Preparation of New 7-Silanorbornene Derivatives and Their Reaction with Some Nucleophiles

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Reduction of the 7-silanorbornene derivatives obtained from Diels–Alder reactions of 1,1,3,4-tetramethylsilacyclopenta-2,4-diene (**1a**), and 2,3-dimethyl-5-silaspiro[4.4]nona-1,3-diene (**1b**) with maleic anhydride was carried out by lithium aluminum hydride (LAH) to give diol derivatives. Attempts to substitute the hydroxyl groups with chlorine using various chlorination agents such as thionyl chloride and triphenylphosphine in carbon tetrachloride were unsuccessful. The latter reaction, however, gave a corresponding ether derivative as a result of intramolecular cyclization. Reactions of the 7-silanorbornene derivatives with some nucleophiles such as LAH, $(n\text{-Bu})_4NF$, *n*-BuLi, and PhLi were also investigated.

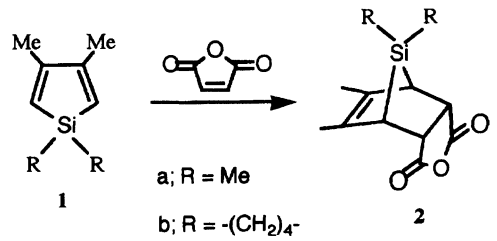
Because of their highly strained structure, the preparation and reaction of 7-silanorbornene derivatives have received much attention. There are many studies on the syntheses and reactions of 7-silanorbornene derivatives.[1] However, most are concerned with derivatives having phenyl substituents on the ring. We are interested in the chemistry of 7-silanorbornene derivatives which have small substituents on the ring,[2] because we supposed that the less hindered 7-silanobornene derivative would show the more essential characteristics of 7-silanobornene itself.

Results and Discussion

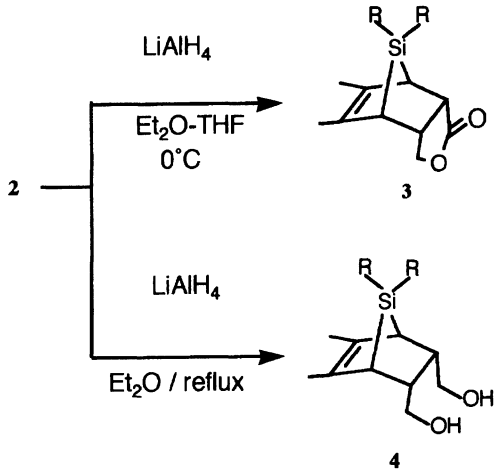
The Diels–Alder reactions of 1,1,3,4-tetramethylsilacyclopenta-2,4-diene (**1a**),[3] and 2,3-dimethyl-5-silaspiro[4.4]nona-1,3-diene (**1b**)[2] with maleic anhydride to give corresponding adducts, i.e., 5,6,7,7-tetramethyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**2a**) and 5,6-dimethylspiro[7-silabicyclo[2.2.1]-hept-5-ene-7,1′-silacyclopentane]-2,3-dicarboxylic anhydride (**2b**), were carried out (Scheme 1).

Seven-silanorbornene derivatives are susceptible to lithium aluminium hydride (LAH) reduction. B. Resibois et al. reported that the reaction of the 7-silanorbornene derivative prepared from the reaction of tetraphenylsilacyclpentadiene derivatives and maleic anhydride with LAH gave the bicycloderivative, formally the silylene extrusion product, in good yield.[4] However, it was found that compounds **2a** and **2b** could be reduced with LAH under carefully controlled reaction conditions to give 8,9,10,10-tetramethyl-4-oxa-10-silatricyclo[5.2.1.$0^{2,6}$]dec-8-en-3-one (**3a**) and 8,9-dimethylspiro[4-oxa-10-silatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-10, 1′-silacyclopentan]-3-one (**3b**) in a mixed solvent of diethyl ether (Et_2O) and tetrahydrofuran (THF) at 0 °C, respectively. Furthermore, the reduction of **2a** and **2b** with LAH under reflux in Et_2O gave, 5,6,7,7-tetramethyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dimethanol (**4a**) and 5,6-dimethylspiro[7-silabicyclo[2.2.1]hept-5-ene-7, 1′-silacyclopentane]-2,3-dimethanol (**4b**) in good yields, respectively (Scheme 2). These differences between the phenyl substituted silacyclopentadiene derivative and methyl substituted **2** for their reduction with LAH might be explained by the increased stability of the anion intermidiate conjugated with phenyl substituents for the former compound.

