

Additions of Hydrogen Bromide to Methylene-cycloalkanes¹

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Received March 12, 1956

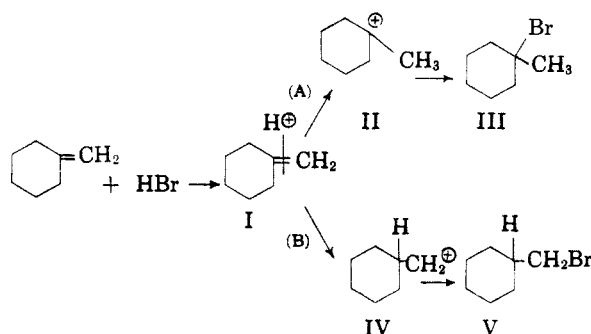
Both ionic and free radical additions of hydrogen bromide to a series of methylenecycloalkanes have been found to proceed normally; *i.e.*, ionic additions lead to tertiary bromides, free radical additions to primary bromides. In the ionic addition to methylenecyclobutane, excess hydrogen bromide led to the formation of 1,2-dibromo-2-methylbutane, but no bromo-methylcyclobutane could be detected. Apparently energy contributions arising from the formation of intermediates with a trigonal carbon in the ring are insufficient to cause abnormal orientations.

As part of a study of the effects of ring size on the orientations of addition reactions with cyclic olefins, we have investigated the addition of hydrogen bromide to a series of methylenecycloalkanes. Previous workers have described the peroxide-catalyzed² and the ionic³ addition of hydrogen bromide to methylenecyclobutane, but other methylenecycloalkanes do not appear to have been investigated. With anhydrous hydrogen bromide as reagent, both photochemically-initiated and ionic addition reactions have now been studied with methylenecyclobutane, methylenecyclopentane, methylenecyclohexane, and methylenecycloheptane.

Recent publications⁴ have emphasized the strain in cyclohexane and cyclobutane derivatives containing a trigonal carbon in the ring, relative to similar cyclopentane and cycloheptane systems. Since additions to olefins proceed in a stepwise manner with the formation of a trigonal atom during the reaction course,⁵ it seemed possible that the relative strain in intermediates derived from methylenecyclohexane and methylenecyclobutane might lead to anomalous orientations.⁶ The fact that "unexpected" products were not found in the reactions with methylenecyclobutane did not seem completely dissuasive because of the possibility of additional stabilization of intermediates leading to

normal products by transannular carbon participation in cyclobutane systems.⁷

The possible reaction paths, with methylenecyclohexane, for ionic addition of hydrogen bromide are illustrated.



Rearrangement⁸ of the protonated olefin to II (Path A) leads to the normal addition product III. However II has the carbonium ion center as part of the 6-membered ring. Although this tertiary carbonium ion would be favored by the usual considerations of hyperconjugation, the ring strain resulting from the trigonal atom in the ring would be expected to modify the stability considerably. Reaction by path B leads to the abnormal product (V). The intermediate IV lacks most of the hyperconjugative stabilization present in II, but it also lacks the unfavorable ring strain present in II. Thus if ring strain effects exceed the stabilization effects associated with a tertiary carbonium ion, path B would become the one of lower energy requirements and the abnormal product would be obtained.⁹

On the basis then of relative degrees of strain in the rings involved, an intermediate analogous to II would be unfavored with methylenecyclobutane and methylenecyclohexane, but favored with methylene-

(1) This work was supported in part by Research Corporation and in part by the Petroleum Research Fund of the American Chemical Society.

(2) Krug, Smith, and Fry, *J. Am. Chem. Soc.*, **76**, 3222 (1954).

(3) Shand, Schomaker, and Fischer, *J. Am. Chem. Soc.*, **66**, 636 (1944). Concentrated hydrobromic acid solution was used.

(4) (a) Brown and Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952); (b) Brown, Brewster, and Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954) and references cited there.

