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Facile 1,4-Silyl Rearrangement with Concomitant Loss of a Benzenesulfonyl Group: One-Pot Synthesis of Allyloxysilanes

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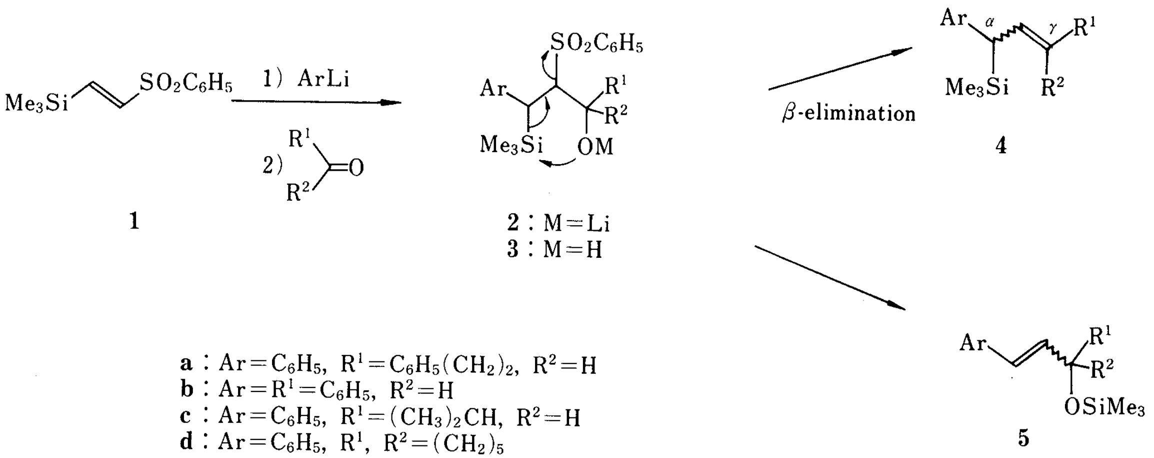
In contrast to the thermal stability of the oxido anions **7**, facile eliminative rearrangement has been shown to occur in the case of the oxido anions **2** which possess an aryl substituent on the carbon atom bearing the trimethylsilyl group. Thus, the one-pot synthesis of the allyloxysilanes **5**, starting from the (*E*)-*β*-(trimethylsilyl)vinyl sulfone **1**, was achieved *via* the facile 1,4-silyl rearrangement of the oxido anions **2** with concomitant loss of the benzenesulfonyl group.

Keywords——1,4-silyl rearrangement; allyloxysilane; (*E*)-trimethylsilylvinyl sulfone; allylsilane; Michael addition; elimination

One of the most valuable features of the reactions of substituted allylsilanes with various kinds of electrophiles is their high regioselectivity for the *γ*-substitution reaction.[1] Therefore the development of methods for the regioselective synthesis of these materials, substituted allylsilanes, is becoming very important. Recently we reported the regioselective synthesis of *α*-substituted allylsilanes, in which (*E*)-*β*-(trimethylsilyl)vinyl phenyl sulfone (**1**) was utilized as a good Michael acceptor for the conjugate addition of lithium salts of carbanions.[2] As an extension of this method, we focused our attention to the regioselective synthesis of *α*,*γ*-substituted allylsilanes **4** utilizing the vinyl sulfone **1**. The synthetic plan is outlined in Chart 1 (**1**→**3**→**4**). Shechter and Hsiao have reported a similar reaction sequence for the preparation of *γ*-substituted allylsilanes **9**, *via* the reductive elimination of the methanesulfonate of **8**, the adduct of the lithium salt of 1-benzenesulfonyl-2-(trimethylsilyl)ethane (**6**) to a carbonyl compound.[3] In this paper we wish to report the unexpected formation of the allyloxysilane **5** by the reaction of the vinyl sulfone **1** with aryllithium and a carbonyl compound.

For the synthesis of the presumed intermediate, *β*-hydroxy-*β*′-trimethylsilyl sulfone **3a**, leading to *α*,*γ*-substituted allylsilane **4**, the *β*-silylvinyl sulfone **1** was treated with 1.2-eq of phenyllthium in tetrahydrofuran (THF) at −78 °C, then phenylpropionaldehyde was added at the same temperature. The reaction mixture was allowed to warm to room temperature. The product thus obtained was not the expected **3a** but a 1 : 1 stereo-isomeric mixture of rearranged allyloxysilane **5a** (85% yield): its infrared (IR) spectrum showed neither the characteristic absorption bands of the sulfonyl group, which usually appear near 1300 and 1150 cm^{-1}, nor those of a hydroxyl group. The nuclear magnetic resonance (NMR) spectrum exhibited peaks attributable to 1,2-disubstituted olefin.

