7.00	6.95
7.64	7.59
10.90	10.85
11.28	11.257

Comparison of the ultraviolet absorption spectra of I and II limits the structure of II to one of three isomers. The ultraviolet spectrum of II (Table III) shows the presence of two isolated diene chromophores, being similar to I but having twice the extinction coefficient.<sup>8</sup> These data can be explained by structures IIa, IIb and IIc

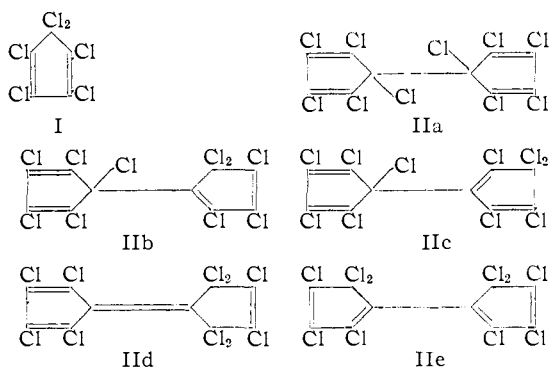


TABLE III  
ULTRAVIOLET ABSORPTION MAXIMA AND INTENSITIES

Compound	$\lambda_{max.}, m\mu$	$\epsilon_{max.}$
Hexachlorocyclopentadiene	323	1490
Compound II	330	2950
Hexachlorofulvene	288	15800
	297	21400
	308	20900
	322	10750
Octachlorocyclopentene	230	10100
Compound III	232	19500
Compound IV	224	15800

IIc and IIe are rejected because these structures possess more extended conjugated systems and would be expected to exhibit quite different absorption<sup>9</sup> (see Table III and comparison of absorption

(6) W. Meiser, *Ber.*, **32**, 2049 (1899).

(7) This band assigned to deformation of an "in-plane" 5-membered ring; F. Miller and R. Inskip, *J. Chem. Phys.*, **18**, 1519 (1950).

(8) E. T. McBee, C. W. Roberts and J. D. Idol, Jr., *Proc. Ind. Acad. Sci.*, in press.

(9) F. A. Miller in Gilman's "Organic Chemistry, An Advanced Treatise," Vol. III, John Wiley and Sons, New York, N. Y., p. 122 ff.

of II with hexachlorofulvene). If either IIb or IIc were the correct structure, the compound should give a ketal with sodium methoxide as does I<sup>10</sup>; II under identical conditions is unreactive. The steric requirements of IIa should militate against this required nucleophilic displacement, as indicated by the possible conformations, II' and II'' (Fig. 1). II reacts sluggishly with alcoholic silver nitrate even in boiling ethanol, whereas I, a *gem*-dichloride, reacts rapidly at room temperature. If either IIb or IIc were correct, a rapid reaction would be expected. II loses a mole of chlorine, on pyrolysis giving a compound  $C_{10}Cl_8$ , presumed to be perchlorofulvalene; structure IIa readily explains such behavior whereas IIb and IIc do not. As noted previously, II can be obtained by hydrogenative coupling of I at atmospheric pressure. If a simple allylic free radical coupling is accepted for this reaction, IIa would result. Bis-(pentachlorocyclopentadienyl) (IIa) is the structure assigned to  $C_{10}Cl_{10}$ .

Bis-(pentachlorocyclopentadienyl) has resisted rigorous attempts to effect a Diels-Alder reaction with maleic anhydride and other dienophiles. An explanation may be found in the steric requirements of the diene. Forms II' and II'' (Fig. 1) represent preferred conformations of the molecule. In both cases approach of the dienophile to one side of either ring is prohibited by the steric requirements of the attached ring. While the obverse side of each ring is still relatively unhindered, the Diels-Alder reaction may be prevented from occurring in II', because the transformation requires the movement of the 2- and 5-chlorine atoms downward past the 2'- and 5'-chlorine atoms, a condition which cannot be met for steric reasons. In II'' a similar argument is based on the steric requirements of the 2'-chlorine atom which projects below the reacting nucleus. II''' representing the *cis*-configuration is probably incapable of existence. I itself reacts slowly in the Diels-Alder synthesis with maleic anhydride.<sup>11</sup> In contrast, 5,5-difluorotetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene both take part readily in the diene synthesis,<sup>11,12a</sup> thus demonstrating the difference in steric requirements of a chlorine and fluorine or hydrogen atoms.