(5) Excellent discussions, with leading references, are given by Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953, pp. 646-653; and by Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956, pp. 202-223.

(6) Such anomalous orientations have been reported for at least one case. Tiffeneau, Weill, and Tchoubar [*Compt. rend.*, **205**, 144 (1937)] have reported that the addition of HOCl to methylenecyclohexane gives (1-chlorocyclohexyl)-methanol rather than the "expected" 1-chloromethylcyclohexanol. We are at present investigating additions of hypohalous acids to a series of methylenecycloalkanes and propose to describe these studies in a subsequent publication.

(7) Roberts and Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

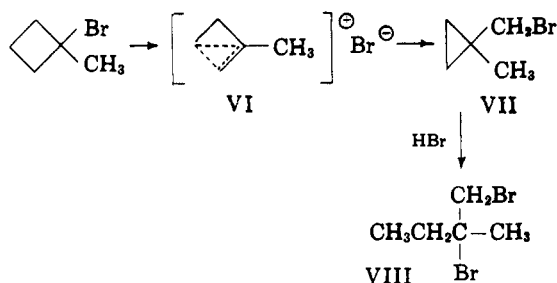
(8) Rearrangement of a protonated olefin (π -complex) to a more conventional carbonium ion has been shown to be an important part of the acid-catalyzed hydration reaction; Taft, *J. Am. Chem. Soc.*, **74**, 5372 (1952); Taft, Purlee, Riesz, and DeFazio, *J. Am. Chem. Soc.*, **77**, 1584 (1955).

(9) This assumes, of course, that the transition state for the slow rearrangement of the π -complex (I) closely resembles the conventional carbonium ion.

cyclopentane and methylenecycloheptane. Similar statements could be made for free radical processes.

However, with all four olefins, by both ionic and free radical paths, the normal products were obtained; that is, ionic addition led to 1-methyl-1-bromocycloalkane and free radical addition to cycloalkylbromomethane. These were the exclusive products from the three higher molecular weight olefins. The products from these olefins were characterized by comparison of their physical properties and infrared spectra with those of authentic samples prepared by independent syntheses.

Some side products, formed in much smaller amounts, were also obtained from the ionic addition to methylenecyclobutane. These were 1,2-dibromo-2-methylbutane and an unidentified lower-boiling, bromine-containing compound.¹⁰ When care was taken to avoid any excess of hydrogen bromide, 1-bromo-1-methylcyclobutane was virtually the exclusive product. Both of these side products were formed at the expense of the major product when an excess of hydrogen bromide was used or when the major product was treated separately with hydrogen bromide under the conditions of the ionic addition reaction.¹¹ These data strongly suggest that these products indeed arise through secondary reactions and may not be formed concurrently with the normal addition product. The very slow rate of solvolysis reported^{4a} for 1-chloro-1-methylcyclobutane makes an ionization mechanism somewhat unattractive for the rather facile reaction of 1-bromo-1-methylcyclobutane with hydrogen bromide. However, the rearrangement of a nonclassical carbonium ion (VI) through a cyclopropane derivative (VII)¹² does provide a more reasonable path for the formation of 1,2-dibromo-2-methylbutane than does simple ring opening (which would have to occur between ring carbon atoms 2 and 3).

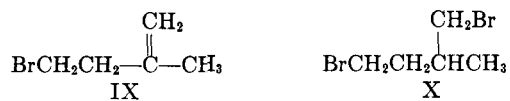


(10) Although the density, infrared spectrum, and carbon-hydrogen analysis of this unidentified fraction strongly suggest the presence of more than one bromine atom per molecule, it is difficult to reconcile this suggestion with the relatively low b.p. and apparent molecular weight of the material.

(11) By contrast, treatment of methylenecyclobutane "at 0° with hydrogen chloride until no more gas was absorbed" has been reported to give an 89% yield of 1-chloro-1-methylcyclobutane.^{4a}

(12) Applequist and Roberts, *J. Am. Chem. Soc.*, **78**, 874 (1956).