Attempted transformations from the alcohols **4** to corresponding halide derivatives failed. The reactions of **4a** and **4b** with thionyl chloride in the presence of triethylamine afforded unexpected products; 10,11,12,12-tetramethyl-4,6-dioxa-5-thia-12-silatricyclo[7.2.1.$0^{2,8}$]-dodec-10-ene 5-oxide (**5a**), and 10,11-dimethylspiro-[4,6-dioxa-5-thia-12-silatricyclo[7.2.1.$0^{2,8}$]dodec-10-ene-12,1′-silacyclopentane] 5-oxide (**5b**), respectively. The



Scheme 1.

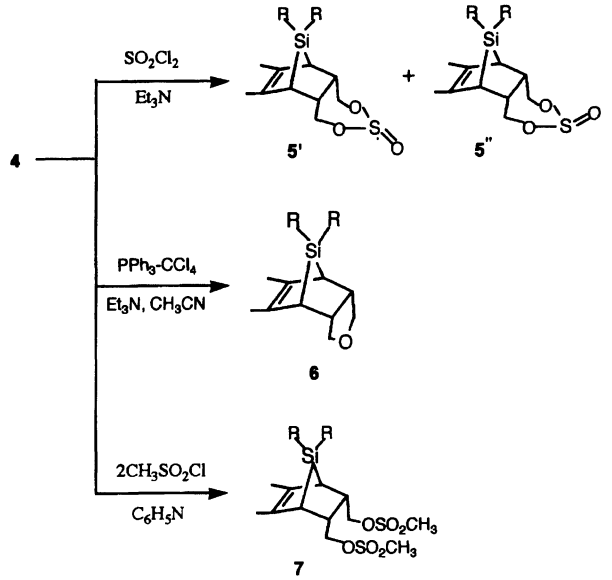


Scheme 2.

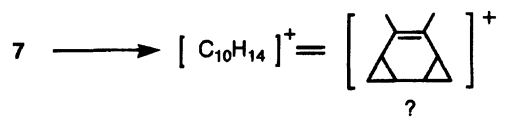
spectrum data, GC-MS, ^{1}H NMR, and ^{13}C NMR of **5a** and **5b**, show that both products **5a** and **5b** consisting of two isomers **5a′** and **5a″**, and **5b′** and **5b″**, may be based on the conformation of the sulfite ring. The isomers were stable enough to be isolated by preparative TLC. The conformers **5a′** and **5a″** could be reduced by LAH to yield **4a** in good yields.

Further attempts to prepare halide derivatives from **4a** and **4b** using triphenylphosphine/carbon tetrachloride in acetonitrile gave unexpected intramolecular cyclized products, i.e., 8,9,10,10-tetramethyl-4-oxa-10-silatricyclo[5.2.1.0^{2,6}]dec-8-ene (**6a**) and 8,9-dimethylspiro[4-oxa-10-silatricyclo[5.2.1.0^{2,6}]dec-8-ene-10,1′-silacyclopentane] (**6b**) in a good yield, respectively (Scheme 3). The formation of cyclic ethers **6** may be explained by faster intramolecular nucleophilic attack of the adjacent hydroxyl group than that of the chloride anion.

On the other hand, **4a** and **4b** were treated with mesyl chloride in the presence of triethylamine to give 2,3,7,7-tetramethyl-5,6-bis(methylsulfonyloxymethyl)-7-silabicyclo[2.2.1]hept-2-ene (**7a**) and 2,3-dimethyl-5,6-bis(methylsulfonyloxymethyl)spiro[7-silabicyclo[2.2.1]hept-2-ene-7,1′-silcyclopentane] (**7b**), respectively. NMR spectra of the products were fully consistent with the structure of **7**. However, no parent peak corresponding to **7** was found in their mass spectra. It is suggested that elimination of silane and two mesyl substituents to give a cyclopropane derivative occurred in the mass spectrometer (Scheme 4).



Scheme 3.



Scheme 4.

The reduction of **7a** with LAH gave 2,3-dimethyl-4-dimethylsilyl-5-(methylsulfonyloxymethyl)bicyclo[4.1.0]hept-2-ene (**8a**) and 2,3,5-trimethyl-4-(dimethylsilyl)bicyclo[4.1.0]hept-2-ene (**9a**). This shows that the product **8a** resulted from the intramolecular nucleophilic cyclization of an initially formed anion by hydride attack on the silicon (Scheme 5).

