Anal. Calcd. for $C_{11}H_{10}O_5$: C, 59.41; H, 4.53. Found: C, 59.17; H, 4.36.

5,7-Dihydroxy-2-carboxy-γ-chromanone (IX).—A mixture of 5.04 g. (0.022 mole) of phloroglucinol and 3.96 g. (0.04 mole) of maleic anhydride in 45 cc. of nitrobenzene was cooled to 10°. During the course of 15 minutes 17.42 g. (0.13 mole) of anhydrous aluminum chloride was introduced with mechanical stirring. External cooling was needed to keep the temperature at 30°. After 0.5 hr. the exothermic reaction subsided and the mixture was stirred at room temperature for 0.75 hr. The aluminum complex was decomposed in a mixture of ice and concentrated hydrochloric acid. The crude acid (4 g.) was recrystallized from water; m. p. of light colored acid 262.5° (dec.).

Anal. Calcd. for $C_{10}H_8O_6$: C, 53.56; H, 3.57; neut. eq., 224. Found: C, 53.14; H, 3.58; neut. eq., 230.

Acknowledgments.—The authors would like to express their thanks to Mr. Glenn B. Hess and Miss Celia Durham for their analytical results.

Summary

An attempt was made to prepare β-(2,6-dihydroxybenzoyl)-acrylic acid and β-(2,4,6-trihydroxybenzoyl)-acrylic acid. The failure of these compounds to add cysteine and their almost white color indicate that cyclization has occurred to give the corresponding 2-carboxy-γ-chromanone.

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

The Chemical Behavior of Hexachlorocyclopentadiene. I. Transformation to Octachloro-3a,4,7,7a-Tetrahydro-4,7-methanoindene-1,8-dione[1]

BY J. S. NEWCOMER[2] AND E. T. MCBEE

During the course of extensive studies conducted in this Laboratory on the chlorination of organic compounds, it was discovered that the pentanes, with the exception of neopentane, can be readily converted to hexachlorocyclopentadiene. The results of preliminary investigations concerning the chemical behavior of this chlorocarbon are shown diagrammatically in Fig. 1.

In view of the recent publication of Prins,[3] the authors were prompted to report[4] the results of concurrent investigations on this versatile chemical intermediate. Since this report,[4] Krynitsky and Bost[5] have described the preparation of tetrachloro-5,5-diethoxycyclopentadiene by the reaction of hexachlorocyclopentadiene with sodium ethoxide.

Prins[3] reported the conversion of hexachlorocyclopentadiene to (a) nonachloromethylcyclopentene by the addition of chloroform, (b) a compound, $C_{10}Cl_{12}$, by the action of aluminum chloride, (c) 3,4,5-trichloro-3-cyclopentene-1,2-dione and 2,3,4,4,5-pentachloro-2-cyclopentenone by the action of sulfuric acid, and (d) octachlorocyclopentene by the addition of chlorine. Recently, Prill[6] described the use of hexachlorocyclopentadiene in the diene synthesis.

The ketals (II), tetrachloro-5,5-dimethoxy- and -diethoxycyclopentadiene, were prepared by the action of the appropriate sodium alkoxides or alcoholic potassium hydroxide on hexachlorocyclopentadiene (I). The ketals were shown to contain a diene system by effecting condensations with maleic anhydride. The adducts, 1,4,5,6-tetrachloro-7,7-dialkoxybicyclo(2.2.1)5-heptene-2,3-dicarboxylic acids (XIV), were converted to 4,5-dichlorobenzene-1,2,3-tricarboxylic acid (XV) upon treatment with sulfuric acid. The position of the two alkoxy groups on the same carbon atom was also established by hydrolysis of II with sulfuric acid to form tetrachlorocyclopentadienone, which immediately dimerized to form an indefinite hydrate of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. Recrystallization of the latter from aqueous acetic acid produced the tetrahydrate (III), which was identified by dehydration to the anhydrous form (IV) and by conversion to hexachloroindone (V) upon treatment with water. The anhydrous form (IV) was shown by the method of mixed melting points to be identical to that prepared as described by Zincke[7] and Meyer by the reduction of a hexachlorocyclopentenone (m. p. 28°) with stannous chloride. Although not reported by Zincke, the initial product isolated from the reaction mixture is an indefinite hydrate of IV. The hydrate is readily differentiated from the anhydrous form by the insolubility of the former in non-polar solvents at room temperature. However, if the hydrate is boiled with such solvents until solution is effected, the product obtained by cooling the solution is the anhydrous form. The reduction of an isomeric hexachlorocyclopentenone (m.p. 92°) with stannous chloride has been reported[5] to form a compound having the molecular formula $C_5H_2Cl_4O$. This material has now been found to be a hydrate of indefinite composition of IV, containing approximately two molecules of water.

