Rearrangement of 3-(Trimethylsilylmethylthio)allyllithium

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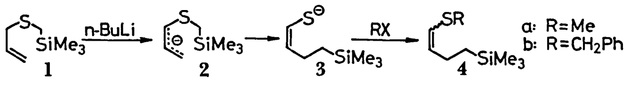
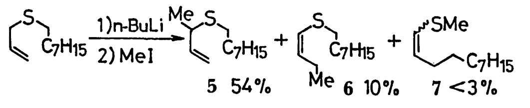
Proton abstraction from 3-trimethylsilylmethylthio-1-propene by butyllithium followed by treatment with iodomethane provided 1-methylthio-4-trimethylsilyl-1-butene. Meanwhile, 1-trimethylsilylmethylthio-2-butene afforded 3-methyl-4-methylthio-1-trimethylsilyl-1-butene upon successive treatment with butyllithium and iodomethane.

Metallation of trimethyl(methylthiomethyl)silane or trimethyl(phenylthiomethyl)silane yields a carbanion which reacts with aldehydes and ketones to provide 1-methylthio-1-alkenes or 1-phenylthio-1-alkenes.[1] We attempted to apply this Peterson type reaction to the synthesis of allyl alkenyl sulfide from 3-trimethylsilylmethylthio-1-propene (**1**) and carbonyl compounds, and found an unexpected rearrangement reaction via 3-(trimethylsilylmethylthio)allyllithium (**2**).

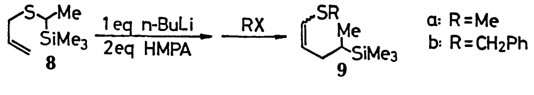


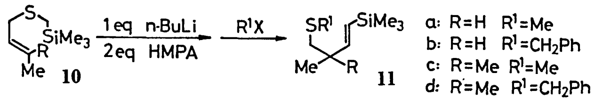
Butyllithium (1.0 mmol) was added to a solution of 3-trimethylsilylmethylthio-1-propene (**1**, 1.0 mmol) and hexamethylphosphoric triamide (HMPA, 2.0 mmol) in tetrahydrofuran (THF, 2 ml) at −60 °C (dry ice-$CHCl_3$) under argon atmosphere. After stirring for 2 h at −50 °C,[2] iodomethane (2.0 mmol)[3] was added to the resulting brown solution. Work-up followed by purification provided 1-methylthio-4-trimethylsilyl-1-butene (**4a**, E/Z=45/55, 91 mg) in 52% yield.

The use of benzyl bromide instead of iodomethane gave the corresponding 1-benzylthio-1-alkene **4b** (45%, E/Z=41/59). Without HMPA, the reaction provided a mixture of methylated products, CH_2=CH–CH(Me)–SCH_2SiMe_3 and $MeCH_2CH$=$CHSCH_2SiMe_3$, which were derived from methylation of α or γ position of ambident allylic anion stabilized by sulfur.[4] The coexistence of HMPA could enhance the nucleophilicity of allylic anion and facilitate the rearrangement. The presence of trimethylsilyl group was also essential for the rearrangement. This was confirmed by the fact that the treatment of 1-allylthiooctane with butyllithium and iodomethane in similar fashion provided methylated products **5** (54%) and **6** (10%) along with a trace amount of the rearranged product **7** (<3%).

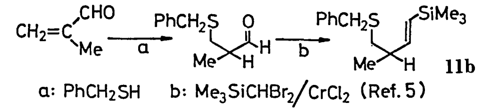


Treatment of **8** with butyllithium and iodomethane afforded the sulfides **9a** (E/Z=66/34) or **9b** (E/Z=67/33) in 70% or 65% yield, respectively. In the meantime, successive treatment of 1-trimethylsilylmethylthio-2-butene or 3-methyl-1-trimethylsilylmethylthio-2-butene (**10a** or **10b**) with butyllithium and iodomethane gave (E)-3-methyl-4-methylthio-1-trimethylsilyl-1-butene (**11a**) or (E)-3,3-dimethyl-4-methylthio-1-trimethylsilyl-1-butene (**11c**) in 51% or 41% yield, respectively. The addition of benzyl bromide instead of iodomethane provided the corresponding sulfide **11b** or **11d** in 62% or 61% yield.

