Anal. Calcd. for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 63.07; H. 9.36.

5-Ethoxycyclopent-2-enone (XIa). 3,4-Diethoxycyclopent-2-ene-ol (2 g., 0.01 mole) was dissolved in 10 ml. of water and 10 ml. of 3 *M* hydrochloric acid solution was added. After standing for 15 min. the solution was extracted with ether, the ether layers were combined, dried, and distilled. The ketone boiled at 81–82°/15 mm. and weighed 1 g. (67% yield), λ_{max} 219 mμ (log ϵ 3.77).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.49; H, 8.21.

A 2,4-dinitrophenylhydrazone was prepared in the usual way, m.p. 154.5–155.5 (dec.).

Anal. Calcd. for $C_{13}H_{14}O_5N_4$: C, 50.98; H, 4.61; N, 18.29. Found: C, 50.55; H, 4.55; N, 18.36.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Rearrangement of 6,6-Dibromobicyclo[3.1.0]hexane[1]

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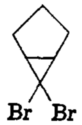
The product of addition of dibromocarbene to cyclopentene, 6,6-dibromobicyclo[3.1.0]hexane, rearranges readily to the allylic dibromide, 2,3-dibromocyclohexene. For this reason, it is isolable as a pure unrearranged material only with care. The 6,6-dibromobicyclo[3.1.0]hexane is converted to 2-bromo-2-cyclohexenol by aqueous silver nitrate or by boiling aqueous acetone. The rearranged allylic dibromide yields the same bromohydrin in aqueous acetone, but a considerable quantity of nitrate ester accompanies the bromohydrin from the silver nitrate treatment. Apparently, the two dibromides do not react by way of a truly common carbonium ion intermediate.

As is well known, the reaction of olefins with dihalocarbene[2] can give rise to dihalocyclopropane derivatives. During the development of synthetic approaches to bicyclo[3.1.0]hexyl systems[3] we investigated briefly the action of dibromocarbene on cyclopentene and found that the expected product, 6,6-dibromobicyclo[3.1.0]hexane (I), was isolable only with mild work-up procedures. Otherwise, the rearranged dibromide II was obtained. This and other observations made at that time are of obvious importance in connection with reported rearrangement reactions[4,5] of the 6,6-dibromide I. For this reason, it seems desirable to report the results of our brief study, and these are presented in the present article.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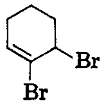
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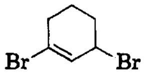
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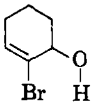
IV

2,3-Dibromocyclohexene. The initial attempts to obtain dibromide I gave a liquid boiling over a wide range with considerable variation in refractive index. After several redistillations, a constant boiling liquid was obtained whose physical properties agreed with those reported for the 6,6-dibromide I by Skell and Garner,[6,7] but which proved to be 2,3-dibromocyclohexene (II) instead.[8] This material had a correct analysis for $C_6H_8Br_2$, showed the presence of unsaturation in the infrared and yielded cyclohexene on reduction with sodium in moist methanol.[2]

In agreement with the structure assigned to dibromide II, only one bromine atom is reactive to silver nitrate and the proton magnetic resonance spectrum shows five proton signals. An alternative structure, 1,3-dibromocyclohexene (III), which also fits the available chemical information, was rejected because the product from hydrolysis of the rearranged dibromide, namely, 2-bromo-2-cyclohexenol[9] (IV), m.p. 38–40°, exhibited intramolecular hydrogen bonding. Only the bromohydrin from 2,3-dibromocyclohexene is capable of an intramolecular interaction between the hydroxyl and bromine groups.

Additional support for the structure of dibromide II is that methyllithium converts it to 2-bromo-3-methylcyclohexene. The latter was re-

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] W. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[3] (a) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

[4] P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958).

[5] W. R. Moore and H. W. Ward, *Chem. & Ind.*, 594 (1961).

[6] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

[7] These authors have more recently recognized that the dibromide sample was very predominantly rearranged material. (P. S. Skell, private communication, March 1959).

[8] The 2,3-dibromocyclohexene is reported to be the product formed when 1,2,3-tribromocyclohexane is heated with potassium hydroxide. [W. G. Christiansen, U. S. Patent 2,146,720 (1939).]

[9] The acetoxybromocyclohexene from treatment of 1,2,3-tribromocyclohexane with potassium acetate in acetic acid gives rise to a bromohydrin,[10] m.p. 39–40°, probably identical to bromohydrin IV.

