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BASE-INDUCED REARRANGEMENT OF 1-TRIMETHYLSILYLPROPARGYL ALCOHOL. GENERATION OF LITHIATED TRIMETHYLSILOXYALLENES AND THEIR REACTIONS

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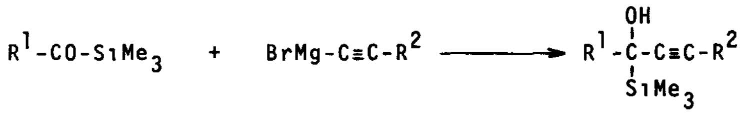
Summary: Under the effect of butyllithium, 1-trimethylsilylpropargyl alcohol undergoes rearrangement to afford the corresponding trimethylsiloxyallene or its lithiated one, which can be used for the preparation of α,β-unsaturated ketone derivatives.

It has been well known that, under the catalytic effect of base, 1-trialkylsilyl alcohol undergoes a facile rearrangement into the corresponding trialkylsilyl ether via transfer of the silyl group from carbon to the adjacent oxygen.[1] In this rearrangement reaction, a 1-trialkylsiloxycarbanionic species has been proved to be formed, but it has hitherto been quite difficult to use such a kind of intermediates for carbon chain elongation because of its high lability under the reaction conditions.[2] We have recently shown a synthetic application of this rearrangement for generating a homoenolate precursor and have reported a stereo- and regio-specific preparative method of silyl enol ethers.[3] In the present paper, we wish to describe a method for generation of lithiated trimethylsiloxyallenes and their reactions, starting from 1-trimethylsilylpropargyl alcohols <u>1</u>, which can easily be prepared by treating the corresponding acyltrimethylsilanes[4] with bromomagnesium acetylides.[5]

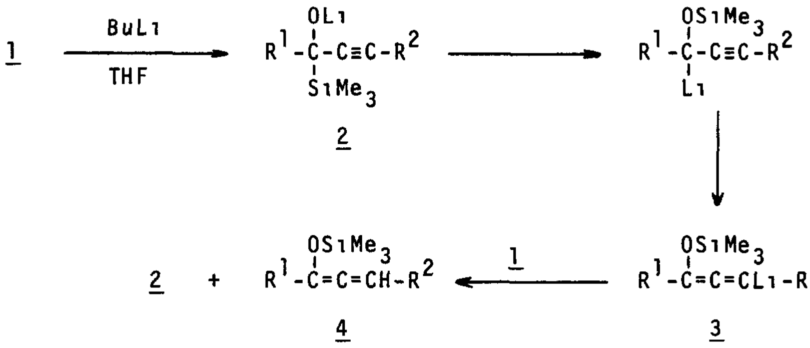


$$R^1\text{-CO-SiMe}_3 \quad + \quad \text{BrMg-C}\equiv\text{C-}R^2 \longrightarrow R^1\text{-}\underset{\text{SiMe}_3}{\overset{\text{OH}}{\text{C}}}\text{-C}\equiv\text{C-}R^2$$

1

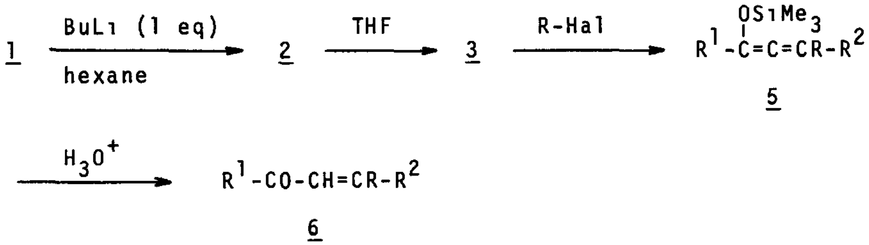
Various examinations have shown that, surprisingly, complete conversion of the alcohol 1 into the corresponding alkoxide 2 appears to be quite difficult even with butyllithium when tetrahydrofuran is employed as the solvent, and the formation of complex mixtures has usually resulted. This may be attributable to an extremely rapid rearrangement of the silyl group of the initially formed alkoxide 2 into the lithiated allenic species 3,[6] and the resulting solution may be a mixture of 3 and 4 together with remaining butyllithium. This assumption is supported by the following observation; an efficient conversion of the alcohol 1 into the corresponding trimethylsiloxyallene 4 can be effected under the influence of a catalytic amount (ca. 5 mol%) of butyllithium in THF as shown in Scheme 1 (see Table 1).

Scheme 1



Employment of a non-polar solvent such as hexane as the reaction solvent has made the rearrangement of 2 into 3 extremely slow. Thus, the alcohol 1 can be converted into the corresponding lithium alkoxide 2 almost completely. Further, addition of tetrahydrofuran to the resulting solution effects the rearrangement efficiently to afford the desired lithiated allene intermediate 3 Carbon chain homologation can be achieved effectively by the in situ reaction of 3 with appropriate alkyl halides, and the corresponding α,β-unsaturated ketone is obtained in high yield after aqueous work-up of the reaction mixture (see Table 2).