The attempted independent synthesis of IIa involved the direct exhaustive chlorination of bicyclopentyl; the compound  $C_{10}Cl_{14}$  (IV) was obtained. It possessed a non-rearranged skeleton as indicated by hydrogenation to bicyclopentyl. The ultraviolet spectrum, by comparison with that of octachlorocyclopentene, shows the presence of two isolated ethylenic chromophores (Table III), while the infrared spectrum confirms the absence of hydrogen. As predicted from the behavior of octachlorocyclopentene,<sup>13</sup> IV does not absorb more chlorine, but appears to possess the maximum number of chlorine atoms which may be accommodated on the bicyclopentyl carbon skeleton. Attempts to re-

(10) J. S. Newcomer and E. T. McBee, *THIS JOURNAL*, **71**, 946 (1949).

(11) E. A. Prill, *ibid.*, **69**, 62 (1947).

(12) E. T. McBee, D. K. Smith and H. E. Ungnade, *ibid.*, **77**, 387 (1955).

(12a) E. T. McBee and D. K. Smith, *ibid.*, **77**, 389 (1955).

(13) J. A. Krinitsky and R. W. Bost, *ibid.*, **69**, 1918 (1947).

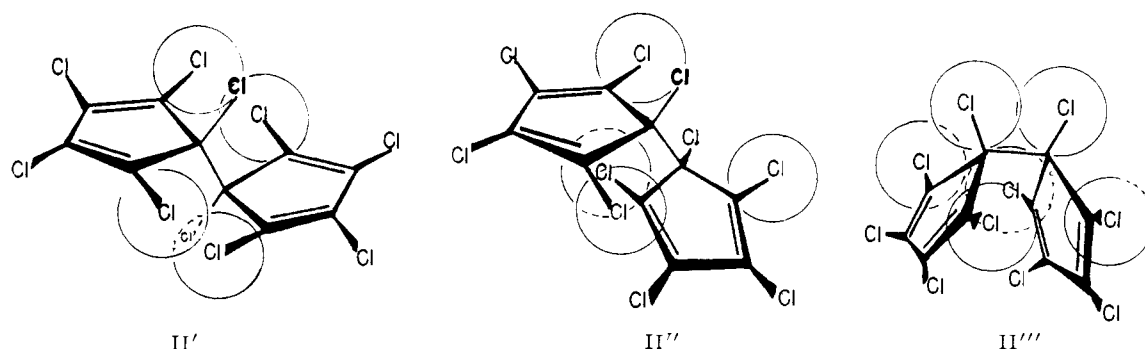


Fig. 1.—Spatial conformation of bis-(pentachlorocyclopentadienyl).

move two moles of chlorine from IV to prepare IIa were unsuccessful.

The chlorination of IIa gave, instead of IV or an isomer, a compound  $C_{10}Cl_{12}$  (III), which resisted further chlorine addition. III could not be hydrogenated to bicyclopentyl which is in contrast to the behavior of II and IV. Hence, III does not possess the bicyclopentyl carbon skeleton. The ultraviolet spectrum of III confirms the presence of isolated, ethylenic chromophores, indicating the destruction of both diene systems (Table III). It was therefore concluded that III was probably a rearranged product. Similarities were noted in the infrared spectra of III and 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VI) (Table IV). It was found that III undergoes thermal depolymerization giving an 80% yield of I. It has been reported that VI under identical conditions is converted in 90% yield to 1,2,3,4,5-pentachlorocyclopentadiene.<sup>12a</sup> It is therefore concluded that III is perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene which may be regarded as a "Diels-Alder dimer" of I. This *cannot* be prepared from I directly, presumably because of the inability of I to act as a dienophile as well as a diene.<sup>14</sup>