Reaction of **6a** with a large excess of LAH gave 3,4-dimethyl-2-dimethylsilyl-8-oxabicyclo[4.3.0]non-3-ene (**10a**) in 50% yield (Scheme 6). Mass spectra analysis showed the existence of small amounts of isomers **11a**, and of diene derivatives **12a**, **13a** in the reaction mixture. These products can be explained by the mechanisms shown in Scheme 6. The hydride attacked the electrophilic silicon to give the anion intermediate. Protonation of the intermediate gave **10a**. After migration of the anion and protonation, the elimination of hydride and dimethylsilane gave the corresponding **11a**, **12a**, and **13a**, respectively. Reactions of **4a** with nucleophiles such as F^-, Bu^-, and Ph^- were carried out. GC-MS analysis of the reaction mixture indicated the existence of the corresponding products (Scheme 7). Recently, M. P. Egorov et al. reported the ring-opening reaction of the 7-sila-2,3-benzo-2,5-norbornadiene derivative with nucleophilic attack on silicon by hydroxide anion to give an anion intermediate, which corresponded to the intermediate shown in Scheme 6.[5]

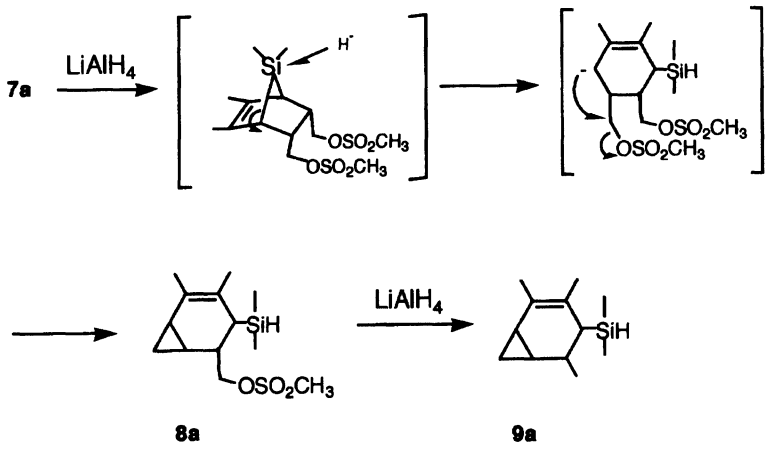
These results show that 7-silanorbornenes are highly reactive for nucleophilic attack on the silicon. Also, the reactivities of the 7-silanorbornene are based on both the release of the strain energy of the ring and the high electrophilicity of the silicon, which are consistent with the relatively low chemical shifts of the ^{29}Si of **2a** (δ= 39.8 in $CDCl_3$).[6]

Experimental

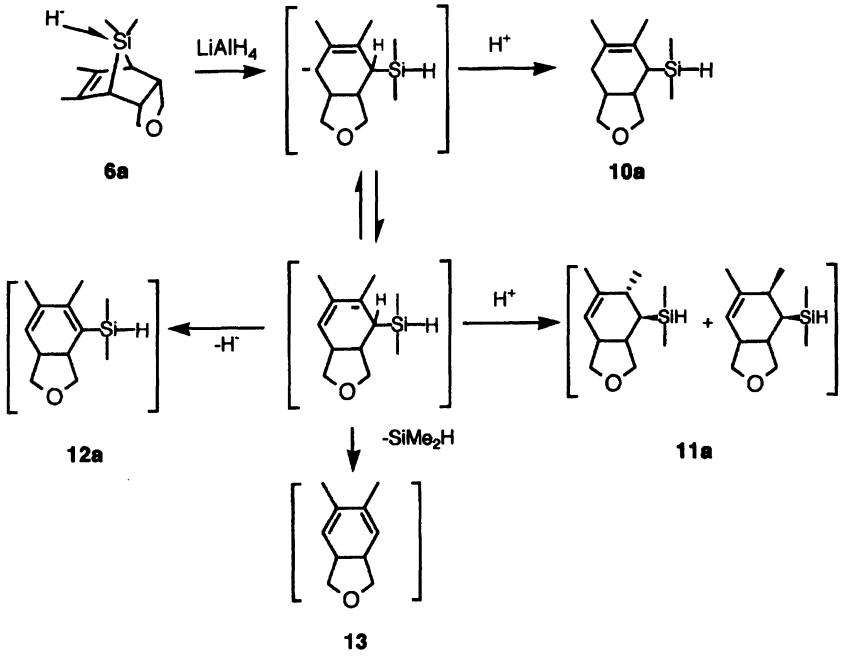
The melting points are uncorrected. The NMR spectra were recorded on a JEOL 60Si (60 MHz), and a Bruker AM400 (400 MHz) spectrometer in $CDCl_3$ using TMS as an internal standard. The mass spectra were measured with a JEOL DX 303 mass spectrometer. All the reactions were carried out under a dry nitrogen atmosphere. Compound **2a** was prepared following a procedure described in the literature,[3] in 47% yield.