The reaction of the *α*-sulfonyl stabilized carbanion, prepared by the conjugate addition of phenyllithium to the sulfone **1**, with benzaldehyde also gave rise to a 1 : 1 mixture of (*E*)- and (*Z*)-allyloxysilane **5b** in 68% yield. The structure of (*E*)-**5b** was confirmed by comparison of the NMR spectrum with that of an authentic sample prepared by the reaction of cinnamaldehyde with phenyllithium and chlorotrimethylsilane in THF. The results of the formation of rearranged allyloxysilanes **5** are summarized in Table I. Usage of ether or hexane



a : Ar$=C_6H_5$, $R^1=C_6H_5(CH_2)_2$, $R^2=H$
b : Ar$=R^1=C_6H_5$, $R^2=H$
c : Ar$=C_6H_5$, $R^1=(CH_3)_2CH$, $R^2=H$
d : Ar$=C_6H_5$, R^1, $R^2=(CH_2)_5$
e : Ar$=p$-$MeOC_6H_4$, $R^1=n$-C_5H_{11}, $R^2=H$
f : Ar$=p$-$MeOC_6H_4$, $R^1=C_6H_5(CH_2)_2$, $R^2=H$

Chart 1

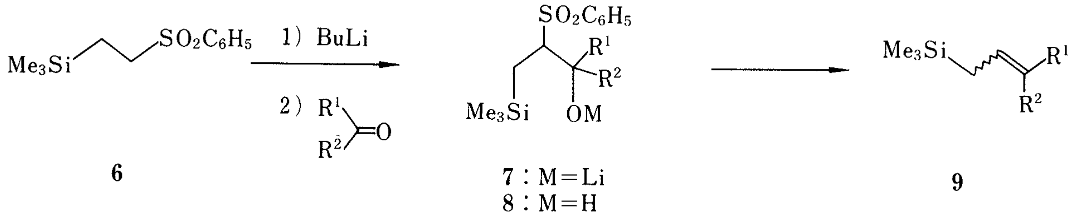
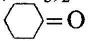


Chart 2

Table I. One-Pot Synthesis of Allyloxysilanes **5**

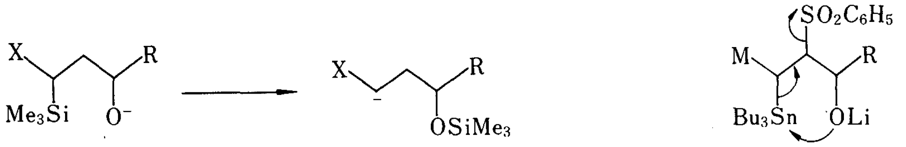
Run	ArLi	Carbonyl compound	Solvent	Reaction conditions[a]	**5**	Product $E:Z$ ratio	Yield (%)[b]
1	C_6H_5Li	$C_6H_5(CH_2)_2CHO$	THF	−78 °C (15 min) then r.t. (1 h)	**5a**	1:1	85
2	C_6H_5Li	$C_6H_5(CH_2)_2CHO$	THF–HMPA[c]	−78 °C (15 min) then r.t. (1 h)	**5a**	2:1	62
3	C_6H_5Li	$C_6H_5(CH_2)_2CHO$	Et_2O	−78 °C (20 min) then r.t. (15 h)	**5a**	3:1	59
4	C_6H_5Li	$C_6H_5(CH_2)_2CHO$	Hexane	−78 °C (30 min) then r.t. (15 h)	**5a**	4:1	19
5	C_6H_5Li	C_6H_5CHO	THF	−78 °C (20 min) then r.t. (1 h)	**5b**	1:1	68
6	C_6H_5Li	$(CH_3)_2CHCHO$	THF	−78 °C (1 h)	**5c**	3:1	51
7	C_6H_5Li		THF–HMPA[c]	−78 °C (1.5 h) then r.t. (1 h)	**5d**	Z	37
8	p-$MeOC_6H_4Li$	n-$C_5H_{11}CHO$	THF	−78 °C (20 min) then r.t. (11 h)	**5e**	1:1	82
9	p-$MeOC_6H_4Li$	$C_6H_5(CH_2)_2CHO$	THF	−78 °C (20 min) then r.t. (24 h)	**5f**	1:1	76

a) r.t.; room temperature.
b) Isolated yield.
c) HMPA; hexamethylphosphoric triamide.

as the reaction solvent gave higher stereoselectivity for the (E)-isomer of **5a**, but the yield of the product mixture dropped markedly (runs 3 and 4).