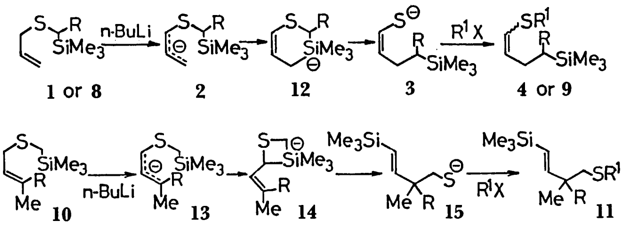




The structure of **11b** was ascertained by the comparison with a sample prepared by the following procedure.



We are tempted to assume following reaction mechanism for the rearrangement of **1** to **4** (or **8** to **9**): (1) Treatment of **1** (or **8**) with butyllithium gave allylic anion **2** by proton abstraction, (2) attack of allylic anion at γ position on Si intramolecularly induced the rearrangement of **2** to **3** via 5-coordinated silicate intermediate (**12**),[6] and (3) trapping of lithium alkenyl sulfide with iodomethane or benzyl bromide provided methylthioalkene or benzylthioalkene **4** (or **9**). On the other hand, the rearrangement of **10** to **11** could



proceed as follows: (1) Metallation with butyllithium gave allylic anion **13**, (2) attack of allylic anion at α position on Si mediated the rearrangement of **13** to **15** via 4-membered 5-coordinated silicate intermediate **14**,[7] and (3) alkylation of the resulting sulfide anion with iodomethane or benzyl bromide gave the alkenylsilane **11**.[8]

Experimental

Distillations of the products were performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. Analytical GLPC was performed with a Shimadzu gas chromatograph, Model GC-8A using thermal conductivity detector and helium as carrier gas. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, chemical shifts being give in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The elemental analyses were carried out at the Elemental Analyses Center of Kyoto University. THF was freshly distilled from sodium benzophenone ketyls just before use.

General Procedure for the Preparation of Allyl Trimethylsilylmethyl Sulfide Derivatives. The preparation of 3-trimethylsilylmethylthio-1-propene (**1**) is representative. Butyllithium (1.6 M, 1 M=1 mol dm^{-3}, 20 ml, 32 mmol) was added dropwise to a solution of 2-propene-1-thiol (2.8 g, 38 mmol) and HMPA (5.6 ml, 32 mmol) in Et_2O (50 ml) at 0 °C. After stirring for 10 min, chloromethyltrimethylsilane (4.5 ml, 32 mmol) was added to the reaction mixture and the resulting mixture was stirred for additional 4 h. The mixture was poured into sat. NH_4Cl (100 ml) and extracted with ether (100 ml). The organic layers were washed with brine (100 ml) and dried over Na_2SO_4 and concentrated in vacuo. Distillation (81—86 °C, 37 Torr, 1 Torr=133.322 Pa) of the crude product gave **1** (3.7 g) in 72% yield: IR(neat) 3078, 2954, 2904, 2878, 1636, 1426, 1250, 989, 913, 845, 736, 695, 653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 9H), 1.68 (s, 2H), 3.10 (dt, *J*=7.2, 1.2 Hz, 2H), 5.00—5.15 (m, 2H), 5.78 (ddt, *J*=16.5, 10.2, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.66, 16.96, 38.76, 116.8, 134.1; MS (70 eV), *m/z* (rel intensity), 160 (33), 145 (17), 120 (9), 119 (85), 103 (9), 91 (9), 74 (9), 73 (100), 41 (10). Found: C, 52.36; H, 10.23%. Calcd for $C_7H_{16}SSi$: C, 52.43; H, 10.06%.

3-[1-(Trimethylsilyl)ethylthio]-1-propene (8). The title compound **8** was prepared in similar fashion to the synthesis of **1** in 69% yield, except that ether was used as a solvent instead of THF: bp 75—80 °C (20 Torr); IR (neat) 3078, 2952, 2862, 1636, 1459, 1449, 1426, 1405, 1249, 1221, 1009, 989, 913, 837, 751, 719, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.07 (s, 9H), 1.25 (d, *J*=7.2 Hz, 3H), 1.91 (q, *J*=7.2 Hz, 1H), 3.05—3.30 (m, 2H), 5.00—5.15 (m, 2H), 5.76 (dddd, *J*=17.6, 9.5, 8.3, 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−3.09, 16.05, 23.01, 33.74, 116.7, 134.5; MS, *m/z* (rel intensity), 174 (15), 133 (9), 131 (9), 91 (9), 73 (100), 69 (39), 68 (15), 59 (11), 45 (11), 41 (9). Found: C, 55.21; H, 10.67%. Calcd for $C_8H_{18}SSi$: C, 55.10; H, 10.40%.

