solvents. The infrared spectra were obtained on a Perkin-Elmer model 21 recording infrared spectrophotometer using carbon tetrachloride and chloroform as solvents.

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[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

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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,[3,4] with granulated zinc,[4] with copper-bronze in methanol,[5] or with cuprous chloride at 60°.[6] It is obtained by thermal isomerization of C_6Cl_8 (liquid),[4] C_6Cl_8, m.p. 72°,[4] C_6Cl_8, m.p. 93°,[7] and C_6Cl_8, m.p. 94°,[7] and by the action of fuming nitric acid on C_6Cl_8 (liquid).[8] The compound is also formed by pyrolysis of octachloro-1,3-pentadiene,[9] treating with aluminum,[10] dehydrochlorination of C_6HCl_9 with potassium hydroxide in ethanol,[11] and by condensing trichloroethylene with chloroform and aluminum chloride.[11]

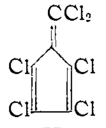
In the present investigation, I has been prepared by refluxing a mixture of hexachlorocyclopentadiene and hexachloropropene. When the tetrachloroethylene, which is formed as a by-product (equations 1 and 3), is allowed to accumulate in the reaction mixture, the reaction temperature drops and only a small 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[9] (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.[5,9] The following reaction sequence accounts for the observed results

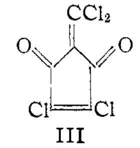
$$C_5Cl_6 + C_3Cl_6 \longrightarrow C_6Cl_8 + C_2Cl_4 \qquad (1)$$

$$C_6Cl_8 \longrightarrow C_6Cl_6 + Cl_2 \qquad (2)$$

$$C_3Cl_6 + Cl_2 \longrightarrow CCl_4 + C_2Cl_4 \qquad (3)$$

The structure of I was first investigated by Prins in 1912.[12] Two early open-chain structures[5,13] were discarded in favor of cyclic formulas based on Raman spectra,[14] interconversion studies[15] and a new synthesis from hexachlorocyclopentadiene.[7] A five-membered ring structure was confirmed by dechlorination of I to the red hexachlorofulvene (II) from which it is regenerated by chlorination.[4] 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.[4,16] The structure of III was established as 1,2-dichloro-4-(dichloromethylene)-cyclopentene-3,5-dione independently by Roedig[4] and by Rakoff[1] by the alkaline hydrolysis of the substance, which yields chloroacetylene[1,4,8] and dichloromaleic acid.[1,4] 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.


II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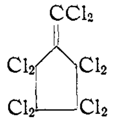
It has been possible to assign a structure to I by comparison of its ultraviolet absorption spectrum and the spectra of the chlorination products IV and V.[4] All three substances have a broad maximum at 223–233 mμ in ethanol corresponding to the ab-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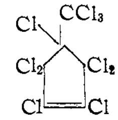
V

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[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.

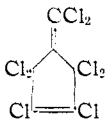
(13) H. J. Prins, *Rec. trav. chim.*, **51**, 1065 (1932).

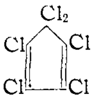
(14) H. V. Brederode, H. Gerding and H. J. Prins, *ibid.*, **65**, 185 (1946).

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

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

sorption band in octachlorocyclopentene (λ_{max} 228 mμ, log ϵ 4.00) but differing from the spectrum of hexachlorocyclopentadiene.[17] The molar absorptivities at the maxima for IV and V are 9060 and 9080, respectively, while the molar absorptivity at 223 mμ for I is 19,400. The data are in agreement with a structure in which the double bonds absorb as isolated rather than conjugated chromophores. Compound I is therefore 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene. Conjugated chlorocarbons


I


VI

show typical bathochromic shifts, as is the case for hexachlorocyclopentadiene (VI) (λ_{max}^{EtOH} 323 mμ, log ϵ 3.17)[15] and the isomer C_6Cl_8, m.p. 91–92° (λ_{max}^{EtOH} 310 mμ, log ϵ 4.19), (VII).

The infrared absorption spectra confirm the structural assignments. Thus, the C=C stretching frequencies for hexachlorocyclopentadiene occur at 6.24 and 6.36 μ and those for VII at 6.19, 6.27 μ, while the corresponding frequencies in I are found at 6.05 and 6.20 μ.

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Experimental

Materials.—Hexachlorocyclopentadiene was obtained through the courtesy of the Hooker Electrochemical Company. Hexachloropropene is available from Halogen Chemicals, Inc., and from Columbia Organic Chemicals Co., Inc.

1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)-cyclopentene (I).—Hexachloropropene (311 g., 1.25 moles) and hexachlorocyclopentadiene (342 g., 1.25 moles) were placed in a one-liter two-necked pot of a two foot rectifying column packed with Pyrex helices. Reaction temperatures were measured by a thermometer immersed in the liquid. The column temperature was maintained at about 140° throughout the entire run. The reactants were heated and the liquid temperature was 218° when boiling commenced. Within two to three hours, tetrachloroethylene refluxed in the column head. As the tetrachloroethylene was removed, the temperature in the pot increased. To avoid the formation of excessive amounts of hexachlorobenzene, heating was discontinued when the temperature of the reactants reached 240°. During the run, 206 g. of liquid distilled. The reaction mixture was cooled, filtered and the precipitate was washed with ice-cold petroleum ether. The solid (230 g.), which was pink in color, was crystallized from petroleum ether (b.p. 90–100°) to give colorless 1,2,-3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene, m. p. 183–184°.