TABLE IV  
INFRARED ABSORPTION BANDS OF 1,2,3,3a,4,5,6,7,7a,8-  
DECACHLORO-3a,4,7,7a-TETRAHYDRO-4,7-METHANOINDENE  
AND  $C_{10}Cl_{12}$  (III)

$C_{10}Cl_{12}H_2$ bands, $\mu$	$C_{10}Cl_{12}$ bands, $\mu$
6.19	6.23-6.28
6.23	7.82
7.85	8.30
8.25	8.95
8.92	9.86
9.90	

It is of interest that strong Lewis acids, *i.e.*, aluminum chloride or antimony pentachloride, effect the transformation of III to the isomer, V, m.p. 485°, described by Prins.<sup>15</sup> Thermal depolymerization of V does not occur at temperatures below 500°; above this temperature chlorine and carbon are the major products. Aluminum chloride is without effect on IV; hence it must be the most thermodynamically stable isomer of its group.

**Acknowledgment.**—The authors express their thanks to the Hooker Electrochemical Company whose financial assistance made this work possible.

(14) H. Rakoff, Ph.D. Thesis, Purdue University, 1950.

(15) H. J. Prins, *Rec. trav. chim.*, **65**, 465 (1946).

### Experimental<sup>16</sup>

**Preparation of IIa. Method A.**—Hexachlorocyclopentadiene<sup>17</sup> (I) (625 g., 2.28 moles) was dissolved in 1500 ml. of 80% ethanol in which was suspended 226 g. (2.26 moles) of cuprous chloride. This mixture was stirred for 2 hr. keeping the temperature below 30°. The water-ethanol layer was decanted from the sludge; the sludge was washed with 1 l. of hot water containing 20 ml. of hydrochloric acid and then with two portions of hot ethanol. The wash liquid was slurried with the sludge while heating the mixture with a Glascol mantle. The crude yield of air dried product, a fine tan powder, amounted to 390 g. (73%). A purified sample, for molecular weight determination,<sup>18</sup> was obtained by passing a solution of 5 g. of the product in petroleum ether (b.p. 60-70°) through a 12" column packed with alumina and evaporating the effluent liquid giving yellow prisms, m.p. 121.5-122°.

*Anal.* Calcd. for  $C_{10}Cl_{10}$ : C, 25.31; Cl, 74.60; mol. wt., 475. Found: C, 25.13; Cl, 74.43, 74.42; mol. wt., 512, 503.

A reaction of this product with alcoholic silver nitrate gave no immediate indication of a reactive halogen.

**Method B.**—I (100 g., 0.37 mole) was treated with copper powder (75 g., 1.18 moles) in boiling petroleum ether (b.p. 90-100°) for 6 hr. After the solvent and unreacted I had been removed by distillation, the residue was recrystallized from chloroform. A second recrystallization from acetone gave 23 g. (25%) of product, m.p. 120-121°, which showed no depression of m.p. on admixture with the compound prepared by method A.

**Effect of Methanolic Potassium Hydroxide on IIa.**—Highly purified IIa (20 g., 0.042 mole) was stirred with 10 g. of potassium hydroxide dissolved in 75 ml. of methanol at reflux temperature for 12 hr. The reaction mixture was poured into 500 ml. of water and extracted with benzene. Decolorization, drying and evaporation of the extracts afforded recovery at 16 g. of IIa, m.p. 120-122°.

**Pyrolysis of IIa.**—IIa (20 g., 0.05 mole) was sealed in a Carius tube *in vacuo*, 35 mm. The tube was maintained at a temperature of 250-275° for ten hours in an electric furnace. After removal from the furnace and cooling in a Dry Ice-Triclene bath, the tube was opened and the contents extracted with 100 ml. of chloroform. The resulting slurry was filtered and the filtrate evaporated to dryness leaving 1.5 g. of residue, m.p. 344-346°, from carbon disulfide. The filtration residue was recrystallized twice from a 1:1 mixture of benzene and glacial acetic acid giving 13 g. of product, m.p. 345-347°. The total yield was 14.5 g. (85%).

