Selective Desilylation of Bis(trimethylsilyl)acetylenes

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Summary Substituted acetylenic carbinols such as (**2**), (**5**), and (**6**) are obtained from the reaction of carbonyl compounds with the potassium or lithium salts of trimethylsilylacetylenes; these are prepared either by the *in situ* cleavage of bis(trimethylsilyl)acetylenes with 1—10 mol % KF–18-crown-6 ether or by the quantitative monodesilylation of bis-silylacetylenes with MeLi–LiBr complex.

4-Substituted-1-trimethylsilylbutadiynes are useful precursors in the stereoselective synthesis of terminal *cis*-enynes,[1] and their preparation therefore merits careful attention. Although a single trialkylsilyl group may be displaced from a bis-silylacetylene by a range of electrophiles, [2,3] this method of approach has its limitations, and a 'nucleophilic' alternative is sometimes desirable. At first sight the latter route is not so promising because, for example, cleavage of a single silyl group from a bis-silylacetylene in protic media (*e.g.*, aqueous methanolic alkali) is not particularly selective.[4] The recent observation[5] that $\mathrm{Bu^n{}_4NF}$ will initiate a smooth reaction between $\mathrm{PhC{\equiv}CSiMe_3}$ or $\mathrm{n\text{-}C_6H_{13}C{\equiv}CSiMe_3}$ and carbonyl compounds has prompted us to investigate the possibility of bringing about analogous single (and double) condensations involving bis-silylacetylenes as a route to secondary and tertiary carbinols. Initial results using Bu^n_4NF were not promising, probably because it is difficult to ensure that this reagent is anhydrous.[6] However use of 1—10 mol % KF–18-crown-6 ether ('naked fluoride') in CH_2Cl_2 or tetrahydrofuran (THF) resulted in a dramatic improvement. For example, the previously described[5] silyl ether (**1**) was obtained in 80% yield by boiling a CH_2Cl_2 solution containing $PhC{\equiv}CSiMe_3$, Ph_2CO (**4b**), and 10 mol % KF–18-crown-6 ether under reflux for 12 h. Other carbonyl compounds such as cyclohexanone and fluorenone reacted analogously. Double condensations using the bis-silylacetylenes, $Me_3SiC{\equiv}CSiMe_3$ (**3a**) [with PhCHO (**4a**)] and $Me_3Si(C{\equiv}C)_2SiMe_3$ (**3b**) [with (**4b**)] gave (**2a**) and (**2b**), respectively. Satisfactory single condensations between (**3a**) or (**3b**) and (**4a**) or Pr^iCHO (**4c**) were also observed, although corresponding reactions with ketones were slow and less efficient. The results are summarized in Table 1.

$PhC{\equiv}CC(OSiMe_3)Ph_2$ (**1**)

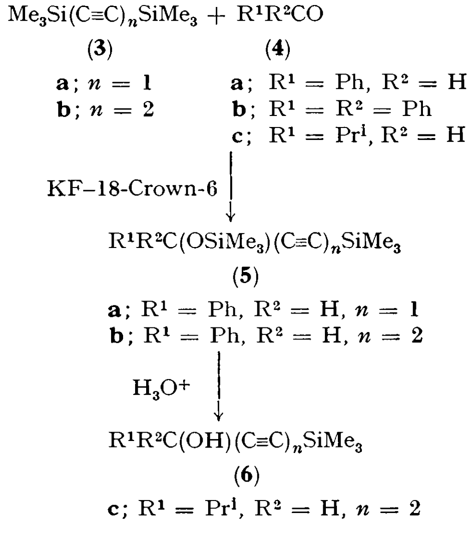
$R^1R^2C(OR^3)(C{\equiv}C)_nC(OR^3)R^1R^2$ (**2**)

a; $R^1{=}Ph$, $R^2{=}H$, $R^3{=}H$, $n = 1$
b; $R^1{=}R^2{=}Ph$, $R^3{=}SiMe_3$, $n{=}2$

TABLE 1

Compound (**3**)	Compound (**4**)	Ratio of (**3**):(**4**)	Solvent	KF–18-Crown-6 [mol % based on (**3**)]	m.p. or b.p. of product /°C (yield/%)
a	**a**	0·5:1[a]	CH_2Cl_2	1	(**2a**), Oil (78)
b	**b**	0·5:1[b]	CH_2Cl_2	10	(**2b**), 85 (90)
a	**a**	1:1[c]	CH_2Cl_2	1	(**5a**), 100 at 0·1 mmHg (60)
b	**a**	2:1[d]	THF	1	(**5b**) 46—47 (36)
b	**c**	2:1[e]	THF	3	(**6c**), 50·5—51·5 (54)

Reaction conditions: [a] mix at 0 °C, reflux 8 h, followed by acid hydrolysis. [b] 20 °C, 5 h. [c] reflux 3 h; 25 °C, 12 h. [d] mix at −20 °C; 20 °C, 14 h, followed by work-up with Me_3SiCl. [e] mix at 0 °C; 40 °C, 3 h, work-up with Me_3SiCl, followed by acid hydrolysis.