1-Trimethylsilylmethylthio-2-butene (10a, *E/Z*=82/18): 93% yield; bp 110 °C (bath temp, 40 Torr); IR (neat) 3018, 2954, 1733, 1452, 1414, 1393, 1249, 1220, 1126, 1070, 963, 846, 749, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.07 (s, 9H), 1.65—1.72 (m, 5H), 3.07 (d, *J*=6.5 Hz, 1.64H), 3.19 (d, *J*=7.5 Hz, 0.36H), 5.35—5.60 (m, 2H); ^{13}C NMR for *E*-isomer ($CDCl_3$) =−1.63, 17.18, 17.64, 37.99, 127.0, 128.1. Found: C, 55.01; H, 10.68%. Calcd for $C_8H_{18}SSi$: C, 55.10; H, 10.40%.

3-Methyl-1-trimethylsilylmethylthio-2-butene (10b): 93% yield; bp 110 °C (bath temp. 30 Torr); IR (neat) 2954, 2914, 1730, 1449, 1391, 1376, 1249, 1120, 1103, 897, 842, 772, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.09 (s, 9H), 1.66 (d, *J*=0.6 Hz, 3H), 1.73 (s, 2H), 1.75 (d, *J*=0.8 Hz, 3H), 3.14 (d, *J*=8.0 Hz, 2H), 5.24 (t, *J*=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.65, 17.54, 17.82, 25.68, 33.46, 120.5, 135.1; MS, *m/z* (rel intensity), 188 (3), 119 (21), 105 (13), 82 (12), 73 (100), 69 (41), 45 (13), 43 (11), 41 (47). Found: C, 57.27; H. 10.99%. Calcd for $C_9H_{20}SSi$: C, 57.37; H, 10.70%.

3-Octylthio-1-propene: ^{1}H NMR ($CDCl_3$) δ=0.80—0.95 (m, 3H), 1.20—1.50 (m, 10H), 1.50—1.65 (m, 2H), 2.45 (t, *J*=7.3 Hz, 2H), 3.13 (d, *J*=7.1 Hz, 2H), 5.00—5.15 (m, 2H), 5.78 (ddt, *J*=17.2, 9.5, 7.1 Hz, 1H).

General Procedure for the Rearrangement of Allyl Trimethylsilylmethyl Sulfide Derivatives. The rearragement of 3-trimethylsilylmethylthio-1-propene as a typical example is as follows. Butyllithium (1.5 M hexane solution, 0.67 ml, 1.0 mmol) was added to a solution of 3-trimethylsilylmethylthio-1-propene (**1**, 0.16 g, 1.0 mmol) and HMPA (0.35 ml, 2.0 mmol) in THF (2 ml) at −60 °C (dry ice-$CHCl_3$) under argon atmosphere. The resulting mixture was stirred at −50 °C for 2 h and then iodomethane (0.12 ml, 2.0 mmol) was added. The mixture was stirred at −60 °C for 30 min and at room temperature for another 30 min. The reaction mixture was poured into sat. NaCl solution and extracted with hexane (20 ml×3). The combined organic layer were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to preparative thin layer chromatography on silica gel to afford 1-methylthio-4-trimethylsilyl-1-butene (**4a**, *E/Z*=45/55, 91 mg) in 52% yield. Analytical samples were prepared by preparative GLPC (OV-1 2%, 2 m, Chromosorb W AW DMCS, 60—80 mesh, 100 °C, t_r=4.98 min for *E*-**4a** and 4.08 min for *Z*-**4a**). *E*-**4a**: bp 75 °C (bath temp, 39 Torr); IR (neat) 2950, 2916, 1729, 1248, 934, 861, 835, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.00 (s, 9H), 0.57—0.65 (m, 2H), 2.06—2.18 (m, 2H), 2.24 (s, 3H), 5.52 (dt, *J*=14.9, 6.6 Hz, 1H), 5.97 (dt, *J*=14.9, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.62, 15.15, 16.47, 27.50, 122.2, 130.6; MS, *m/z* (rel intensity), 174 (11), 159 (11), 105 (30), 87 (11), 74 (10), 73 (100), 59 (13), 45 (18), 43 (13). Found: C, 55.05; H, 10.66%. Calcd for $C_8H_{18}SSi$: C, 55.10; H, 10.40%. *Z*-**4a**: bp 73 °C (bath temp, 39 Torr); IR (neat) 2950, 2918, 1727, 1248, 860, 835, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) =0.01 (s, 9H), 0.58—0.67 (m, 2H), 2.06—2.19 (m, 2H), 2.27 (s, 3H), 5.56 (dt, *J*=9.3, 7.0 Hz, 1H), 5.81 (dt, *J*=9.3, 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.65, 16.23, 17.09, 23.53, 125.1, 131.9; MS, *m/z* (rel intensity), 174 (11), 159 (13), 105 (31), 86 (13), 84 (22), 74 (11), 73 (100), 59 (14), 45 (17), 43 (14), 36 (18). Found: C, 54.91; H, 10.49%. Calcd for $C_8H_{18}SSi$: C, 55.10; H, 10.40%.

