Generation of Silylethynolates via C–Si Bond Cleavage of Disilylketenes Induced by *t*-BuOK[1]

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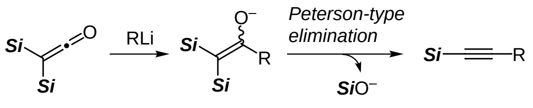
Abstract: Disilylketenes undergo selective mono-desilylation upon treatment of *t*-BuOK in the presence of HMPA. The resulting silylethynolates are convertible to other disilylketenes in good yields. The intermediary silylethynolate was analyzed by NMR and IR spectroscopy.

Key words: disilylketene, silylethynolate, potassium *t*-butoxide, carbon-silicon bond cleavage, HMPA

Recently we reported that α,α-disilylenolate intermediates derived from disilylketenes and organolithiums subsequently undergo Peterson-type elimination to give silylacetylenes (Scheme 1).[3]

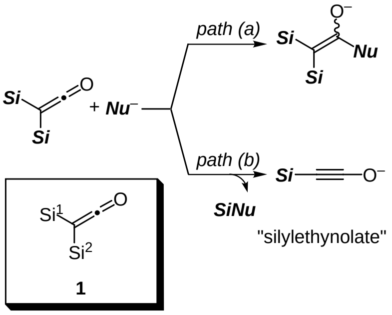
This finding suggests that disilylketenes may be synthetically equivalent to SiC≡C$^+$ in organic synthesis.



Si = triorganosilyl

Scheme 1

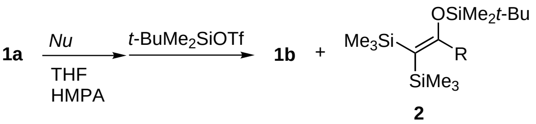
In the course of our synthetic exploitation of disilylketenes, we have now found that disilylketenes (**1**) undergo nucleophilic desilylation with organolithium reagents at the ketene *sp*^{2}-carbon [Scheme 2, path (b)] as well as nucleophilic addition to the ketene *sp*-carbon [Scheme 2, path (a)]. The selective nucleophilic desilylation from **1** may provide a new method for the generation of silylethynolate intermediates,[4,5] which should be useful for organic synthesis.



1	Si^1	Si^2
a	Me$_3$Si	Me$_3$Si
b	Me$_3$Si	*t*-BuMe$_2$Si
c	Me$_3$Si	*i*-Pr$_3$Si
d	Me$_3$Si	PhMe$_2$Si
e	Me$_3$Si	Ph$_2$MeSi
f	Me$_3$Si	Ph$_3$Si
g	*t*-BuMe$_2$Si	*t*-BuMe$_2$Si
h	*t*-BuMe$_2$Si	PhMe$_2$Si
i	*t*-BuMe$_2$Si	Ph$_2$MeSi
j	*t*-BuMe$_2$Si	Ph$_3$Si
k	Ph$_3$Si	Ph$_3$Si

Scheme 2

First, we examined the reaction of bis(trimethylsilyl)ketene (**1a**)[6] with various nucleophilic reagents in the presence of HMPA[7,8] (Scheme 3). The reaction was carried out by adding organolithiums to a solution of equimolar amounts of **1a** and HMPA in THF at 0 °C. After stirring for 1 h, the reaction mixture was quenched by *t*-BuMe$_2$SiOTf at 0 °C and then stirred at r.t. for 2 h. Then, the product was isolated by an aqueous work-up and then purified by preparative HPLC. The use of PhLi as a nucleophile resulted in the formation of **1b**[5a] (39% yield) in addition to **2** (R = Ph, 51% yield).[9a] While the chemoselectivity was not noticeably changed in the case of MeLi [**1b**, 32% and **2** (R = Me), 53% yield],[9b] the formation of **2** (R = *t*-Bu) was completely suppressed in the case of *t*-BuLi, although the yield of **1b** was modest (47%). Finally, we found that the use of *t*-BuOK instead of organolithiums improved the yield remarkably (**1b**, 84%) with excellent chemoselectivity. These results clearly show that *t*-BuOK prefers the silicon center rather than the ketene carbonyl of **1a** in the initial step to form a potassium silylethynolate selectively.[10] The synthesis of various disilylketenes by means of *t*-BuOK is summarized in Table 1.[11] The silylethynolate derived from **1a** and *t*-BuOK upon treatment with organosilyl halides such as *i*-Pr$_3$SiCl, PhMe$_2$SiCl, Ph$_2$MeSiCl, and Ph$_3$SiCl gave unsymmetrical disilylketenes **1c**–**f** in good yields (entry 2–5). When unsymmetrical disilylketenes **1b**, **1e**, or **1f** bearing at least one Me$_3$Si group were employed, the less bulky Me$_3$Si group was selectively substituted by other R$_3$Si group to afford the corresponding unsymmetrical disilylketenes **1g**–**k** in good yields (entry 6, 7, 9–11). However, the reaction of unsymmetrical disilylketene **1d** gave a mixture of **1h** and **1b** (47% and 32%, respectively) upon treatment with *t*-BuMe$_2$SiOTf, probably because there is no remarkable difference in the steric congestion between two silicon groups in **1d** (entry 8).



