

A Lewis Acid Mediated Rearrangement of 1-(Trimethylsilyl)prop-2-ynyl Trimethylsilyl Ethers to 2-Trimethylsilyl Enones

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Treatment of 1-(trimethylsilyl)prop-2-ynyl trimethylsilyl ethers with methylaluminium dichloride leads to the formation of the 3-metallated 2-(trimethylsilyl)enones, which, on quenching with water, afford the corresponding 2-(trimethylsilyl)enones in good yields.

2-(Trimethylsilyl)enones (1) are excellent Michael acceptors owing to the stabilizing effect of the silyl group of the anionic species resulting from conjugate addition.¹ Further, in contrast to the relatively unstable character of terminal unsubstituted enones, silylated enones (1) are quite stable and easy to handle, which has made them convenient reagents for conjugate addition reactions. However, the need for multistep operations as well as the rather low efficacy involved in their preparation² appears to call for the development of simple synthetic methods.

We previously reported synthetic reactions involving rearrangement of the silyl group of 1-(trimethylsilyl)prop-2-ynyl alcohols.³ In the present paper, we describe another type of

rearrangement of the silyl group mediated by a Lewis acid which leads to the formation of 2-(trimethylsilyl)enones (1). Treatment of acyltrimethylsilanes⁴ with magnesium acetylide followed by silylation with chlorotrimethylsilane affords the corresponding prop-1-ynyl ethers (2) in high yields. We have found that, on exposure to an equimolar amount of methylaluminium dichloride, the ethers (2)† undergo rapid isomerization and afford the corresponding structures (1) (>80% yield) after quenching with water (equation 1).

Deuteriated prop-2-ynyl ethers afforded the corresponding (Z)-isomers‡ exclusively. Further, before quenching, treatment of the reaction mixture with deuterium oxide or chloromethyl methyl ether afforded the 3-(E)-deuteriated‡ or 3-(E)-methoxymethylated enones exclusively. These results clearly show the formation of 3-(E)-metallated enones (3) (equations 2 and 3).

According to these results, the reaction is considered to proceed through an initial co-ordination of aluminium to the acetylenic linkage of (2), which facilitates the 1,2-rearrangement of the silyl group to the neighbouring carbon atom followed by removal of another silyl group from oxygen (equation 4). Stronger Lewis acids such as titanium tetrachloride or aluminium trichloride did not effect this transformation.

Thus, in addition to a new aspect on the rearrangement of silicon to cationic centres,⁵ this reaction offers a convenient method for synthesis of compounds (1) because the starting acyltrimethylsilanes are now readily prepared from enol silyl ethers of thiol esters. Further, the metallated intermediates (3) appear to be quite useful, considering recent progress in organoaluminium chemistry.

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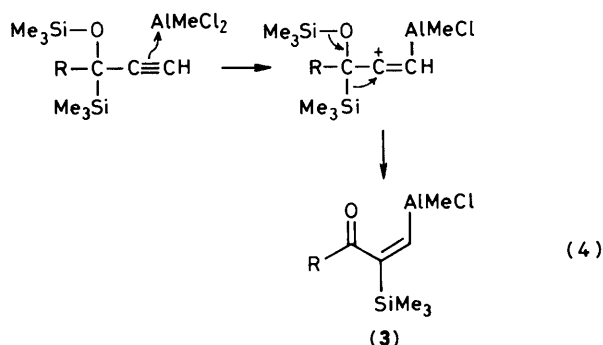
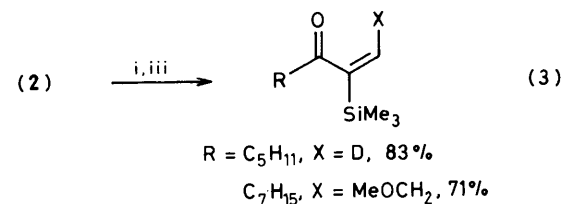
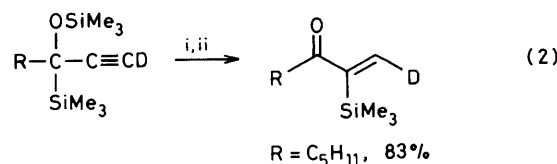
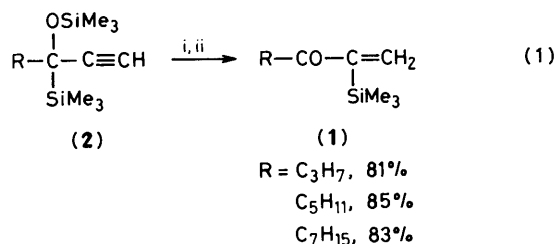
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† In contrast, 3-substituted prop-2-ynyl ethers do not undergo this type of rearrangement.

‡ The vinyl proton of the (Z)-isomer appears at δ 6.43, whereas that of the (E)-isomer is at δ 6.08.



Reagents: i, MeAlCl_2 ; ii, H_2O ; iii, D_2O or MeOCH_2Cl .