[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

New Methods of Preparation and the Chemistry of 1,2-Dichlorocyclopentene-3,5-dione

BY E. T. MCBEE, C. W. ROBERTS AND K. DINBERGS[1]

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New methods are presented for the preparation of 1,2-dichlorocyclopentene-3,5-dione (I), m.p. 163–164°, by acid hydrolysis of methoxy derivatives of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene and by the cleavage of 1,2-dichloro-4-(dichloromethylene)-cyclopentene-3,5-dione with 95% ethanol. The chlorination and bromination products of I were prepared and the correct melting point for 1,2,4,4-tetrachlorocyclopentene-3,5-dione established.

Discussion

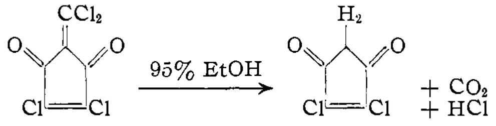
The preparation of 1,2-dichlorocyclopentene-3,5-dione (I), m.p. 163–164°, was first reported in 1898 by the tin–hydrochloric acid reduction of amines obtained from the reaction of ammonia with hexachloro-2-cyclopentenone, m.p. 28°[2]. The compound has been prepared also by the action of sulfuric acid on the chlorination or bromination products of 1,2,3,4-tetrachlorocyclopentadiene.[3] This investigation presents new methods for the preparation of I and certain aspects of its chemistry.

The attempted preparation of a tetramethoxy derivative of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene (II) by replacement of the four allylic chlorines using methanolic potassium hydroxide gave unexpected results. Two products were obtained; a higher melting compound, III, having the composition $C_{10}H_{13}Cl_3O_4$, m.p. 115.5–116.5°, and a lower melting product, IV, of undetermined composition, m.p. 78–79°.[4]

The formula $C_6HCl_3(OCH_3)_4$ of III indicated that besides nucleophilic displacement reactions, a reduction had occurred, one chlorine atom being replaced by hydrogen. Compound III forms white prisms from petroleum ether, is inert toward hot alcoholic silver nitrate solution, and decomposes if exposed for several weeks to the atmosphere. It can be kept unchanged in a sealed tube. The infrared spectrum of III shows two types of carbon-hydrogen bands, a medium strength band at 3.42 and a weak band at 3.56 μ. Two bands (6.16 and 6.28 μ) are found in the carbon–carbon double bond region and the ether linkages are indicated by a strong band at 9.05 μ. The ultraviolet spectrum (λ_{max} 300 mμ, log ε 3.37) of III indicates conjugation.[5]

The hydrolysis of III with concentrated sulfuric acid at 5–9° or with hydrochloric acid in boiling methanol gave I. That this reaction involved decarboxylation was shown by the fact that carbon dioxide was obtained as by-product. The identity of I was proved by its melting point (163–164°) and analysis. A typical ultraviolet spectrum of a conjugated ketone was obtained, λ_{max} 258 mμ, log ε 4.19 and λ_{max} 328 mμ, log ε 1.63. The infrared spectrum of I shows a strong, broad carbonyl absorption at 5.76 μ and a carbon–carbon double bond frequency at 6.20 μ. Compound I is obtained also by the sulfuric acid hydrolysis of IV at 95°.

The preparation of 1,2-dichloro-4-(dichloromethylene)-cyclopentene-3,5-dione (VI) and 2,3,4,4-tetrachloro-5-(dichloromethylene)-cyclopentene-1-one (VII) by the oxidation of II with nitric acid has been reported.[6] The same publication reports that VI gives a compound of unknown constitution, m.p. 163.5–164°, upon boiling with methanol or ethanol. This reaction was reinvestigated and the structure of the unknown compound determined. The reaction takes place in the following manner



VI I

The identity of I was proved by mixed melting points with a known sample. The infrared spectrum was identical with the spectrum of a known sample of I. The presence of carbon dioxide was shown by bubbling the exit gases through a barium hydroxide solution and by the infrared absorption bands characteristic of carbon dioxide (4.29 and 14.98 μ). The reaction mixture gave a strong test for chlorine with silver nitrate and was acid to litmus. The carbon dioxide formed in the reaction indicates that the dichloromethylene group is hydrolyzed to an acid which subsequently decarboxylates. Several attempts to isolate the acid were unsuccessful. That two adjacent keto groups are necessary to cleave the dichloromethylene group was shown by the fact that VII is stable toward 95% ethanol.

