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STOICHIOMETRIC GENERATION OF 3-SILOXYALLENYLLITHIUM AND ITS REACTIONS WITH ELECTROPHILES

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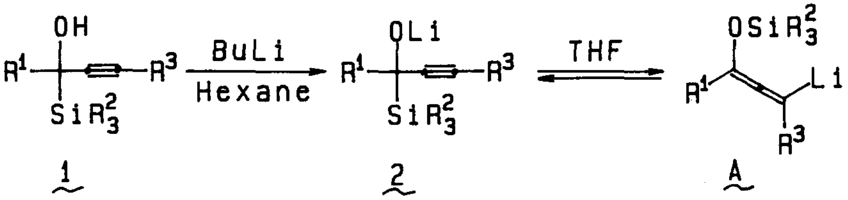
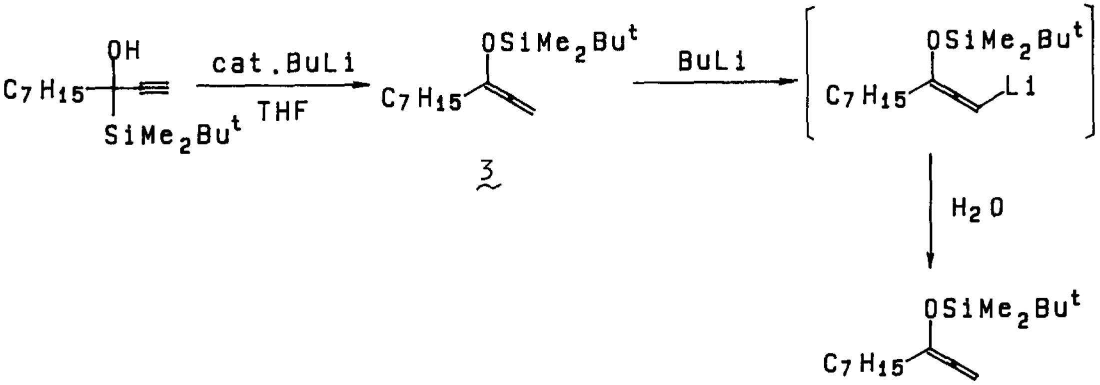
Summary: A 3-(t-butyldimethylsiloxy)allenyllithium generated quantitatively from the 1-silylpropargyl alcohol can be used as a synthetic equivalent of α,β-unsaturated ketone having nucleophilic center at its β-position through transmetallation.

As reported previously,[1] a siloxyallenyllithium **A-1** ($R^2 = CH_3$) generated from a 1-(trimethylsilyl)propargyl alcohol **1** ($R^2 = CH_3$) has a potential synthetic utility as an equivalent of α,β-unsaturated ketones bearing nucleophilic centers on both α- and β-positions.



However, there exists a great drawback on the generation of **A** through such procedure because the equilibrium with the alkoxide **2** usually greatly disfavors generation of the desired nucleophile **A**. This was not a serious problem in the reaction with alkyl halides, which proceeds only with **A** to allow a shift of the equilibrium. But, in order to use **A** for carbon chain homologation reactions involving other organometallic species, e.g. organocopper compounds, a preferable or possibly stoichiometric generation is required for achieving a transmetallation effectively.[2] For such purpose, we attempted to generate terminal unsubstituted siloxyallenyllithium **A**(R^3 = H). Treatment of the alcohol **1** ($R^1 = C_7H_{15}$, $R^2 = CH_3$, R^3 = H) with an equimolar amount of butyllithium in hexane followed by the addition of THF[3] led to the unexpected result that non- and dilithiated siloxyallenes[4,5] were formed and the desired monolithiated species **A-1**($R^2 = CH_3$, R^3 = H) was not obtained in a detectable amount. Use of 2 equiv of butyllithium resulted in the preferable formation of this dilithiated species. This interesting phenomenon may be induced by an acidic acetylenic proton.

In the next, we examined on a generation of **A** through lithiation of an allenic proton of the siloxyallene. Desilylation mainly took place in the reaction of butyllithium with (trimethylsiloxy)allenes, but use of t-butyldimethylsilyl substituted alcohol **1** has circumvented such difficulty. Thus, under the influence of 0.1 equiv of butyllithium in THF, the propargyl silyl alcohol **1** ($R^1 = C_7H_{15}$, $SiR^2_3 = SiMe_2Bu^t$, $R^3 = H$) was converted to the siloxyallene 3^1 almost quantitatively after stirring at 0°C for 30 min. Addition of further 0.9 equiv of butyllithium to the resulting solution yielded the siloxyallenyllithium **A-2** ($R^1 = C_7H_{15}$, $SiR^2_3 = SiMe_2Bu^t$) after stirring for 70 min at -46°C. Quenching the reaction mixture with deuterium oxide afforded the monodeuterated siloxyallene exclusively without any formation of the alcohol. This result indicated that a t-butyldimethylsilyl group blocks an equilibration of **A-2** with the alkoxide to allow a use of such nucleophile in stoichiometric quantity. Even in the presence of terminal alkyl group, an equilibrium composition appears to favor on the siloxyallenyllithium **A-2** ($R^1 = C_7H_{15}$, $SiR^2_3 = SiMe_2Bu^t$, $R^3 = C_4H_9$), and on quenching, the siloxyallene and the alcohol were obtained in 80 and 20% yields, respectively.



