[CONTRIBUTION NO. 2026 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XII. The Bromine Addition Products of Methylenecyclobutane[1]

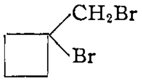
BY DOUGLAS E. APPLEQUIST[2] JOHN D. ROBERTS

RECEIVED AUGUST 22, 1955

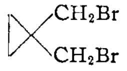
The dibromide(s) (I) from addition of bromine to methylenecyclobutane has been studied by several workers[3–9] but the structural evidence is confusing and inconclusive. Compound I has been reported to be reconverted to methylenecyclobutane by treatment with zinc[4,9] and hydrolyzed to cyclopentanone in the presence of lead dioxide.[4,6] It reacts with potassium cyanide in aqueous ethanol to give an unidentified dinitrile,[5,10] and with dimethylamine or trimethylamine to give both saturated (permanganate) and unsaturated products in which both bromines are displaced.[7,8] Dibromides prepared from methylenecyclobutane either by direct bromination or by Ziegler bromination have been found to contain unsaturated material by permanganate test and possess boiling ranges of 4–7°.[7]

Slobodin and Shokhor[9] considered the dibromide, prepared in ice-cold ether solution, to be 1-bromomethyl-1-bromocyclobutane (II), and reported that it was converted to pure 1-(hydroxymethyl)-cyclobutanol diacetate by treatment with silver acetate in acetic acid, but no satisfactory proofs of structure were presented.

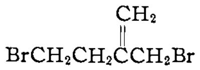
We have found that addition of bromine to methylenecyclobutane in carbon tetrachloride gives a mixture of three dibromides II–IV, containing approximately 61% of II, 32% of III, and 6% of IV. Partial separation of the mixture was effected by fractional distillation, which afforded II in about 93% purity as judged by infrared analysis. Pure III was obtained by treatment of the crude bromination mixture with powdered potassium hydroxide, which selectively destroyed II and IV. The properties of IV were inferred by comparison of the properties of fractions containing only III and IV with those of pure III.



II



III

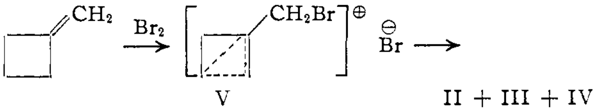


$BrCH_2CH_2\overset{\overset{CH_2}{\|}}{C}CH_2Br$

IV

II was saturated to permanganate, reacted with sodium iodide in acetone to give a red color and a white precipitate, and showed no double-bond or methyl-group infrared absorptions. III was likewise saturated to permanganate and showed no double-bond or methyl absorption in the infrared. III reacted with sodium iodide in acetone on warming to give only a white precipitate. III reacted instantly with alcoholic silver nitrate at room temperature. IV rapidly reduced permanganate in acetone, reacted with sodium iodide in acetone at room temperature to give a white precipitate, and showed a strong C=C stretching band at 6.05 μ. The infrared spectrum showed no methyl group absorption.

The assignment of structures II–IV is in agreement with mechanistic expectations if the bromine addition goes by way of a non-classical carbonium-ion intermediate, which might be represented as V.[11] That the three dibromides are actually anionotropically related was proved by treatment of mixtures of variable compositions with zinc bromide at room temperature, which caused interconversions of the isomers. The equilibrium constant between II and III was found to be 5.7 ± 2.1 in favor of II at room temperature, as expected from strain considerations. The concentration of IV increased in every run, so its relative free energy was not determined.



The structural assignments of II and III were confirmed also by their nuclear-magnetic-resonance spectra.[12]

Experimental[13]

Methylenecyclobutane Dibromides.—To a stirred solution of 34 g. (0.5 mole) of methylenecyclobutane[14] (b.p. 41.0–42.0°, 739 mm.) in 100 ml. of carbon tetrachloride was added 73.6 g. (0.46 mole) of bromine in 50 ml. of carbon tetrachloride. The reaction temperature was kept between −5° and −2°. Simple distillation of the reaction mixture gave a forerun, b.p. 28–48° (3.4 mm.), 6.2 g.; the dibromide mixture, b.p. 48–59° (3.4 mm.), 72.3 g.; and a dark residue, 12.3 g.