Preparation of 2b. A solution of **1b** (2.8 g, 17 mmol) in chloroform (10 ml) was added to a solution of maleic anhydride (2.5 g, 26 mmol) in chloroform (10 ml) with stirring. The reaction mixture was stirred at room temperature for 24 h. Precipitates were filtered off. Evaporation and recrystallization of the residue from hexane gave 2.4 g (53%) of **2b**. Mp 98—101 °C; ^{1}H NMR ($CDCl_3$) δ=0.55 (2H, t, J=7.2 Hz, Si–CH_2), 0.68 (2H, t, J=7.2 Hz, Si–CH_2), 1.58—1.63 (4H, m, SiCCH_2), 1.72 (6H, s, =CCH_3), 2.35 (2H, t, J=1.5 Hz, SiCH); ^{13}C NMR ($CDCl_3$) δ=5.1, 11.1 (SiCH_2), 25.1, 26.1 (SiC$\underline{C}H_2$), 16.2 (=C$\underline{C}H_3$), 38.4 (SiCH), 47.4 (SiC$\underline{C}$H), 133.0 (=C), 173.6 (C=O). Found: m/z 262.1026. Calcd for $C_{14}H_{18}O_3Si$: M, 262.1025.

Preparation 3a. A solution of **2a** (90 mg, 0.38 mmol) in dry THF (3 ml) was added to a mixture of LAH (15 mg,



Scheme 5.



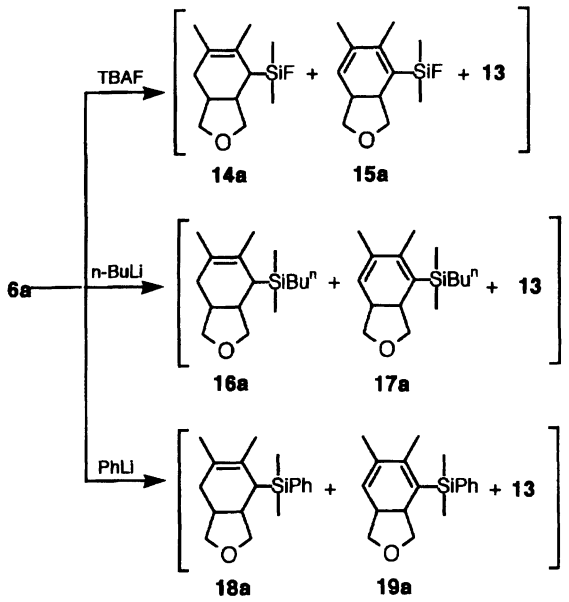
Scheme 6.

0.38 mmol) in dry Et_2O (6 ml) at 0 °C with stirring. The mixture was stirred for 1 h at 0 °C. Aqueous HCl (0.5 M, 8 ml, 1 M=1 mol dm^{-3}) was added to the mixture. The reaction mixture was extracted with Et_2O (5 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and recrystallization from a mixed solvent (hexane : benzene=3 : 2) gave a crystalline solid. Yield 71 mg (85%).

Compound **3b** was prepared using **2b** in a manner similar to that described above. Yield, 71%, ^{1}H NMR ($CDCl_3$) δ= 0.49—0.65 (4H, m, $SiCH_2$), 1.53—1.66 (4H, m, $SiCCH_2$), 1.72, 1.78 (3H, s, $=CCH_3$), 1.89, 2.24 (2H, two s, SiCH), 3.31 (2H, s, SiCCH), 3.77—3.80, 4.35—4.39 (2H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=5.1, 11.3 ($SiCH_2$), 16.5, 18.0 (=C<u>C</u>H_3), 25.3, 26.2 (Si<u>C</u>CH_2), 38.1, 39.9 (SiCH), 40.4, 46.5 (Si<u>C</u>CH), 72.7 (OCH_2), 131.5, 133.9 (C=), 179.9 (C=O). Found: m/z 248.1250. Calcd for $C_{14}H_{20}O_2Si$: M, 248.1233.

