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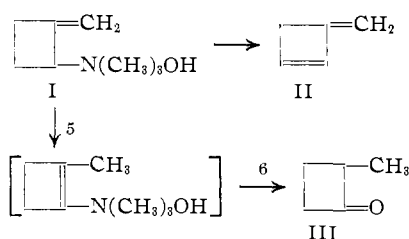
## The Thermal Decomposition of (2-Methylenecyclobutyl)-trimethylammonium Hydroxide<sup>1</sup>

BY DAVID R. HOWTON<sup>2</sup> AND EDWIN R. BUCHMAN

RECEIVED JANUARY 16, 1956

The pyrolysis of (2-methylenecyclobutyl)-trimethylammonium hydroxide (I) proceeds principally in two ways leading, respectively, to methylenecyclobutene (II) and to 2-methylcyclobutanone (III).

In connection with a proposed study of the thermal decomposition of 2-cyclobutenyltrimethylammonium hydroxide,<sup>3</sup> it was of interest to carry out the pyrolysis of the more readily accessible (2-methylenecyclobutyl)-trimethylammonium hydroxide (I). This latter base, obtained in the conventional manner from the corresponding bromide,<sup>4</sup> was decomposed by heat under a variety of conditions; the course of the reaction is indicated on the chart.



The best yield<sup>7</sup> of diolefin (approximately 13%) was achieved when I in concentrated aqueous solution was brought into contact with powdered Pyrex glass maintained at *ca.* 310°. The basic fraction formed consisted of dimethylamine and trimethylamine<sup>8</sup>; no unsaturated base was encountered. From the neutral portion was isolated a fraction containing 2-methylcyclobutanone (III, structure based on analogy),<sup>5a</sup> also higher boiling material, presumably condensation products<sup>6</sup> derived from III.

The diolefin (b.p. *ca.* 37°) polymerized readily even at 0°; in benzene solution one mole of bromine was added to the molecule<sup>9</sup>; in the ultraviolet a well-defined absorption maximum at 221  $\mu$  was observed. The data are consistent with the formulation of the diene as methylenecyclobutene (II). This tentative assignment of struc-

ture has been confirmed by Applequist and Roberts<sup>10</sup> through a comparison with authentic II<sup>10</sup> of a sample of hydrocarbon<sup>11</sup> obtained in the present research.

### Experimental<sup>12</sup>

**Thermal Decomposition of I.**—Aqueous solutions of I were prepared by shaking 2-methylenecyclobutyltrimethylammonium bromide<sup>4</sup> in water with silver oxide; carbonate-free reagents were employed and all operations were conducted in an atmosphere of nitrogen. The solution of I, after centrifuging from solids, was concentrated to a small volume *in vacuo* at 40°; extensive loss of product occurred during this evaporation step. Two pyrolysis experiments will be described; in the first (A), 12.1 g. (0.059 mole) of bromide<sup>4</sup> was used and in the second (B), 4.6 g. (0.022 mole). In procedure A the concentrated solution of I was decomposed simply by heating with a free flame, while in B the solution was introduced dropwise into a tube<sup>13</sup> containing powdered Pyrex glass and maintained at 310–325°. The products of pyrolysis were suitably condensed and treated with 6 *N* hydrochloric acid; the diolefin was separated from higher-boiling neutral materials by taking advantage of its volatility.

Procedure B gave the better yield of diene II (*ca.* 0.25 ml. = 13%); a separate experiment indicated that the yield of II was lowered when no special precautions were taken to exclude carbon dioxide during the preparation of I. Using a micro method, the b.p. of II was found at 37°, a solution in *n*-hexane showed an ultraviolet absorption maximum, free of fine-structure, at 221  $\mu$ . The diene polymerized rapidly on distillation; even on standing overnight at 0°, an appreciable portion was converted to a yellow resinous material (compare, however, its stability<sup>11</sup> in carbon tetrachloride solution). Thirty milligrams of II placed in a sealed tube with 25 mg. of freshly sublimed maleic anhydride showed no apparent signs of reaction after two hours at 0°; on standing at room temperature, the mixture turned to a brownish material insoluble in common solvents and swelling to a jelly-like mass in pyridine. Freshly distilled II (*ca.* 0.15 g.) in 1 ml. of benzene was treated dropwise with a 10% solution of bromine in benzene until color persisted (end-point quite sharp). One milliliter of an 18% solution of trimethylamine in benzene was then added. The resulting precipitate of fine colorless needles (very hygroscopic) was separated, taken up in a small amount of water and treated with a warm concentrated solution of sodium picrate until no further precipitate formed. The initially oily picrate soon solidified completely (crude m.p. 134–138°) and was recrystallized from acetonitrile, forming groups of yellow rectangular plates, m.p. 133.6–133.8°, and gave a positive test for halogen.