These results can be rationalized by assuming an initial 1,4-trimethylsilyl migration from the carbon atom to the oxygen atom of **2** because of the strong affinity of the silyl group for oxygen, followed by the loss of the benzenesulfonyl group. A similar type of 1,4-rearrangement of a silyl group from carbon to oxygen has been reported:[4] the 1,4-trimethylsilyl shifts in the anions **10a**—**c** occur smoothly to produce the corresponding carbanions **11a**—**c**, in which the negative charge is stabilized by the conjugation with electron-withdrawing groups such as amide, nitrile, and sulfonyl groups.[5] In contrast to the ready rearrangements of **2a**—**f**, the oxido anions **7** have been shown to be stable even at room temperature and their rearrangements to the corresponding allyloxysilanes were not observed at all.[3] It seems reasonable to assume that the facile 1,4-silyl rearrangement in the oxido anions **2a**—**f** may be attributable to the presence of the phenyl or *p*-methoxyphenyl group on the carbon atom attached to the silyl group. These aryl groups may stabilize considerably the developing negative charge on the carbon atom in the transition state. A similar type of eliminative 1,4-stannyl rearrangement of the oxido anion **12** has been reported.[6]

Thus we developed a new method for the one-pot synthesis of the protected allyl alcohols **5**.



10 **11** **12** : M = $SiMe_3$ or $SnBu_3$

a : X = $CONMe_2$
b : X = CN
c : X = $SO_2C_6H_5$

Chart 3

Experimental

IR spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer. NMR spectra were obtained with a JEOL JNM-FX 100 or a JEOL JNM-PMX 60 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a JEOL JMS-DX-300 spectrometer. Column chromatography was carried out on Woelm neutral alumina (Activity grade III). Analytical thin layer chromatography (TLC) was carried out on Merck DC-Fertigplatten (Kieselgel 60 F-254).

General Procedure for Synthesis of Allyloxysilanes 5——A THF solution of phenyllithium or *p*-methoxyphenyllithium (1.2 mmol) (prepared from the corresponding aryl bromide by reaction with *tert*-butyllithium at −78 °C for 1 h) was added dropwise to a stirred solution of (*E*)-1-phenylsulfonyl-2-(trimethylsilyl)ethylene (**1**) (1 mmol) in the solvent (5 ml) listed in Table I at −78 °C under nitrogen. The reaction mixture was stirred at −78 °C for 1 h and the complete disappearance of the vinyl sulfone **1** was confirmed by analytical TLC using ethyl acetate–hexane (3 : 7). A solution of a carbonyl compound (1.2 mmol) in the solvent (2.5 ml) listed in Table I was added dropwise at −78 °C. The reaction mixture was stirred under the conditions described in Table I, quenched with cold brine, and extracted with ether. The organic layer was washed with brine and dried over sodium sulfate. Evaporation *in vacuo* left an oil, which was chromatographed on a column of neutral alumina and eluted with ethyl acetate–hexane (15 : 85) to give an oily mixture of stereoisomers of allyloxysilanes **5**. Their *E* : *Z* ratios were determined from the NMR spectra.

1,5-Diphenyl-3-trimethylsilyloxy-1-pentene (5a)——IR $^{\text{film}}_{\text{max}}$ cm^{-1}: 1600, 1500, 1250, 965, 870, 840, 745. MS *m*/*e*: 310 (M^+), 220, 205, 129, 91, 73 (base peak). High resolution MS: Found 310.1776. Calcd for $C_{20}H_{26}OSi$ (M^+) 310.1753. NMR ($CDCl_3$) δ: −0.01 (s, $SiMe_3$ for (*Z*)-isomer), 0.14 (s, $SiMe_3$ for (*E*)-isomer), 1.7—2.1 (2H, m, $C\underline{H}_2CHO$), 2.5—2.9 (2H, m, $C\underline{H}_2C_6H_5$), 4.24 (q, $J=6$ Hz, CHO for (*E*)-isomer), 4.58 (dt, $J=5$, 9 Hz, CHO for (*Z*)-isomer), 5.65 (dd, $J=12$, 9 Hz, $C\underline{H}CHO$ for (*Z*)-isomer), 6.14 (dd, $J=16$, 6 Hz, $C\underline{H}CHO$ for (*E*)-isomer), 6.38 (d, $J=12$ Hz, $C\underline{H}C_6H_5$ for (*Z*)-isomer), 6.45 (d, $J=16$ Hz, $C\underline{H}C_6H_5$ for (*E*)-isomer), 6.9—7.6 (5H, m, C_6H_5).