*Anal.* Calcd. for  $C_{10}Cl_8$ : C, 29.70; Cl, 70.30. Found: C, 29.48; Cl, 70.59, 70.86.

**Catalytic Hydrogenation of IIa.**—A typical run is described. IIa (15 g., 0.032 mole) in 200 ml. of ethanol was treated with hydrogen over Adams catalyst (0.2 g. platinum

(16) Melting points are uncorrected; analyses were performed by Mrs. T. P. Yeh, Purdue University and the Galbraith Microanalytical Laboratory.

(17) Hexachlorocyclopentadiene was generously supplied by the Hooker Electrochemical Company.

(18) Molecular weights were determined by vapor pressure method using tetrahydrofuran as solvent; H. C. Brown, L. P. Eddy and R. Wong, *THIS JOURNAL*, **75**, 6275 (1953).

oxide—a trace of iron oxide was added as a catalyst promoter) in a standard Parr apparatus. After 12 hr. a pressure drop of 28 p.s.i. corresponding to that calculated to remove all chlorine from the molecule and saturate all double bonds was observed. In the absence of iron, the reaction was complete in 24 hours. After catalyst removal, the solution was diluted with twice its volume of water and extracted with two 200-ml. portions of petroleum ether (b.p. 35–37°). The combined extracts were dried over Drierite, the solvent distilled, and the residue distilled to give 2 g. (46%) of bicyclopentyl, b.p. 70–75° (25 mm.). This was further purified by redistillation at atmospheric pressure to give 1.5 g. of the pure hydrocarbon, b.p. 188–190°,  $n_D^{20}$  1.4650. Further proof of identity was obtained by comparison of the infrared spectrum of the product with that of an authentic specimen of the hydrocarbon prepared from sodium and cyclopentyl bromide.

**Preparation of Bicyclopentyl.**—This is essentially the procedure indicated but not described by Meiser.<sup>6</sup>

One mole of sodium sand in a 1-l., three-necked flask equipped with a mercury-sealed Herslberg stirrer and a reflux condenser was prepared in xylene. The xylene was removed with a filter stick; the sodium sand was washed six times with anhydrous ether and finally covered with 300 ml. of anhydrous ether. Cyclopentyl bromide (149 g., 1.0 mole) dissolved in 100 ml. of ether was added dropwise during 2 hr. After stirring the mixture for an additional 2 hr., 10 ml. of ethanol was added to destroy the unreacted sodium. The reaction mixture was poured, with caution, into 500 ml. of water; the organic layer was separated and dried over Drierite. The dried ether solution was rectified in a metal helices-packed column. There was obtained 37 g. (53%) of bicyclopentyl, b.p. 107–109° (50 mm.),  $n_D^{20}$  1.4645.

**Chlorination of Bicyclopentyl.**—The hydrocarbon (0.36 mole, 50 g.) was placed in a vertical Pyrex tube, 12" by 1.25" and the tube and contents chilled to 0°. Chlorine was passed into the liquid until the latter assumed a green color indicating that hydrogen substitution was no longer occurring. The ice-bath was removed and the tube strongly irradiated with a 100 w. mercury lamp. When hydrogen chloride was no longer detected in the exhaust gases, the temperature was raised to 75° with external heating coils; the temperature was ultimately raised to 175°. The dark brown liquid solidified on cooling to a mass of crystals which were recrystallized twice from petroleum ether (b.p. 60–70°) to give 149 g. (74%) of colorless needles (IV), m.p. 166.2–166.6°.

*Anal.* Calcd. for  $C_{10}Cl_4$ : C, 19.41; Cl, 80.49. Found: C, 19.54; Cl, 80.08.

**Catalytic Hydrogenation of IV.**—IV (18.9 g., 0.03 mole) was treated with hydrogen using the same equipment and amount of catalyst which had been promoted with iron oxide. The drop of 26 p.s.i. corresponded to absorption of 87% of the calculated amount of hydrogen. After 12 hr. no more hydrogen was absorbed. Following the previously described procedure there was obtained 1.8 g. (43%) of bicyclopentyl, b.p. 186–190° (745 mm.),  $n_D^{20}$  1.4651.

