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.

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

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

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

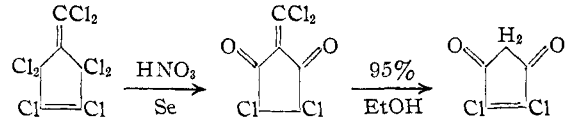
BY E. T. MCBEE, C. W. ROBERTS AND K. DINBERGS[1]

RECEIVED AUGUST 18, 1955

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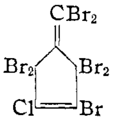
(1) From a thesis submitted by Kornelijs Dinbergs to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1956.

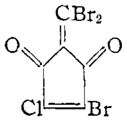
(2) U. S. Patent 2,553,518, Dow Chemical Corporation, May, 1951.

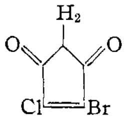
(3) E. T. McBee, C. W. Roberts and K. Dinbergs, THIS JOURNAL, **78**, 489 (1956).

(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.

ture of IV was obtained by oxidation to 1-bromo-2-chloro-4-(dibromomethylene)-cyclopentene-3,5-dione (V). Compound V was cleaved to 1-bromo-2-chlorocyclopentene-3,5-dione (VI) by 95% ethanol. Previous studies[3] have shown that for such a cleavage to occur a dihalomethylene group must be located between two adjacent keto groups.

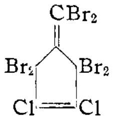

IV

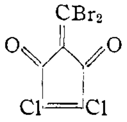

V

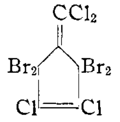

VI

Compound VI has ultraviolet and infrared spectra very similar to the spectra of 4,5-dichloro-2-(dichloromethylene)-cyclopentene-1,3-dione (II), and the bathochromic shifts due to the bromines are present also in this compound, but in the ketones the bromines produce a hypochromic effect.

During attempts to improve the yield of IV by varying the reaction conditions new compounds were formed. Prolonged heating (3 hr.) at 95° resulted in a very low yield (2%) of IV. Bromination in liquid bromine under reflux gave 1,2-dichloro-3,3,5,5-tetrabromo-4-(dibromomethylene)-cyclopentene (VII). This compound is similar to IV. The spectral data support the assigned structure. The final structure proof of VII was its


VII


VIII


IX

oxidation by fuming nitric acid to 4,5-dichloro-2-(dibromomethylene)-cyclopentene-1,3-dione (VIII) which upon boiling with 95% ethanol gave 1,2-dichlorocyclopentene-3,5-dione (III), m.p. 163–164°.

If the reaction is carried out at room temperature with aluminum bromide and carbon tetrabromide or with aluminum bromide in bromine the same compound, 1,2-dichloro-3,3,5,5-tetrabromo-4-(dichloromethylene)-cyclopentene (IX) was obtained. Compound IX is more soluble in organic solvents than IV and VII, but in other respects it is similar to them. That IX has the same basic structure as I was shown by spectral data, and the positions of the chlorines was proved unequivocally by the oxidation of IX to II. The identity of II was proved by a mixed melting point with a known sample.

Spectral Studies.—Data in the literature indicate that substitution of bromine for a chlorine or a hydrogen produces a bathochromic shift. In α,β-unsaturated ketones and acids a bromine substituted for a hydrogen in the α-position results in a 20–30 mμ shift; if chlorine is replaced by bromine the shift is only 6 mμ.[5,6] In the α,β-unsaturated ketones the introduction of bromine in the β-position results in a greater (30 mμ) shift.[6] The introduction of a second α-bromine produces an additional 22 mμ bathochromic shift.[6] In both the acids and ketones the introduction of a bromine causes a hypochromic effect.

The exchange of chlorine by bromine in hydrocarbons or ketones of the cyclopentane series results in a bathochromic shift and a decrease in absorption intensity. In contrast to the ketones the exchange of chlorine by bromine in the hydrocarbon series results in a hyperchromic shift. The shifts observed per bromine in the hydrocarbon (2.5–7 mμ) and for the ketone (5–11 mμ) series are smaller than the ones reported earlier.[5,6] This is explained by the fact that the number of bromines introduced is greater than in the earlier investigations. Some regularity may be observed in the infrared spectra of the halogenated hydrocarbons. The carbon–carbon double bond stretching frequencies increase by about 0.25 μ per bromine introduced.

