

Reactions of gem-Dibromocyclopropanes with Alkyllithium Reagents. Formation of Allenes, Spiropentanes, and a Derivative of Bicyclopropylidene¹

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 allenes²; 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 intermediates³ 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°, C₁₄H₂₀ (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 C₁₃H₂₀, were isolated by gas chromatography.⁵ In the absence of cyclohexene, II was obtained but III and IV were not formed.



Structure II has been assigned on the basis of the following data: reaction with bromine, high end absorption in the ultraviolet $(\lambda^{C_2H_6OH} 206 \text{ m}\mu)$,

(4) Determined by mass spectrometry. We thank Prof. K. Biemann for measuring the mass spectra.

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

(6) (a) $r = 10.00 - \delta_{\text{Metsi-}}^{\text{int}}$ (b) Tertiary cyclopropane protons in certain fused-ring systems (e.g., norcarane) show signals below r = 9. (c) We thank Dr. G. E. Maciel for measuring NMR spectra.

 $\epsilon \sim 13,000$), NMR⁶ absorption in the region $\tau = 8 - 9$ only (no olefinic protons), $\nu_{max}^{\rm CCL_4} 2977$ cm.⁻¹ (cyclopropane C—H). Hydrogenation of II (platinum, acetic acid, 25°, 1 atm.) has given mixtures of dihydro-II ($\nu_{max}^{\rm CCL_4} 3000$ cm.⁻¹; Anal. Found: C, 88.31; H, 11.55), tetrahydro-II ($\nu_{max}^{\rm CCL_4} 3000$ 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 $(\lambda^{C_1H_0OH} 206 \text{ m}\mu, \epsilon < 300)$, NMR⁶ absorption in the region $\tau = 8 - 9$ only, $\nu_{\max}^{CCl_4} 2988 \text{ cm.}^{-1}$ 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; $\nu_{\max}^{CCl_4} 2996 \text{ cm.}^{-1}$).

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.



The formation of spiropentanes III⁷ and V⁷ 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 II⁷ may also involve this intermediate. We hope that work in progress may shed some light on these questions.

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(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)}.

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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).