Octachlorocyclopentene (VI) was prepared by the addition of chlorine to I at atmospheric pressure and in the presence of a catalytic amount of aluminum chloride. The rapid absorption of

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(1) Abstracted from the doctoral thesis of J. S. Newcomer.

(2) Present address: Sharples Chemicals, Inc., Wyandotte, Michigan.

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

(4) Presented before the Division of Organic Chemistry at the 111th Meeting of the American Chemical Society, April, 1947.

(5) J. A. Krynitsky and R. W. Bost, THIS JOURNAL, **69**, 1918 (1947).

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

(7) T. Zincke and K. H. Meyer, *Ann.*, **367**, 9 (1909).

chlorine under these conditions provides a convenient method for preparing large quantities of VI in a short period of time.

Hexachlorocyclopentenone (m.p. 28°) used in this investigation was derived by the action of sulfuric acid on VI. The conversion of this ketone to (a) an isomeric hexachlorocyclopentenone (m.p. 92°) by the application of heat and (b) a pentachloropentadienoic acid (m.p. 124–125°) by treatment with alkali showed it to be identical to the ketone obtained from a hexachlorocyclohexenedione[8] through a series of reactions and also by the action of sulfuric acid on octachloropentadiene.[3] Considerable work has been performed[8,9,10] in attempts to determine the position of the ethylenic bond in the two isomeric hexachlorocyclopentenones (VIII) and (IX). van Brederode[11] states that "none of the reactions of the two ketones C_5Cl_6O permits a definite choice between the two isomers." An attempt to identify the ketones by Raman spectra[11] was not decisive. The last attempt of Zincke[7] to establish the identity of the ketones was based upon the reduction of the isomer having a melting point of 28° to form a compound tentatively identified as 2,3,4,4,5-pentachloro-2-cyclopentenone, since it decomposed upon treatment with alkali. A more rigorous determination of the structure of the pentachlorocyclopentenone performed in this Laboratory has substantiated the proposed structure. It was assumed previously[7] that 2,3,4,4,5-pentachloro-2-cyclopentenone could be derived only from the conjugated hexachloroketone, apparently because (a) it was considered improbable that rearrangement might occur under similar treatment of the unconjugated hexachloroketone and (b) reduction of the hexachloroketone melting at 92° gave a compound $C_5H_2Cl_4O$ of unknown structure. Since this compound is now shown to be a hydrate of IV, rearrangement must have occurred upon reduction of the unconjugated ketone. Consequently, due to the lack of knowledge concerning the mechanisms of reduction and rearrangement of the unconjugated isomer, either hexachloroketone might have formed 2,3,4,4,5-pentachloro-2-cyclopentenone.

Based upon the data presented herein and further interpretation of published information, it seems probable that the ketone melting at 28° has the structure shown as compound VIII and that its isomer melting at 92° has the structure IX. It was known[12] that cleavage of the hexachloroketone melting at 28° produces a high yield of only one product, a pentachloropentadienoic acid (m.p. 124–125°), whereas cleavage of the isomeric ketone melting at 92° produces an isomeric acid (m.p. 96°) contaminated with a small quantity of the higher melting acid. Furthermore, separation of the two isomeric acids has been accomplished only by microscopic techniques. Investigations in this Laboratory show that pure pentachloropentadienoic acid (m.p. 124–125°) can be obtained in high yield by (a) treatment of octachlorocyclopentene with sodium methoxide to form a ketal of hexachlorocyclopentenone, (b) hydrolysis of the ketal to a hexachlorocyclopentenone, and (c) cleavage of the ketone with alkali to form the acid. The enhanced reactivity of chlorine atoms in a position allylic to a double bond is well known, and is used to establish the structure of the ketal as 1,2,4,4,5,5 - hexachloro - 3,3 - dimethoxycyclopentene. Hydrolysis of the ketal to form hexachloro-2-cyclopentenone may be readily explained. On the other hand, hexachloro-3-cyclopentenone could have been formed only through a rearrangement. Consideration of the equilibrium mixtures[10,11] of the two ketones at various temperatures shows that if a rearrangement had occurred upon hydrolysis of the ketal, the product would have been a mixture of the two ketones containing at least 5% of the isomer melting at 92°. Since the ketone melting at 28° was the only product, a rearrangement could not have taken place. Further evidence supporting structure VIII as that of the ketone melting at 28° is obtained by an interpretation of the results of Zincke and co-workers.[13,14,15,16] Whereas ammonia converted the higher melting ketone to an amide of a pentachloropentadienoic acid, the other ketone was converted to a pentachloro-3-iminocyclopentanone which was believed to be either 2,4,4,5,5-pentachloro-3-iminocyclopentanone or 2,2,4,5,5-pentachloro-3-iminocyclopentanone. The action of basic reagents on the lower melting ketone proceeds by two distinct modes of attack. Cleavage occurs by the action of aqueous potassium hydroxide to produce a pentachloropentadienoic acid. Addition to the conjugated system occurs by the action of both ammonia and aniline resulting in the ultimate formation of pentachloro-3-iminocyclopentanones. On the other hand, the higher melting ketone does not show the properties of a conjugated system, since both aqueous alkali and ammonia convert it to straight chain derivatives, while aniline reacts with it only on long standing to form an amorphous material.