*Anal.* Calcd. for C<sub>4</sub>H<sub>17</sub>BrN<sub>3</sub>O: C, 38.81; H, 3.96; N, 12.93. Found: C, 39.16; H, 4.05; N, 13.47.

The higher-boiling neutral material from procedure A

(10) D. E. Applequist and J. D. Roberts, *THIS JOURNAL*, **78**, 4012 (1956).

(11) A carbon tetrachloride solution of diolefin (from degradation of I *in vacuo*) which had been stored at room temperature for more than 5 years had only partly polymerized. Its infrared spectrum was nearly identical with that of a carbon tetrachloride solution of II prepared by a different route.<sup>10</sup>

(12) Melting points are corrected; microanalyses by Dr. G. Oppenheimer and staff (this Institute) and by Huffman Microanalytical Laboratories.

(13) Cf. M. J. Schlatter, *THIS JOURNAL*, **63**, 1733 (1941).

(1) Aided by a grant from the Research Corporation.

(2) Medical School, University of California at Los Angeles.

(3) Cf. E. R. Buchman and D. R. Howton, *THIS JOURNAL*, **70**, 3510 (1948).

(4) E. R. Buchman and D. R. Howton, *ibid.*, **70**, 2517 (1948).

(5) Regarding the shift of the double bond from the allylic to the vinylic position, see (a) D. R. Howton, *J. Org. Chem.*, **14**, 1 (1949); (b) R. B. Woodward and W. J. Brehm, *THIS JOURNAL*, **70**, 2109, footnote 19 (1948).

(6) Cf. E. R. Buchman, M. J. Schlatter and A. O. Reims, *ibid.*, **64**, 2701 (1942).

(7) Very substantial amounts of diolefin were obtained when the decomposition of I was accomplished *in vacuo* (2 mm.) at *ca.* 50°; the yield was not measured.

(8) The amount of trimethylamine formed may be taken as a measure of the diolefin-producing reaction (trimethylamine formation from the vinylic quaternary base is unlikely and allylic alcohol production is apparently insignificant); by an extension of this reasoning dimethylamine measures the reaction leading to III.

(9) Giving a dibromide only one of whose bromines was displaced on treatment with trimethylamine in benzene.

was taken up in ether and dried over magnesium sulfate. Distillation gave 0.87 g. of colorless oil (odor like that of cyclopentanone), b.p. 50–58° at 100 mm., an intermediate fraction (0.22 g.), 0.77 g. of pale yellow oil, b.p. 83–102° at 9 mm. and 0.73 g. of residue. Distillation of like material from B gave 0.27 g., b.p. *ca.* 50° at 100 mm. The two fractions, 0.87 g. from A and 0.27 g. from B, were found to consist largely of ketone III. On treating such crude III with saturated aqueous sodium bisulfite, heat was evolved and the bulk of the material dissolved. After removing the small insoluble portion with ether, the ketone was regenerated from the soluble bisulfite compound by treatment with alkali. Following this purification, the ketone still slowly decolorized aqueous potassium permanganate (cyclopentanone stable in parallel experiment). Analyses<sup>14</sup> of crude III for alcohol were not conclusive but left open the possibility that these fractions contain 5–10% of alcohol calculated as C<sub>5</sub>H<sub>7</sub>OH. Attempts to prepare a *p*-nitrobenzal derivative gave an oil. A semicarbazone was obtained from crude III, tiny square plates with corners extended, m.p. 195.8–196.3° from ethanol.

*Anal.* Calcd. for C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>O: C, 51.04; H, 7.86; N, 29.77. Found: C, 51.22; H, 7.88; N, 29.43.

The 2,4-dinitrophenylhydrazone formed thin square orange-brown plates from methanol; m.p. 120.6–121.0°.

(14) J. W. Petersen, K. W. Hedberg and B. E. Christensen, *Ind. Eng. Chem., Anal. Ed.*, **15**, 225 (1943).

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>N<sub>4</sub>O<sub>4</sub>: C, 50.00; H, 4.58; N, 21.20. Found: C, 50.22; H, 4.60; N, 21.52.

The boiling point (83–102° at 9 mm.) of the less-volatile neutral fraction corresponds roughly to that expected for aldol-type dimers<sup>8</sup> of III. The absence of appreciable amounts of an  $\alpha,\beta$ -unsaturated ketone was indicated by the ultraviolet absorption spectrum which was devoid of peaks in the region 225–320 m $\mu$ . Attempts to prepare crystalline derivatives were generally unsuccessful; in one experiment with 2,4-dinitrophenylhydrazine, a small amount of yellow-brown crystals was obtained, m.p. *ca.* 184° from acetonitrile.