[10] R. Cornubert, A. Rio, and P. Senechal, *Bull. soc. chim. France*, **22**, 46 (1955).

TABLE I

Physical Properties of the Isomeric Dibromides

Dibromide	B.P.	(Mm.)	n^{25}_D	d^{25}_4	M_D		Ref.
					Found	Calcd.	
I	63°	(2.9)	1.5568	1.858	41.5	41.8	This study
I			1.5568				11
II	94–95°	(4.5)	1.5760	1.851	42.9	42.8	This study
	105–106°	(9.5)	1.5759				
II			1.5761				11
II	110°	(11)	1.5744				6, 7
II	110–111°	(7)					8

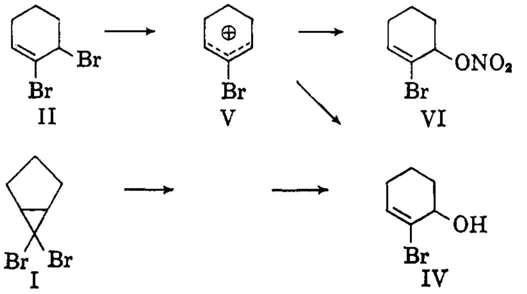
ported recently[8] as arising from the action of methyllithium on the 6,6-dibromide I, but it arises instead[11] from the rearranged dibromide II.

6,6 - Dibromobicyclo[3.1.0]hexane. Authentic 6,6-dibromobicyclo[3.1.0]hexane (I) was obtained when the reaction product from cyclopentene and dibromocarbene was distilled rapidly at low temperature. The 6,6-dibromide I had an analysis corresponding to $C_6H_8Br_2$, and showed the absence of unsaturation in the infrared spectrum. On reduction with sodium in wet methanol[2] the 6,6-dibromide I yielded bicyclo[3.1.0]hexane contaminated with a trace of cyclohexene. The structural assignment is supported by the proton magnetic resonance spectrum of dibromide I; also, the molar refraction of I is in excellent agreement with the calculated value.

A subsequent experiment showed that the 6,6-dibromide I, in the absence of solvent, undergoes isomerization to the 2,3-dibromide II when heated at 155° for a short time. It appears probable that milder conditions will also suffice to cause the rearrangement. The 6,6-dibromide I can be distilled at low temperatures without appreciable rearrangement, but slow fractional distillation at higher temperatures results in conversion to the rearranged dibromide.

The physical properties of the isomeric dibromides I and II are listed in Table I. In the experimental section are summarized the infrared absorption spectra of these dibromides along with that of bromhydrin IV derived from them.

Rearrangement and hydrolysis. The thermal rearrangement of the 6,6-dibromide I, probably promoted by trace electrophilic catalysts, is akin to other examples of unstable dihalocyclopropane derivatives reported in the recent literature[12]; in some cases these dihalocyclopropanes are merely postulated intermediates. In these examples[12] hydrogen halide or alkyl halide is lost with ring expansion or ring opening, while in the present case, ring expansion occurs without the loss of any elements.



During the course of this investigation, a communication by Skell and Sandler[4] appeared, which reported the behavior of 1,1-dihalocyclopropanes toward aqueous silver nitrate. In these laboratories, the 6,6-dibromide I was found to be converted rather cleanly to the bromohydrin IV when refluxed with aqueous acetone or on treatment with aqueous silver nitrate. The 2,3-dibromide II gave the same bromohydrin when refluxed with aqueous acetone. However, with aqueous silver nitrate, the 2,3-dibromide gave, not only bromohydrin IV, but a considerable quantity of a nitrate ester VI, as identified by infrared spectrum.[13] As regards relative reactivity of the isomeric dibromides I and II, the precipitation of one mole of silver bromide in the silver nitrate treatment occurs more rapidly for the allylic dibromide II than for the 6,6-dibromide I.

The formation of bromohydrin IV by hydrolysis of the 2,3-dibromide II and the formation of a mixture of bromohydrin and nitrate ester VI by treatment with aqueous silver nitrate may be formulated most simply by way of an intermediate allylic cation[14] V. The 6,6-dibromide I gives the bromohydrin IV in hydrolysis, but it does not lead to an appreciable quantity of nitrate ester VI accompanying the bromohydrin from treatment with silver nitrate. This difference in behavior of the isomeric dibromides I and II is quite significant

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(11) W. R. Moore, private communication, July 1961.