Prins[3] reported the preparation of a pentachlorocyclopentenone (m.p. 82–83°) by the action of sulfuric acid on hexachlorocyclopentadiene at 100–105°, "the lowest temperature at which reaction occurs." Under these conditions, or at

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(8) T. Zincke and K. W. Kuster, *Ber.*, **21**, 2719 (1888).

(9) (a) T. Zincke and F. W. Kuster, *ibid.*, **22**, 486 (1899); (b) **23**, 820, 2200 (1890); (c) **26**, 2104 (1893).

(10) F. W. Kuster, *Z. physik. Chem.*, **18**, 161 (1895).

(11) H. van Brederode, *Rec. trav. chim.*, **65**, 174 (1946).

(12) T. Zincke and F. W. Kuster, *Ber.*, **26**, 2111 (1893).

(13) T. Zincke and F. Kuster, *Ber.*, **21**, 2728 (1888); **22**, 494 (1889); **23**, 2222 (1890); **26**, 2107 and 2116 (1893).

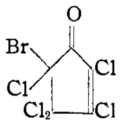
(14) T. Zincke, *ibid.*, **23**, 2208 (1890); **25**, 2230 (1892); **27**, 3364 (1894); **28**, 1644 (1895).

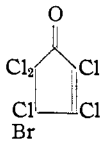
(15) T. Zincke and A. Rohde, *Ann.*, **299**, 367 (1897).

(16) T. Zincke and O. Fuchs, *Ber.*, **26**, 1680 (1893).

higher temperatures, the main product was 3,4,5-trichloro-3-cyclopentene-1,2-dione. It has been shown in this Laboratory that a compound C_5HCl_5O (m.p. 82-83°) (X) can be obtained in 78% yield by performing the reaction at 80°. Both pentachlorocyclopentenones are identical to those obtained[7] by the reduction of VIII.

During the course of the identification of the pentachlorocyclopentenone, attempts were made to replace the hydrogen atom by a halogen atom. Although chlorination was not successful, bromination occurred readily to form a compound C_5BrCl_5O (m.p. 3-4°). The identification of the bromo derivative as 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone (XI) and the reduction of the bromoketone to the original pentachloroketone provides evidence useful in establishing the structure of the pentachloroketone.


XI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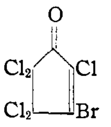
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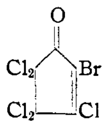
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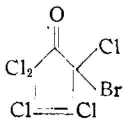
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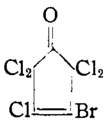
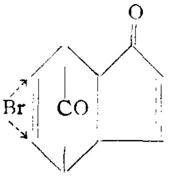
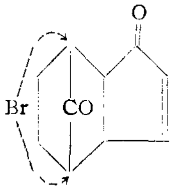
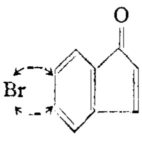
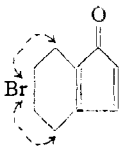

XIE

Of the six possible bromopentachlorocyclopentenones (XI-XIE), structures XIB and XIC were readily eliminated, since treatment of the bromoketone with potassium iodide in acetone solution formed hexachloroindone (V). Structures XIB and XIC would have formed the intermediates XVI and XVII, in which a bromine atom is attached to either position 5 or 6 and 4 or 7, as indicated. The elimination of COX_2 from these intermediates would have formed bromoindone derivatives, represented by structures XVIII and XIX. The reduction of the bromoketone (XI) to form a stable pentachlorocyclopentenone eliminates structures XID and XIE. Structure XID would be expected to behave similarly to hexachloro-3-cyclopentenone, in which case an unstable intermediate, C_5HCl_5O, would immediately dehydrochlorinate and dimerize to form a hydrate of IV. Structure XIE is likewise improbable, since reduction with stannous chloride should form a bromocyclopentenone or the dimer of a tetrahalocyclopentadienone. Structure XIA, as well as XIB, XIC, and XIE was eliminated by cleavage of the bromoketone with aqueous alkali to form a bromotetrachloropentadienoic acid (XII), in which the bromine atom was shown to be on the terminal carbon atom. The salt solution obtained after removal of the acid was free of bromide ion. The bromo acid was identified by its synthesis from tetrachloro-5,5-dimethoxycyclopentadiene (II), involving (a) addition of bromine, (b) hydrolysis of the dibromoketal to a dibromotetrachlorocyclopentenone (XIIIA) or (XIIIB), and (c) cleavage of the dibromoketone with alkali. Irrespective of the structure of the dibromoketone, the resulting bromo acid, $C_4BrCl_4CO_2H$, must be 5-bromo-2,3,4,5-tetrachloropentadienoic acid. Since it is identical to the acid obtained by cleavage of the bromopentachlorocyclopentenone, only structure XI readily accounts for all the experimental results.


