

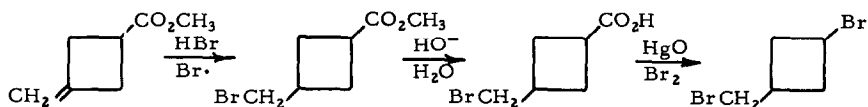
THE REACTION OF 3-BROMOCYCLOBUTANE-1-METHYL BROMIDE
WITH SODIUM : BICYCLO[1.1.1]PENTANE¹

By Kenneth B. Wiberg, Daniel S. Connor and Gary M. Lampman
Department of Chemistry, Yale University, New Haven, Conn.

(Received 20 January 1964)

In recent years, the syntheses of a number of bicyclic small ring compounds such as the bicyclo[1.1.0]butanes,^{2,3} bicyclo[2.1.0]pentane,^{4,5} bicyclo[2.2.0]hexane,^{5,6} the bicyclo[2.1.1]hexanes,⁷ the bicyclo[3.1.0]hexanes,⁸ the bicyclo[3.1.1]heptanes,^{9,10} and the bicyclo[3.2.0]heptanes¹⁰ have been reported. The one member of this group for which no representatives have been obtained is bicyclo[1.1.1]pentane although it appears to have a crucial role in the interpretation of the effects of bond angle deformation on the properties of compounds.

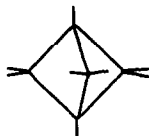
Encouraged by our success in effecting a ring closure of 1-bromo-3-chlorobutane to bicyclobutane using sodium,³ we have attempted a similar reaction with 3-bromocyclobutane-1-methyl bromide. This compound was prepared from methyl 3-methylenecyclobutane-1-carboxylate¹¹ by the anti-Markownikoff addition of hydrogen bromide followed by hydrolysis and brominative decarboxylation.¹²



The reaction of the bromoacid with mercuric oxide and bromine gave a 50% yield of the dibromide when the acid and bromine were added simultaneously to the mercuric oxide.

The reaction of the dibromide with sodium in dioxane led to a rapid gas evolution. Initial gas chromatographic separation of the mixture using β, β' -oxydipropionitrile as the substrate, gave a mixture of hydrocarbons having a retention time of 4.6 min., followed by a saturated hydrocarbon (I) (5.5 min.) and 1,4-pentadiene (II) (6.3 min.) in an approximate ratio of 80 : 1 : 20. The separation of I and II was not quantitative, but they could be separated using nitrobenzene as the substrate (I, 13.8 min., II, 11.5 min.).

The hydrocarbon, I, was saturated and gave two sharp n. m. r. signals at 8.16 and 7.55 τ in the ratio of 3 : 1. The mass spectrum indicated a molecular weight of 68. These data permit only one structure, bicyclo[1.1.1]pentane. Here, six carbon-hydrogen bonds lie in an



I

equatorial belt and the two bridgehead carbon-hydrogen bonds lie at right angles to the six. This is a case in which a small spin-spin coupling constant might be expected¹³ and is in good accord with the assigned structure.

The hydrocarbon mixture obtained as the first fraction in the initial gas chromatographic separation could be resolved using nitrobenzene as the substrate and was found to contain methylcyclobutane and 1-pentene in about equal quantity. The details of the ring forming reactions, and the reactions of bicyclo[1.1.1]pentane will be discussed in a subsequent manuscript.

We wish to thank Mr. H. Hoberecht, Olin Matheson Chemical Corp., for obtaining the mass spectrum.

REFERENCES

1. This work was supported by the U.S. Army Research Office (Durham).
2. K. B. Wiberg and R. P. Ciula, J. Am. Chem. Soc., 81, 5261 (1959); W. R. Moore, H. R. Ward and R. F. Merritt, ibid., 83, 2019 (1961); D. M. Lemal, F. Menger and G. W. Clark, ibid., 85, 2529 (1963).
3. K. B. Wiberg and G. M. Lampman, Tetrahedron Letters, 2173 (1963).
4. R. Criegee and A. Rimmelin, Chem. Ber., 90, 414 (1957).
5. C. E. Griffin, N. F. Hepfinger and B. L. Shapiro, J. Am. Chem. Soc., 85, 2683 (1963).
6. S. Cremer and R. Srinivasan, Tetrahedron Letters, No. 21, 24 (1960).
7. J. Meinwald and P. Gassman, J. Am. Chem. Soc., 82, 2857 (1960); 82, 5445 (1960); K. B. Wiberg, B. R. Lowry, and T. H. Colby, ibid., 83, 3998 (1961); K. B. Wiberg, and B. R. Lowry, ibid., 85, 3188 (1963).
8. M. S. Kharasch, Jerome S. Sullo, and Walter Nudenberg, J. Org. Chem., 21, 129 (1956); Howard E. Simmons and Ronald D. Smith, J. Am. Chem. Soc., 81, 4256 (1959).
9. W. H. Brown, Ph. D. Thesis, Columbia University, 1928; E. Wenkert and D. P. Strike, J. Org. Chem., 27, 1883 (1962); F. Nerdel, D. Frank and H. Marschall, Angew. Chem. Int. Ed., 1,

- 457 (1962).
10. K. B. Wiberg and G. W. Klein, Tetrahedron Letters, 1043 (1963).
 11. H. K. Cripps, J. K. Williams and W. H. Sharkey, J. Am. Chem. Soc. 81, 2723 (1959).
 12. S. J. Cristol and W. C. Firth, J. Org. Chem., 26, 280 (1961).
 13. M. Karplus, J. Chem. Phys., 30, 11 (1959); M. Karplus and D. H. Anderson, ibid., 30, 6 (1959); H. Conroy, Advances in Organic Chemistry, Methods and Results, Vol. 2, p. 308, Interscience Publishers, New York.