**Attempted Reaction of IIa with Benzoquinone.**—Compound IIa (10 g., 0.021 mole) and benzoquinone (4.5 g., 0.043 mole) were dissolved in 50 ml. of benzene and the solution was refluxed for 12 hr. The benzene was then evaporated on the steam-cone, and the residue was redissolved in ethanol and the solution decolorized with Norite. On cooling, 8.5 g. of the IIa was recovered as light yellow prisms, m.p. 121–122°.

**Attempted Reaction of IIa with Maleic Anhydride.**—The compound IIa (4 g., 0.0084 mole) and maleic anhydride (4 g., 0.041 mole) were sealed in a Carius tube and heated to 200° for 12 hr. After cooling and opening the tube, the contents were extracted with hot acetone and the resulting extracts decolorized with Norite. The acetone was evaporated on the steam-cone and the starting materials were separated by dissolving the residue in hot ethanol. On cooling, 3 g. of IIa was recovered as light yellow prisms, m.p. and mixed m.p. 120–122°.

**Chlorination of IIa. Method A.**—A solution of IIa (50 g., 0.105 mole) in 200 ml. of carbon tetrachloride was placed in a Vycor tube 50 mm. by 250 mm. equipped with a gas dispersion disk, internal cooling coils, and a reflux condenser. The tube was irradiated by two fluorescent

lamps while chlorine was admitted into the solution at a moderate rate for 12 hr. at a temperature of approximately 15°. The solution was removed from the tube and the solvent evaporated. The residue was dissolved in 150 ml. of benzene and decolorized with Norite. Partial evaporation of the solution and isolation of III gave 37 g. (65%) of colorless needles, m.p. 221–223°.

*Anal.* Calcd. for  $C_{10}Cl_2$ : C, 22.01; Cl, 77.98. Found: C, 22.12; Cl, 78.05, 77.89.

**Method B.**—IIa (5 g., 0.01 mole) was sealed in a Carius tube at –194° with 10 g. (0.14 mole) of chlorine. The tube was heated in a furnace at 200° for 12 hours. After cooling the tube was chilled to –194°, opened, and the excess chlorine allowed to evaporate. The residue was recrystallized from benzene giving 4 g. (75%) of III as colorless needles, m.p. and mixed m.p. with III from method A, 221–223°.

**Chlorination of III.**—III (10 g., 0.018 mole) and chlorine (15 g., 0.22 mole) were sealed in a Carius tube at 1 mm. pressure at –194°. The tube and contents were allowed to come to room temperature and then irradiated for 18 days with a 500 w. mercury lamp. The tube was chilled in liquid nitrogen, opened, and the chlorine allowed to evaporate. The white, crystalline residue was dissolved in hot benzene, the solution concentrated to a volume of 100 ml., and chilled giving white needles, m.p. 212–214°. A recrystallization from a mixture of equal volumes of benzene and petroleum ether (b.p. 60–70°) gave 9.5 g. of recovered III, m.p. 220–221°.

**Conversion of III to V (Prins Dimer).**—III (4 g., 0.007 mole) was dissolved in 100 ml. of methylene chloride distilled from anhydrous aluminum chloride. Powdered aluminum chloride (0.5 g.) was added and the mixture was refluxed overnight. The darkened mixture was poured in water which had been made acidic with hydrochloric acid and the organic layer separated and washed with water and dried. Evaporation of the solvent left 3.7 g. of very light yellow crystals, m.p. 485°; no depression with an authentic sample of "Prins dimer."

*Anal.* Calcd. for  $C_{10}Cl_2$ : C, 22.01; Cl, 77.99. Found: C, 22.42; Cl, 77.31.

**Attempted Fluorination of III.**—Antimony trifluoride (96 g., 0.53 mole) and antimony pentachloride (78 g., 0.26 mole) were mixed and heated to 150° to form a liquid melt; to this stirred melt, III (54.6 g., 0.1 mole) was added and the mixture maintained at 140–160° for 3.5 hr. The reaction mixture was poured into 1:1 hydrochloric acid and the flocculent yellow precipitate extracted with chloroform. The chloroform solution was washed with dilute hydrochloric acid and dried over calcium chloride. Evaporation of the solution and subsequent chilling resulted in the precipitation of a crude product. This was first recrystallized from petroleum ether (b.p. 60–70°); a final purification by vacuum sublimation gave a product, m.p. 470–475°, which proved to be, by infrared spectra, impure V. Analysis indicated no fluorine present.

