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A NOVEL ROUTE TO CUMULENES. THE ADDITION OF DIHALOCARBENES TO 2,5-DIMETHYL-2,3,4-HEXATRIENE.

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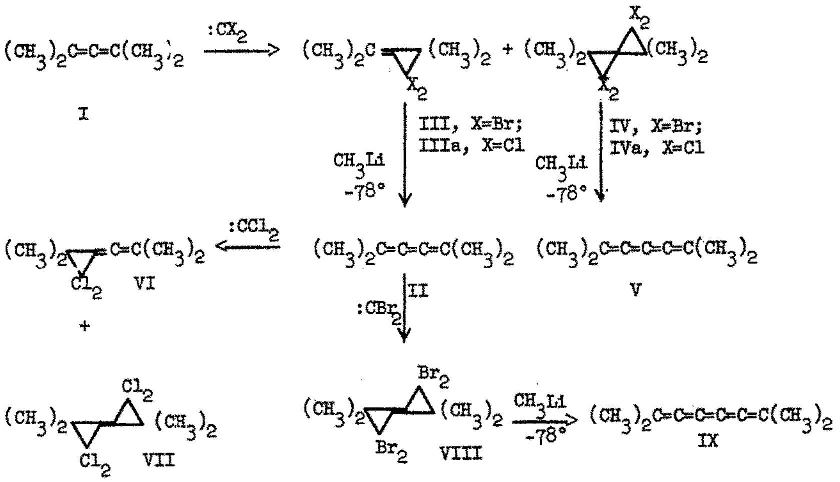
Doering and Hoffmann[1] discovered that gem-dihalocyclopropanes can be formed by the addition to olefins of dihalocarbenes, generated from the respective haloform and potassium t-butoxide. An impressive amount of work has since been carried out on this and related reactions.[2] Ball and Landor[3] described the addition of dibromocarbene to allenes yielding methylenecyclopropanes, but the formation of diadducts, i.e. spiropentanes, has not been described, nor has successful addition to a cumulene been reported in the literature.

This preliminary communication describes the addition of dichloro- and dibromocarbene to 2,4-dimethyl-2,3-pentadiene (I) and 2,5-dimethyl-2,3,4-hexatriene (II) to give the corresponding gem-dihalocyclopropane derivatives. The treatment of the dibromo derivatives with methyllithium[4] afforded cumulenes, and this sequence of two reactions, starting from allenes, constitutes a novel route to this class of compounds.[5] It appears particularly promising as a method for the synthesis of alkyl-substituted cumulenes.

The following chart summarizes the reactions carried out:



The reaction of an excess of two molar equivalents of dibromocarbene with 2,4-dimethyl-2,3-pentadiene (I) gave a mixture of the monoadduct III,[6] m.p. 42-43°, and the diadduct IV,[6] m.p. 216° (dec.), in 67 and 6% yields, respectively. A similar reaction of I with dichlorocarbene yielded 73% of the monoadduct IIIa, m.p. 38°, and 3% of the diadduct IVa, m.p. 208°. The compounds were characterized by elemental analyses and spectroscopic evidence. It is interesting to note that compound III exhibited an ultraviolet absorption maximum at 214.5 mμ (ε 15700), which can be ascribed to the strained double bond. The treatment of this compound with ethereal methyllithium at -78° afforded in practically theoretical yield a highly oxygen-sensitive crystalline compound, m.p. 40°; λ_{max} (n-hexane) 230 mμ (ε ~ 7000) and 262.5 mμ (ε ~ 17000);[7] ν_{max} 1900, 1645 cm^{-1} (C=C).[9] The n.m.r. spectrum shows only a single peak at τ 8.19, and hydrogenation (Pd-charcoal catalyst) gave exclusively 2,5-dimethylhexane. On the basis of this evidence the structure 2,5-dimethyl-2,3,4-hexatriene (II)[10] has been assigned.

The reaction of the spiropentane IV with methyllithium gave a very unstable liquid together with some polymeric material. The n.m.r. spectrum exhibits a single peak at τ 8.13; ultraviolet absorption maxima were observed at 224 and 250 mμ, and the infrared spectrum shows a weak band at 2010 cm^{-1}. Catalytic hydrogenation yielded 2,6-dimethylheptane. The compound underwent rearrangement to 2,6-dimethyl-1,5-heptadien-3-yne on attempted gas chromatography. On the basis of this evidence the structure 2,6-dimethyl-2,3,4,5-heptatetraene (V) has been assigned to this compound. It is the first reported aliphatic cumulene with an even number of double bonds. Recently Kuhn, Fischer and Fischer[13] described for the first time the synthesis of two aryl-substituted pentatetraenes.