(*Z*)-1-Benzylthio-4-trimethylsilyl-1-butene (*Z*-4b): GLPC t_r=8.23 min (OV-1 2%, 2 m, Chromosorb W AW DMCS, 60—80 mesh, 160 °C); bp 110 °C (bath temp, 1 Torr); IR (neat) 3026, 2950, 2920, 1728, 1495, 1454, 1303, 1247, 1072, 860, 835, 744, 693, 658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.04 (s, 9H), 0.52—0.62 (m, 2H), 2.00—2.20 (m, 2H), 3.84 (s, 2H), 5.56 (dt, *J*=9.2, 7.2 Hz, 1H); 5.82 (dt, *J*=9.2, 1.4 Hz, 1H), 7.15—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−1.66, 16.16, 23.59. 37.97, 122.1, 127.1, 128.5, 128.8, 133.5, 138.2; MS, *m/z* (rel intensity), 250 (7), 159 (22), 92 (8), 91 (100), 74 (7), 73 (95), 65 (9), 45 (10). Found:

C, 67.40; H, 8.89%. Calcd for C$_{14}$H$_{22}$SSi: C, 67.13; H, 8.85%.

(*E*)-1-Benzylthio-4-trimethylsilyl-1-butene (*E*-4b): GLPC t_r=8.99 min (OV-1 2%, 2 m, Chromosorb W AW DMCS, 60—80 mesh, 160 °C); bp 110 °C (bath temp, 1 Torr); IR (neat) 3026, 2950, 2914, 1495, 1454, 1248, 1071, 946, 861, 835, 744, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.05, 0.52—0.62 (m, 2H), 2.00—2.20 (m, 2H), 3.83 (s, 2H), 5.72 (dt, J=15.0, 6.5 Hz, 1H), 5.90 (d, J=15.0 Hz, 1H), 7.20—7.40 (m, 5H), ^{13}C NMR (CDCl$_3$) δ=−1.66, 16.16, 27.54, 37.62, 120.6, 127.0, 128.5, 128.8, 135.1, 137.9; MS, m/z (rel intensity), 250 (10), 159 (20), 92 (9), 91 (100), 74 (7), 73 (84), 65 (9), 45 (10). Found: C, 67.42; H, 8.89%. Calcd for C$_{14}$H$_{22}$SSi: C, 67.13; H, 8.85%.