Preparation of 4a. A solution of **2a** (500 mg, 2.1 mmol) in dry Et_2O (30 ml) was added to a mixture of LAH (240 mg, 6.3 mmol) in dry Et_2O (15 ml) at 0 °C with stirring. The mixture was refluxed for 1 h with stirring. Aqueous HCl (0.5 M, 50 ml) was added to the mixture. The organic layer was separated and the reaction mixture was extracted with Et_2O (15 ml×3). The combined organic layer extracts were dried (Na_2SO_4). Evaporation and recrystallization (hexane : benzene=3 : 2) gave white crystals. Yield, 324 mg (74%); Mp 150—152 °C; ^{1}H NMR ($CDCl_3$) δ=−0.02, 0.15 (6H, two s, Si–CH_3), 1.49 (2H, s, SiCH), 1.65 (6H, s, $=CCH_3$), 2.75—2.77 (2H, m, SiCCH), 3.57—3.60, 3.64—3.67 (2H, m, OCH_2), 3.57—3.67 (2H, broad s, OH); ^{13}C NMR ($CDCl_3$) δ=−9.0, −2.2 ($SiCH_3$), 17.3 (=C<u>C</u>H_3), 41.3 (SiCH), 44.1 (Si<u>C</u>CH), 65.4 (OCH_2), 130.9 (C=). Found: m/z 226.1400. Calcd for $C_{12}H_{22}O_2Si$: M, 226.1389.

Compound **4b** was prepared using **2b** in a manner similar to that described above. Yield, 332 mg (75%); Mp 156—157 °C; ^{1}H NMR ($CDCl_3$) δ=−0.45—0.48 (4H, m, Si–CH_2), 1.43—1.54 (4H, m, $SiCCH_2$), 1.50 (2H, s, SiCH), 2.70—2.72 (2H, m, SiCCH), 3.49—3.52, 3.56—3.61 (2H, m, OCH_2),



Scheme 7.

3.49—3.61 (2H, broad s, OH); ^{13}C NMR ($CDCl_3$) δ=4.5, 10.9 ($SiCH_3$), 17.3 (=C$\underline{C}H_3$), 25.5, 26.3 (Si$\underline{C}CH_2$), 40.2 (SiCH), 44.7 (Si$\underline{C}$CH), 65.1 (OCH_2), 131.4 (C=). Found: m/z 252.1546. Calcd for $C_{14}H_{24}O_2Si$: M, 252.1546.

Reaction of 4a with Thionyl Chloride. A solution of thionyl chloride (66 mg, 0.55 mmol) in dry ether (1 ml) was added to a mixture of **4a** (50 mg, 0.22 mmol) and pyridine (87 mg, 1.10 mmol) in dry ether (3 ml) at 0 °C. The mixture was stirred for 1 h at room temperature. To the reaction mixture, water (5 ml) was added. The mixture was extracted with ether (5 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and preparative silica-gel chromatography (hexane : dichloromethane=3 : 5) gave 48 mg (80%) of two isomers of **5a**.

Yield 18 mg (30%), R_f = 0.6 (hexane : dichloromethane=2 : 5); ^{1}H NMR ($CDCl_3$) δ=0.03, 0.20 (6H, two s, $SiCH_3$), 1.46 (2H, s, SiCH), 1.71 (6H, s, =CCH_3), 2.97—2.99 (2H, m, SiCCH), 3.60—3.64, 4.73—4.76 (4H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=−8.5, −2.0 ($SiCH_3$), 17.4 (=C$\underline{C}H_3$), 39.9 (SiCH), 44.2 (Si$\underline{C}$CH), 63.2 (OCH_2), 131.0 (C=). Found: m/z 272.0900. Calcd for $C_{12}H_{20}O_3SSi$: M, 272.0903.

Yield 30 mg (50%), R_f = 0.3 (hexane : dichloromethane=2 : 5); ^{1}H NMR ($CDCl_3$) δ=0.01, 0.18 (6H, two s, $SiCH_3$), 1.50 (2H, s, SiCH), 1.70 (6H, s, =CCH_3), 2.96—2.98 (2H, m, SiCCH), 3.98—4.04, 4.19—4.22 (4H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=−8.3, −2.1 ($SiCH_3$), 17.3 (=C$\underline{C}H_3$), 40.2 (SiCH), 42.3 (Si$\underline{C}$CH), 65.9 (OCH_2), 131.2 (C=). Found: m/z 272.0898. Calcd for $C_{12}H_{20}O_3SSi$: M, 272.0903.