XVI


XVII


XVIII


XIX

The reduction of hexachloro-2-cyclopentenone with stannous chloride to form a pentachlorocyclopentenone might be initiated at the carbonyl group, or at positions 4 or 5. Possible attack at the carbon to carbon double bond necessitates a consideration of allylic shifts involving carbon atoms 2, 3, and 4. On the other hand, the reduction of 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone to a pentachlorocyclopentenone could conceivably occur only at the carbonyl group or at position 5. The replacement of the bromine atom by a hydrogen atom is not concerned with the position allylic to the carbon to carbon double bond, and there is no reason to suspect an allylic shift involving carbon atoms 2, 3, and 4. Consequently, whether the reduction involves direct replacement of the bromine atom by a hydrogen atom, or conversion of the carbonyl group to an alcohol followed by dehydrobromination and ketolization, the only possible product is 2,3,4,4,5-pentachloro-2-cyclopentenone (X).

It is interesting to note that the reaction of hexachlorocyclopentadiene with sulfuric acid produces 2,3,4,4,5-pentachloro-2-cyclopentenone, whereas fluorosulfonic acid produces octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione, and chlorosulfonic acid produces a compound having the molecular formula $C_{10}H_2SCl_{12}O_3$, the identification of which is in progress.

Experimental

Materials.—The hexachlorocyclopentadiene used in this investigation was supplied by the Hooker Electrochemical Company. Other reagents were obtained from the usual chemical supply houses.

1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene.—A solution containing 684 g. (12.2 moles) of potassium hydroxide dissolved in 3 liters of methanol was added to a