1,3-Diphenyl-1-trimethylsilyloxy-2-propene (5b)——IR $\nu^{\text{film}}_{\text{max}}$ cm^{-1}: 1600, 1495, 1445, 1250, 1060, 885, 840, 695. MS *m*/*e*: 282 (M^+), 205, 193, 115, 91, 73 (base peak). High resolution MS: Found 282.1433. Calcd for $C_{18}H_{22}OSi$ (M^+) 282.1438. NMR ($CDCl_3$) δ: 0.0 (s, $SiMe_3$ for (*Z*)-isomer), 0.14 (s, $SiMe_3$ for (*E*)-isomer), 5.28 (d, $J=6$ Hz, CHO for (*E*)-isomer), 5.59 (d, $J=9.5$ Hz, CHO for (*Z*)-isomer), 5.85 (dd, $J=11$, 9.5 Hz, $C\underline{H}CHO$ for (*Z*)-isomer), 6.23 (dd, $J=16$, 6 Hz, $C\underline{H}CHO$ for (*E*)-isomer), 6.54 (d, $J=16$ Hz, $C\underline{H}C_6H_5$ for (*E*)-isomer), 6.56 (d, $J=11$ Hz, $C\underline{H}C_6H_5$ for (*Z*)-isomer), 7.1—7.5 (5H, m, C_6H_5). The structure of (*E*)-**5b** was confirmed by comparison of the NMR spectrum with that of an authentic sample prepared from (*E*)-cinnamaldehyde as follows. A solution of (*E*)-cinnamaldehyde (100 mg, 0.76 mmol) in THF (1 ml) was added dropwise at −20 °C to a stirred solution of phenyllithium (0.6 M, 1.26 ml, 0.76 mmol) in THF under nitrogen and the mixture was stirred for 15 min at -20 °C, then cooled to -78 °C. Trimethylchlorosilane (82 mg, 0.76 mmol) was added, and the reaction mixture was warmed to room temperature and stirred for 12 h. After the addition of cold brine, the mixture was extracted with ether. The organic layer was washed with brine and dried. Evaporation left an oil, which was chromatographed on a column of neutral alumina. Elution with ethyl acetate–hexane (15 : 85) afforded the (*E*)-allyloxysilane **5b** (170 mg, 79%).

4-Methyl-1-phenyl-3-trimethylsilyloxy-1-pentene (5c)——IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1600, 1500, 1250, 1055, 965, 880, 840, 740. MS *m/e*: 248 (M$^+$), 205, (base peak), 179, 73. High resolution MS: Found 248.1566. Calcd for $C_{15}H_{24}OSi$ (M$^+$) 248.1596. NMR ($CDCl_3$) δ: -0.04 (s, $SiMe_3$ for (*Z*)-isomer), 0.12 (s, $SiMe_3$ for (*E*)-isomer), 0.8—1.0 (6H, CH$\underline{Me_2}$), 1.4—1.9 (1H, m, C$\underline{H}$Me$_2$), 3.91 (t, $J=6$ Hz, CHO for (*E*)-isomer), 4.30 (dd, $J=10$, 6 Hz, CHO for (*Z*)-isomer), 5.62 (dd, $J=12$, 10 Hz, C$\underline{H}$CHO for (*Z*)-isomer), 6.11 (dd, $J=16$, 6 Hz, C$\underline{H}$CHO for (*E*)-isomer), 6.43 (d, $J=16$ Hz, C$\underline{H}C_6H_5$) for (*E*)-isomer), 6.46 (d, $J=12$ Hz, C$\underline{H}C_6H_5$ for (*Z*)-isomer), 7.0—7.6 (5H, m).

(*Z*)-1-(2-Phenylethylenyl)-1-(trimethylsilyloxy)cyclohexane (5d)——IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1600, 1500, 1245, 1045, 835, 700. MS *m/e*: 274 (M$^+$), 231, 217, 205, 179, 73 (base peak). High resolution MS: Found 274.1714. Calcd for $C_{17}H_{26}OSi$ (M$^+$) 274.1752. NMR ($CDCl_3$) δ: 0.07 (9H, s, $SiMe_3$), 1.1—1.8 (10H, $(CH_2)_5$), 5.68 (1H, d, $J=13$ Hz, C$\underline{H}$CO), 6.36 (1H, d, $J=13$ Hz, C$\underline{H}C_6H_5$), 7.1—7.6 (5H, m, C_6H_5).

