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CONVERSION OF 1,1-DICHLORO-2-ALKYLCYCLOPROPANES TO ALLENES AND CYCLOPROPANES

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We wish to report the reaction of 1,1-dichloro-2-alkylcyclopropanes with Mg metal and alkyl or aryl halides to yield 1,2-alkadienes (allenes) and alkylcyclopropanes as the principal products. To our knowledge, this is the first reported preparation of allenes from the dichlorocarbene ($:CCl_2$) adducts of olefins.

Doering and La Flamme have reported[1,2] that the dibromocarbene adducts of some olefins, such as 1-pentene, react readily with active metals (e.g. Na or Mg) to yield allenes, but that the corresponding dichloro compounds do not react under similar or more vigorous conditions. Moore and Ward have recently reported[3] that allenes are produced in high yields by the

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[1] Wm. von E. Doering and P. M. La Flamme, Tetrahedron 2, 75 (1958).

[2] Wm. von E. Doering and P. M. La Flamme, "Process for Increasing the Carbon Chain Length of an Olefin," U.S. Patent 2,933,544, April 19, 1960.

[3] W. R. Moore and H. R. Ward, J. Org. Chem. 25, 2073 (1960).

reaction of 1,1-dibromocyclopropanes with n-butyllithium. The reaction reported herein differs from the Moore reaction since we have found that n-butyllithium reacts with the corresponding dichloro compounds to give only a small yield of allene, accompanied by a multiplicity of other products. In addition, cyclopropanes are not formed in the Moore reaction.

In a typical example, 1,1-dichloro-2-decylcyclopropane, 6.3 g (0.025 mole), Mg shavings, 12.15 g (0.5 mole), and 200 ml of anhydrous ether were placed in a 500 ml, 3-necked flask equipped with stirrer, reflux condenser, and dropping funnel. Over a period of 1 hr, 54.5 g (0.5 mole) of ethyl bromide was added at a rate sufficient to maintain reflux. When the addition was completed, the contents were refluxed an additional hour, then carefully hydrolyzed by the dropwise addition of water, followed by 10% HCl. The ether layer was separated, dried, and distilled to give 2.6 g of liquid, b.p. 68-94° (0.85 mm), and 1.2 g of high boiling hydrocarbon residue. By gas chromatographic analysis, the distillate consisted of 44% decyl allene, 33% decylcyclopropane, 5% starting material, and 18% of unidentified minor components (assuming that peak area percentages are equal to weight percentages). By gas chromatographic comparison with known samples of 1- and 2-tridecyne, it was shown that neither of these products was present in the distillate. Infrared analysis also showed the absence of the 1-alkyne.

The two major components were separated by preparative-scale gas chromatography[4] for identification. Decylcyclopropane was identified by

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[4] We are indebted to Dr. C. H. Orr for this separation.

comparing an infrared spectrum and a gas chromatogram of an authentic sample (prepared by the Na-MeOH reduction[5] of 1,1-dibromo-2-decylcyclopropane) with those of the product. Decyl allene was identified by the strong infrared absorption at 5.1 μ and by hydration[6] to 2-tridecanone. The 2,4-dinitrophenylhydrazone derivative m.p. and mixture m.p. with an authentic sample was 71.8-72.0°.

Other halides which have been successfully employed in this reaction are methyl iodide, ethyl iodide, ethyl chloride, t-butyl chloride, bromobenzene, and *p*-bromoanisole. Dichlorocarbene adducts of 1-octene and 1-octadecene were also prepared and reacted with alkyl halides and Mg as above to give the corresponding allenes and cyclopropanes. In all examples studied thus far, the allene and cyclopropane are the major products and no evidence for acetylene formation has been observed.

The reaction of dibromo compounds with Mg, which was described by Doering[1], resembles the reaction of dichloro compounds with Mg and alkyl or aryl halides reported herein, since both reactions yield allene-cyclopropane mixtures. Although Doering reported that the other products of his reaction apparently were isomeric acetylenes, formed by an active metal-catalyzed allene-acetylene interconversion, we have now demonstrated that the alkylcyclopropane is the other major product from the reaction of either 1,1-dibromo-2-propylcyclopropane or 1,1-dibromo-2-hexylcyclopropane with Mg metal.

Attempts to trap a possible carbene intermediate with cyclohexene have thus far proven unsuccessful. Further work on the mechanism of this reaction is in progress and will be reported at a later date.

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[5] Wm. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.* **76**, 6162 (1954).

[6] G. F. Hennion and J. J. Sheehan, *ibid.* **71**, 1964 (1949).