Part of the dibromide mixture was distilled through a 61-cm. modified-Podbielniak (spiral-wire) column with a total reflux head, and collected in 14 fractions over the range 53–

---

[1] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[2] National Science Foundation Predoctoral Fellow, 1953–1955.

[3] G. Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896).

[4] G. Gustavson and H. Bulatoff, *ibid.*, **56**, 93 (1897).

[5] H. Fecht, *Ber.*, **40**, 3883 (1907).

[6] N. J. Demjanow and M. Dojarenko, *ibid.*, **55**, 2730 (1922).

[7] E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517 (1948).

[8] E. R. Buchman and D. R. Howton, unpublished results.

[9] Ya. M. Slobodin and I. N. Shokhor, *Sbornik Stateĭ Obscheĭ Khim.*, **2**, 846 (1953); *C. A.*, **49**, 6843 (1955).

[10] (a) K. Mereshkovski, *J. Russ. Phys. Chem. Soc.*, **46**, 517 (1914); *J. Chem. Soc.*, **106**, 923 (1914); (b) R. Curtis and J. Kenner, *ibid.*, **105**, 282 (1914).

[11] (a) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951); (b) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951); (c) J. D. Roberts and E. F. Cox, unpublished work.

[12] Determined by Dr. C. A. Reilly of the Shell Development Corp., to whom the authors are indebted. It was found possible to distinguish and determine quantitatively by graphical integration methylene hydrogens of types $C-CH_2-C$ and $C-CH_2-Br$. The ratio of the former to the latter was 0.985 (theoretical 1.000) in III and 2.94 (theoretical 3.00) in II.

[13] Boiling points are uncorrected. Infrared spectra were obtained with a Model 21 Perkin–Elmer spectrophotometer. Microanalyses were performed by Dr. A. Elek.

[14] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

65° (5 mm.). Indices of refraction were not useful in following composition changes during the distillation, but the infrared spectra of the various fractions revealed that the mixture probably contained three main constituents and one minor one (VI) which appeared only in the lowest-boiling fractions. From these spectra and from the spectrum of pure III, extinction coefficients were deduced for useful analytical peaks for each of the four components of the mixture. The fractions were analyzed by the base-line method.[15] The compositions were plotted against total distillate and the curves integrated graphically to obtain the over-all composition: II, 61%; III, 32%; IV, 6%; and the fourth constituent VI, 1%. The first five fractions, b.p. 53-58°, contained primarily II, so were combined and redistilled through the same column. A fraction was obtained of b.p. 56.1-56.6° (5.1 mm.), $n^{25}\text{D}$ 1.5370, which had an infrared spectrum (Fig. 1) indicating 93% of II, about 5% of III, and about 4% of VI. The last four fractions of the first distillation, b.p. 65.0-65.0° (5.3 mm.), contained primarily III and IV, and neither of these could be separated conveniently by distillation.

Chemical tests on the various fractions from the first fractional distillation showed that fraction 4 was nearly inert to permanganate in acetone, while fraction 13 reacted rapidly with that reagent. Fraction 4 (containing II, III and VI) reacted with sodium iodide in acetone to give a white precipitate and a red color, both at a moderate rate, while fraction 7 (68% II, 29% III, 3% IV, and no trace of VI) reacted with the same reagent to give a white precipitate readily and a red solution slowly. Fraction 13 (containing only III and IV) gave a white precipitate rapidly but no color. A carbon-hydrogen analysis was obtained on fraction 13.

Anal. Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54. Found: C, 26.41; H, 3.58.