Reaction of **4b** with thionyl chloride was carried out in a manner similar to that described above. **5b**: Yield 53%.

Yield 23%, R_f = 0.8 (hexane : dichloromethane=2 : 5); ^{1}H NMR ($CDCl_3$) δ=0.55—0.59 (4H, m, $SiCH_2$), 1.52—1.62 (4H, m, $SiCCH_2$), 1.54 (2H, s, SiCH), 1.72 (6H, s, =CCH_3), 2.99—3.02 (2H, m, SiCCH), 3.60—3.63, 4.72—4.78 (4H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=5.0, 11.1 ($SiCH_2$), 17.4 (=C$\underline{C}H_3$), 25.4, 26.2 (Si$\underline{C}CH_2$) 38.8 (SiCH), 44.8 (Si$\underline{C}$CH), 63.0 (OCH_2), 131.6 (C=). Found: m/z 298.1074. Calcd for $C_{14}H_{22}O_3SSi$: M, 298.1060.

Yield 30%; R_f = 0.5 (hexane : dichloromethane=2 : 5); ^{1}H NMR ($CDCl_3$) δ=0.53—0.60 (4H, m, $SiCH_2$), 1.54—1.62 (4H, m, $SiCCH_2$), 1.59 (2H, s, SiCH), 1.71 (6H, s, =CCH_3), 2.97—2.99 (2H, m, SiCCH), 3.96—4.01, 4.25—4.27 (4H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=4.5, 11.1 ($SiCH_2$), 17.2 (=C$\underline{C}H_3$), 25.4, 26.2 (Si$\underline{C}CH_2$) 39.5 (SiCH), 43.3 (Si$\underline{C}$CH), 65.6 (OCH_2), 131.7 (C=). Found: m/z 298.1042. Calcd for $C_{14}H_{22}O_3SSi$: M, 298.1060.

Preparation of 6a. Triphenylphosphine (145 mg, 0.55 mmol) was added to a solution of **4a** (50 mmg, 0.22 mmol), triethylamine (49 mg, 0.49 mmol) in carbon tetrachloride (2 ml) and acetonitrile (4 ml). The mixture was stirred for 1 h at room temperature. The solvents was evaporated and the residue was purified by preparative silica-gel chromatography (dichloromethane) to gave 38 mg (83%) of **6a**. ^{1}H NMR ($CDCl_3$) δ=0.05, 0.16 (6H, two s, $SiCH_3$), 1.53 (2H, s, SiCH), 1.70 (6H, s, =CCH_3), 3.11 (2H, s, SiCCH), 3.11—3.13, 3.88—3.90 (2H, m, OCH_3); ^{13}C NMR ($CDCl_3$) δ=−7.3, −1.6 ($SiCH_3$), 18.1 (=C$\underline{C}H_3$), 38.2 (SiCH), 47.1 (Si$\underline{C}$CH), 72.7 (OCH_2), 132.0 (=C). Found: m/z 208.1278. Calcd for $C_{12}H_{20}OSi$: M, 208.1284.

Compound **6b** was prepared using **4b** in a manner similar to that described above. Yield 64%; ^{1}H NMR ($CDCl_3$) δ=0.53, 0.60 (4H, t, J=7.2 Hz, $SiCH_2$), 1.51—1.63 (4H, m, $SiCCH_2$), 1.61 (2H, s, SiCH), 1.71 (6H, s, =CCH_3), 3.11 (2H, s, SiCCH), 3.11—3.13, 3.86—3.91 (4H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=5.9, 11.5 ($SiCH_2$), 18.1 (=C$\underline{C}H_3$), 25.5, 26.3 (Si$\underline{C}CH_2$), 37.2 (SiCH), 47.5 (Si$\underline{C}$CH), 72.0 (OCH_2), 132.5 (=C). Found: m/z 234.1456. Calcd for $C_{12}H_{20}OSi$: M, 234.1441.