Rearrangement¹² of VI might be expected to lead also to IX or X



but no evidence for the presence of these nor of VII was found. Particularly important for the present considerations is the fact that no bromomethylcyclobutane could be detected in the product mixture.

No addition products other than bromomethylcyclobutane could be found in the mixture from the free radical reaction. The structure assignment for this product was confirmed by its nuclear-magnetic-resonance spectrum.¹³

Apparently the effects of ring strain in intermediates derived from methylenecyclobutane and methylenecyclohexane are insufficient to outweigh the stabilizing influence favoring the tertiary carbonium ion or radical.¹⁴

EXPERIMENTAL

1-Methylcycloalkyl acetates. 1-Methylcyclopentanol, 1-methylcyclohexanol and 1-methylcycloheptanol were prepared by reaction of a methylmagnesium halide reagent with the appropriate cycloalkanone. The tertiary alcohols were then converted to corresponding acetates by treatment with acetyl chloride in pyridine solution.¹⁵

A mixture of tertiary alcohol and dry pyridine (1:1.05 mole ratio) was placed in a 1-liter, 3-neck flask fitted with a stirrer, condenser, and dropping-funnel. While the flask was chilled by an ice-bath, 1.05 molar equivalents of acetyl chloride were added slowly. The cooling bath was removed and stirring was continued until the spontaneous reaction had subsided. The mixture was heated for 3 hours at approximately 60°. To the cooled mixture were added convenient quantities of petroleum ether (b.p. 30–38°) and water. The organic layer was separated and was washed with water, with dilute sodium carbonate solution, and again with water. After being dried over potassium carbonate, the mixture was distilled. Some starting alcohol was always recovered and the yields of acetates reported are based on

(13) The authors are indebted to Drs. Homer Hix and John R. Zimmerman of the Magnolia Petroleum Company, Dallas, Texas, for the nuclear magnetic resonance spectrum and its interpretation. The n-m-r spectrum indicated that there were hydrogens with 4 distinctly different electronic environments in the molecule and provided strong evidence for a single hydrogen attached to one of the carbons. Although the infrared spectrum showed strong absorption at 7.27 μ , the n-m-r spectrum provided no evidence for the presence of a methyl group.

(14) On the basis of the stabilization energies quoted by Baker (*Hyperconjugation*, Oxford Univ. Press, London, 1952, p. 35), one may estimate that the difference in stabilization energy of a tertiary free radical (with 7 α -hydrogens) and a primary free radical (with 1 α -hydrogen) is about 5–7 kcal./mole. Similarly the difference in stabilization energy of a tertiary carbonium ion (7 α -hydrogens) and a primary carbonium ion (1 α -hydrogen) is about 16 kcal./mole.

(15) In our hands, this procedure gave higher conversions and yields than one prescribing powdered magnesium and acetic anhydride (Reference 16).

unrecovered alcohol. The figures in parentheses represent the proportion of alcohol recovered.

Prepared were: 1-methylcyclopentyl acetate, b.p. 155–156°, d_4^{20} 0.946, n_D^{20} 1.4320, yield 75% (7.6%); 1-methylcyclohexyl acetate,¹⁶ b.p. 178–179°, d_4^{20} 0.957, n_D^{20} 1.4375, yield 70% (18%); and 1-methylcycloheptyl acetate, b.p. 110–111° (40 mm.), d_4^{20} 1.032, n_D^{20} 1.4528, yield 58% (23%).