Isolation of 1,1-Bis-(bromomethyl)-cyclopropane (III).—A mixture of 8.74 g. of mixed methylenecyclobutane dibromides (over 50% III from infrared analysis) and 13.1 g. of powdered potassium hydroxide was heated at 100° for 2.5 hours. The reaction mixture was diluted with ether and filtered. Distillation of the filtrate through a semi-micro column gave 2.06 g. of III, b.p. 63.7-64.0° (5.1 mm.), $n^{25}\text{D}$ 1.5346. There was a viscous residue (0.5 g.) and a substantial forerun of lower-boiling, unsaturated material, which was not further investigated. The infrared spectrum of III is shown in Fig. 1. III was unreactive to permanganate in acetone. It reacted with sodium iodide in acetone at 50° and with alcoholic silver nitrate at room temperature to give precipitates of sodium and silver bromides, respectively.

Anal. Calcd. for $C_5H_8Br_2$: C, 26.34; H, 3.54. Found: C, 26.48; H, 3.55.

Isomerization of Methylenecyclobutane Dibromides.—In each experiment, a few drops of dibromide mixture was treated with a small amount of powdered zinc bromide at room temperature for 17 hr. The volatile material was removed *in vacuo* with gentle warming and analyzed by its infrared spectrum. A very small amount of undistillable tar was formed in each reaction. The results are shown in Table I.

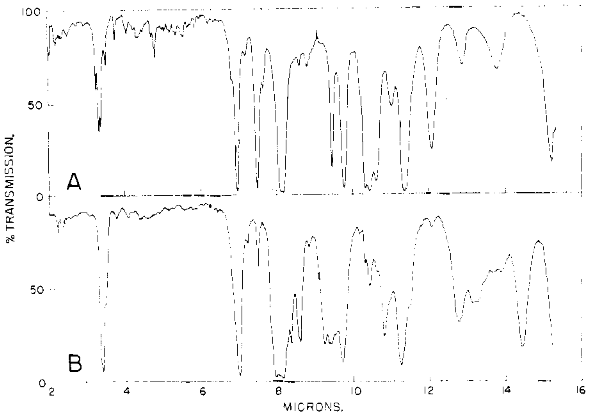


Fig. 1.—Infrared spectra taken in 0.054-mm. cells (no solvent) with a Perkin-Elmer model 21 spectrophotometer and NaCl prism: A, 1,1-bis-(bromomethyl)-cyclopropane (III); B, 1-bromomethyl-1-bromocyclobutane (II), about 93% containing about 5% of III and 4% of VI.

TABLE I

ISOMERIZATION OF METHYLENECYCLOBUTANE DIBROMIDES WITH ZINC BROMIDE AT ROOM TEMPERATURE

	Dibromide mixtures, percentage composition			
	Sample A		Sample B	
Compound	Before $ZnBr_2$	After $ZnBr_2$	Before $ZnBr_2$	After $ZnBr_2$
II	7.7	36.6	89.0	60.9
III	71.3	19.2	4.0	8.4
IV	14.2	38.2	0.0	20.3
VI	0.0	0.0	5.1	5.0
Total	93.3	94.0	98.1	94.6

VI is tentatively considered to be 1,2-dibromo-2-methylbutane, since it is saturated to permanganate, shows methyl group absorption in the infrared (7.23 μ), and is not interconvertible with II-IV by zinc bromide (Table I). 2-Methyl-1-butene, from which VI could have been formed with bromine, is known to contaminate methylenecyclobutane prepared by the zinc debromination of pentaerythrityl tetrabromide.[16]

If the interconversions of II and III are assumed to be first-order reactions and fast relative to isomerization of either to the IV,[11a] then the equilibrium constant between II and III is calculated from the data in Table I to be 5.7 ± 2.1 in favor of II. The error was estimated from maximum errors in the infrared analyses and does not include errors inherent in the foregoing assumptions.

PASADENA 4, CALIFORNIA

---

(15) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

(16) F. C. Whitmore and P. H. Williams, private communication to S. H. Bauer and J. Y. Beach, THIS JOURNAL, **64**, 1142 (1942).