Controlled Carbon–Sulphur or Carbon–Silicon Bond Cleavage in the Reactions of Alkyl-lithium Reagents with a 1-Silyl-1-thioallene

Alexander J. Bridges,* Victor Fedij, and Eugene C. Turowski

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.

3-Methyl-1-phenylthio-1-trimethylsilylbuta-1,2-diene (**3**) reacts with different alkyl-lithium reagents by C–Si or C–S bond cleavage, rather than by Michael addition or metallation; one product, the α-silyl-α-lithioallene (**6**), is alkylated mainly γ with carbonyl compounds, but is silylated α with Et_3SiCl to form the 1,1-bis-silylallene $Me_2C{=}C{=}C(SiEt_3)SiMe_3$.

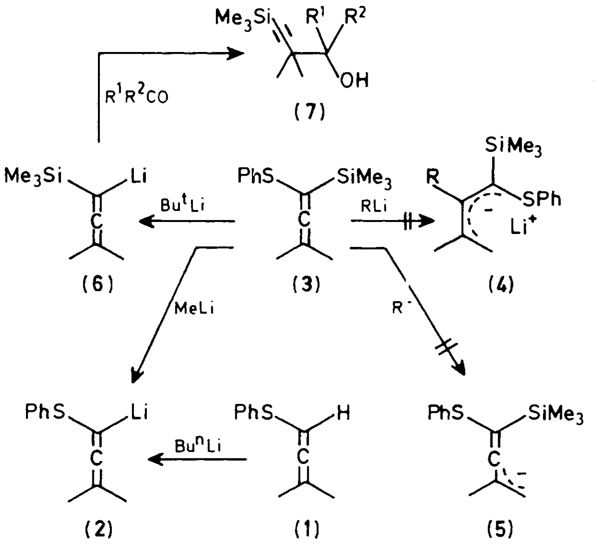
The phenylthioallene (**1**)[1] is readily lithiated by n-butyl-lithium–tetramethylethylenediamine (TMEDA) to form the lithioallene (**2**).[2] The anion of (**2**) reacts with chlorotrimethylsilane, exclusively at the α position, to give 3-methyl-1-phenylthio-1-trimethylsilylbuta-1,2-diene (**3**) in 87—98% isolated yields. The allene (**3**) contains many interesting functionalities, and might be expected to undergo reactions of both allenic silanes[3] and sulphides.[2,4] Since alkyl,[5] vinyl,[6] and allyl[7] carbon atoms, disubstituted with both silicon and sulphur, have recently been utilised as versatile acyl equivalents, the allene (**3**) might be expected to be similarly useful. In order to explore this facet of the chemistry of (**3**), its reactions with alkyl-lithium reagents were investigated, as reported in this communication.

Michael addition of an alkyl-lithium to the central carbon atom of the allene (**3**)[6,8] should give the allyl anion (**4**), whereas

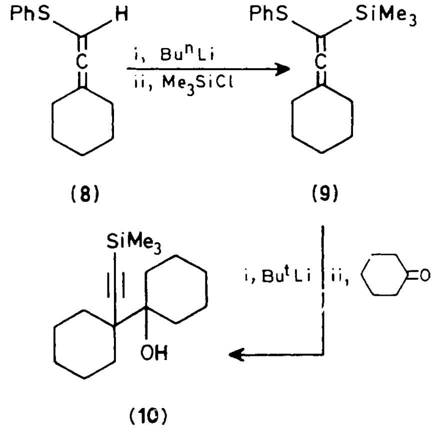
Table 1. Coupling reactions between (**6**) and various electrophiles.

Run	E^+	Product(s)[a]	Yield[b] (%)
i	Ph_2CO	(**7**; $R^1 = R^2 = Ph$)	66
ii	PhC(O)Me	(**7**; $R^1 = Me$, $R^2 = Ph$)	46
iii	Me_2CO	(**7**; $R^1 = R^2 = Me$)	26
iv	EtCHO	(**7**; $R^1 = Et$, $R^2 = H$)	55
v	DMF	$Me_3SiC{\equiv}CCMe_2CHO$	23
vi	CO_2	$HC{\equiv}CCMe_2CO_2H$ + $Me_2C{=}C{=}CHCO_2H$ 2:1	63
vii	$MgBr_2$ CO_2	$HC{\equiv}CCMe_2CO_2H$	49
viii	$MeCHCH_2O$	$Me_3SiC{\equiv}CCMe_2CH_2CHMeOH$ + $Me_2C{=}C{=}C(SiMe_3)CH_2CHMeOH$	33 17
ix	$MgBr_2$ $MeCHCH_2O$	$Me_3SiC{\equiv}CCMe_2CH_2CHMeOH$	10
x	Et_3SiCl	$Me_2C{=}C{=}C(SiEt_3)SiMe_3$	55