The addition of dichlorocarbene[1] to the cumulene II produced the compounds VI and VII in 65 and 16% yields, respectively. The structure of VI,[6] m.p. 80-84° (dec.), has been assigned on the following evidence besides elemental analysis: the infrared spectrum shows a strong band at 2010 cm^{-1} due to the allenic linkage,[14] and the absence of olefinic absorption. The n.m.r. spectrum consists of two singlets of equal intensity at τ 8.44 and 8.65 corresponding to the methyl groups attached to the double bond and the cyclopropane ring, respectively. The ultraviolet spectrum exhibits only end absorption.

The bicyclopropylidene VII,[6] m.p. 152°, is surprisingly stable. The infrared spectrum shows no bands due to unsaturation, but the ultraviolet spectrum shows a maximum at 216.5 mμ (ϵ 18700).[15] In accordance with the structure VII the twelve equivalent methyl protons give rise to one singlet at τ 8.48 in the n.m.r. spectrum. The configuration about the double bond has been shown to be trans on the basis of X-ray crystallography.[17]

The reaction of II with dibromocarbene has so far invariably produced a complex mixture. We have only been able to separate a small amount of a compound, m.p. 155-159° (dec.), which has been assigned the structure VIII[6] on the basis of similar evidence to that obtained for VII. In addition, the reaction of VIII with methyllithium gave a compound too unstable to be isolated which exhibited ultraviolet maxima at 215, 228, 308, and 321 mμ.[18] We assume that the compound has the structure 2,7-dimethyl-2,3,4,5,6-octapentaene (IX).[19]

References

1. W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).
2. For a review see W. E. Parham and E. E. Schweizer, *Organic Reactions*, **13**, 55 (1963).
3. W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 246 (1961).
4. Allenes can be formed from *gem*-dibromocyclopropanes and methyllithium; L. Skattebøl, *Acta. Chem. Scand.*, **17**, 1683 (1963).
5. For a review on cumulenes, see P. Cadiot, W. Chodkiewicz and J. Rauss-Godineau, *Bull. Soc. Chim.* (France), 2176 (1961).
6. Consistent names: III, 1,1-dibromo-2,2-dimethyl-3-isopropylidenecyclopropane; IIIa, 1,1-dichloro-2,2-dimethyl-3-isopropylidenecyclopropane; IV, 2,2,2',2'-tetrabromo-3,3,3',3'-tetramethylspiropentane; IVa, 2,2,2',2'-tetrachloro-3,3,3',3'-tetramethylspiropentane; VI, 1-(2-methylpropenylidene)-2,2-dichloro-3,3-dimethylcyclopropane; VII, 2,2,2',2'-tetrachloro-3,3,3',3'-tetramethyl-1,1'-bicyclopropylidene; VIII, 2,2,2',2'-tetrabromo-3,3,3',3'-tetramethyl-1,1'-bicyclopropylidene.
7. This is in good agreement with maxima at 230 and 271.5 mμ observed for the similar triene bis[2,2,6,6-tetramethylcyclohexylidene]ethylene.[8]
8. F. Bohlmann and K. Kieslich, *Ber.*, **87**, 1363 (1954).

9. Butatriene absorbs at 2030 and 1610 cm^{-1}, W. M. Schubert, T. H. Liddicoet and W. A. Lanka, *J. Am. Chem. Soc.*, **76**, 1929 (1954).

10. The reaction of 2,5-dichloro-2,5-dimethyl-3-hexyne with either methylmagnesium bromide[11] or zinc[12] gave a compound with identical physical and chemical properties.

11. L. Skattebøl, *Tetrahedron*, in press.

12. W. Krestinsky, *Ber.*, **59**, 1930 (1926).

13. R. Kuhn, H. Fischer and H. Fischer, *Ber.*, **97**, 1760 (1964).

14. H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961), has shown that the allenic infrared absorption of a number of alkenylidenecyclopropanes lies in the 2020 cm^{-1} region, as compared with 1950 cm^{-1} for strainless allenes.

15. The only other bicyclopropylidene derivative reported,[16] *viz*. 7,7'-(bicyclo[4.1.0] heptylidene), exhibited an ultraviolet absorption maximum at 198 mμ ($\epsilon \sim 15000$), L. Skattebøl, *Tetrahedron Letters*, 167 (1961).

16. W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

17. Private communication from G. S. D. King.

18. The UV spectrum compares very well with that of the pentaene bis[2,2,6,6-tetramethylcyclohexylidene] butatriene, which shows maxima at 225, 238, 317, and 339 mμ.[8]

19. A compound with the same ultraviolet spectrum has been prepared by dechlorination of 2,7-dichloro-2,7-dimethyl-3,5-octadiyne with either methylmagnesium bromide or zinc.[11]