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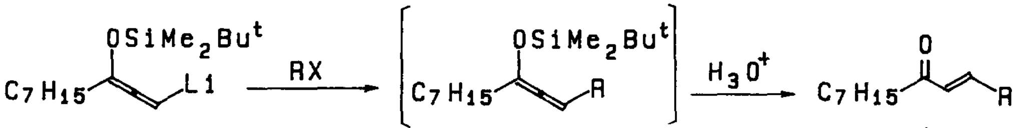
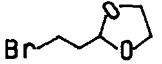
Following are the reactivities of the siloxyallenyllithium **A-2** thus generated toward several electrophiles.

Reactions with alkyl halides proceeded to give trans-α,β-unsaturated ketones **4** in good yields after hydrolysis (1M HCl-THF, room temp, 30min). As suggested by required longer reaction period and higher temperature,[1] reactivity of **A-2** seems to be lower than that of **A-1**, but it reacted not only with iodides but also with a bromide in good yields as shown below.

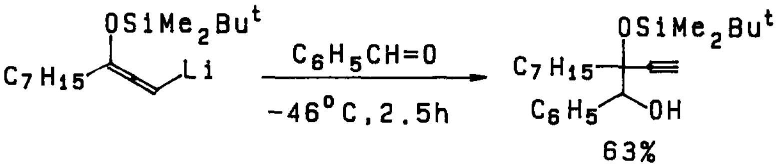


4

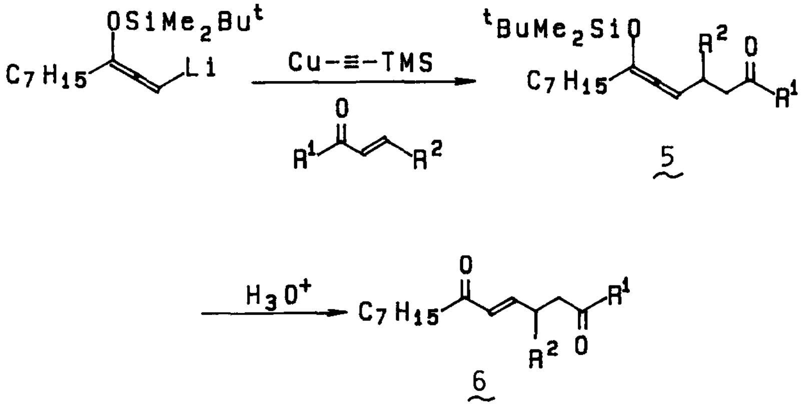
RX	Yield,% [a)]
CH_3I	87
$C_6H_{13}I$	73
	71[b)]

a) Reactions were performed with 1.5 equiv of A-2. Isolated yield of 4. b) Yield of the siloxyallene based on NMR.

Reaction with benzaldehyde proceeded at the propargylic position, suggesting the six-membered-like transition state.

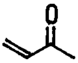
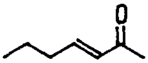
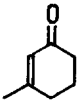
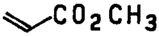


In order to effect a conjugate addition of siloxyallenic species, we now examined the transmetallation reaction to Cu(I). Using a mixed cuprate prepared from **A-2** and copper(I) trimethylsilylacetylide,[6] addition reaction proceeded smoothly at the terminal position in a 1,4-manner. All the adducts could be isolated as siloxyallenyl ketones **5** and gave 2-ene-1,6-diones **6** in good yields after hydrolysis (1M HCl-THF, room temp, 30min). Use of chlorotrimethylsilane sometimes accelerated the addition reaction.[7] Several types of enones including acetylenic ester can be used as acceptors, but **A-2** failed to react with relatively unreactive ones such as β-disubstituted enones and α,β-unsaturated ester.



5

6

Enone	Yield,%$^{\mathrm{a)}}$	
	5	**6** (E:Z)
	96	72(100:0)
	81	54(100:0)
	80	76(60:40)
$\equiv$—CO_2CH_3	65	63(60:40)
	N.R.	
	N.R.	

a) Reactions were performed with 1.5 equiv of **A-2**. Isolated yield.

Thus, use of 1-(t-butyldimethylsilyl)propargyl alcohol has allowed almost quantitative generation of 3-siloxyallenyllithium **A-2**, which further broadens the scope of synthetic utility as a homoenolate equivalent of α,β-unsaturated ketone through transmetallation.

References

1) I. Kuwajima and M. Kato, Tetrahedron Lett., **21**, 623 (1980). M. Kato and I. Kuwajima, Bull. Chem. Soc. Jpn., **57**, 827 (1984).
2) J. Enda and I. Kuwajima, J. Am. Chem Soc., **107**, 5495 (1985).
3) M. Kato, A. Mori, H. Oshino, J. Enda, K. Kobayashi, and I. Kuwajima, J. Am. Chem. Soc., **106**, 1773 (1984).
4) Formation of the dilithiated species was confirmed by deuteration and silylation with deuterium oxide and chlorotrimethylsilane, respectively.
5) The dilithiated siloxyallene thus generated was not so reactive as expected. It reacted only with reactive reagents such as methyl iodide or a chlorosilane. The alkylation reaction could not be controlled to yield the monoalkylation products, but gave dialkylation ones.
6) An effect of this Cu(I) salt for conjugate addition, see ref 2.
7) Y. Horiguchi, S. Matsuzawa, E. Nakamura, and I. Kuwajima, Tetrahedron Lett., **27**, 4025 (1986). E. Nakamura, S. Matsuzawa, Y. Horiguchi, and I. Kuwajima, ibid., **27**, 4029 (1986).

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