Table I

Hydrocarbons

Cmpd.	Infrared stretching frequencies (C=C), μ	Ultraviolet λ_{max}, mμ	log ϵ
I	6.05, 6.20	224	4.29
IX	6.15, 6.30	234	4.39
VII	6.18, 6.37	235	4.39
IV	6.22, 6.39	242	4.33

Table II

Ketones

Cmpd.	Infrared stretching frequencies, μ C=O	C=C	Ultraviolet λ_{max}, mμ	log ϵ
II	5.80	6.13	248	4.35
			255	4.34
			270	4.29
			280	4.18
			295	3.84
VIII	5.88	6.21	258	4.33
			273	4.32
V	5.93	6.38	267	4.30
			278	4.29
			289	4.26
III	5.76	6.20	258	4.19
			327	1.64
VI	5.85	6.36	269	4.12
$C_5Cl_4O_2$[a]	5.60	6.24sh[c]	264	4.15
	5.74	6.39		
	5.83			
$C_5Br_4O_2$[b]	5.66	6.45	283	4.05
	5.74			

[a] Perchlorocyclopentene-1,3-dione.[3] [b] Perbromocyclopentene-1,3-dione.[3] [c] sh = shoulder.

Experimental[7]

Preparation of 1-Chloro-2,3,5,5-pentabromo-4-(dibromomethylene)-cyclopentene (IV).—In a 500-ml., 3-necked flask fitted with a stirrer, a reflux condenser protected by a calcium chloride drying tube, and a 50-ml. erlenmeyer flask connected by a wide rubber tubing with the 3-necked flask were placed 100 g. (0.27 mole) of carbon tetrabromide. The

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

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

[7] All melting points are corrected. The microanalyses were carried out by Dr. C. S. Yeh, Purdue University, and by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. The ultraviolet spectra were determined in heptane or cyclohexane 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 Nujol with a Perkin-Elmer model 21 recording spectrophotometer.

flask was heated on a steam-cone, and, while the carbon tetrabromide melted, 50 g. (0.14 mole) of 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)-cyclopentene (I) was added from the erlenmeyer flask during two minutes. As the reaction mixture was stirred, the temperature was let fall during 1 hr. from 95 to 50°, then it was stirred for 30 min. at 25°. The reaction mixture was poured into an ice-ethanol mixture. The viscous reaction mixture is practically unattacked by water. The yield of the once recrystallized product was 54 g. (58%); after several recrystallizations from benzene, white prisms were obtained which turned brown at 190°, sintered at 225° and melted at 240–248°.

Anal. Calcd. for C_6Br_7Cl (IV): C, 10.80; H, 0.00; silver halide from a 3.021-mg. sample, 6.604 mg. AgX. Found: C, 10.84, 10.77; H, 0.17, 0.00; AgX, 6.565 mg.

Preparation of 1-Bromo-2-chloro-4-(dibromomethylene)-cyclopentene-3,5-dione (V) by the Oxidation of IV with Fuming Nitric Acid.—Thirty-one grams (0.046 mole) of IV, a trace of selenium and 40 g. of fuming nitric acid were placed in an evaporating dish. The reaction was initiated on a steam-bath and after the reaction subsided the heating was resumed for 20 min.; the reaction mixture was then filtered. The product was recrystallized from ligroin (b.p. 90–100°) and gave 17 g. (97%) of green plates, m.p. 218–220°. Several recrystallizations from ligroin (b.p. 90–100°) with decolorization gave pure V as light green plates, m.p. 222–223°. The compound may be purified also by sublimation.

Anal. Calcd. for $C_6Br_3ClO_2$ (V): C, 19.00; H, 0.00; silver halide obtained from a 3.566-mg. sample, 6.645 mg. AgX. Found: C, 19.02; H, 0.00; AgX, 6.650 mg.

Preparation of 1-Bromo-2-chlorocyclopentene-3,5-dione (VI) by the Hydrolysis of V with 95% Ethanol.—Seven and a half grams (0.020 mole) of V was boiled with 400 ml. of 95% ethanol until solution was complete; 200 ml. of water was added and three-fourths of the solvent removed overnight in a stream of air. The product was recrystallized from ligroin (b.p. 90–100°) to give 2 g. (45%) of VI, m.p. 150–156°. Recrystallization was carried out from the same solvent and the pure product, green plates, melted at 157–158°.

Anal. Calcd. for $C_5H_2BrClO_2$ (VI): C, 28.66; H, 0.97; silver halide obtained from a 4.665-mg. sample, 7.376 mg. AgX. Found: C, 28.57; H, 1.06; AgX, 7.372 mg.

Bromination of 1,2,3,3,5,5-Hexachloro-4-(dichloromethylene)-cyclopentene (I) with Aluminum Bromide in Carbon Tetrabromide at 95°.—The same apparatus was used as in the preparation of IV. In the 3-necked flask were placed 25 g. (0.070 mole) of I, 67 g. (0.25 mole) of anhydrous aluminum bromide and 45 g. (0.14 mole) of carbon tetrabromide; the stirred reaction mixture was heated on a steam-cone for 3 hr. The reaction mixture was poured into ice-cooled ethanol. The yield of the crude benzene soluble product was 45 g. After one recrystallization from ligroin (b.p. 90–100°) this benzene soluble product formed green-brown plates, m.p. 155–160°. The benzene-insoluble product amounted to 1 g. (2%) (IV).