$Me_3Si(C{\equiv}C)_nSiMe_3$ + R^1R^2CO
(**3**) **a**; $n = 1$; **b**; $n = 2$
(**4**) **a**; $R^1 = Ph$, $R^2 = H$; **b**; $R^1 = R^2 = Ph$; **c**; $R^1 = Pr^i$, $R^2 = H$

$\downarrow$ KF–18-Crown-6

$R^1R^2C(OSiMe_3)(C{\equiv}C)_nSiMe_3$ (**5**)
a; $R^1 = Ph$, $R^2 = H$, $n = 1$
b; $R^1 = Ph$, $R^2 = H$, $n = 2$

$\downarrow$ H_3O^+

$R^1R^2C(OH)(C{\equiv}C)_nSiMe_3$ (**6**)
c; $R^1 = Pr^i$, $R^2 = H$, $n = 2$

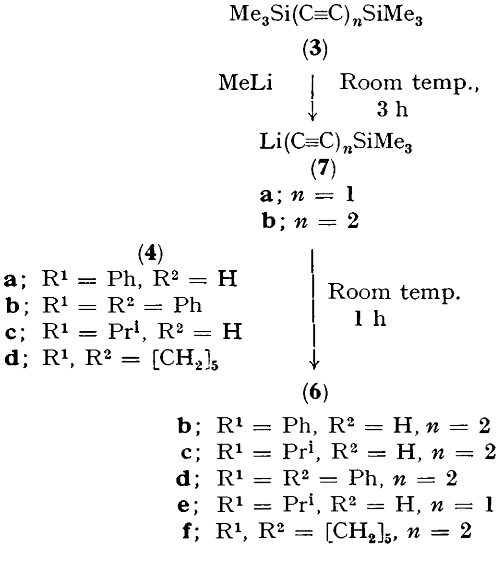
The desire to prepare a reagent which would react more effectively with ketones, coupled with the difficulty inherent in the existing methods of preparing $Me_3SiC{\equiv}CH$[7] and $Me_3Si(C{\equiv}C)_2H$,[3] led us to investigate the feasibility of cleaving silylacetylene bonds with methyl-lithium. Treatment of (**3b**) in Et_2O with the MeLi–LiBr complex at room temperature resulted in monodesilylation of (**3b**) and quantitative formation of $Me_3Si(C{\equiv}C)_2Li$ (**7b**) as revealed by ^1H n.m.r. spectral monitoring of the reaction mixture.

TABLE 2

Compound (**7**)	Compound (**4**)	Solvent[a]	Product (**6**)	m.p./°C	Yield/ %
a	**c**	THF	**e**[b]	Oil	88
b	**a**	Et_2O	**b**	Oil	58
b	**c**	Et_2O	**c**	50·5—51·5	72
b	**b**	Et_2O	**d**	91—93	72
b	**d**	Et_2O	**f**	108—109	46

[a] A solution of (**4**) was added to a solution containing a 1·2-fold excess of (**7**) at 0 °C, followed by stirring at room temperature for 1 h and quenching at 0 °C with saturated aqueous NH_4Cl solution. [b] Ref. 2b.

Similarly, MeLi–LiBr reacts with (**3a**) to give (**7a**) in THF but not in Et_2O. Compounds (**7a**) and (**7b**) reacted with a wide range of aldehydes and ketones to give carbinols (**6**) in high yield (Table 2).



$Me_3Si(C{\equiv}C)_nSiMe_3$ (**3**)

$\downarrow$ MeLi, Room temp., 3 h

$Li(C{\equiv}C)_nSiMe_3$ (**7**)
a; $n = 1$
b; $n = 2$

$\downarrow$ (**4**) Room temp. 1 h
a; $R^1 = Ph$, $R^2 = H$
b; $R^1 = R^2 = Ph$
c; $R^1 = Pr^i$, $R^2 = H$
d; R^1, R^2 = $[CH_2]_5$

(**6**)
b; $R^1 = Ph$, $R^2 = H$, $n = 2$
c; $R^1 = Pr^i$, $R^2 = H$, $n = 2$
d; $R^1 = R^2 = Ph$, $n = 2$
e; $R^1 = Pr^i$, $R^2 = H$, $n = 1$
f; R^1, R^2 = $[CH_2]_5$, $n = 2$

Formation of (**7a**) from the very readily available (**3a**) offers an alternative method for the preparation of substituted trimethylsilylacetylenes; for example alkylation of (**7a**) with an excess of MeI gave $MeC{\equiv}CSiMe_3$ (76%).

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