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

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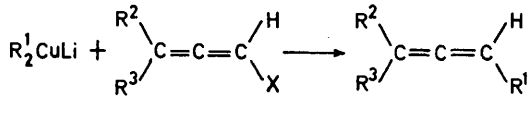
Summary Reaction of 1-halogenoallenes or 3-chloroalk-1-ynes with dialkylcopperlithium reagents at low temperature gives a new general route to the synthesis of allenic hydrocarbons.

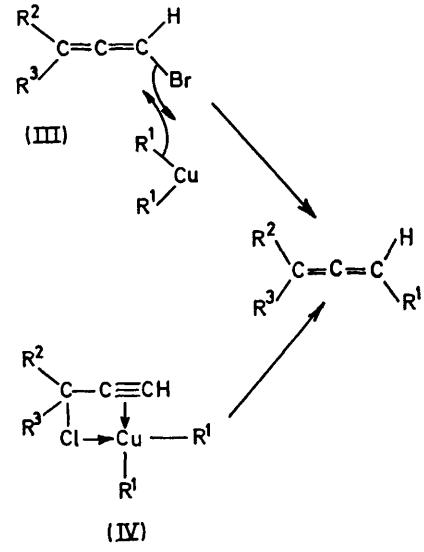
WE have described[1] a synthesis of 1-cyanoallenes from 1-halogenoallenes by the direct replacement of the halogen atom by CN^- from CuCN; rearranged acetylenic nitriles due to a propargylic rearrangement were not detected. With R_2CuLi replacement of halogen on C-1 again takes place, this time by an alkyl group and no rearrangement products were isolated. As 1-bromoallenes are readily available[2] this constitutes an effective general method for the synthesis of 1,3-di- and 1,3,3-tri-alkyl substituted allenes. In contrast, the reaction of 1-haloallenes with alkyl lithium compounds[4] gives allenic carbenes and hence mixtures of products in which acetylenes predominate.



(I) (II)

R^1	R^2	R^3	X	Yield (%)
Me	Me	Et	Br	85
Me	H	Pr	Br	85
Me	H	Pr	I	68
Et	H	Pr	Br	68
Bu	Me	Et	Br	87
Bu	H	Pr	I	64

The R_2CuLi reagents were prepared according to published procedure,[2] and the allenic halide was added to the complex (2·5 mol. equiv.) in ether under nitrogen. Reactions with Me_2CuLi were carried out at −5 °C, with Et_2CuLi at −30°, and those with Bu_2CuLi at −60° for 1—3 h. Pure samples of (II) were obtained by g.l.c. and characterised by elemental analyses and i.r. and n.m.r. spectra. We tentatively suggest a four-centred transition state (III) similar to the one proposed for the reaction with cuprous cyanide.[1]



(III) (IV)

Allenic hydrocarbons are also the main products from the reaction of 3-chloroalk-1-ynes and R_2CuLi under similar conditions and this provides an alternative preparative method. The reaction is believed to proceed *via* the π-complex (IV).[5]

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