(12) (a) A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283, (1958); (b) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959); (c) E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960); (d) R. W. Murray, *Tetrahedron Letters*, **7**, 27 (1960); (e) (i) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961) and ref. (3) therein; (ii) M. F. Dull and P. G. Abend, *J. Am. Chem. Soc.*, **81**, 2588 (1959).

(13) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley and Sons, Inc., New York, 1958.

(14) W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

because it shows that the 6,6- and 2,3-dibromides do not react by way of a truly common intermediate with the same relative reactivities towards water and nitrate ion as nucleophiles.

EXPERIMENTAL

6,6-Dibromobicyclo[3.1.0]hexane. Following the procedure of Skell and Garner,[6] a stirred solution of equimolar amounts of cyclopentene (20.5 g., 0.30 mole) and bromoform (75.5 g., 0.30 mole) in dry *t*-butyl alcohol (50 ml.) was maintained at temperatures between −3 and +8° while 1.04*M* potassium *t*-butylate (450 ml.) was added at a rate of approximately 50 ml./hr. At the conclusion of the addition of base, the mixture was stirred an additional hour. Following the addition of water (200 ml.) and pentane (350 ml.), the organic layer was separated and washed throughly with water (4 × 500 ml.). The pentane solution was dried over anhydrous magnesium sulfate, filtered, and the pentane removed. The amber residue (57 g.) was distilled rapidly through a small Vigreux column. Fractions (a) 1.5 g., b.p. 42–56° (4.5 mm.); (b) 7 g., b.p. 57–60° (4.5 mm.), n^{25}_{D} 1.5418; (c) 6 g., b.p. 61–65° (4.0 mm.); (d) 11 g., b.p. 65–68° (3.2 mm.); (e) 12 g., b.p. 68–70° (3.2 mm.); and (f) 12 g., b.p. 70° (3.2 mm.), n^{25}_{D} 1.5568, were collected; a 1-g. residue remained. Fraction (f) did not discolor bromine in carbon tetrachloride but reacted with alcoholic silver nitrate and gave an immediate precipitate of silver bromide. The infrared spectrum of fraction (f) showed the absence of an absorption band in the 6.0-μ region. The 6,6-dibromobicyclo[3.1.0]hexane was a colorless liquid, sweet smelling, and neutral to litmus, which did not crystallize on cooling.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found for fraction (f): C, 30.18; H, 3.38.

After all the above fractions were combined, the material was rapidly fractionated through a Podbielniak column. Fractions (a) 2.0 g., b.p. 32–36° (3.9 mm.); (b) 1.5 g., b.p. 36–39° (3.9 mm.); (c) 1.6 g., b.p. 39° (3.9 mm.) to 61° (3.3 mm.), n^{25}_{D} 1.5383; (d) 1.6 g., b.p. 63° (3.3 mm.), n^{25}_{D} 1.5524; (e) 16.65 g., b.p. 63° (3.1 mm.) to 63° (2.9 mm.), n^{25}_{D} 1.5562; (f) 11.90 g., b.p. 63–63.5° (2.9 mm.), n^{25}_{D} 1.5570; and (g) 2.40 g. b.p. 64–61° (2.9 mm.), n^{25}_{D} 1.5576, were collected. A black higher boiling liquid (9.35 g.) remained. Fractions (f) and (g) were slightly yellow.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36; Br; 66.61. Found for fraction (e): C, 29.98; H, 3.35; Br, 66.27.

Fractions (e) and (f) were combined and considered pure, all further work being done on the sample. A colorless fraction, n^{25}_{D} 1.5568 gave d_4^{25} 1.858; M_D calcd.[15] 41.8, M_D found 41.5. Infrared absorption maxima were observed at the following wave numbers: 3025mw, 2925s, 2865m, 1465m, 1439ms, 1350w, 1315m, 1282m, 1270sh, 1225m, 1185mbr, 1070s, 1036vw, 1002s, 965m, 886mw, 821mw, 780sh, and 738s.

The rearranged dibromide: 2,3-dibromocyclohexene. In the initial attempts to synthesize 6,6-dibromobicyclo[3.1.0]-hexane, a procedure similar to that described above was followed. The product was, however, slowly distilled through a Podbielniak column at 11 mm. (bath temperature 155°). The high-boiling fraction, b.p. 90–105° (11 mm.), collected from the first distillation gave on redistillation a small forerun, b.p. 90.5–104° (9.5 mm.), and material, b.p. 105–106° (9.5 mm.), n^{25}_{D} 1.5759, whose infrared spectrum showed an appreciable absorption maximum for carbon-carbon unsaturation (1624 cm.$^{-1}$).