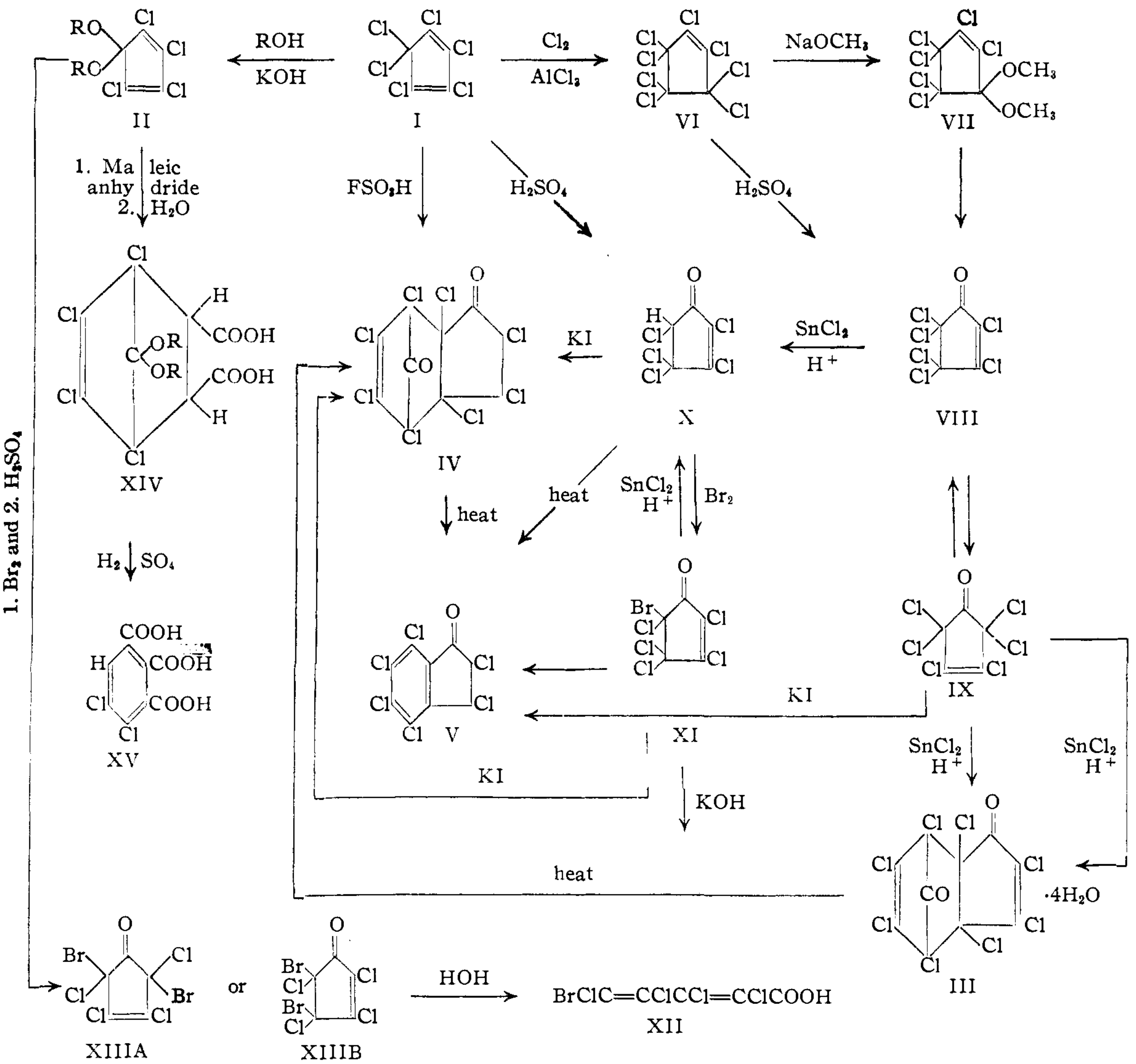


Fig. 1.

solution of 1270 g. (4.7 moles) of hexachlorocyclopentadiene in 4 liters of methanol during a period of four hours. The temperature increased from 48° at the beginning of the addition to 60° at the end. After dilution with water, the organic layer was separated, washed with water, dried, distilled, and rectified. There was obtained 841 g. (3.2 moles) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, a yellow liquid having a sweet odor and the following physical properties: b. p. (11 mm.) 108–110°, d^{20}_4 1.5010, n^{20}_{D} 1.5288.

Anal. Calcd. for $C_7H_6Cl_4O_2$: Cl, 53.8. Found: Cl, 53.8.

1,2,3,4-Tetrachloro-5,5-diethoxycyclopentadiene.—This acetal, b. p. (5 mm.) 101–103°, d^{20}_4 1.3932, and n^{20}_{D} 1.5063, was prepared from hexachlorocyclopentadiene in a manner similar to that described for the dimethoxy derivative using ethanol as a solvent and reactant in place of methanol.

Anal. Calcd. for $C_9H_{10}Cl_4O_2$: Cl, 48.7; mol. wt., 292. Found: Cl, 49.2; mol. wt. (cryoscopic in benzene), 287.

1,2,3,4,11,12,13,14-Octachloro-6,9,15,18-tetraoxadispiro(4.4.4.4)-1,3,11,13-octadecatetraene.—Hexachlorocyclopentadiene (540 g., 2.0 moles) was added to a solution of potassium hydroxide (600 g., 10.7 moles) in ethylene glycol (750 g., 12.1 moles) at 50–60° during a period of two hours. After cooling, the reaction mixture was diluted with water and the organic layer separated and dissolved in petroleum ether. Upon cooling in a bath of Dry Ice and trichloroethylene, fine white needle-like crystals separated. Recrystallization of the solid from a mixture of acetone and benzene produced 63 g. of the octadecatetraene, m. p. 279–280°.

Anal. Calcd. for $C_{14}H_8Cl_8O_4$: Cl, 54.2; mol. wt., 524. Found: Cl, 54.1; mol. wt. (Rast), 511, 518.

1,4,5,6-Tetrachloro-7,7-dimethoxybicyclo(2.2.1)-5-heptene-2,3-dicarboxylic Acid and Anhydride.—A solution containing 53 g. of tetrachloro-5,5-dimethoxycyclopentadiene, 19 g. of maleic anhydride, and 300 ml. of xylene was refluxed for 1.25 hours. During this period, the pale yellow solution became orange and a solid crystallized. The solvent was removed by steam distillation. Upon cooling, tan crystals separated from the water and collected on the orange residue. After filtration, the solid product was washed repeatedly with petroleum ether (90–100°) at room temperature. The resulting white product (62 g.) was recrystallized from water to produce 1,4,5,6-tetrachloro-7,7-dimethoxybicyclo(2.2.1)-5-heptene-2,3-dicarboxylic acid, m. p. 196–197°.

Anal. Calcd. for $C_{11}H_{10}Cl_4O_6$: Cl, 37.4; neut. equiv., 190. Found: Cl, 38.0; neut. equiv., 192.

The dibasic acid (14 g.) was heated at 220–225° until the evolution of gases ceased. The product was cooled, extracted with hot benzene, filtered, and recrystallized from benzene to obtain the anhydride, m. p. 192°.

Anal. Calcd. for $C_{11}H_8Cl_4O_5$: Cl, 39.2; neut, equiv. (in methanol), 362. Found: Cl, 39.7; neut. equiv., 360.

