# Simple Route to Mono-, Di-, and Tri-substituted Allenic Compounds

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*Summary* Allenic compounds can be prepared in high yields without appreciable rearrangement by alkylation of allenic lithium reagents.

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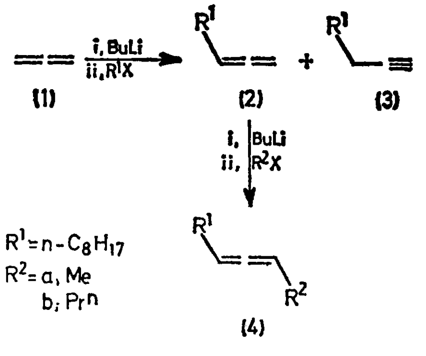
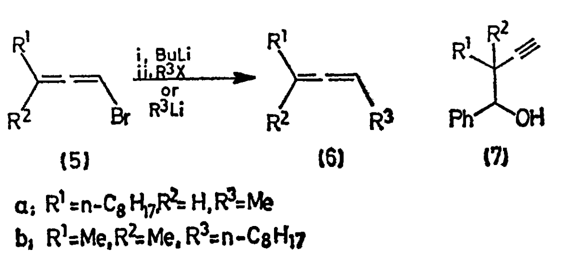
Double bonds have been synthesised stereospecifically by alkylation of vinylic lithium reagents.[1] We report a high yield synthesis of mono-, di-, and tri-substituted allenes *via* allenic lithium reagents derived from terminal allenic-hydrocarbons or from bromoallenes. Although classically one might expect the formation of both allenic and acetylenic products corresponding to the allenic anion and the related acetylenic species, the formation of acetylenic compounds was of little importance in the present case.



Scheme 1



Scheme 2

Propa-1,2-diene (**1**) was lithiated in tetrahydrofuran at $-70°$ with $Bu^nLi$[2] (1 equiv.). Reaction with octyl iodide or bromide (1 equiv.) gave 86% of a mixture (87 : 13) of the allene (**2**) and the acetylene (**3**).[3] The allene (**2**) was easily purified by treatment with aqueous $AgNO_3$ and was identical to an authentic sample;[4,5] $M^+$ 152; δ ($CCl_4$) 4·47—5·30 (3H, m).

Lithiation of the monosubstituted allene (**2**) occurs at the terminal position. A convenient procedure for the synthesis of 1,3-disubstituted allenes has been developed: for example, undeca-1,2-diene (**2**) was treated sequentially with equimolecular quantities of $Bu^nLi$ and MeI to provide dodeca-2,3-diene (**4a**) in 93% yield (94% purity); $M^+$ 166; $\nu$ 1964 $cm^{-1}$; $\delta$ ($CCl_4$) 1·55—1·73 (3H, m) and 4·72—5·26 (2H, m). $Bu^nLi$ and $Pr^nI$ similarly gave (96%) tetradeca-4,5-diene (**4b**) (95% purity), b.p. 130—140 °C at 15 mmHg; $M^+$ 194; $\nu$ 1963 $cm^{-1}$; $\delta$ ($CCl_4$) 4·81—5·18 (2H, m).

Allenic lithium reagents could also be obtained from bromoallenes by the action of Li or $Bu^nLi$.[6] Treatment of 1-bromoundeca-1,2-diene (**5a**) (prepared from undec-1-yn-3-ol according to a known procedure[7]) with $Bu^nLi$ (1 equiv.) in ether at −70° followed by addition of tetrahydrofuran and MeI (1 equiv.) gave (90%) dodeca-2,3-diene (**6a**) (purity 92%). The bromoallene (**5b**),[7] under the same conditions, provided (91%) the pure trisubstituted allene (**6b**), b.p. 65 °C at 0·1 mmHg; $M^+$ 180; $\nu$ 1970 $cm^{-1}$; $\delta$ ($CCl_4$) 1·64 (6H, d, $J$ 3 Hz) and 4·87 (1H, m).

The allene (**6b**) could also be generated (65%) directly by action of an alkyl-lithium upon the bromoallene (**5b**) (*via* halogen–metal interconversion and coupling).

Except in the case (**1**) → (**2**) + (**3**) where 13% of the acetylene (**3**) was formed, the allenic compounds described here were generated without significant isomerization (<5%) to the acetylenic isomers.

The reactivity of these allenic lithium reagents with alkyl halides contrasts with their reactivity with carbonyl compounds; the acetylenic alcohols (**7a**) and (**7b**) were formed in good yield (70 and 59%) without noticeable amounts of the allenic alcohols.[2,8]

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