Anal. Calcd. for C_6Cl_8: C, 20.2; Cl, 79.8. Found: C, 20.4, 20.5; Cl, 79.5.

The distillate was rectified to yield 15.5 g. (0.1 mole) of carbon tetrachloride and 164.5 g. (0.98 mole) of tetrachloroethylene. From the mother liquors, 11.5 g. (0.046 mole) of hexachloropropene and 67 g. (0.245 mole) of hexachlorocyclopentadiene were recovered. The conversion to 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene was 51% while the yield, based upon hexachlorocyclopentadiene utilized, was 64%.

1,2-Dichloro-4-(dichloromethylene)-cyclopentene-3,5-dione (II).—A mixture of 40 g. (0.11 mole) of I and concentrated sulfuric acid (250 ml.), in a one-liter three-necked flask, was heated on a steam-bath with stirring for 2 hr. Hydrogen chloride was evolved. As the solution cooled to room temperature, a yellow solid precipitated. The cooled mixture was poured onto ice and the solid, obtained by filtration, was recrystallized from petroleum ether (b.p. 90–100°) to yield 13 g. (47%) of II, shiny white plates, m.p. 231–232°, λ_{max} 248 mμ (log ϵ 4.35) in heptane (the spectrum has four fine structure bands of lesser intensity at 255 mμ (log ϵ 4.34), 270 mμ (log ϵ 4.29), 280 mμ (log ϵ 4.18), 295 mμ (log ϵ 3.84)), λ_{max} (C=O) 5.80 μ, λ_{max} (C=C) 6.13 μ.

Anal. Calcd. for $C_6Cl_4O_2$: C, 29.2; Cl, 57.7. Found: C, 29.0, 29.3; Cl, 57.3.

Action of Potassium Hydroxide Solution on II.—Three grams of II was added slowly to a solution of 5 g. of potassium hydroxide in 50 ml. of water. Small flames were observed and a black soot formed due to the explosions of the liberated monochloroacetylene.[2] After the reaction had ceased, the liquid was filtered, acidified and continuously extracted with ether for 16 hr. On evaporation of the ether, a red oil remained which crystallized on boiling with petroleum ether (b.p. 30–60°). The crude material was sublimed under reduced pressure to yield a white solid, m.p. 119–120°, the melting point of dichloromaleic anhydride.[18]

The product melting at 119–120° was treated with anthracene according to the method of Diels and Thiele.[19] Petroleum ether (b.p. 90–100°) was employed as the recrystallization solvent rather than the recommended mixture of acetic anhydride and acetonitrile. The colorless solid melted at 233–234°, the reported melting point of anthracene-9,10-endodichlorosuccinic anhydride.

Chlorination of I.—A mixture of 1,2,3,3,4,4-hexachloro-4-(dichloromethylene)-cyclopentene (8 g.) and liquid chlorine (10 ml.) was sealed in a Carius tube and illuminated with a blue fluorescent light for 10 days.[4] The excess chlorine was evaporated and the remaining oil was crystallized from petroleum ether. The solid fractions, which were recrystallized from methanol, weighed 1.0 g. (10%) and melted at 130.5–131.5°,[4,15] (V), λ_{max}^{EtOH} 233 mμ (log ϵ 3.96), λ_{max} (C=C) 6.19 μ. The mother liquors were evaporated and the residual oil was crystallized from methanol to give 6 g. (63%) of the isomer melting at 36.8–37.5°,[4] (IV), λ_{max}^{EtOH} 233 mμ (log ϵ 3.96), λ_{max} (C=C) 6.27 μ.

The Reaction of I with Nitric Acid.—A mixture of 53 g. of I, m.p. 178–183°, 45 ml. of fuming nitric acid and a trace of selenium metal was warmed on a steam-cone. After the vigorous reaction subsided, the mixture was evaporated to dryness on a steam-cone. Concentrated hydrochloric acid (30 ml.) was added and the mixture was again evaporated to dryness. The residue was crystallized from benzene and gave 15 g. (41%) of colorless diketone (II), m.p. 224–232° which melted at 232–233° after one recrystallization from benzene. The mother liquors were evaporated to dryness and the residue was recrystallized from petroleum ether (b.p. 60–70°) to give 16 g. (36%) of monoketone, m.p. 70–89°. After recrystallization from the same solvent and vacuum sublimation the pure ketone melted at 84–85.5°, $\lambda_{max_1}^{heptane}$ 228 mμ (log ϵ 4.18), $\lambda_{max_2}^{heptane}$ 278 mμ (log ϵ 4.21), $\lambda_{max_3}^{heptane}$ 327 mμ (log ϵ 1.41), $\lambda_{max_4}^{heptane}$ 340 mμ (log ϵ 1.42), $\lambda_{max_5}^{heptane}$ 353 mμ (log ϵ 1.35), $\lambda_{max_6}^{heptane}$ 370 mμ (log ϵ 1.19), λ_{max} (C=O) 5.77 μ, λ_{max} (C=C) 6.22, 6.32 μ.

When the hydrolysis reaction was carried out at 100° with 124 g. of hexachloro-4-(dichloromethylene)-cyclopentene, 140 ml. of fuming nitric acid, and a trace of selenium, the yield of diketone was 85%.

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[17] E. T. McBee, C. W. Roberts and J. D. Idol, Jr., *Proc. Indiana Acad. Sci.*, in press.

[18] T. Zincke and O. Fuchs, *Ann.*, **267**, 20 (1892).

[19] O. Diels and W. E. Thiele, *Ber.*, **71**, 1173 (1938).