Compound I was chlorinated following the method of Zincke[2] who reported the isolation of perchlorocyclopentane-1,3-dione (VIII), m.p. 70°. In this investigation a different compound was obtained, namely, 2,2,4,5-tetrachlorocyclopentene-1,3-dione (IX) in a 60% yield.

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(1) From a thesis submitted by Kornelijs Dinbergs to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1956.

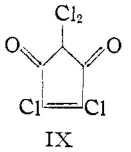
(2) T. Zincke and A. Rohde, *Ann.*, **299**, 367 (1898).

(3) R. K. Meyers, Ph.D. Thesis, Purdue University, 1950.

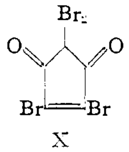
(4) Based on carbon–hydrogen analysis the empirical formula $C_7H_6Cl_4O_2$ could be assigned to the compound but the chlorine analysis did not check with the calculated value.

(5) An attempt to prove the structure of III by hydrolysis with dilute hydrochloric acid at room temperature resulted in partial hydrolysis of the methoxy groups. The product, V, was a white solid, m.p. 35.5–36.5°, b.p. 110° (1–1.5 mm.), having the composition $C_8H_7Cl_3O_3$. The infrared spectrum of V shows the same type of carbon–hydrogen bands (3.44 and 3.58 μ) that III does and a very strong absorption in the ether region (8.5–9.3 μ). Besides these bands a strong carbonyl band is present at 5.88 μ and a strong broad band in the carbon–carbon double bond region with a shoulder at 6.24 μ and a peak at 6.40 μ. These data indicate that only one ketal or acetal has been cleaved. The failure of the compound to give a Tollens test indicates that the free carbonyl group is a ketone. The ultraviolet spectrum of V (λ_{max} 3.18 mμ, log ε 3.52) is very similar to that of III. The compound is inert toward hot alcoholic silver nitrate solution. Definite structures are not assigned for compounds III and V.

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



IX



X

Compound IX forms greenish prisms from petroleum ether, m.p. 65–66.5° and has a strong disagreeable quinone-like odor. The structure of IX is supported by spectral data. The ultraviolet spectrum clearly indicates a conjugated ketone system, $\lambda_{\max_1}$ 219 mμ, log ε 3.81, $\lambda_{\max_2}$ 264 mμ, log ε 4.15, and $\lambda_{\max_3}$ 350 mμ, log ε 1.63. The infrared spectrum shows a strong band in the carbonyl region with three peaks at 5.60, 5.74 and 5.83 μ. There is also a strong band in the carbon–carbon double bond region with a shoulder at 6.24 and a peak at 6.39 μ.

The preparation of IX, m.p. 65°, by heating a perchlorotriketocyclohexene is reported by Zincke.[7] The same investigator in two earlier papers[8,9] described the preparation of the same dione by a different method but reported a higher melting point (75–76°). Since there is no possibility for stereoisomerism in IX, one of the two reported melting points is wrong. The work reported here supports the findings of the later investigation[7] and indicates the correct melting point for IX to be 65–66.5°.[10]

The bromination of I in acetic acid gave 2,2,4,5-tetrabromocyclopentene-1,3-dione (X), m.p. 140–142.5°, the yield being 80%. No bromination could be obtained in refluxing carbon tetrachloride as solvent. The ultraviolet spectrum ($\lambda_{\max}$ 283 mμ, log ε 4.05) indicates conjugation and is very similar to the spectrum of the corresponding chloro compound (IX), showing the expected bathochromic and hypochromic shifts.[11,12] The infrared spectrum has two bands in the carbonyl region; one weak at 5.66 and a strong one at 5.74 μ. A carbon–carbon double bond frequency is present at 6.45 μ. It should be noted here that in the preparation of X only two moles of bromine was used for one mole of X. Since the yield is well over 50% it is assumed that the hydrogen bromide obtained by the bromination of the methylene group acts further as brominating agent on the vinylic chlorines.