The bases which had been absorbed in dilute hydrochloric acid were liberated into ether by addition of sodium hydroxide and converted to picrates with ethereal picric acid. Fractionation of the crude picrate mixture gave only dimethylamine and trimethylamine picrates; a careful search for picrates of other bases was fruitless. In order to analyze the picrate mixtures, a melting point diagram was constructed from the following data obtained on mixtures of the two authentic picrates: 20.7 weight % dimethylamine picrate, final m.p. 210.7°; 40.4%, 186.2°; 50.3%, 176.4°; 68.2%, 146.2°; 75.8%, 149.4°; 87.2%, 154.3°; 92.5%, 157.3°; 97.4%, 159.8° (eutectic *ca.* 63%, 132°). Procedure A gave 11.1 g. of mixed picrates (*ca.* 50% dimethylamine picrate by weight) equivalent to a 67% yield of both bases, while the recovered picrates from B (*ca.* 35% dimethylamine picrate) corresponded to a 54% yield.

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## Small-Ring Compounds. XV. Methylenecyclobutene and Related Substances<sup>1</sup>

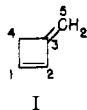
BY DOUGLAS E. APPLEQUIST<sup>2a</sup> AND JOHN D. ROBERTS<sup>2b</sup>

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Methylenecyclobutene has been synthesized from diethyl methylenemalonate by way of 3-methylenecyclobutanecarboxylic acid and 3-methylenecyclobutylamine. The synthesis featured the use of anthracene as a blocking group for the exocyclic double bond during malonic-ester closure of the cyclobutane ring. 4,4-Dimethyl-3-methylenecyclobutene has been obtained by degradation of  $\alpha$ -pinene and 1-phenyl-3-methylenecyclobutene by condensation of allene with phenylacetylene. Bromine addition and three types of polymerization of methylenecyclobutene have been found to proceed in accordance with predictions based on simple molecular-orbital theory. 3-Methylenetrimethylene oxide, of interest because of the possibility that it might have demonstrable  $\pi$ -bonding across the ring, has been prepared.

### Introduction

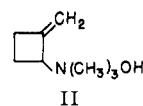
Simple molecular-orbital (LCAO) calculations<sup>3</sup> indicate the substantial delocalization energy of 1.59  $\beta$  for the cyclobutadienylcarbiny radical, cation and anion. Cyclobutadienylcarbiny intermediates could conceivably be obtained either from methylcyclobutadiene or from methylenecyclobutene (I), in the latter case by removal of a



proton, hydrogen atom or hydride ion from the 4-position. Synthesis of methylcyclobutadiene appeared less promising than the synthesis of methylenecyclobutene,<sup>4</sup> and the objective of the present

research was to find a practical synthesis of methylenecyclobutene (or simple derivatives thereof) and to test the validity of the predictions based on the molecular-orbital calculations.

The structure I was once tentatively assigned to pirylyene, a hydrocarbon obtained by a degradation of piperidine, by von Braun in 1928.<sup>5</sup> However, more recent chemical<sup>6</sup> and electron diffraction<sup>7</sup> evidence has demonstrated that pirylyene is methylvinylacetylene. Howton and Buchman have achieved the preparation of I, by pyrolysis of 2-methylenecyclobutyltrimethylammonium hydroxide (II)<sup>4,8</sup> (obtained from the previously described<sup>9</sup> corresponding quaternary bromide).



**Synthesis of Methylenecyclobutenes.**—The synthesis of methylenecyclobutene developed in the

(1) Supported in part by the Petroleum Research Fund of the American Chemical Society and presented before the Meeting of the American Chemical Society at Minneapolis, September 16, 1955.

(2) (a) National Science Foundation Predoctoral Fellow, 1953–1955; (b) Gates and Crellin Laboratories, California Institute of Technology.

(3) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952).

(4) E. R. Buchman, *Abst. of A. C. S. meeting*, Sept. 13, 1954, p. 9-O.

(5) J. von Braun and W. Teuffert, *Ber.*, **61**, 1092 (1928).

(6) H. Sargent, E. R. Buchman and J. P. Farquhar, *THIS JOURNAL*, **64**, 2692 (1942).

(7) R. Spurr and V. Schomaker, *ibid.*, **64**, 2693 (1942).

(8) D. R. Howton and E. R. Buchman, *ibid.*, **78**, 4011 (1956).

(9) E. R. Buchman and D. R. Howton, *ibid.*, **70**, 2517 (1948).