

Silicon in Synthesis. Methoxymethyltrimethylsilane, a New Reagent for Reductive Nucleophilic Acylation

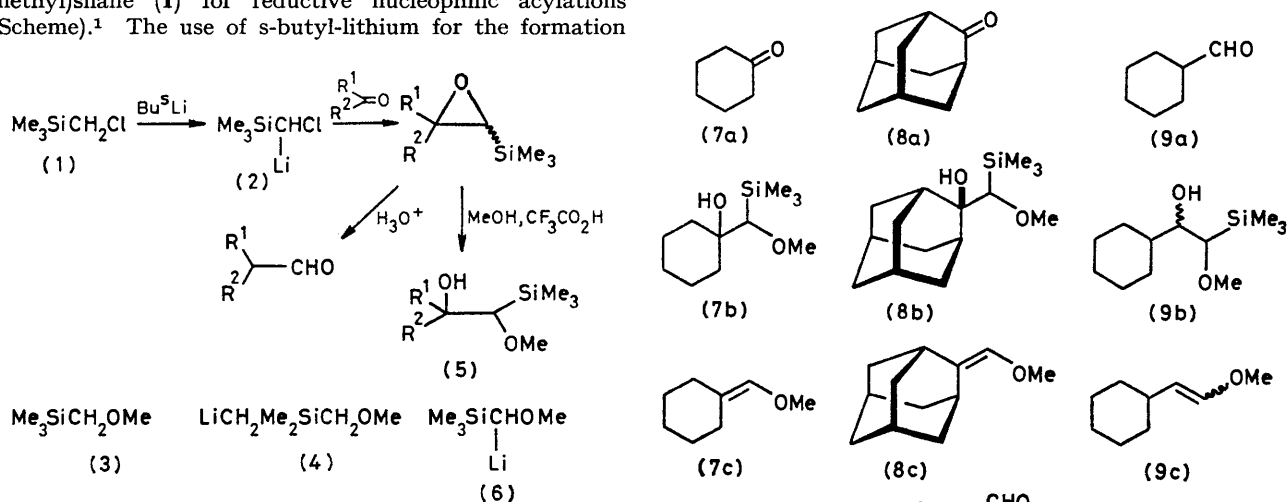
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Summary Lithium methoxy(trimethylsilyl)methylide (6), prepared by deprotonation of methoxymethyltrimethylsilane (3) using *s*-butyl-lithium reacts with ketones and aldehydes to give adducts (7b)—(9b) that can be converted into aldehydes.

RECENTLY we described the use of α -chloromethyl(trimethyl)silane (1) for reductive nucleophilic acylations (Scheme).¹ The use of *s*-butyl-lithium for the formation

to us that reported attempts to deprotonate methoxymethyl(trimethyl)silane (3) using *n*-butyl-lithium resulted in nucleophilic attack at silicon and subsequent cleavage of the $-\text{CH}_2\text{OMe}$ group; *t*-butyl-lithium gave the α -lithio-species (4), which could be regarded as a kinetic product.² Furthermore it has been reported that $\alpha\beta$ -epoxysilanes are opened with $\text{MeOH}-\text{BF}_3\cdot\text{Et}_2\text{O}$ or $\text{MeOH}-\text{CF}_3\text{CO}_2\text{H}$ to give

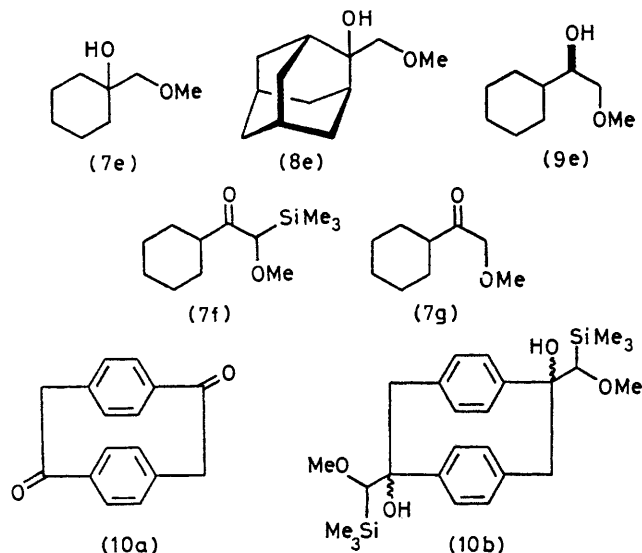


SCHEME

of the α -lithio species (2) from (1) is essential, and we have not yet discovered any other base that will accomplish this deprotonation so specifically. It was of particular interest

exclusively the α -methoxy-adduct (5).³ The adduct (5) would result from the nucleophilic addition of the α -lithio-species (6) to an aldehyde or ketone.

Treatment of methoxymethyltrimethylsilane (3)⁴ in tetrahydrofuran (THF) with *s*-butyl-lithium (1.4M in hexane) at -70°C followed by warming to -25°C gave the lithium methoxy(trimethylsilyl)methylide (6), as judged by



its subsequent reactions with aldehydes and ketones (7a)—(9a). The initial adducts (7b)—(9b) did *not* undergo *syn*-elimination of $-\text{OSiMe}_3$ *in situ*, but upon treatment with KH in THF at 25°C the corresponding enol ethers (7c)—(9c) were formed in excellent yields.[†] Treatment of the adducts (7b)—(9b) with 90% aqueous formic acid gave the aldehydes (7d)—(9d) in $>90\%$ yields. Previously (8d) had been reported as an unstable compound;⁵ using the new procedure described here (8d) was isolated as a stable crystalline compound, m.p. $99-102^\circ\text{C}$. We were unable to hydrolyse the adduct (10b) with formic acid without causing extensive degradation. When the adducts (7b)—(9b) were treated with caesium fluoride in dimethyl sulphoxide at 80°C with the objective of eliminating HOSiMe_3 under essentially neutral conditions, surprisingly the $-\text{SiMe}_3$ group was cleanly removed to give the desilylated adducts (7e)—(9e), with no trace of the enol ethers (7c)—(9c). The adduct (9b) was rapidly oxidized with pyridinium chlorochromate⁶ to give (7f), chromatography of which on silica gel effected desilylation to give (7g).

The reagent methoxymethyltrimethylsilane (3) provides a new procedure for conducting reductive nucleophilic acylations and a source of the $-\text{CH}_2\text{OMe}$ anion.⁷

All new compounds gave satisfactory spectral data.

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[†] It should be noted that Peterson olefinations conducted with $\text{Me}_3\text{SiCHLiSiMe}$ under similar conditions to those reported here provide directly the vinyl sulphide through the *in situ syn*-elimination of $-\text{OSiMe}_3$ (ref. 2).

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