Experimental[13]

The Preparation of Methoxy Derivatives, M.p. 115.5–116.5° (III) and M.p. 78–79° (IV).—In a 3-l., 3-necked flask fitted with a reflux condenser, a mercury-sealed stirrer and a separatory funnel was placed a suspension of 178 g. (0.50 mole) of II in 800 ml. of methanol. During one hour 112 g. (2 moles) of potassium hydroxide, dissolved in 600 ml. of methanol, was added to the cooled reaction mixture. After 2 hr. the ice-bath was removed and, after an additional hour, the reaction mixture warmed to 50° for 30 min.; cooling was again applied. During this time the reaction mixture turned brown. After 6 hr. the reaction was stopped and the light brown reaction mixture filtered. The residue contained 130 g. (87%) of potassium chloride and 40 g. of unreacted starting material. The filtrate was poured into 2 l. of water and the resulting precipitate filtered. The crude and moist product amounted to 130 g. This was fractionally recrystallized from petroleum ether (b.p. 60–70°) to give the following fractions: m.p. 104–115° (19 g.), m.p. 92–111° (20 g.), m.p. 60–77° (23 g.), and m.p. 78–125° (12 g.); total, 74 g. After extensive recrystallization from petroleum ether (b.p. 60–70°) compound III was obtained pure, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{10}H_{13}Cl_3O_4$ (III): C, 39.54; H, 4.32; Cl, 35.06. Found: C, 39.58; H, 4.31; Cl, 34.80.

Also compound IV was recrystallized from the same solvent. After numerous recrystallizations the observed melting point was 78–79°.

Anal. Calcd. for $C_7H_6Cl_4O_2$ (IV): C, 31.84; H, 2.29; Cl, 53.73. Found: C, 31.79; H, 2.27; Cl, 51.30.

Preparation of III.—A 3-l., 3-necked flask was fitted with a reflux condenser, a separatory funnel and a stirrer. One hundred and twelve grams (0.31 mole) of II was suspended in 300 ml. of methanol. A solution of 105 g. (1.90 moles) of potassium hydroxide in 300 ml. of methanol was added during 4 hr. with stirring. During the addition the exothermic reaction kept the temperature at about 60°. The total reaction time was 8 hr. The reaction mixture was filtered and the residue suspended in water; this separated part of the product from the inorganic salts. The filtrate was poured into water and the resulting solid was filtered. No starting material was recovered. The yield was 69 g. (73%) of III, m.p. 110–115°.

Hydrolysis of III with Sulfuric Acid.—Ten grams (0.033 mole) of III was placed into a 200-ml., 3-necked flask and 70 ml. of concentrated sulfuric acid added all at once. The reaction mixture was stirred and a stream of nitrogen carried the exit gases through a Dry Ice trap and a barium hydroxide solution. The reaction mixture was kept at about 50° for 30 min. and the same length of time at room temperature. During the reaction time the barium hydroxide solution gradually became cloudy and a precipitate formed. This precipitate was dissolved in dilute hydrochloric acid and no odor of sulfur dioxide could be detected; the precipitate was barium carbonate. The sulfuric acid mixture was filtered and poured on ice. Two and a half grams (50%) of I, m.p. 159–162°, was obtained. After several recrystallizations from ligroin (b.p. 90–100°), the pure compound melted at 163–164°.

Anal. Calcd. for $C_5H_2Cl_2O_2$ (I): C, 36.39; H, 1.22; Cl, 42.97. Found: C, 36.43; H, 1.30; Cl, 42.90.

Gradual addition of III and lower reaction temperatures (5–9°) did not increase the yield of I.

Hydrolysis of III with Hydrochloric Acid in Boiling Methanol.—Compound III upon treatment with 5% hydrochloric acid and methanol gave an oil. This oil (3 ml.) was then boiled with 50 ml. of a 50-50 mixture of concentrated hydrochloric acid and methanol until most of the liquid dissolved. The solution was then poured into water and the resulting precipitate after several recrystallizations from ligroin (b.p. 90–100°) melted at 163–164°.