Pyrolysis of acetates. Methylene-cyclopentane, methylene-cyclohexane, and methylene-cycloheptane were prepared by pyrolysis¹⁶ at 450° of the appropriate tertiary acetate. In the absence of the Hoskins furnace recommended,¹⁶ a Sargent Carius combustion apparatus, arranged vertically, was found to be quite satisfactory. The pyrolysis tube was a 45-cm. length of 9-mm. Pyrex tubing; the 25-cm. length that was heated by the Carius Combustion Apparatus was packed with 3-mm. Pyrex glass helices. The acetates were added at the rate of one drop per second. A slow stream of nitrogen minimized oxidation and swept the pyrolysate vapor into the condenser. The condensed pyrolysate was taken up in petroleum ether (b.p. 30–38°) and the solution was washed successively with water, with sodium carbonate solution, and with water. It was dried over potassium carbonate and then distilled through a 6-inch Vigreux column. The yields reported are based on unrecovered acetate; the figures in parentheses represent the proportion of acetate recovered.

Prepared were: methylene-cyclopentane,¹⁷ b.p. 75–76°, d_4^{20} 0.778, n_D^{20} 1.4310, yield 69% (26%); methylene-cyclohexane,^{16–19} b.p. 108–109°, d_4^{20} 0.804, n_D^{20} 1.4508, yield 83% (32%); and methylene-cycloheptane,¹⁹ b.p. 138–139°, d_4^{20} 0.823, n_D^{20} 1.4609, yield 72% (30%).

Identity of methylenecyclohexane sample. Although several previous investigators^{16–19} have reported a b.p. for methylene cyclohexane in the range 101–106° (most frequently at about 103°), in about 12 preparations we have consistently obtained material boiling at 108–109°. The isomer, 1-methylcyclohexene, has been reported^{16–18} to boil in the range 109–112° (most frequently at about 110°) and we have also observed a b.p. of 110–111° (d_4^{20} 0.810, n_D^{20} 1.4502). Small differences in position and relative intensities of the infrared absorption bands distinguished the spectra of the two isomers. A weak band at 10.15 μ , which was absent in the spectrum of the *endo*-olefin, was present in that of the *exo*-olefin. In order to confirm the identity of our sample of methylenecyclohexane, it was converted into the glycol¹⁹ with peroxyformic acid²⁰; 52% yield, m.p. 76–77°. The glycol derived from 1-methylcyclohexene is reported²¹ to melt at 84°.

Further, our methylenecyclohexane glycol, when heated with concentrated hydrobromic acid, gave an 81% yield of cyclohexanecarboxyaldehyde²²; b.p. 49.5° (10 mm.), n_D^{20} 1.4490; m.p. of 2,4-dinitrophenylhydrazones,²² 172–173°.

We believe the identification of our sample of methylenecyclohexane to be valid and are unable to account for the b.p. differences described above.

Independent syntheses of 1-bromo-1-methylcycloalkanes. Each of the tertiary bromides was synthesized, independent of the addition reactions, by reaction of concentrated hydro-

bromic acid (48%) with the appropriate 1-methylcycloalkanol.²³

1-Bromo-1-methylcyclopentane: 47% yield, b.p. 56–57° (36 mm.), d_4^{20} 1.298, n_D^{20} 1.4815.

1-Bromo-1-methylcyclohexane: 52% yield, b.p. 78–79° (38 mm.), d_4^{20} 1.251, n_D^{20} 1.4866.²⁴

1-Bromo-1-methylcycloheptane: 52% yield, b.p. 102–103° (39 mm.), d_4^{20} 1.236, n_D^{20} 1.4966.

Independent syntheses of bromomethylcycloalkanes. Each of the primary bromides was synthesized, independent of the addition reactions, from the appropriate cycloalkyl halide by reaction of the corresponding Grignard reagent with formaldehyde²⁵ and subsequent treatment of the cycloalkylcarbinol so obtained with phosphorus tribromide.²⁶

Cyclopentylcarbinol²⁶: 65% yield, b.p. 162–163°, d_4^{20} 0.930, n_D^{20} 1.4576. Bromomethylcyclopentane: 47% yield, b.p. 72–73° (38 mm.), d_4^{20} 1.271, n_D^{20} 1.4831.

Cyclohexylcarbinol²⁷: 62% yield, b.p. 69–70° (5 mm.), d_4^{20} 0.927, n_D^{20} 1.4650. Bromomethylcyclohexane²⁸: 53% yield, b.p. 93–94° (38 mm.), d_4^{20} 1.283, n_D^{20} 1.4928.