(*Z*)-1-Methylthio-4-trimethylsilyl-1-pentene (*Z*-9a): GLPC t_r=6.85 min (OV-1 2%, 2 m, Chromosorb W AW DMCS 60—80 mesh, 100 °C); bp 73—78 °C (bath temp, 40 Torr); IR (neat) 2952, 2920, 2862, 1730, 1453, 1437, 1248, 853, 833, 745, 687 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.01 (s, 9H), 0.73 (dqd, J=9.5, 7.0, 4.3 Hz, 1H), 0.94 (d, J=7.0 Hz, 3H), 1.96 (dddd, J=14.7, 9.5, 7.6, 1.1 Hz, 1H), 2.24 (dddd, J=14.7, 6.6, 4.3, 1.5 Hz, 1H), 2.27 (s, 3H), 5.58 (ddd, J=9.3, 7.6, 6.6 Hz, 1H), 5.90 (ddd, J=9.3, 1.5, 1.1 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−3.21, 14.13, 17.10, 20.25, 31.44, 126.6, 129.6; MS, m/z (rel intensity), 188 (10), 105 (24), 99 (10), 87 (35), 74 (50), 73 (100), 59 (9), 36 (8). Found: C, 57.28; H, 10.96%. Calcd for C$_9$H$_{20}$SSi: C, 57.37; H, 10.70%.

(*E*)-1-Methylthio-4-trimethylsilyl-1-pentene (*E*-9a): GLPC t_r=8.10 min (OV-1 2%, 2 m, Chromosorb W AW DMCS 60—80 mesh, 100 °C); bp 75—80 °C (bath temp, 35 Torr); IR (neat) 2952, 2918, 2862, 1728, 1453, 1437, 1248, 936, 853, 834, 747, 687 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.03 (s, 9H), 0.69 (dqd, J=9.0, 7.2, 4.4 Hz, 1H), 0.92 (d, J=7.2 Hz, 3H), 1.90 (dddd, J=14.2, 9.0, 7.8, 1.1 Hz, 1H), 2.24 (s, 3H), 2.27 (dddd, J=14.2, 6.2, 4.4, 1.2 Hz, 1H), 5.45 (ddd, J=14.6, 7.8, 6.2 Hz, 1H), 5.95 (ddd, J=14.6, 1.2, 1.1 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−3.17, 13.95, 15.18, 20.36, 35.71, 123.6, 128.0; MS, m/z (rel intensity), 188 (9), 173 (9), 105 (18), 99 (10), 87 (13), 74 (41), 73 (100), 57 (13), 43 (10), 41 (10), 38 (10), 36 (35). Found: C, 57.34; H, 10.97%. Calcd for C$_9$H$_{20}$SSi: C, 57.37; H, 10.70%.

(*Z*)-1-Benzylthio-4-trimethylsilyl-1-pentene (*Z*-9b): GLPC t_r=4.5 min (OV-1 2%, 2 m, Chromosorb W AW DMCS 60—80 mesh, 180 °C); bp 140 °C (bath temp, 1 Torr); IR (neat) 2950, 2862, 1728, 1494, 1453, 1248, 1121, 1071, 852, 833, 743, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.05 (s, 9H), 0.55—0.80 (m, 1H), 0.88 (d, J=7.0 Hz, 3H), 1.82—2.12 (m, 1H), 2.18—2.32 (m, 1H), 3.85 (s, 2H), 5.62 (ddd, J=9.5, 7.5, 6.5 Hz, 1H), 5.97 (dt, J=9.5, 1.2 Hz, 1H), 7.20—7.40 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−3.21, 14.07, 20.21, 31.48, 38.02, 123.7, 127.0, 128.5, 128.8, 131.1, 138.2; MS, m/z (rel intensity), 264 (7), 173 (17), 99 (9), 92 (8), 91 (100), 74 (7), 73 (75), 65 (8), 45 (10). Found: C, 68.10; H, 9.16%. Calcd for C$_{15}$H$_{24}$SSi: C, 68.11; H, 9.15%.

(*E*)-1-Benzylthio-4-trimethylsilyl-1-pentene (*E*-9b): GLPC t$_r$=6.1 min (OV-1 2%, 2 m, Chromosorb W AW DMCS 60—80 mesh, 180 °C), IR (neat) 3026, 2950, 2898, 2862, 1495, 1454, 1247, 852, 834, 746, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=−0.07 (s, 9H), 0.55—0.80 (m, 1H), 0.83 (d, J=7.0 Hz, 3H), 0.75—1.95 (m, 1H), 2.17—2.32 (m, 1H), 3.84 (s, 2H), 5.70 (ddd, J=15.0, 7.8, 6.5 Hz, 1H), 5.95 (d, J=15.0, Hz, 1H), 7.20—7.38 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−3.22, 13.83, 20.07, 35.69, 37.68, 122.1, 127.0, 128.8, 132.9, 137.9; MS, m/z (rel intensity), 264 (8), 173 (17), 99 (9), 92 (8), 91 (100), 73 (72), 65 (8), 45 (9). Found: C, 68.40; H, 9.34%. Calcd for C$_{15}$H$_{24}$SSi: C, 68.11; H, 9.15%.