1-(4-Methoxyphenyl)-3-(trimethylsilyloxy)-1-octene (5e)——IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1610, 1520, 1250, 1035, 880, 840, 750. MS *m/e*: 306 (M$^+$), 235 (base peak), 217, 121, 73. High resolution MS: Found 306.2017. Calcd for $C_{18}H_{30}O_2Si$ (M$^+$) 306.2016. NMR ($CDCl_3$) δ: -0.01 (s, $SiMe_3$ for (*Z*)-isomer), 0.13 (s, $SiMe_3$ for (*E*)-isomer), 0.7—1.0 (3H), 1.1—1.7 (8H), 3.78, 3.80 (total 3H, each s, OMe), 4.16 (m, CHO for (*E*)-isomer), 4.56 (m, CHO for (*Z*)-isomer), 5.53 (dd, $J=12$, 9 Hz, C$\underline{H}$CHO for (*Z*)-isomer), 5.97 (dd, $J=16$, 6.5 Hz, C$\underline{H}$CHO for (*E*)-isomer), 6.31 (d, $J=12$ Hz, C$\underline{H}C_6H_4$ for (*Z*)-isomer), 6.36 (d, $J=16$ Hz, C$\underline{H}C_6H_4$ for (*E*)-isomer), 6.80, 6.83, 7.10, 7.23 (total 4H, each d, $J=8.5$ Hz, C_6H_4).

1-(4-Methoxyphenyl)-5-phenyl-3-(trimethylsilyloxy)-1-pentene (5f)——IR $\nu_{\max}^{\text{film}}$ cm^{-1}: 1605, 1520, 1250, 1080, 1030, 870, 840, 745. MS *m/e*: 340 (M$^+$), 250, 235 (base peak), 159, 91, 75, 73. High resolution MS: Found 340.1861. Calcd for $C_{21}H_{28}O_2Si$ (M$^+$) 340.1859. NMR ($CDCl_3$) δ: 0.0 (s, $SiMe_3$ for (*Z*)-isomer), 0.12 (s, $SiMe_3$ for (*E*)-isomer), 1.7—2.1 (2H, m, C$\underline{H_2}$CHO), 2.5—2.9 (2H, m, C$\underline{H_2}C_6H_4$), 3.75 (3H, s, OMe), 4.22 (q, $J=6.5$ Hz, CHO for (*E*)-isomer), 4.58 (dt, $J=5$, 9 Hz, CHO for (*Z*)-isomer), 5.56 (dd, $J=12$, 9 Hz, C$\underline{H}$CHO for (*Z*)-isomer), 6.00 (dd, $J=16$, 6.5 Hz, C$\underline{H}$CHO for (*E*)-isomer), 6.30 (d, $J=12$ Hz, C$\underline{H}C_6H_4$ for (*Z*)-isomer), 6.40 (d, $J=16$ Hz, C$\underline{H}C_6H_4$ for (*E*)-isomer), 6.6—7.4 (9H, C_6H_4, C_6H_5).

References and Notes

1) *a*) H. Sakurai, *Pure Appl. Chem.*, **54**, 1 (1982); *b*) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London, 1981, pp. 97—124; *c*) I. Fleming, *Chem. Soc. Rev.*, **10**, 83 (1981); *d*) T. H. Chan and I. Fleming, *Synthesis*, **1979**, 761.

2) M. Ochiai, K. Sumi, E. Fujita, and S. Tada, *Chem. Pharm. Bull.*, **31**, 3346 (1983).

3) C-N. Hsiao and H. Shechter, *Tetrahedron Lett.*, **23**, 1963 (1982).

4) A. G. Brook and A. R. Bassindale, "Rearrangements in Ground and Excited States," Vol. 2, ed. by P. de Mayo, Academic Press, New York, 1980, pp. 216—218.

5) *a*) R. P. Woodbury and M. W. Rathke, *J. Org. Chem.*, **43**, 1947 (1978); *b*) I. Matsuda, S. Murata, and Y. Ishii, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 26; *c*) I. Matsuda, S. Murata, and Y. Izumi, *Bull. Chem. Soc. Jpn.*, **52**, 2389 (1979); *d*) M. Isobe, M. Kitamura, and T. Goto, *Tetrahedron Lett.*, **1979**, 3465.

6) *a*) M. Ochiai, T. Ukita, and E. Fujita, *Tetrahedron Lett.*, **24**, 4025 (1983); *b*) *Idem*, *J. Chem. Soc., Chem. Commun.*, **1983**, 619.