4,5-Dichlorobenzene-1,2,3-tricarboxylic acid.—1,4,5,6-Tetrachloro-7,7-dimethoxybicyclo(2.2.1)-5-heptene-2,3-dicarboxylic acid (14 g.) was heated with concentrated sulfuric acid (150 g.) at 90° for twenty minutes. Upon cooling the resulting solution, crystals of 4,5-dichlorobenzene-1,2,3-tricarboxylic acid anhydride crystallized. The anhydride was filtered, dissolved in water, extracted with ether, and recrystallized from an ether–benzene mixture to produce 4 g. of 4,5-dichlorobenzene-1,2,3-tricarboxylic acid, m. p. 124–126°.

Anal. Calcd. for $C_9H_4Cl_2O_6$: Cl, 25.4; neut. equiv., 93. Found: Cl, 25.8; neut. equiv., 95.

Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. Method A.—1,2,3,4-Tetrachloro-5,5-diethoxycyclopentadiene (11 g.) was added slowly to 45 g. of concentrated sulfuric acid at 0–5°. Immediately upon the addition of each drop of the acetal, a red color formed which disappeared with the simultaneous precipitation of a white solid. The mixture was poured onto cracked ice and the solid was washed repeatedly with water and "dried" by exposure to the atmosphere. There was obtained 8.9 g. of a hydrate of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. This material melted with decomposition at 157–163°.

Anal. Calcd. for $C_{10}Cl_8O_2 \cdot 2H_2O$: Cl, 60.2; mol. wt., 462. Found: Cl, 59.2; mol. wt. (cryoscopic in nitrobenzene), 455.

A hydrate of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione was also obtained by the reduction of hexachloro-3-cyclopentenone with stannous chloride as described by Zincke,[5] who reported the product to have the formula $C_5H_2Cl_4O_2$. The hydrate was converted to the tetrahydrate by recrystallizing from aqueous acetic acid. The tetrahydrate was converted to the anhydrous material by recrystallizing from petroleum ether as well as by heating to constant weight at 90–95° at 20 mm.

Anal. Calcd. for $C_{10}Cl_8O_2 \cdot 4H_2O$: Cl, 55.9; mol. wt., 508. Found: Cl, 55.9; mol. wt. (cryoscopic in glacial acetic acid), 509, 482, 508.

Anal. Calcd. for $C_{10}Cl_8O_2$: Cl, 65.2. Found: Cl, 65.2.

Method B.—A mixture containing 30 g. of potassium iodide, 27 g. (0.11 mole) of 2,3,4,4,5-pentachloro-2-cyclopentenone and 1 liter of acetone was refluxed for thirty minutes, cooled, and poured into water. There was an immediate precipitation of a red solid followed by the separation of a flocculent orange solid. Separation by decantation gave 4 g. of hexachloroindone, orange in color, and a red solid which was washed with aqueous potassium iodide and water to remove the color. Recrystallization from petroleum ether (90–100°) gave 19 g. of anhydrous octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. The yields were 11 and 88%, respectively.

Method C.—Fluorosulfonic acid (200 g., 2.0 moles) was added to hexachlorocyclopentadiene (544 g., 2.0 moles) at 120° during a period of twenty-five minutes. After addition of the fluorosulfonic acid was completed, the mixture was heated at 80–100° with vigorous stirring for one and one-fourth hours. The orange-red reaction mixture was poured onto cracked ice and the organic layer separated and washed with water. The semi-solid product was filtered and the solid recrystallized from petroleum ether (90–100°). There was obtained 146 g. of octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.

Octachlorocyclopentene.—Chlorine was bubbled rapidly into a stirred mixture of 2580 g. (9.49 moles) of hexachlorocyclopentadiene and 40 g. of anhydrous aluminum chloride. The temperature of the reaction mixture was maintained at 40–45° by absorbing the heat of the rapidly occurring exothermic reaction in an ice–water-bath. The mixture was washed with warm water and then purified by crystallization from ethanol. The purified product weighed 3245 g. (9.46 moles) and melted at 39°.

Anal. Calcd. for C_5Cl_8: Cl, 82.6. Found: Cl, 82.3.