**Depolymerization of III.**—III (12 g., 0.02 mole, m.p. 223°) was passed, under a positive nitrogen pressure, through a heavy-walled Pyrex tube maintained at 340° by an electric furnace. The entrance of the tube was curved upward to receive the solid reactant while the exit was curved downward to connect with an ice-trap where the product was collected. The center portion of the tube, 12" long, was inclined 20° from the horizontal to ensure flow of the melted reactant into the heated chamber. Distillation of the liquid product gave 8.1 g. (81% yield) of (I), b.p. 86–89° (2 mm.),  $n_D^{20}$  1.5658. Two grams of starting material, m.p. 220–222°, was recovered from the distillation residue.

**Action of Aluminum Chloride on IV.**—IV (10 g., 0.016 mole) dissolved in 100 ml. of methylene chloride was treated with 1 g. of powdered aluminum chloride and the resulting mixture was refluxed for 48 hr. Isolation of the product in the manner previously described and recrystallizations from petroleum ether (b.p. 60–70°) gave 7 g. of recovered IV, m.p. 165–166°.

**Absorption Spectra.**<sup>19</sup>—Ultraviolet absorption spectra were determined with a Cary recording spectrophotometer in purified *n*-hexane, cyclohexane<sup>20</sup> and 95% ethanol as

(19) Ultraviolet spectra by Mr. Robert Curry; infrared spectra by Mrs. Laverne Walsh and Mr. H. Sasi.

(20) M. E. Maclean, P. J. Jencks and S. F. Acree, *J. Research Natl. Bur. Standards*, **34**, 271 (1945).

solvents. The infrared spectra were obtained on a Perkin-Elmer model 21 recording infrared spectrophotometer

using carbon tetrachloride and chloroform as solvents. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

## Chemistry of Hexachlorocyclopentadiene. IV. The Synthesis and Structure of 1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)-cyclopentene

BY E. T. MCBEE, H. E. UNGNADE, H. RAKOFF<sup>1</sup> AND K. DINBERGS<sup>2</sup>

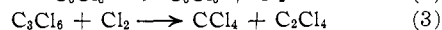
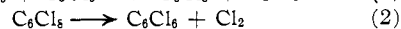
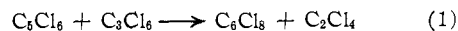
RECEIVED FEBRUARY 23, 1955

A new synthetic method is described for the preparation of the chlorocarbon  $C_6Cl_8$  (I), m.p. 182–183°. The chemical reactions and absorption spectra of the compound are in agreement with the proposed structure of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene.

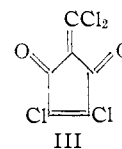
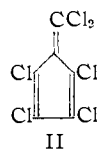
### Discussion

The chlorocarbon  $C_6Cl_8$  (I), m.p. 182–183°, one of six isomers which have been described in the literature, has been prepared by dechlorination of hexachloropropene with aluminum in ether,<sup>3,4</sup> with granulated zinc,<sup>4</sup> with copper-bronze in methanol,<sup>5</sup> or with cuprous chloride at 60°.<sup>6</sup> It is obtained by thermal isomerization of  $C_6Cl_8$  (liquid),<sup>4</sup>  $C_6Cl_8$ , m.p. 72°,<sup>4</sup>  $C_6Cl_8$ , m.p. 93°,<sup>7</sup> and  $C_6Cl_8$ , m.p. 94°,<sup>7</sup> and by the action of fuming nitric acid on  $C_6Cl_8$  (liquid).<sup>8</sup> The compound is also formed by pyrolysis of octachloro-1,3-pentadiene,<sup>9</sup> treating with aluminum,<sup>10</sup> dehydrochlorination of  $C_6HCl_8$  with potassium hydroxide in ethanol,<sup>11</sup> and by condensing trichloroethylene with chloroform and aluminum chloride.<sup>11</sup>