Scheme 2



Sometimes, isolation of trimethylsiloxyallene 5 is difficult by a simple distillation due to its lability on heating, but the crude product is usually

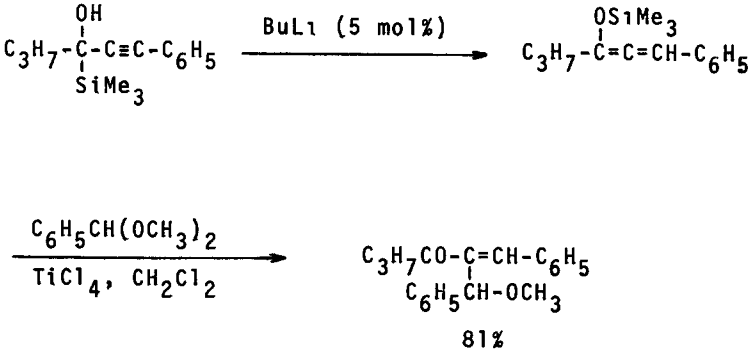
Table 1. Preparation of Trimethylsiloxyallene 4.

R^1	R^2	Yield(%) of 4
C_3H_7	C_6H_5	96
$C_6H_5CH_2CH_2$	C_4H_9	97
$C_6H_5CH_2CH_2$	C_6H_5	89
$C_6H_5CH_2CH_2$	Me_3Si	63
$C_6H_5CH_2CH_2$	$CH_3O\text{-}CH_2$	80

Table 2. Preparation of α,β-Unsaturated Ketone 6.

R^1	R^2	R-Hal	Yield(%) of 6
C_3H_7	C_6H_5	CH_3I	92
$C_6H_5CH_2CH_2$	C_4H_9	CH_3I	94
$C_6H_5CH_2CH_2$	C_6H_5	CH_3I	92
$C_6H_5CH_2CH_2$	C_6H_5	C_4H_9I	86
$C_6H_5CH_2CH_2$	Me_3Si	CH_3I	87
$C_6H_5CH_2CH_2$	$(C_2H_4O_2)CHCH_2CH_2$	CH_3I	82

highly pure enough to be used for further synthetic purposes. For example, another carbon chain can also be introduced on the central carbon of the allenic linkage under the influence of a Lewis acid as shown below.



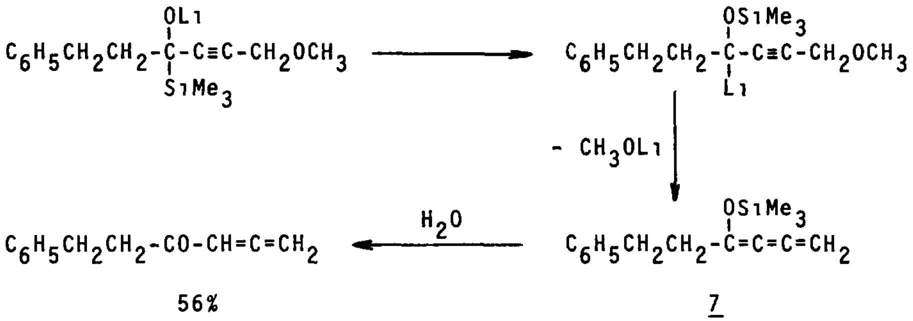
$$C_3H_7\text{-}\underset{SiMe_3}{\overset{OH}{C}}\text{-}C\equiv C\text{-}C_6H_5 \xrightarrow{BuLi\ (5\ mol\%)} C_3H_7\text{-}\overset{OSiMe_3}{C}{=}C{=}CH\text{-}C_6H_5$$

$$\xrightarrow[TiCl_4,\ CH_2Cl_2]{C_6H_5CH(OCH_3)_2} C_3H_7CO\text{-}\underset{C_6H_5CH\text{-}OCH_3}{C}{=}CH\text{-}C_6H_5$$

81%

On treating a 4-alkoxypropargyl alcohol derivative with butyllithium (1eq), rearrangement of the lithium alkoxide appears to be followed by successive 1,4-elimination of lithium alkoxide as shown in Scheme 3. The corresponding allenic ketone was isolated in good yield after aqueous work-up of the reaction mixture. The reaction is considered to proceed through the formation of the cumulated triene 7.

Scheme 3



References and Notes

1) A. G. Brook, Acc. Chem. Res., 7, 77 (1974); A. Wright and R. West, J. Am. Chem. Soc., 96, 3214 (1974).

2) About synthetic applications of this type of rearrangement, see:
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4) For the preparation of acyltrimethylsilane derivatives, see: I. Kuwajima, M. Kato, and T. Sato, J. Chem. Soc., Chem. Commun., 478 (1978);
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A. Hosomi, H. Hashimoto, and H. Sakurai, J. Organometal. Chem., 175, C1 (1979), and references cited therein.

5) Employment of lithium acetylides usually resulted in the formation of complex mixtures. This might be attributable to the same reason with that described in the text.

6) For generation of lithiated allene derivatives, see: G. Linstrumelle and D. Michelot, J. Chem. Soc., Chem. Commun., 561 (1975); D. Michelot and G. Linstrumelle, Tetrahedron Lett., 275 (1976); J. C. Clinet and G. Linstrumelle, ibid., 1137 (1978).

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