Cycloheptylcarbinol²⁹: 59% yield, b.p. 114–115° (40 mm.), d_4^{20} 0.932, n_D^{20} 1.4678. Bromomethylcycloheptane: 34% yield, b.p. 106–107° (38 mm.), d_4^{20} 1.254, n_D^{20} 1.4987.

Ionic additions of hydrogen bromide to methylenecycloalkanes. While the temperature of the mixture was kept at 5–10°, slightly more than 0.1 mole of anhydrous hydrogen bromide was passed into a solution of approximately 0.1 mole of methylenecycloalkane in 50 ml. of glacial acetic acid in a 200-ml. flask equipped with stirrer. The gaseous hydrogen bromide was added at such a rate that virtually all of it was absorbed (about 2 hours). For a total of 8 hours, the reaction mixture was stirred at 5–10°. It was then poured into 100 ml. of water. The water-insoluble material was extracted into petroleum ether (b.p. 30–38°), washed with dilute sodium carbonate solution and with water, dried over sodium sulfate, and distilled. The data are summarized in Table I.

Ionic addition to methylenecyclobutane. By the general procedure described above, three products were obtained from methylenecyclobutane: A, unidentified, b.p. 76–77°, d_4^{20} 1.563, n_D^{20} 1.4582, Mol. wt. (C₄H₈ f.p. depression) 153; *Anal.*,³⁰ C, 8.76, 8.90%; H, 0.60, 0.42%; unreactive toward KMnO₄, Br₂ in CCl₄, and NaI in acetone (solution turned dark yellow but no precipitate appeared); immediate precipitate formation with alcoholic AgNO₃. B, 1-bromo-1-methylcyclobutane,³ b.p. 111–112°, d_4^{20} 1.319, n_D^{20} 1.4695, C, 1,2-dibromo-2-methylbutane,³¹ b.p. 83–84° (40 mm.), d_4^{20} 1.670, n_D^{20} 1.5090.

The proportions of the three products depended upon the

(23) The procedure described by Norris, Watt, and Thomas, *J. Am. Chem. Soc.*, **38**, 1071 (1916), for the preparation of α -chloroethylbenzene was used with HBr solution being substituted for HCl solution.

(24) Goering, Abell, and Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952), report n_D^{20} 1.4468. This may be a misprint since the values of n_D^{20} for the lower and higher homologous 1-bromo-1-methylcycloalkanes are 1.4815 and 1.4966 respectively.

(25) Gilman and Catlin, in *Org. Syntheses*, Coll. Vol. 1, 2nd ed., 188–190 (1941).

(26) Noller and Adams, *J. Am. Chem. Soc.*, **48**, 1080 (1926).

(27) Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, London, 1953, Vol. I, p. 640.

(28) Perlman, Davidson, and Bogert, *J. Org. Chem.*, **1**, 288 (1936).

(29) Rosanov, *Zhur. Russ. Fiz. Khim. Obshchestva*, **61**, 2313 (1929) [*Chem. Zentr.*, **101**, (II), 229 (1930)].

(30) Analyses by Geller Laboratories, Hackensack, N. J.

(31) Sherill and Walter, *J. Am. Chem. Soc.*, **58**, 742 (1936).

(16) Bailey, Hewitt, and King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

(17) Vogel, *J. Chem. Soc.*, 1323 (1938).

(18) Egloff, *Physical Constants of Hydrocarbons*, Reinhold Pub. Corp., New York, N. Y., 1940, vol. 2, pp. 160, 326.

(19) Wallach, *Ann.*, **347**, 316 (1906).

(20) Roberts and Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

(21) Adkins and Roebuck, *J. Am. Chem. Soc.*, **70**, 4041 (1948).

(22) Heilbron, Jones, Richardson, and Sondheimer, *J. Chem. Soc.*, 737 (1949).