Nu: RLi (R = Ph, Me, *t*-Bu), or OK*t*-Bu

Scheme 3

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Table 1 Preparation of Various Disilylketenes using *t*-BuOK[a]

Entry	Substrate	R_3SiX	Product	Yield (%)
1	**1a**	*t*-$BuMe_2SiOTf$	**1b**	84
2	**1a**	*i*-Pr_3SiCl	**1c**[5a]	60
3	**1a**	$PhMe_2SiCl$	**1d**[12a]	71
4	**1a**	$Ph_2MeSiCl$	**1e**[3,13a,b]	75
5	**1a**	Ph_3SiCl	**1f**[13b]	76
6	**1b**	*t*-$BuMe_2SiOTf$	**1g**[5b,13c]	75
7	**1b**	$PhMe_2SiCl$	**1h**[5b]	67
8	**1d**	*t*-$BuMe_2SiOTf$	**1h** (**1b**)	47 (32)[b]
9	**1e**	*t*-$BuMe_2SiOTf$	**1i**[5b]	79
10	**1f**	*t*-$BuMe_2SiOTf$	**1j**[5b]	81
11	**1f**	Ph_3SiCl	**1k**[12b]	94

[a] Reaction conditions; substrate: *t*-BuOK:HMPA:R_3SiX = 1:1:1:1, [substrate] = 0.33 M in THF, 0 °C for 1 h.

[b] *t*-$BuOSiMe_2Ph$[13d] was obtained as a by-product in 31% yield.

Table 2 Selected Spectroscopic Data for Ketenes and Alkynyl Ethers

compound		^{13}C NMR ($CDCl_3$)		IR	Ref.
$R_{(2-n)}$	$C^{\beta}C^{\alpha}OR_n$	C^{α} (ppm)	C^{β} (ppm)	ν_{CCO} (cm^{-1})	
Ph_2	C=C=O	201.2	47.6	2090	13f
(*n*-C_6H_{13})(Me_3Si)	C=C=O	182.6	13.0	2090	13e
$(Me_3Si)_2$	C=C=O	166.8	1.7	2050	13f
(Me_3Si)(Me_3Sn)	C=C=O	164.4	–5.8	2080	8a,13f
$(Me_3Sn)_2$	C=C=O	161.7	–13.9	2040–2060	8a,13f
t-$BuMe_2Si$	C≡C–$OSiMe_2$*t*-Bu	–	–	2185	13c
t-$BuMe_2Si$	C≡C–O*t*-Bu	106.7	37.9	2180	13g
t-Bu	C≡C–$OSiMe_2$*t*-Bu	85.5	40.3	2270	13h
n-Bu	C≡C–O*t*-Bu	85.6	40.1	2280	13i

The present reaction was not applicable to monosilylketenes. For instance, the reaction of *n*-hexyl(trimethylsilyl)ketene[13e] with *t*-BuOK in the presence of HMPA gave a complex mixture including *t*-butyl octanoate. This may be attributable to the difference of thermodynamic stability between alkynolates and silylethynolates. In other words, the interaction of the Si–C σ* orbital with the π-orbital in silylethynolates should stabilize their negative charge,[14] inducing better leaving ability than in the case of alkynolates.

To gain deeper insight into the structure of the silylethynolate, the mixture of **1a** and *t*-BuOK in THF–HMPA was concentrated in vacuo and the resulting red residue was analyzed by spectroscopic methods. Its ^{13}C NMR spectrum in d_8-THF showed two signals at 132.8 and 33.4 ppm, in addition to 38.1 and 5.2 ppm which are assignable to HMPA ($^3J_{CP}$ = 3.7 Hz) and Me_3Si group, respectively. Although the absence of any characteristic ketene carbonyl signal above 160 ppm may support its structure as 'O-ynolate, $Me_3SiC{\equiv}C{-}OK$', the observed signals do not fall within the typical range for the acetylenic ethers (see Table 2). Moreover, IR spectra (d_8-THF) showed a strong absorption at 2076 cm^{-1}, which is typical for ketenes (see Table 2). Therefore, the contribution from the 'C-ynolate, $Me_3Si(K)C{=}C{=}O$' structure cannot be ruled out. Currently we are trying to get a suitable crystalline for this material, to determine its structural property in the solid state via single-crystal X-ray diffraction analysis.

