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ADDITION REACTIONS OF BUTYLLITHIUM WITH PROPARGYLIC ALCOHOLS[1]

Lars-Inge Olsson and Alf Claesson*
Department of Organic Chemistry, Faculty of Pharmacy, University of Uppsala
Box 574, S-751 23 Uppsala, Sweden

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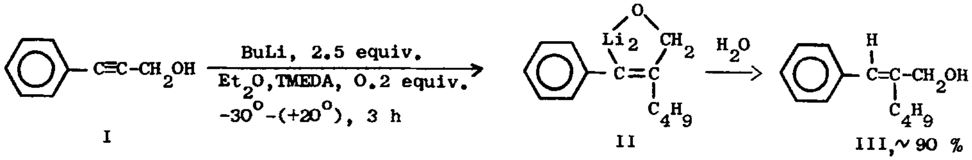
The hydroxyl function of acetylenic alcohols promotes the addition of Grignard reagents to the triple bond.[2] Other neighbouring groups, like amino and ether functions, are also known to have an activating effect in this respect.[3]

It has been reported that alkyllithium reagents add to the double bond of allylic alcohols[4], but to our knowledge no such reaction has been described for propargylic alcohols. On the other hand additions of alkyllithium to diphenylacetylene and derivatives of it are known.[5]

We wish to report on some reactions, where butyllithium adds to the triple bond of 3-phenylpropargyl alcohol and 4-methoxy-2-butyn-1-ols. The reactions can be syntetically utilized as they give rise to α-allenic alcohols or to a vinyl carbanion suitable for further transformations.

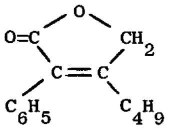
3-Phenylpropargyl alcohol (I) easily reacts with butyllithium to give the known cinnamyl alcohol derivative III upon hydrolysis of the intermediate carbanion II.



The addition of 0.2 equivalents of tetramethylethylenediamine (TMEDA),[4,5] had a marked effect on the reaction rate and prevented darkening of the mixture.

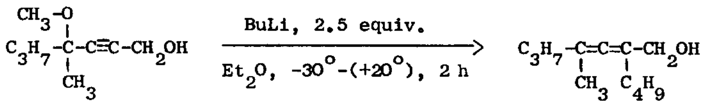
The alcohol III is homogeneous on GLC (Carbowax 20M and OV-25) indicating a single stereoisomer. The stereochemical course of the reaction as well as its preparative value was indicated through the carbonation of II, which on work up at pH 4 gave the lactone IV in 77 % yield (GLC), thus proving the E configurations of II and III. The exclusive trans addition of alkyllithiums to diphenylacetylene has been shown.[5] IV: IR 1750 and 1650 cm^{-1}. NMR: δ (rel. to TMS in $CDCl_3$) = 7.45-7.20 (m,5H), 4.75 (s,2H), 2.55 (t,2H), 1.70-1.00 (m,4H) and

0.86 ppm (t,3H). MS: Mol.wt.216.



IV

The acetylenic derivative V reacts with butyllithium in an addition-elimination sequence with formation of an α-allenic alcohol VI. NMR: ($CDCl_3$) δ = 3.97 (s,2H), 2.40 (s,1H), 2.15-1.70 (m,4H), 1.70 (s,3H), 1.70-0.70 ppm (two m centered at 1.40 and 0.90 ppm, 12H). MS: Mol.wt. 182. IR: 1960 cm^{-1}.



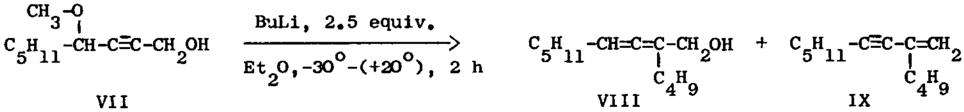
$$C_3H_7-\overset{CH_3-O}{\underset{CH_3}{C}}-C\equiv C-CH_2OH \xrightarrow[Et_2O,\ -30^{\circ}-(+20^{\circ}),\ 2\ h]{BuLi,\ 2.5\ equiv.} C_3H_7-\underset{CH_3}{C}=C=\underset{C_4H_9}{C}-CH_2OH$$

V VI

~80 %

The reaction rate is not significantly increased by TMEDA.

The acetylene VII also reacts with butyllithium to give an α-allenic alcohol VIII, but in addition there is formed an alkenyne (IX), probably through proton abstraction by butyllithium at the δ-position of the lithium alcoholate of VIII leading to a 1,4-elimination of Li_2O. VIII: IR 1960 cm^{-1}. NMR: ($CDCl_3$) δ = 5.55-5.10 (M,1H), 4.00 (d,2H), 2.30 (s,1H), 2.25-1.82 (m,4H), 1.70-1.05 (m,10H) and 1.05-0.70 ppm (m,6H). MS: Mol.wt. 196. IX: IR 2215, 1608 and 890 cm^{-1} ($=CH_2$). NMR ($CDCl_3$) δ = 5.27-5.03 (m,2H), 2.50-1.97 (m,4H), 1.75-1.12 (m,10H) and 0.92 (t,6H). MS: Mol.wt. 178.



$$C_5H_{11}-\overset{CH_3-O}{CH}-C\equiv C-CH_2OH \xrightarrow[Et_2O,-30^{\circ}-(+20^{\circ}),\ 2\ h]{BuLi,\ 2.5\ equiv.} C_5H_{11}-CH=C=\underset{C_4H_9}{C}-CH_2OH + C_5H_{11}-C\equiv C-\underset{C_4H_9}{C}=CH_2$$

VII VIII IX

~40 % ~35 %

4-Bromo-3,4-butadien-1-ol is reported to undergo the same elimination reaction when allowed to react with butyllithium.[6]

2-Heptyn-1-ol does not undergo an addition reaction with butyllithium, but is mainly isomerized (~60%) to the known allenic alcohol, 2,3-heptadien-1-ol, when refluxed in ether + TMEDA for 5 h.

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