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.22; H, 3.26.

In another run a rapid first distillation at 9.5 mm. gave: (a) 8 g., b.p. 42–75°; (b) 10 g., b.p. 75–79°, n^{25}_{D} 1.5493; and (c) 32 g., b.p. 79.5–83.0°, n^{25}_{D} 1.5556. A slow redistillation of this combined material through a glass center-rod column at 9.5 mm. gave material whose boiling point increased rapidly after reaching 70°. As the bath temperature was increased from 107–140°, the pot became progressively darker. Distillation was stopped when the distillate came over black. The distillate and residue were combined and after a rapid distillation at 9.5 mm. now gave material with n^{25}_{D} 1.5741. The final redistillation of the material through a small Vigreux column gave: (a) 4 g., b.p. 78–82.5° (3.7 mm.), (light yellow); (b) 23 g., b.p. 82.5–83.5° (3.5 mm.), n^{25}_{D} 1.5749, (light yellow); and (c) 9 g., b.p. 83.5–85.0° (3.5 mm.), n^{25}_{D} 1.5760, (colorless).

The distillates from three runs with refractive indices n^{25}_{D} 1.574 and higher, were combined with pentane and washed with 2*N* sodium hydroxide (25 ml.) followed by water (2 × 50 ml.). After the pentane solution was dried over potassium carbonate, the pentane was removed under aspirator vacuum and the residue distilled carefully through a Podbielniak column. Five fractions were collected: (a) 1.6 g. forerun up to 92° at 4.5 mm.; (b) 5.6 g., b.p. 93° (4.2 mm.), n^{25}_{D} 1.5742; (c) 23.2 g., b.p. 92° (4.0 mm.) to 94° (4.5 mm.), n^{25}_{D} 1.5760; (d) 22.8 g., b.p. 95° (4.5 mm.) to 95.5° (4.8 mm.), n^{25}_{D} 1.5760; and (e) 18.6 g., b.p. 94–94.5° (4.6 mm.), n^{25}_{D} 1.5762. A very small residue remained.

Anal. Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36; Br, 66.61. Found for fraction (d): C, 30.25; H, 3.36; Br, 66.96.

Fractions (c), (d), and (e) were combined and considered to be pure in all further chemical tests. A sample of the dibromide, n^{25}_{D} 1.5764, had d_4^{25} 1.851; M_D calcd.[15] 42.8; M_D found 42.9.

The infrared spectrum shows a definite absorption in the 6.0-μ region. Infrared absorption maxima were observed at the following wave numbers: 3025w, 2925s, 2865sh, 2835w, 1680vw, 1624m, 1449m, 1435ms, 1425ms, 1346m, 1330m, 1315s, 1284m, 1249m, 1186s, 1171m, 1135m, 1080m, 1025m, 988s, 936m, 913m, 882s, 840m, 800m, and 733s.

The 2,3-dibromocyclohexene is a colorless liquid which forms white circular crystals which melt below 0°. It gives an immediate precipitate of silver bromide when treated with alcoholic silver nitrate but only slowly discharges bromine in carbon tetrachloride with evolution of hydrogen bromide.

Thermal rearrangement of 6,6-dibromobicyclo[3.1.0]hexane. A small sample of 6,6-dibromobicyclo[3.1.0]hexane, n^{25}_{D} 1.5562, was put into a 155° bath at atmospheric pressure. After a few seconds, it started to boil vigorously and change color. A small quantity of gas was liberated which proved to be acidic to litmus and came off as a white gas when exposed to air. Simultaneously, the remaining liquid became light brown. After an hour in the 155–160° bath, the liquid residue appeared black. After some small droplets on the side of the tube and receiver were removed, the residue was distilled at low temperature under full vacuum. A liquid was collected, n^{25}_{D} 1.5762, whose infrared spectrum was identical to that of the rearranged dibromide, n^{25}_{D} 1.5760. In addition four very weak bands at 1470, 1100, 1044, and 867 cm.$^{-1}$ were observed.