Hydrolysis of III with Dilute Hydrochloric Acid at Room Temperature.—Fifty grams (0.16 mole) of III, 27 ml. of 1:1 hydrochloric acid and 30 ml. of methanol was placed in a 250-ml. beaker and stirred occasionally for 1.5 hr. until all of the solid had liquefied. The product, a yellow oil, was washed three times with distilled water, dried and weighed; yield of crude product was 39 g. (92%). The oil was fractionated through a 1 × 32 cm. column to give 37 g. of yellow oil, b.p. 105–109° (1 to 1.5 mm.), collected in four fractions. The middle fractions were refractionated to give pure V, water-white oil, b.p. 110° (1–1.5 mm.), n^{20}_{D} 1.5293. The compound can be kept for weeks at room temperature without solidification, but when placed in Dry Ice crystallization can be induced, m.p. 35.5–36.5°.

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[7] T. Zincke and E. Weishaupt, *Ann.*, **437**, 86 (1924).

[8] T. Zincke, *Ber.*, **24**, 912 (1891).

[9] T. Zincke and H. V. Lohr, *ibid.*, **25**, 2219 (1892).

[10] The failure to obtain VIII by the chlorination of I as was described by Zincke[2] may be due to different experimental conditions since Zincke's paper does not give any experimental detail.

[11] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

[12] A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz and C. Djerassi, This Journal, **73**, 3263 (1951).

[13] All melting points are corrected. Microanalysis by Dr. Ching S. Yeh of Purdue University, or by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. The ultraviolet spectra were determined in heptane solutions in concentrations of 1 × 10^{-2} to 1 × 10^{-5} mole per liter with a Cary recording spectrophotometer. The infrared spectra were obtained in carbon tetrachloride or Nujol with a Perkin-Elmer model 21 recording spectrophotometer.

Anal. Calcd. for $C_8H_7Cl_3O_3$ (V): C, 37.32; H, 2.74; Cl, 41.32. Found: C, 37.49; H, 2.91; Cl, 41.21.

Hydrolysis of IV with Sulfuric Acid at 95°.—A 50-ml. flask fitted with a reflux condenser and containing a mixture of 25 ml. of concentrated sulfuric acid and 2.5 g. of IV was placed on a steam-cone and heated for 2.25 hr. The mixture was allowed to stand for 3 hr. and then poured on ice. The precipitated material was filtered and dried, m.p. 158–162°. After several recrystallizations from ligroin (b.p. 90–100°) the melting point was raised to 163–164°. A mixed melting point with a known sample of I showed no depression.

Reaction of VI with 95% Ethanol.—Forty-eight grams (0.19 mole) of VI and 1 l. of 95% ethanol were placed in a 2-l., round-bottomed flask fitted with a reflux condenser. The exit gases after passing through a Dry Ice trap were bubbled into a 7% barium hydroxide solution. A flow of nitrogen was passed constantly through the apparatus. When the ethanol started to boil the solid dissolved slowly, and a precipitate was formed in the barium hydroxide solution. This precipitate was filtered, and upon acidification a colorless and odorless gas was evolved. After all of the solid had dissolved (1.5 hr.) the yellow reaction mixture was poured into water and turned red. Most of the ethanol was removed in a stream of air and this resulted in the precipitation of the product which weighed 13 g. (41%), m.p. 160–163°. Several recrystallizations from ligroin (b.p. 90–100°) and treatment with activated carbon gave pure I, m.p. 163–164°. A mixed melting point with a sample obtained by the sulfuric acid hydrolysis of III showed no depression.

Preparation of IX.—Ten grams (0.060 mole) of I was placed in a 200-ml., round-bottomed flask and 140 ml. of glacial acetic acid added. A slow stream of chlorine was passed through the reaction mixture while the flask was heated on a steam-cone for 7.5 hr. Heating was discontinued and chlorination was continued for one hour while the mixture cooled to room temperature. After most of the solvent was distilled under vacuum the residue was poured onto water and an oil formed which solidified immediately. The product was crystallized from petroleum ether (b.p. 60–70°); first fraction 10 g., m.p. 59–65°; second fraction 1 g., m.p. 55–62°; total yield was 11 g. (60%). After several recrystallizations from the same solvent the pure compound was obtained, m.p. 65–66.5°.