Preparation of 7a. A solution of methanesulfonyl chloride (93 mg, 0.99 mmol) in CH_2Cl_2 (1 ml) was added to a solution of **4a** (40 mg, 0.18 mmol) and triethylamine (263 mg, 1.61 mmol) in CH_2Cl_2 (2 ml) at 0 °C. The mixture was stirred for 1 h at room temperature. Aqueous HCl (0.5 M, 7 ml) was added to the reaction mixture, and the mixture was extracted with CH_2Cl_2 (5 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and purification by preparative silica-gel TLC (CH_2Cl_2) gave 52 mg (75%) of **7a**. ^{1}H NMR ($CDCl_3$) δ=0.05, 0.17 (6H, two s, $SiCH_3$), 1.74 (6H, s, =CCH_3), 1.77 (2H, s, SiCH), 2.92—2.95 (2H, m, SiCCH), 3.02 (6H, s, SCH_3), 3.94—3.98, 4.14—4.18 (2H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=−8.8, −2.1 ($SiCH_3$), 17.1 (=C$\underline{C}H_3$), 37.3 (SCH_3), 40.7 (Si$\underline{C}$CH), 70.0 (OCH_2), 131.9 (C=). Found: m/z 134.1111. Calcd for $C_{10}H_{14}$: (M−$SiMe_2$−$2SO_3Me$), 134.1096.

Compound **7b** was prepared using **4b** in a manner similar to that described above. Yield 45%; ^{1}H NMR ($CDCl_3$) δ=0.54, 0.59 (4H, two t, J=7.2 Hz, $SiCH_2$), 1.51—1.63 (4H, m, $SiCCH_2$), 1.75 (6H, s, =CCH_3), 1.86 (2H, s, SiCH), 2.94—2.97 (2H, m, SiCCH), 3.02 (6H, s, SCH_3), 3.94—3.99, 4.13—4.17 (2H, m, OCH_2); ^{13}C NMR ($CDCl_3$) δ=4.5, 11.0 ($SiCH_2$), 17.1 (=C$\underline{C}H_3$), 25.3, 26.2 (Si$\underline{C}CH_2$), 37.4 (SCH_3), 41.3 (S$\underline{C}$H), 69.8 (OCH_2), 132.5 (C=). Found: m/z 134.1093. Calcd for $C_{10}H_{14}$: (M−$Si(CH_2)_4$−$2SO_3Me$), 134.1096.

Reaction of 7a with LAH. A solution of **7a** (115 mg, 0.30 mmol) in ether (3 ml) was added to a solution of LAH (20 mg, 0.53 mmol) in ether (2 ml) at 0 °C. The mixture was stirred for 30 min. at room temperature. Aqueous HCl (0.5 M, 12 ml) was added to the reaction mixture, and the

mixture was extracted with ether (5 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and purification by preparative silica-gel TLC (CH_2Cl_2) gave 30 mg (48%) of **8a**. ^{1}H NMR ($CDCl_3$) δ=0.03 (1H, q, J=4.6 Hz, cyclopropane ring), 0.12, 0.13 (6H, two d, J=3.7 Hz, $SiCH_3$), 0.69 (1H, dt, J_1=4.6 Hz, J_2=8.7 Hz, cyclopropane ring), 1.03—1.08 (1H, m, SiCCCH), 1.23—1.25 (1H, m, SiCC=CCH), 1.26—1.29 (1H, m, SiCH), 1.58, 1.73 (6H, two s, $=CCH_3$), 2.66—2.71 (1H, m, SiCCH), 2.98 (3H, s, SCH_3), 3.79—3.83, 3.97—4.01 (2H, m, OCH_2), 3.91—3.93 (1H, m, SiH); ^{13}C NMR ($CDCl_3$), δ=−7.8, −4.4 ($SiCH_3$), 11.4 (SiC), 12.2 (cyclopropane ring), 16.8 (SiCC$\underline{C}$H), 17.7, 20.2 (=C$\underline{C}H_3$), 32.2 (SiCC=C$\underline{C}$H), 37.3 (SCH_3), 72.2 (OCH_2), 125.0, 125.7 (=C). Found: m/z 288.1227. Calcd for $C_{13}H_{24}O_3SSi$: M, 288.1216.