Reduction of 6,6-dibromobicyclo[3.1.0]hexane with sodium and alcohol. The 6,6-dibromobicyclo[3.1.0]hexane, n^{25}_{D} 1.5562–1.5570), (25.7 g., 0.11 mole) was reduced with sodium and wet methanol by the procedure of Doering and Hoffmann.[2] Fractional distillation of the dried ether solution through a Podbielniak column gave, after most of the ether was removed, a 6.15 g. fraction boiling at 55°. When this homogeneous fraction was cooled below room temperature, two layers formed suggesting the presence of an azeotrope of methanol and hydrocarbon. All the fractions were recombined with ether, and dried over an excess of anhydrous calcium chloride for 5 hr. After most of the ether was removed, fractionation through a Podbielniak column at 746 mm. gave: (a) 0.35 g., b.p. 75–78°; (b) 3.75 g., b.p. 78–

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(15) A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 514 (1952); A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 2nd ed., Longmans, Green and Co., London, 1951.

80.5°, n^{20}_{D} 1.4381; and (c) 1.30 g., b.p. 80.5°, n^{20}_{D} 1.4400 (reported[16] for bicyclo[3.1.0]hexane, b.p. 81–82°, n^{25}_{D} 1.4373). A 57.5% yield of the highly volatile bicyclo[3.1.0]-hexane, b.p. 78–80.5°, was thus obtained.

Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found for fraction (c): C, 87.87; H, 12.32.

Vapor phase chromatographic analysis of fraction (c) using a column of tetraethylene glycol saturated with silver nitrate indicated 89% bicyclo[3.1.0]hexane and 11% cyclohexene. The infrared spectrum of fraction (c) had a strong band at 1017 cm.$^{-1}$ (cyclopropane ring) and showed the presence of some cyclohexene.

Reduction of 2,3-dibromocyclohexene with sodium and alcohol. The rearranged dibromide n^{25}_{D} 1.5760, (25.7 g., 0.11 mole) was also reduced by the procedure of Doering and Hoffmann.[2] As described above, the ether solution was dried over anhydrous magnesium sulfate and later with anhydrous calcium chloride. Fractionation through a Podbielniak column gave two fractions after most of the ether and pentane was removed: (a) 0.75 g., b.p. 73–82.2°; and (b) 5.05 g., (57.5%) b.p. 82.2° (746 mm.), n^{20}_{D} 1.4462. The infrared spectrum of fraction (b) was identical to that of authentic cyclohexene, b.p. 82.2°, n^{20}_{D} 1.4463. A vapor phase chromatographic analysis of fraction (b) on a column of tetraethylene glycol saturated with silver nitrate indicated 99.5% purity. The other 0.5% had a retention time corresponding to bicyclo[3.1.0]hexane.

6,6-Dibromobicyclo[3.1.0]hexane with aqueous acetone. A solution of the 6,6-dibromide (0.6 g., 2.5 mmoles) was refluxed for 24 hr. with acetone (10 ml.) and water (5 ml.). Following, potassium carbonate (7 g., 5 mmoles) was added and the basic solution extracted with ether and pentane and then dried over anhydrous magnesium sulfate. Distillation through a small distilling head gave 0.49 g. of a very slightly yellow liquid, b.p. 75–77° (4 mm.), n^{25}_{D} 1.5352, which solidified after being cooled in a Dry Ice–acetone bath. The infrared spectrum of this product was identical to that of the bromohydrin from the hydrolysis of 2,3-dibromocyclohexene, but it contained a trace of carbonyl material (1688 cm.$^{-1}$).

The infrared absorption maxima observed for purified 2-bromo-2-cyclohexenol occurred at the following wave numbers: 3385vs br, 3050w, 2925s, 2870s, 2845sh, 2690w, 1675vw, 1636m, 1450m, 1435m, 1381m, 1350m, 1328s, 1294m, 1267m, 1245m, 1204w, 1176m, 1162m, 1075s, 1048vs, 975vs, 950vw, 935m, 905m, 868m, 830m, 805m, and 698m.

2,3-Dibromocyclohexene with aqueous acetone. A solution of the rearranged dibromide (1.2 g., 5 mmoles) was refluxed for 24 hr., with acetone (20 ml.) and water (10 ml.). Following, potassium carbonate (1.4 g., 10 mmoles) was added and the basic solution extracted continuously with ether containing some pentane. The resulting extract was dried over anhydrous magnesium sulfate and distilled through a small distilling head to give 0.92 g. of colorless material, b.p. *ca.* 50–55° (1 mm.), which crystallized in an ice bath. Recrystallization from pentane gave 0.56 g. of product, m.p. 38.2–40.2°. Another recrystallization from pentane did not change the melting point. A melted sample gave n^{25}_{D} 1.5404. The remaining mother liquor (0.36 g.) crystallized partially. The liquid portion, n^{25}_{D} 1.5305, displayed a very slight trace of carbonyl absorption (1690 cm.$^{-1}$) in the infrared region but proved to be primarily the bromohydrin IV by infrared analysis.

