Reactions of Lithio and Grignard Derivatives of 6-Halogenohexa-1,2-dienes with an Azirine

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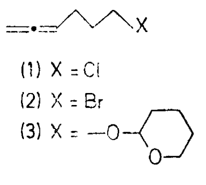
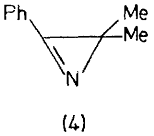
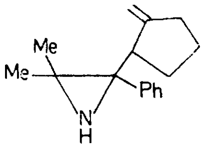
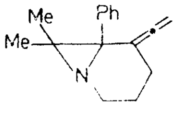
Summary The lithio and Grignard derivatives of the 6-halogeno-1,2-dienes (**1**) and (**2**) react with 3,3-dimethyl-2-phenyl-Δ^1-azirine (**4**) to give the methylenecyclopentylaziridine (**5**), indicating that they probably exist in the form of the metallated methylenecyclopentane (**9**).

Much work has been devoted recently to the cyclisation of Grignard reagents[1] or lithio derivatives[2] of unsaturated halides. We report here the behaviour of metallic derivatives of the γ-halogenoallenes (**1**) and (**2**); the only allenic halides studied up to now are β-bromoallenes, which give allenic Grignard reagents which isomerise thermally to cyclopropane homologues.[3]


(1) X = Cl
(2) X = Br
(3) X = —O—


(4)


(5)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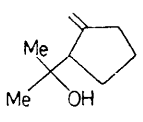
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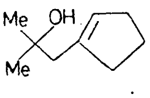
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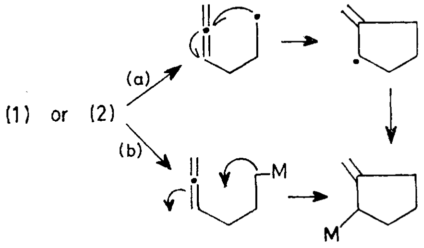
We were interested in the synthesis of aziridines substituted with an allenic chain, and have investigated the reaction of lithio and Grignard derivatives of the halides (**1**) and (**2**) with the azirine (**4**) following the method previously described for metallic derivatives of saturated halides.[4]

The halide (**1**) is easily prepared (yield 60—70%) by the reaction of allenyl-lithium with 1-bromo-3-chloropropane in tetrahydrofuran (THF) at −40 °C.[5] The same reaction with the tetrahydropyranyloxy-derivative of 3-bromopropanol gives (**3**) which is transformed using PPh_3–Br_2 into the bromide (**2**), isolated by preparative g.l.c.

The halide (**1**) (1·5 mol) was treated with metallic lithium (3 equiv.) in THF at −10 °C in the presence of the azirine (**4**) (1 mol). The mixture was stirred for 1 h at −10 °C, then hydrolysed. After usual work-up, the products were separated by column chromatography over silica gel with light petroleum–ether (70 : 30) as eluent. The aziridine (**5**) was isolated in 50% yield together with small amounts (5%) of the bicyclic compound (**6**). Both compounds were identified by microanalysis, and i.r., n.m.r., and mass spectroscopy. The chloride (**1**) is unreactive toward magnesium, even under conditions appropriate for alkyl halides of poor reactivity.[6]

The Grignard reagent of (**2**) was prepared at 0 °C in THF. It reacts at 0 °C with (**4**) giving, after 2 h, a mixture of dimerization products of the reagent and the same aziridine (**5**) (40%).



(9)

M = Li or MgBr

The reaction at 0 °C in THF of metallic lithium with (**1**) in the presence of acetone was more sluggish. A mixture (60:40) of the alcohols (**7**) and (**8**) was obtained in only 10% yield, the product being mainly composed of unidentified polymeric material.

All these results suggest that the metallic derivatives of (**1**) and (**2**) exist predominantly in the cyclic form (**9**), and further work should determine whether the cyclisation takes place *via* path (a) or path (b).

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[6] R. D. Rieke and S. E. Bales, *J. Amer. Chem. Soc.*, 1974, **96**, 1775.