TABLE I
 DATA FOR ADDITIONS OF HBr TO METHYLENECYCLOALKANES

Ring Size	Yield, %	Ionic Addition Product			Free Radical Addition Product			
		B.p., °C. (37-38 mm.)	d_4^{20}	n_D^{20}	Yield, %	B.p., °C. (37-38 mm.)	d_4^{20}	n_D^{20}
C ₄ ^a	61	111-112 ^b	1.319	1.4695	59	123-124 ^b	1.326	1.4726
C ₅	53	56-57	1.299	1.4817	60	71-72	1.372	1.4831
C ₆	65	77-78	1.250	1.4865	71	92-93	1.283	1.4928
C ₇	63	101-102	1.235	1.4962	61	107-108	1.253	1.4989

^a Data for only the major ionic addition product are included. ^b Atmospheric pressure.

amount of HBr used. When care was taken to avoid any excess of HBr, B was obtained in 62% yield from 0.12 mole of olefin but less than 0.1 g. each of A and C was obtained. Treatment of 0.15 mole of olefin with an excess of HBr under similar conditions yielded 8.4 g. of A, 7.8 g. (36%) of B, and 9.5 g. (28%) of C.

Substitution of 6.2 g. (0.04 mole) of B for methylenecyclobutane in the general procedure led to the isolation of 1.5 g. of A, 0.5 g. (8%) of recovered B and 3.5 g. (37%) of C.

Summary of features of infrared spectra. All infrared spectra were obtained with a Perkin-Elmer model 21 spectrophotometer with 0.035-mm. and 0.053-mm. cells (NaCl windows). Because of the proclivity toward rearrangement in cyclobutane systems, the spectra of the products obtained from methylenecyclobutane are summarized here. Only bands with absorbancy (A) greater than 0.3 are included. The relative intensities of the bands are indicated: s (strong), A greater than 0.7; m (medium), A between 0.4 and 0.7; w (weak), A less than 0.4.

1-Bromo-1-methylcyclobutane: 3.38 (s), 5.97 (m), 6.86-6.92 (s), 7.27 (s), 7.44 (w), 7.77 (w), 7.94 (w), 8.17 (s), 8.32 (s), 8.47 (s), 8.8 broad (s), 9.18 (s), 9.47 (w), 9.87 (m), 10.90 (w), 11.95 (m), 12.7-13.1 (s), and 14.55 μ (w).

1,2-Dibromo-2-methylbutane: 3.35 (s), 3.41 (s), 6.87 (s),

6.97 (s), 7.23 (s), 8.15 (s), 9.01 (s), 9.06 (s), 9.74 (m), 9.95 (m), 11.57 (w), 12.57 (s), and 13.07 μ (w).

Unidentified fraction (A). Essentially identical with spectrum of CCl₄ except for additional weak bands (C-H) at 3.37, 6.84, and 7.24 μ .

Bromomethylcyclobutane. 3.41 (s), 3.45 (s), 6.94 (s), 7.01 (s), 7.27 (s), 8.09 (s), 8.29 (s), 8.92 (s), 10.95 (w), 12.78 (s), 13.38 (w), and 14.55 μ (m).

Free radical additions of hydrogen bromide to methylenecycloalkanes. A solution of approximately 0.1 mole of methylenecycloalkane in 50 ml. of purified petroleum ether (b.p. 35-40°) was placed in a quartz reaction flask equipped with a gas inlet tube and a thermometer. While the olefin solution was kept cool at -20° to -25° by a CO₂-CCl₄ bath and was irradiated with a 250-watt G.E. type H mercury vapor lamp, a slow stream of anhydrous hydrogen bromide was passed into the solution during 2 hours. The mixture then was poured into 100 ml. of water. The organic material was washed successively with a dilute ferrous sulfate solution, a dilute sodium carbonate solution, and water. It was dried over sodium sulfate and distilled.

The data are summarized in Table I.

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