In conclusion, we have developed the *t*-BuOK-induced C–Si bond cleavage reaction of disilylketenes.[15] Our method may provide a general method for the generation of silylethynolates efficiently from disilylketenes. Its operational simplicity based on the remarkable stability of the precursors should be beneficial to the development of the potential utility of silylethynolates in organic synthesis.

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(9) Analytical data for **2**: (a) 1,1-Bis(trimethylsilyl)-2-[(1,1-dimethylethyl)dimethylsilyl]oxy-2-phenylethene (**2**, R = Ph). ^{1}H NMR ($CDCl_3$) δ: –0.31 (s, 9 H), –0.29 (s, 6 H), 0.25 (s, 9 H), 0.86 (s, 9 H), 7.18–7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ: –3.1, 2.1, 2.4, 18.6, 26.3, 109.9, 127.8, 128.0, 129.6, 142.0, 165.9. Anal. Calcd for $C_{20}H_{38}OSi_3$: C, 63.42; H, 10.11. Found: C, 63.31; H, 10.35. (b) 1,1-Bis(trimethylsilyl)-2-[(1,1-dimethylethyl)dimethylsilyl] oxy-1-propene (**2**, R = Me). This compound was not obtained in pure form and thus only ^{1}H and ^{13}C NMR spectral data were shown. ^{1}H NMR ($CDCl_3$) δ: 0.12 (s, 9 H), 0.14 (s, 9 H), 0.20 (s, 6 H), 0.95 (s, 9 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ: –2.3, 0.1, 2.7, 2.9, 19.1, 26.5, 107.1, 164.5.

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(11) (a) **General Procedure for the Preparation of Disilylketenes using *t*-BuOK**: Preparation of [(1,1-dimethylethyl)dimethylsilyl](trimethylsilyl)ketene(**1b**) from **1a** is representative. Disilyllketene **1a** (296.5 mg, 1.59 mmol) was dissolved in THF (1.6 mL) and HMPA (0.28 mL, 1.61 mmol). To the resulting yellow solution was added a solution of *t*-BuOK (180.0 mg, 1.60 mmol) in THF (3.2 mL) at 0 °C. The mixture was stirred for 1 h at the same temperature and quenched by *t*-BuMeSiOTf (0.37 mL, 1.61 mmol). After stirring the resulting solution for 2 h at room temperature, the reaction mixture was diluted with pentane and washed with water. Then the organic layer was dried by Na_2SO_4 and filtered through Florisil. Evaporation of the solvent followed by silica-gel chromatography (Wakogel C-200) afforded **1b** as a colorless oil (305.4 mg, 84% yield). (b) We were unable to detect the formation of any *O*-silylated product (silyl silylethynyl ether) under these conditions. See ref.[13c]. (c) The use of carbon electrophiles (MeI, Me_2SO_4, Me_3OBF_4, or PhCHO) instead of R_3SiX resulted in the formation of intractable mixtures under similar conditions.

(12) Analytical data for new disilylketenes (silicon-attached quarternary carbon was not observed in ^{13}C NMR spectra): (a) (Dimethylphenylsilyl)(trimethylsilyl)ketene(**1d**). ^{1}H NMR ($CDCl_3$) δ: 0.14 (s, 9 H), 0.52 (s, 6 H), 7.40–7.43 (m, 3 H), 7.59–7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ: –0.2, 1.2, 127.8, 129.4, 133.6, 138.3, 166.9; IR(neat) 2084 cm^{-1} (CCO); MS (70 eV) *m/z* 248 (M^+); bp 62–70 °C (0.05 mmHg). Anal. Calcd for $C_{13}H_{20}OSi_2$: C, 62.84; H, 8.11. Found: C, 63.10; H, 8.28. (b) Bis(triphenylsilyl)ketene(**1k**). ^{1}H NMR ($CDCl_3$) δ: 7.21-7.49 (m, 30 H); ^{13}C NMR ($CDCl_3$) δ: 127.7, 127.8, 129.7, 129.8, 133.7, 135.2, 135.4, 135.9, 166.2; IR(nujol) 2080 cm^{-1} (CCO); MS (70 eV) *m/z* 558 (M^+); mp 165-166 °C. Anal. Calcd for $C_{38}H_{30}OSi_2$: C, 81.67; H, 5.41. Found: C, 81.40; H, 5.32.

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