Anal. Calcd. for $C_5Cl_4O_2$ (IX): C, 25.67; H, 0.00; Cl, 60.64. Found: C, 25.78; H, 0.16; Cl, 60.68.

Preparation of X.—In a 200-ml., 3-necked flask fitted with a reflux condenser and a dropping funnel was placed 6 g. (0.036 mole) of I and 50 ml. of glacial acetic acid added. While the flask was heated on a steam-cone a solution of 12 g. (0.075 mole) of bromine in 50 ml. of acetic acid was added during 10 min. The bromine color disappeared immediately. The reaction mixture was heated on a steam-cone for 3 hr., during which time hydrogen halide was evolved. The reaction mixture was then poured into water and 12 g. (82%) of product was obtained, m.p. 125–134°. The product was recrystallized several times from petroleum ether (b.p. 60–70°) and carbon tetrachloride to give a product, yellow needles, m.p. 140–142.5°.[14]

Anal. Calcd. for $C_5Br_4O_2$ (X): C, 14.58; H, 0.00; Br, 77.62. Found: C, 14.80; H, 0.18; Br, 77.02.

When the bromination was carried out with 4 g. of I and 5 g. of bromine in 100 ml. of refluxing carbon tetrachloride for 14 hr., 88% of the starting material was recovered unchanged. No product could be isolated.

Acknowledgment.—The authors wish to thank the Charles H. Viol Memorial Fellowship for support of this work.

WEST LAFAYETTE, INDIANA

[14] Zincke[7] reported m.p. 142–143°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Bromination of 1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)-cyclopentene

BY E. T. MCBEE, C. W. ROBERTS AND K. DINBERGS[1]

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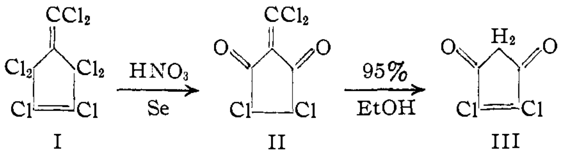
1-Chloro-2,3,3,5,5-pentabromo-4-(dibromomethylene)-cyclopentene, 1,2-dichloro-3,3,5,5-tetrabromo-4-(dibromomethylene)-cyclopentene and 1,2-dichloro-3,3,5,5-tetrabromo-4-(dichloromethylene)-cyclopentene have been prepared from 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene by a halogen exchange reaction with anhydrous aluminum bromide. The structures of the compounds were proved by oxidation to the corresponding 1,2-dihalo-4-(dihalomethylene)-cyclopentene-3,5-diones and subsequent degradation to the 1,2-halocyclopentene-3,5-diones. Ultraviolet and infrared spectra of the compounds were studied.

Discussion

The use of anhydrous aluminum bromide in halogen exchange bromination has been reported by the Dow Chemical Corporation[2] where methylene chloride has been converted to bromochloromethane. The studies reported in this work are concerned with the bromination of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene (I). Since I contains eight replaceable chlorine atoms several products can be obtained depending on the bromination conditions. The results of this investigation show that the halogen exchange occurs without rearrangement or isomerization of the double bonds. The proof of the positions of the halogen atoms was effected by using the same sequence of reactions as was described for the chlorocompound I.[3]



I II III

1 - Chloro - 2,3,3,5,5 - pentabromo - 4 - (dibromomethylene)-cyclopentene (IV) was obtained in 58% yield by the bromination of I with anhydrous aluminum bromide in carbon tetrabromide for a short time at 95°. The ultraviolet spectrum (see Table I) indicates non-conjugation.[4] Proof for the struc-

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[1] From a thesis submitted by Kornelijs Dinbergs to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1956.

[2] U. S. Patent 2,553,518, Dow Chemical Corporation, May, 1951.

[3] E. T. McBee, C. W. Roberts and K. Dinbergs, THIS JOURNAL, **78**, 489 (1956).

[4] The observed bathochromic shift (19 mμ) calculated from the perchlorocompound is too small to arise from conjugation. A shift of such magnitude is caused by the exchange of chlorine by bromine substituents. A hyperchromic shift of 0.05 log ε unit was observed.