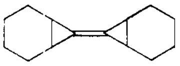
Communications TO THE EDITOR

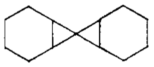
Reactions of *gem*-Dibromocyclopropanes with Alkyllithium Reagents. Formation of Allenes, Spiropentanes, and a Derivative of Bicyclopropylidene[1]

Sir:

We have found that treatment of *gem*-dibromocyclopropanes with methyl- or butyllithium in ether at 0 to −80° presents a general method for the synthesis of allenes[2]; 1,2-undecadiene (*Anal.* Found: C, 86.77; H, 13.04), 2,3-heptadiene (*Anal.* Found: C, 87.52; H, 12.60), 1,2-cyclodecadiene (*Anal.* Found: C, 88.13; H, 11.96), and 1,2-cycloundecadiene (*Anal.* Found: C, 87.81; H, 12.12) have been obtained in 70–90% yields.

In these reactions, no evidence of carbene intermediates[3] has been found in experiments employing cyclohexene as a trapping agent. However, treatment of 7,7-dibromobicyclo [4.1.0]heptane (I) with methyllithium in ether-cyclohexene at −80° gave a mixture of products from which a white solid (II) (30%), m.p. 120.5–121°, $C_{14}H_{20}$ (*Anal.* Found: C, 89.56; H, 10.54; mol. wt.,[4] 188) and liquids (III) (10%; *Anal.* Found: C, 88.43; H, 11.53; mol. wt.,[4] 176) and IV (5%; *Anal.* Found: C, 88.68; H, 11.45; mol. wt.,[4] 176), both $C_{13}H_{20}$, were isolated by gas chromatography.[5] In the absence of cyclohexene, II was obtained but III and IV were not formed.

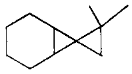

II

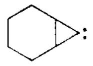

III

Structure II has been assigned on the basis of the following data: reaction with bromine, high end absorption in the ultraviolet ($\lambda^{C_2H_5OH}$ 206 mμ, ε ∼ 13,000), NMR[6] absorption in the region $\tau = 8 - 9$ only (no olefinic protons), $\nu_{max}^{CCl_4}$ 2977 cm.$^{-1}$ (cyclopropane C—H). Hydrogenation of II (platinum, acetic acid, 25°, 1 atm.) has given mixtures of dihydro-II ($\nu_{max}^{CCl_4}$ 3000 cm.$^{-1}$; *Anal.* Found: C, 88.31; H, 11.55), tetrahydro-II ($\nu_{max}^{CCl_4}$ 3000 cm.$^{-1}$; *Anal.* Found: C, 87.08; H, 12.51) and 1,2-dicyclohexylethane (hexahydro-II). At higher temperatures, both di- and tetrahydro-II are slowly hydrogenated to give 1,2-dicyclohexylethane.

Structure III has been assigned on the basis of the following data: no reaction with bromine, essentially no end absorption in the ultraviolet ($\lambda^{C_2H_5OH}$ 206 mμ, ε < 300), NMR[6] absorption in the region $\tau = 8 - 9$ only, $\nu_{max}^{CCl_4}$ 2988 cm.$^{-1}$ Hydrogenation of III (platinum, acetic acid, 120°, 34 atm.) gave only cyclohexylcycloheptane (identified by gas chromatography on three columns and comparison of infrared spectra. *Anal.* Found: C, 86.61; H, 13.49). Less vigorous conditions (platinum, propionic acid, 100°, 1 atm.) gave 74% of cyclohexylcycloheptane, 1% of a compound with retention times (four columns) identical to those of dicyclohexylmethane, and 24% of dihydro-III (mol. wt.[4] 178; $\nu_{max}^{CCl_4}$ 2996 cm.$^{-1}$).

Present results indicate that the formation of spiropentanes related to III may be general. A liquid, $C_{11}H_{18}$ (*Anal.* Found: C, 87.91; H, 12.04; mol. wt.[4] 150), assigned structure V on the basis of evidence similar to that presented for III, has been obtained from the reaction of I with methyllithium in the presence of isobutylene.


V


VI

The formation of spiropentanes III[7] and V[7] must involve a common intermediate which may be carbene VI, or the highly strained 1,2-cycloheptadiene, or a species which is intermediate in structure between carbene and allene. The formation of bicyclopropylidene II[7] may also involve this intermediate. We hope that work in progress may shed some light on these questions.

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Received July 11, 1960

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958) have reported related reactions.

[3] Certain polyhalomethylenes produce carbenes when treated with alkyllithium reagents. (a) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959). (b) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

[4] Determined by mass spectrometry. We thank Prof. K. Biemann for measuring the mass spectra.

[5] (a) Relative retention times: Carbowax 20 M (142°) $t_{II}/t_{III} = 2.70$, $t_{IV}/t_{III} = 1.00$; silver nitrate (15%) – tetraethylene glycol (115°), $t_{IV}/t_{III} = 1.41$. (b) The structure of IV (an olefin) and the structures of lower boiling products will be discussed in the future.

[6] (a) $\tau = 10.00 - \delta^{int}_{Me_4Si}$. (b) Tertiary cyclopropane protons in certain fused-ring systems (*e.g.*, norcarane) show signals below $\tau = 9$. (c) We thank Dr. G. E. Maciel for measuring NMR spectra.

[7] Consistent names: II, 7,7′-{bicyclo[4.1.0]heptylidene}; III, 7,7′-spirobi{bicyclo[4.1.0]heptane}; IV, spiro{bicyclo[4.1.0]heptane-7,1′-(2′,2′-dimethylcyclopropane)}.

[8] National Science Foundation Summer Fellow, 1959.