Hexachloro-2-cyclopentenone.—A mixture containing 1832 g. (5.3 moles) of octachlorocyclopentene and 2600 g. of concentrated sulfuric acid was heated with vigorous stirring for seven hours at 105°. After cooling to 25°, the pale yellow upper layer was separated, washed with water and recrystallized twice from *n*-pentane. There was obtained 1138 g. (3.9 moles) of hexachloro-2-cyclopentenone, m. p. 28°. This product was converted to hexachloro-3-cyclopentenone (m. p. 92°) and to pentachloropentadienoic acid (m. p. 124.5–125° cor.).[8]

Pentachloropentadienoic Acid.—Sixty-seven grams of sodium (2.9 moles) was added to 1.5 liters of methanol. The solution was added to a suspension of 548 g. (1.6 moles) of octachlorocyclopentene in 2 liters of methanol at 45–50° during a three and one-half-hour period. Water was added to the reaction mixture and the solid which precipitated was separated and recrystallized from pentane. A 95-g. portion of a crude product was stirred with concentrated sulfuric acid at 45° for ten minutes. The sulfuric acid mixture was poured onto cracked ice, the resulting liquid was washed with water, and then it was added to a solution of 50 g. of potassium hydroxide in 400 g. of water at 25°. After stirring for ten minutes, the mixture was filtered to obtain 23 g. of unreacted octachlorocyclopentene. The filtrate was acidified with dilute hydrochloric acid. The pentachloropentadienoic acid, which precipitated, melted at 118–120°. This acid was readily purified by recrystallizing from a mixture of carbon tetrachloride and pentane. After two recrystallizations, the acid melted at 124.5–125° (cor.). This material was shown by a method of mixed melting points to be identical with pentachloropentadienoic acid obtained by cleavage of hexachloro-2-cyclopentenone.

2,3,4,4,5-Pentachloro-2-cyclopentenone. Method A.—A mixture of 814 g. (3.0 moles) of hexachlorocyclopentadiene and 1600 g. of concentrated sulfuric acid was heated with vigorous stirring at 80° until the solution was complete. This required eleven hours. A portion (790 ml.) of the homogeneous reaction mixture (total volume 1270 ml.) was poured onto cracked ice and the resulting solid was separated by filtration. The crude material was purified by recrystallization from petroleum ether (90–100°). There was obtained 372 g. (1.5 moles) of 2,3,4,4,5-pentachloro-2-cyclopentenone, m. p. 82–83°, yield 78%. This material did not depress the melting point of the compound C_5HCl_5O prepared previously.[7]

Anal. Calcd. for C_5HCl_5O: Cl, 69.7; mol. wt., 254. Found: Cl, 69.6; mol. wt. (cryoscopic in benzene), 257.

Method B.—Thirty-one grams (0.14 mole) of stannous chloride dihydrate was dissolved in a mixture of 62 g. of glacial acetic acid and 150 g. of concentrated hydrochloric acid. The resulting solution was added to a mixture of 30 g. (0.9 mole) of 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone in 300 g. of glacial acetic acid at 10–15° during a period of twenty minutes. The reaction mixture was diluted with water and the solid material which separated was recrystallized from a pentane-carbon tetrachloride mixture. Eighteen grams (0.07 mole) of 2,3,4,4,5-pentachloro-2-cyclopentenone, m. p. 82–83°, was obtained in a yield of 78%. Attempts to convert this material to hexachlorocyclopentenone by reaction with liquid chlorine at 30° and by reaction with gaseous chlorine at 70° (carbon tetrachloride solution) were unsuccessful.

5-Bromo-2,3,4,4,5-pentachloro-2-cyclopentenone.—Two hundred and ten grams of bromine (1.3 moles) and 275 g. (1.08 moles) of 2,3,4,4,5-pentachloro-2-cyclopentenone were added to 1.5 liters of carbon tetrachloride. The mixture was allowed to stand at 25° for twenty-two hours in the presence of light from two 40-w. 360 B. L. lamps. Carbon tetrachloride, bromine, and dissolved gases were removed by heating on a steam-bath under reduced pressure. The liquid product which remained was crystallized from petroleum ether (90–100°) to obtain 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone (221 g., 0.66 mole), m. p. 3–4°, and 102 g. of starting material. The conversion and yield were 62 and 98%, respectively.

Anal. Calcd. for C_5BrCl_5O: total halogen (calculated chloride, grav. anal.) 63.9. Found: total halogen, 62.8.

Dibromotetrachlorocyclopentenone.—A mixture containing 150 g. (0.94 mole) of bromine, 200 g. (0.73 mole) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, and 500 g. of carbon tetrachloride was allowed to stand at room temperature for fifteen hours. The mixture was then heated on a steam-bath to remove excess bromine and carbon tetrachloride. The viscous liquid which remained was added slowly to 800 g. of concentrated sulfuric acid at 30°. The mixture was poured onto cracked ice and the organic product was crystallized from pentane. After repeated recrystallizations, a white solid melting at 156–157° was obtained. The odor of bromine was readily detected in the pure solid, and upon warming with water bromine vapors were evolved.

Anal. Calcd. for $C_5Br_2Cl_4O$: total halogen (calculated as chloride), 56.4. Found: total halogen, 56.4.