In the present investigation, I has been prepared by refluxing a mixture of hexachlorocyclopentadiene and hexachloropropene. When the tetrachloroethylene, which is formed as a by-product (equations 1 and 3), is allowed to accumulate in the reaction mixture, the reaction temperature drops and only a small amount of hexachlorocyclopentadiene reacts. Continuous distillation of the tetrachloroethylene from the mixture and maintenance of the temperature near 240° favors the formation of I. At higher temperatures, I is converted to hexachlorobenzene<sup>9</sup> (equation 2). The formation of I from hexachloropropene and hexachlorocyclopentadiene does not involve equimolar amounts of the reactants since the yield of tetrachloroethylene is larger than one molar equivalent. The additional tetrachloroethylene and the carbon tetrachloride which is also formed may result from chlorinolysis of hexachloropropene.<sup>5,9</sup> The following reaction sequence accounts for the observed results

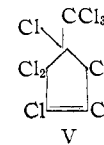
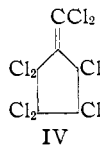


The structure of I was first investigated by Prins in 1912.<sup>12</sup> Two early open-chain structures<sup>5,13</sup> were discarded in favor of cyclic formulas based on Raman spectra,<sup>14</sup> interconversion studies<sup>15</sup> and a new synthesis from hexachlorocyclopentadiene.<sup>7</sup> A five-membered ring structure was confirmed by dechlorination of I to the red hexachlorofulvene (II) from which it is regenerated by chlorination.<sup>4</sup> Compound I is hydrolyzed by heating with sulfuric acid to give a diketone  $C_6O_2Cl_4$  (III), m.p. 231–232°. The same diketone accompanied by a monoketone, m.p. 84–85.5°, is obtained by heating I with fuming nitric acid and a trace of selenium.<sup>4,16</sup> The structure of III was established as 1,2-dichloro-4-(dichloromethylene)-cyclopentene-3,5-dione independently by Roedig<sup>4</sup> and by Rakoff<sup>1</sup> by the alkaline hydrolysis of the substance, which yields chloroacetylene<sup>1,4,8</sup> and dichloromaleic acid.<sup>1,4</sup> Chemical evidence establishes the carbon skeleton for I. The



position of ethylenic bonds, however, cannot be assigned from hydrolysis experiments using sulfuric acid because of the possibility of allylic rearrangements in strongly protonic media.

It has been possible to assign a structure to I by comparison of its ultraviolet absorption spectrum and the spectra of the chlorination products IV and V.<sup>4</sup> All three substances have a broad maximum at 223–233  $m\mu$  in ethanol corresponding to the ab-



(1) A portion of the thesis by H. Rakoff submitted to Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) In part from a thesis to be submitted by K. Dinbergs to Purdue University.

(3) A. Roedig, *Experientia*, **4**, 305 (1948).

(4) A. Roedig, *Ann.*, **569**, 161 (1950).

(5) H. J. Prins, *J. prakt. Chem.*, [2] **89**, 423 (1914).

(6) E. T. McBee, and J. S. Newcomer, U. S. Patent 2,506,428 (1950).

(7) H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

(8) A. Roedig, *Ann.*, **580**, 24 (1953).

(9) J. A. Krynitsky and H. W. Carhart, *THIS JOURNAL*, **71**, 816 (1949).

(10) L. Metz and A. Roedig, *Chem. Ing. Tech.*, **21**, 191 (1949).

(11) H. J. Prins, *Rec. trav. chim.*, **72**, 253 (1953).

(12) H. J. Prins, Doctoral Dissertation, Delft, 1912.

(13) H. J. Prins, *Rec. trav. chim.*, **51**, 1065 (1932).

(14) H. V. Brederode, H. Gerdiug and H. J. Prins, *ibid.*, **65**, 185 (1946).

(15) H. J. Prins, *ibid.*, **68**, 419, 898 (1949).

(16) Pure fuming nitric acid does not react with this chlorocarbon.