Preparation of 1,2-Dichloro-3,3,5,5-tetrabromo-4-(dibromomethylene)-cyclopentene (VII).—In a 500-ml., 3-necked flask fitted with a stirrer, dropping funnel and a reflux condenser protected by a calcium chloride drying tube were placed 50 g. (0.14 mole) of I, 112 g. (0.42 mole) of anhydrous aluminum bromide and during 10 min. 350 g. (2.2 moles) of bromine added. The reaction mixture was refluxed for 1.5 hr., then poured on ice, the product filtered off and washed with ethanol and petroleum ether (b.p. 35–37°); yield of crude product 75 g.; one recrystallization from benzene gave 60 g. (69%) m.p. 205–220°. After several recrystallizations from benzene the pure compound was obtained; on heating it turns brown at 180°, sinters at 215° and melts at 226–231°.

Anal. Calcd. for $C_6Br_6Cl_2$ (VII): C, 11.58; H, 0.00; silver halide obtained from a 3.421-mg. sample, 7.768 mg. AgX. Found: C, 11.85; H, 0.00; AgX, 7.740 mg.

Preparation of 1,2-Dichloro-4-(dibromomethylene)-cyclopentene-3,5-dione (VIII) by the Oxidation of VII with Fuming Nitric Acid.—Twenty-four grams (0.039 mole) of VII, 57 g. of fuming nitric acid and a trace of selenium were placed in an evaporating dish; a reaction started at once. After the initial reaction ceased, the reaction mixture was placed on a steam-cone and evaporated to dryness. The product (VIII) was recrystallized from ligroin (b.p. 90–100°) and gave 11 g. (85%) of green plates, m.p. 228–229.5°.

Anal. Calcd. for $C_6Br_2Cl_2O_2$ (VIII): C, 21.52; H, 0.00. Found: C, 21.51; H, 0.00.

Hydrolysis of VIII with 95% Ethanol.—Two grams (0.060 mole) of compound VIII was boiled with 200 ml. of 95% ethanol until solution was complete and then 200 ml. of water was added. During 3 hr. most of the ethanol was evaporated; the resulting precipitate was removed by filtration and recrystallized from ligroin (b.p. 90–100°) to give 0.5 g. (50%) of greenish plates, m.p. 162–163°. An additional recrystallization and decolorization gave white plates (III), m.p. 163–164°. A mixed melting point with an authentic sample of III showed no depression.

Preparation of 1,2-Dichloro-3,3,5,5-tetrabromo-4-(dichloromethylene)-cyclopentene (IX) in Bromine as Solvent.—The same apparatus was used as in the preparation of VII. In the flask were placed 25 g. (0.070 mole) of I and 50 g. (0.19 mole) of anhydrous aluminum bromide. The stirrer was started and, during 5 min., 110 g. (0.69 mole) of bromine was added. Solution occurred and a small amount of heat was given off. The reaction was carried out for 4.5 hr. at 30°; the mixture was poured onto ice and the resulting precipitate filtered. The product was recrystallized from benzene and gave 30 g. (80%) of white prisms, m.p. 192–207°. After several recrystallizations from the same solvent the pure product (IX) turned brown at 160°, sintered at 180°, and melted at 204–213°.

Anal. Calcd. for $C_6Br_4Cl_4$ (IX): C, 13.51; H, 0.00; silver halide obtained from a 2.811-mg. sample, 6.979 mg. AgX. Found: C, 13.50; H, 0.00; AgX, 6.958.

Preparation of IX in Carbon Tetrabromide as Solvent.—The same apparatus was used as in the preparation of IV. In the flask were placed 50 g. (0.14 mole) of I, 112 g. (0.42 mole) of anhydrous aluminum bromide and 62 g. (0.19 mole) of carbon tetrabromide. A very low flame was applied at the beginning of the reaction for one minute to hasten the liquefaction of the reaction mixture. The mixture was stirred for 7 hr. at 25°, and was poured into cold ethanol and 54 g. of crude product was obtained. Two recrystallizations from ligroin (b.p. 90–100°) gave 45 g. (60%) of white prisms, m.p. 203–212°. After several recrystallizations from the same solvent the compound IX was obtained pure.

Oxidation of IX with Fuming Nitric Acid.—Six grams (0.011 mole) of IX, 13 g. of fuming nitric acid and a trace of selenium was placed into an evaporating dish. After the initial reaction subsided the reaction mixture was evaporated to dryness on a steam-cone. The product was recrystallized from ligroin (b.p. 90–100°). The first crop of crystals weighed 2 g., m.p. 232–235°, the second crop weighed 0.5 g., m.p. 230–233°; total yield 2.5 g. (90%). A mixed melting point of the first crop of crystals with a known sample of II, melting 233–234°, was 232–234°.

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WEST LAFAYETTE, INDIANA