Anal. Calcd. for C_6H_9BrO: C, 40.70; H, 5.12. Found: C, 40.81; H, 4.87.

The infrared spectrum of this product was identical with that of the bromohydrin derived from the 6,6-dibromobicyclo[3.1.0]hexane. The infrared spectrum of a dilute solution of the crystalline bromohydrin in carbon tetrachloride was examined for the position and shape of the hydroxyl absorption. A single symmetrical peak at 1.4229 μ and a single peak at 3600 cm.$^{-1}$ were observed, suggesting an intramolecular hydrogen bond.

6,6-Dibromobicyclo[3.1.0]hexane with aqueous silver nitrate. The 1*M* silver nitrate (5 ml.) was added to 6,6-dibromobicyclo[3.1.0]hexane (0.6 g., 2.5 mmoles) in a 25 ml. flask and the heterogeneous mixture stirred magnetically at 0–25°. Silver bromide precipitated almost immediately, 0.16 g. being obtained after several minutes. The total weight of silver bromide recovered after 1 hr. was 0.44 g. (2.3 mmoles).

The acidic aqueous solution was extracted with ether and pentane and dried. After most of the solvent was distilled on a steam bath, ether was added, and the ether solution washed successively with water, 5% sodium bicarbonate, and water. After being dried over anhydrous magnesium sulfate, distillation through a small simple distilling head gave 0.35 g. of a colorless liquid, b.p. 74–76° (4 mm.), n^{25}_{D} 1.5387, which solidified upon cooling in a Dry Ice–acetone bath. The infrared spectrum of the distillate was identical with that of the bromohydrin IV prepared from aqueous hydrolysis. No covalent nitrate was observed.

2,3-Dibromocyclohexene with aqueous silver nitrate. The 1*M* silver nitrate (10 ml.) was added to the rearranged dibromide (1.2 g., 5 mmoles) in a 50 ml. flask and the heterogeneous mixture stirred magnetically at 0–25°. Silver bromide precipitated immediately. The weight of silver bromide recovered after being washed with water, ether, and acetone was 0.94 g. (5 mmoles).

After 1 hr., the acidic aqueous solution was extracted with ether. The ether solution was washed successively with water, 5% sodium bicarbonate, and water, and then dried over anhydrous magnesium sulfate. Distillation through a small distilling head at 3.0 mm. gave 0.85 g. of a very slightly yellow liquid, n^{25}_{D} 1.5284, which only partially solidified on cooling in a Dry Ice–acetone bath. The infrared spectrum of this product indicated the presence of some bromohydrin. In addition, absorption maxima at 1630 and 1272 cm.$^{-1}$ (covalent nitrate) and 845 and 683 cm.$^{-1}$ were observed. Apparently a covalent nitrate is the major product. Redistillation indicated the presence of two main components, b.p. 82–83° (4.5 mm.) and b.p. 93–94° (4.8 mm.), which were not well separated. The combined material had n^{25}_{D} 1.5281.

The above reaction was repeated in as nearly the same manner as possible with the following exception—the dibromide was dissolved in acetone (20 ml.) before the 1*M* silver nitrate (10 ml.) was added. Silver bromide (0.94 g.) was recovered after 5 min. at 0–20°. Distillation gave 0.85 g. of a very slightly yellow liquid, b.p. 75° (3.5 mm.) to 90° (4.5 mm.), n^{25}_{D} 1.5280. The infrared spectrum of the mixture was very similar to that in the previous run.

The products from the above two runs were combined and distilled through a Podbielniak column at 8.5 mm. with the final bath temperature up to 160°. Three fractions were collected: (a) b.p. 93°, n^{25}_{D} 1.5388; (b) b.p. 93–109°, n^{25}_{D} 1.5325; and (c) b.p. 109–110°, n^{25}_{D} 1.5236 (yellow). A small amount of residue remained, apparently resulting from some decomposition. Analysis of the infrared spectra indicated that fraction (a) was mainly bromohydrin IV while fraction (c) was mainly a covalent nitrate.

Infrared and NMR spectra. The infrared spectra were determined on neat samples using a Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride optics. The proton magnetic resonance spectra were obtained on the liquid dibromides with a Varian V-4300-B high resolution NMR spectrometer at 40 mc./sec., using a magnetic field of about 9400 gauss.

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[16] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).