5-Bromo-2,3,4,5-tetrachloropentadienoic Acid. Method A.—Cleavage of 14 g. (0.042 mole) of 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone was accomplished by adding the ketone, with stirring, to 30 g. of potassium hydroxide in 270 ml. of water at 25°. The reaction mixture was diluted and filtered. A tan solid precipitated upon acidification of the filtrate with dilute hydrochloric acid. This solid was recrystallized from carbon tetrachloride to give 6 g. (0.02 mole) of 5 bromo 2,3,4,5-tetrachloropentadienoic acid: white solid, m. p. 118–119°.

Anal. Calcd. for $C_5HBrCl_4O_2$: total halogen (calculated as chloride), 56.4; neut. equiv., 315. Found: total halogen, 56.0; neut. equiv., 317.

Method B.—Excess bromine was added slowly to a few grams of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and the reaction mixture was allowed to stand until it cooled to room temperature. The mixture was dropped into concentrated sulfuric acid at room temperature, poured onto cracked ice, washed with water, and dissolved in 10% aqueous potassium hydroxide solution. After filtration and acidification, a white solid, m. p. 119°, was obtained. It did not depress the melting point of the acid obtained by Method A.

Hexachloroindone,—5-Bromo-2,3,4,4,5-pentachloro-2-cyclopentenone (60 g., 0.18 mole), potassium iodide (70 g., 0.42 mole) and acetone (1 liter) were mixed and refluxed for two and one-half hours. The reaction mixture was then cooled and diluted with water. The orange solid which precipitated was washed with aqueous potassium iodide and recrystallized from acetone to give 25 g. (0.074 mole) of hexachloroindone, m. p. 149°, yield 83%. This product is identical to that obtained by heating octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione with water.

Anal. Calcd. for C_9Cl_6O: Cl, 63.1. Found: Cl, 63.1.

Reaction of Hexachlorocyclopentadiene with Chlorosulfonic Acid.—A mixture of 1000 g. of hexachlorocyclopentadiene (3.68 moles) and 1000 g. (8.62 moles) of chlorosulfonic acid was stirred vigorously for two hours at 90°. Solid began to crystallize from the reaction mixture after one half hour. After cooling in an ice-bath, the thick slurry was filtered through a sintered glass funnel and the solid was washed with water, refiltered, and washed with petroleum ether (90–100°) saturated with the final product. The resulting product, 987 g., m. p. 143–147°, was a white, crystalline solid. Recrystallization from petroleum ether-benzene increased the melting point to 146–147°.

Anal. Calcd. for $C_{10}H_2Cl_{12}O_3S$: C, 19.11; H, 0.32; Cl, 67.8; S, 5.09; mol. wt., 627. Found: C, 19.02, 19.10; H, 0.26, 0.25; Cl, 67.6, 67.8, 67.8; S, 5.05, 5.12; mol. wt. (ebull. in benzene), 611, 639.

Distillation of the original filtrate produced 674 g. (5.81 moles) of chlorosulfonic acid and 130 g. of tar, whereas decomposition of the filtrate by dropping onto ice produced 97.5 g. of a mixture of hexachlorocyclopentadiene and the sulfur-containing product. The conversion and yield are 86 and 95%, respectively. The structure of the product is being investigated.

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Summary

Hexachlorocyclopentadiene reacts with alcoholic alkali to form the ketals, tetrachloro-5,5-dialkoxycyclopentadiene. The ketals react with dienophiles to form Diels–Alder adducts and undergo hydrolysis to give octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione. The tricyclic ketone was also prepared by treatment of 2,3,4,4,5-pentachloro-2-cyclopentenone and 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone with potassium iodide in acetone solution, as well as by the reaction of hexachlorocyclopentadiene with fluorosulfonic acid.

The reaction of hexachlorocyclopentadiene with sulfuric acid may be controlled to produce a 78% yield of 2,3,4,4,5-pentachloro-2-cyclopentenone, which was identified by bromination to 5-bromo-2,3,4,4,5-pentachloro-2-cyclopentenone, reduction of the bromoketone to the same pentachloroketone, and conversion of the pentachloroketone to octachlorotetrahydromethanoindenedione. Identification of the bromoketone was based primarily upon cleavage to form 5-bromo-2,3,4,5-tetrachloropentadienoic acid, the structure of which was demonstrated by synthesis involving (a) addition of bromine to tetrachloro-5,5-dimethoxycyclopentadiene, (b) hydrolysis of the acetal linkage to form a dibromotetrachlorocyclopentenone, and (c) cleavage of the dibromoketone with alkali.

Octachlorocyclopentene, prepared by the catalytic addition of chlorine to hexachlorocyclopentadiene, was found to produce hexachloro-2-cyclopentenone by reaction with sulfuric acid. Strong chemical evidence is presented in regard to the aged controversy as to the structure of the isomeric hexachlorocyclopentenones (m. p. 28° and 92°). The former is believed to be hexachloro-2-cyclopentenone; the latter, hexachloro-3-cyclopentenone.

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