

# Synthesis of Allenic Hydrocarbons from 1-Halogenoallenes and Dialkylcopper-lithium Reagents

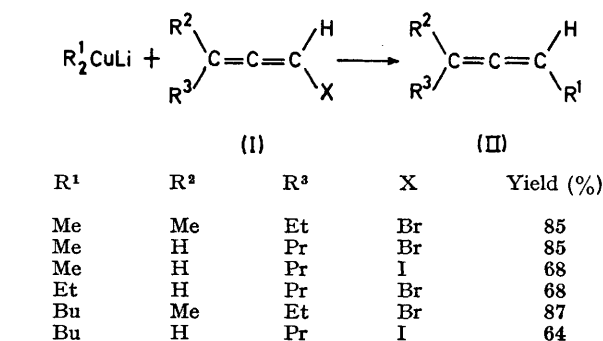
By M. KALLI, PHYLLIS D. LANDOR, and S. R. LANDOR\*

(Makerere University, Kampala and Woolwich Polytechnic, London, S.E.18)

**Summary** Reaction of 1-halogenoallenes or 3-chloroalk-1-ynes with dialkylcopperlithium reagents at low temperature gives a new general route to the synthesis of allenic hydrocarbons.

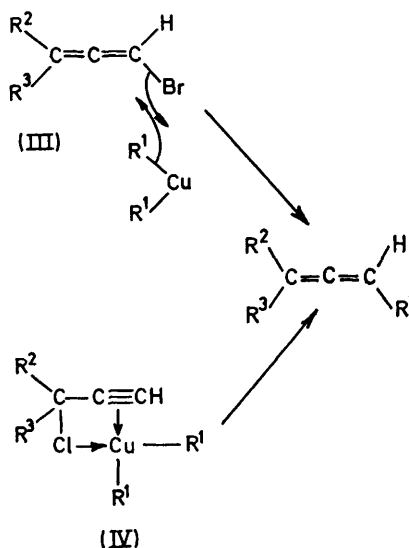
We have described<sup>1</sup> a synthesis of 1-cyanoallenes from 1-halogenoallenes by the direct replacement of the halogen atom by CN<sup>-</sup> from CuCN; rearranged acetylenic nitriles due to a propargylic rearrangement were not detected. With R<sub>2</sub>CuLi replacement of halogen on C-1 again takes place, this time by an alkyl group and no rearrangement products were isolated. As 1-bromoallenes are readily available<sup>2</sup> this constitutes an effective general method for the syn-

thesis of 1,3-di- and 1,3,3-tri-alkyl substituted allenes. In contrast, the reaction of 1-haloallenes with alkyl lithium compounds<sup>4</sup> gives allenic carbenes and hence mixtures of products in which acetylenes predominate.



thesis of 1,3-di- and 1,3,3-tri-alkyl substituted allenes. In contrast, the reaction of 1-haloallenes with alkyl lithium compounds<sup>4</sup> gives allenic carbenes and hence mixtures of products in which acetylenes predominate.

The R<sub>2</sub>CuLi reagents were prepared according to published procedure,<sup>3</sup> and the allenic halide was added to the complex (2.5 mol. equiv.) in ether under nitrogen. Reactions with Me<sub>2</sub>CuLi were carried out at -5 °C, with



Allenic hydrocarbons are also the main products from the reaction of 3-chloroalk-1-ynes and R<sub>2</sub>CuLi under similar conditions and this provides an alternative preparative method. The reaction is believed to proceed *via* the  $\pi$ -complex (IV).<sup>5</sup>

(Received, 6th March 1972; Com. 364.)

\* P. M. Greaves, S. R. Landor, and D. R. J. Laws, *J. Chem. Soc. (C)*, 1968, 291.

<sup>2</sup> H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, 1952, 17, 1630; E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, 1967, 89, 3911; *ibid.*, 1968, 90, 5615; G. M. Whitesides, W. F. Fischer, J. S. Filippo, R. W. Bashe, and H. O. House, *ibid.*, 1969, 91, 4871.

<sup>3</sup> S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc.*, 1966, 1223.

<sup>4</sup> S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 1965, 5625.

<sup>5</sup> P. M. Greaves, M. Kalli, P. D. Landor, and S. R. Landor, *J. Chem. Soc. (C)*, 1971, 667; S. R. Landor, B. Demetriou, R. J. Evans, R. Grzeskowiak, and D. Pavey, *J.C.S. Perkin II*, in the press.