Compound **7a** (110 mg, 0.29 mmol) was treated with LAH (90 mg, 2.4 mmol) in a manner similar to that described above to give 20 mg (38%) of **9a**. ^{1}H NMR ($CDCl_3$) δ=0.09—0.11 (6H, m, $SiCH_3$), 0.12—0.15, 0.49—0.55 (2H, m, cyclopropane ring), 0.84 (3H, d, J=8.0 Hz, CH_3), 0.92—0.95 (2H, m, SiCCCH, SiCC=CCH), 1.24—1.30 (1H, m, SiCH), 1.58, 1.74 (6H, two s, $=CCH_3$), 2.48—2.52 (1H, m, SiCCH), 3.87—3.91 (1H, m, SiH); ^{13}C NMR ($CDCl_3$) δ=−4.5, −4.1 ($SiCH_3$), 12.1 (cyclopropane ring), 15.7 (SiCH), 17.7 (SiCC$\underline{C}$H), 17.8, 20.6 (=C$\underline{C}H_3$), 22.1 (CH_3), 28.1 (SiC$\underline{C}$H), 39.3 (SiCC=C$\underline{C}$H), 124.1, 126.4 (=C). Found: m/z 194.1493. Calcd for $C_{12}H_{22}Si$: M, 194.1492.

Reaction of 6a with LAH. A solution of **6a** (137 mg, 0.66 mmol) in ether (4 ml) was added to a mixture of LAH (105 mg, 2.8 mmol) in ether (2 ml) at 0 °C. The reaction mixture was stirred at room temperature for 8 h. Aqueous HCl (0.5 M, 30 ml) was added to the reaction mixture, and the mixture was extracted with ether (10 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and purification by preparative TLC (dichloromethane : hexane) gave 69 mg (50%) of **10a**. ^{1}H NMR ($CDCl_3$) δ=0.10, 0.11 (6H, d, J=3.6 Hz, $SiCH_3$), 1.42 (1H, s, SiCCH), 1.65 (6H, s, $=CCH_3$), 1.6—1.8, 2.1—2.3 (2H, m, $=CCH_2$), 2.4—2.6 (2H, m, OCCH), 3.2—3.3, 3.3—3.4 (2H, m, OCH), 3.8—4.0 (3H, m, OCH, SiH); ^{13}C NMR ($CDCl_3$) δ=−4.5, −4.3 ($SiCH_3$), 19.8, 20.6 (=C$\underline{C}H_3$), 31.6 (=C$\underline{C}H_2$), 32.0 (SiCH), 36.0 (SiC$\underline{C}$H), 39.1 (SiCC$\underline{C}$H), 74.3, 75.5 (OCH_2), 122.4, 124.9 (=C). Found: m/z 210.1435. Calcd for $C_{12}H_{22}OSi$: M, 210.1440.

11a; ^{1}H and ^{13}C NMR spectra of the reaction mixture show the existence of isomers. The isomers were not isolated. Found: m/z 210.1420. Calcd for $C_{12}H_{22}OSi$: M, 210.1440.

12a; Found: m/z 208.1290. Calcd for $C_{12}H_{20}OSi$: M, 208.1284.

13a; Found; m/z 150.1039. Calcd for $C_{10}H_{14}O$: M, 150.1049.

Reaction of 6a with Tetrabutylammonium Fluoride (TBAF). A solution of TBAF (0.5 ml of 1M solution in THF, 0.5 mmol) was added to a solution of **6a** (40 mg, 0.19 mmol) in THF at −20 °C. The reaction mixture was stirred at room temperature for 2 h, and then passed through a short column (silica gel).

14a; Found: m/z 228.1348. Calcd for $C_{12}H_{21}OSiF$: M, 228.1346.

15a; Found: m/z 226.1184. Calcd for $C_{12}H_{19}OSiF$: M, 226.1190.

Reaction of 6a with *n*-BuLi. A solution of *n*-BuLi (0.25 ml of 1.66 M solution in hexane) was added to a solution of **6a** (54 mg, 0.26 mmol) in ether (2 ml) at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and successive 2 h at room temperature. The mixture was passed through a short column (silica gel).

16a; Found; m/z 266.2059. Calcd for $C_{16}H_{30}OSi$: M, 266.2067.

17a; Found; m/z 264.1914. Calcd for $C_{16}H_{28}OSi$: M, 264.1910.

Reaction of 6a with PhLi. A solution of PhLi (0.4 ml of 1.8 M solution in ether) was added to a solution of **6a** (52 mg, 0.25 mmol) in ether (2 ml) at −78 °C. The reaction mixture was stirred for 2 h at −78 °C, and for one more hour at room temperature. The mixture was passed through a short column (silica gel).

18a; Found: m/z 286.1759. Calcd for $C_{18}H_{26}OSi$: M, 286.1754.

19a; Found: m/z 284.1590. Calcd for $C_{18}H_{24}OSi$: M, 284.1597.

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