[a] All products were fully characterised by spectroscopic methods and in most cases elemental analysis. [b] Isolated purified yields.



(**7**) (**6**) (**3**) (**4**) (**2**) (**1**) (**5**)



(**8**) (**9**) (**10**)

allylic metallation[9] should give the allyl anion (**5**). At −78 °C (**3**) did not react with any alkyl-lithium, being recovered quantitatively even after prolonged treatment with t-butyl-lithium–TMEDA followed by quenching with acetone. The failure to observe metallation *anywhere* was rather surprising as the corresponding allyl compound is initially aromatically metallated under similar conditions.[10] When the allene (**3**) was treated with t-butyl-lithium (1 equiv.) at −25 °C carbon–sulphur bond cleavage[11] occurred cleanly within an hour to give (**6**), which was trapped with a variety of electrophiles (Table 1) and t-butyl phenyl sulphide. In contrast, methyl-lithium (3 equiv.) in tetrahydrofuran (THF) at 25 °C, reacted with (**3**) over several hours to give the allene (**1**) after aqueous quenching. Thus methyl-lithium induces carbon–silicon bond cleavage[12] producing the anion of (**2**) initially. This reaction did not occur with only one equivalent of methyl-lithium, or with diethyl ether as the solvent, and, if it was allowed to go to completion, usually led to extensive decomposition. n-Butyl-lithium cleaved the allene (**3**) at −25 °C in THF but the results varied from run to run. Sometimes clean C–S bond cleavage was seen, but usually C–Si bond cleavage also occurred, and sometimes was the predominant pathway. The t-butyl-lithium cleavage proved to be very satisfactory for preparation of (**6**), but since (**2**) is the precursor to the allene (**3**) the methyl-lithium cleavage was not investigated further. The change in reaction pathways presumably reflects both the greater steric hindrance to attack at silicon, and the greater thiophilicity of t-butyl-lithium.

Compound (**6**) was not stable above −20 °C, but at −78 °C it coupled efficiently with a variety of electrophiles as shown in Table 1. With aldehydes and ketones, (entries i—iv) exclusive γ-attack occurred.[13] G.c. and n.m.r. analysis of the crude reaction mixtures showed that the reactions are essentially quantitative, and the purified yields often showed large losses due to product volatility. Dimethylformamide (DMF) (entry v) gave an acetylenic aldehyde in 23% yield, but both CO_2 and propylene oxide gave mixtures of α- and γ-products (entries vi and viii). However, the corresponding Grignard reagent[14] [(**6**) plus $MgBr_2$] gave only γ-attack (entries vii and ix). In both cases the carboxylic acids produced were completely desilylated when isolated. Compound (**6**) reacted exclusively at the α-position with chlorotriethylsilane to give the 1,1-disilylallene (entry x). This was unexpected since the corresponding Grignard reagent is silylated exclusively γ with chlorotrimethylsilane.[14] Since the allene (**1**) is obtained in one step from 2-methylbut-3-yn-2-ol in *ca.* 70% yield,[2] this represents a convenient 2 step preparation of 1,1-disilylallenes in *ca.* 35% overall yield from a ketone–acetylene adduct. Several attempts were made to alkylate (**6**) with primary alkyl and allyl bromides, but no identifiable products were obtained from the rather complex reaction mixtures.

The cyclohexyl allene (**8**) is also silylated in good yield to form the allene (**9**). This also underwent C–S bond cleavage with t-butyl-lithium and C–Si bond cleavage with methyl-lithium. Reaction of the silylallenyl-lithium with cyclohexanone gave the adduct (**10**) in 30% yield illustrating the ability of this methodology to put two sterically crowded centres adjacent to one another.

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