(*E*)-3-Methyl-4-methylthio-1-trimethylsilyl-1-butene (11a): Bp 80 °C (bath temp, 16 Torr); IR (neat) 2954, 2914, 2868, 1728, 1655, 1616, 1453, 1438, 1431, 1371, 1248, 1128, 989, 865, 838, 756, 721, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.03 (s, 9H), 1.07 (d, J=6.4 Hz, 3H), 2.07 (s, 3H), 2.35—2.65 (m, 3H), 5.68 (dd, J=19.0, 1.0 Hz, 1H), 6.02 (dd, J=19.0, 6.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−1.21, 16.27, 18.99, 39.68, 41.25, 128.6, 150.4; MS, m/z (rel intensity), 188 (12), 173 (44), 120 (12), 115 (50), 105 (64), 99 (28), 85 (12), 73 (100), 61 (79), 59 (54), 45 (19), 43 (20). Found: C, 57.50; H, 10.84%. Calcd for C$_9$H$_{20}$SSi: C, 57.37; H, 10.70%.

(*E*)-4-Benzylthio-3-methyl-1-trimethylsilyl-1-butene (11b): Bp 85—90 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2868, 1732, 1613, 1494, 1454, 1248, 989, 864, 837, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.05 (s, 9H), 1.05 (d, J=6.5 Hz, 3H), 2.28—2.54 (m, 3H), 3.70 (s, 2H), 5.63 (dd, J=18.6, 0.8 Hz, 1H), 5.93 (dd, J=18.6, 5.9 Hz, 1H), 7.23—7.33 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−1.19, 19.12, 36.85, 38.08, 39.82, 126.9, 128.4, 128.8, 128.9, 138.6, 150.3; MS, m/z (rel intensity), 264 (3), 191 (5), 181 (5), 173 (28), 137 (8), 99 (9), 92 (7), 91 (100), 74 (7), 73 (78), 59 (8). Found: C, 67.95; H, 9.33%. Calcd for C$_{15}$H$_{24}$SSi: C, 68.11; H, 9.15%.

(*E*)-3,3-Dimethyl-4-methylthio-1-trimethylsilyl-1-butene (11c): Bp 85 °C (bath temp, 18 Torr); IR (neat) 2956, 2916, 2868, 1730, 1610, 1465, 1247, 993, 867, 837, 727, 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.03 (s, 9H), 1.05 (s, 6H), 2.08 (s, 3H), 2.47 (s, 2H), 5.59 (d, J=19.0 Hz, 1H), 5.99 (d, J=19.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−1.15, 18.17, 26.18, 39.53, 48.31, 125.3, 154.5; MS, m/z (rel intensity), 202 (5), 141 (11), 105 (8), 99 (21), 82 (24), 74 (9), 73 (100), 61 (17), 59 (24), 57 (6), 45 (13), 43 (13), 41 (8). Found: C, 59.47; H, 11.05%. Calcd for C$_{10}$H$_{22}$SSi: C, 59.33; H, 10.95%.

(*E*)-4-Benzylthio-3,3-dimethyl-1-trimethylsilyl-1-butene (11d): Bp 130 °C (bath temp, 1 Torr); IR (neat) 3026, 2954, 2924, 1605, 1493, 1454, 1247, 993, 867, 837, 725, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.05 (s, 9H), 1.03 (s, 6H), 2.42 (s, 2H), 3.69 (s, 2H), 5.58 (d, J=19.0 Hz, 1H), 5.98 (d, J=19.0 Hz, 1H), 7.20—7.35 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−1.12, 26.28, 38.16, 39.18, 44.61, 125.5, 126.8, 128.4, 128.9, 138.7, 154.3; MS, m/z (rel intensity), 278 (2), 187 (28), 181 (11), 141 (11), 137 (8), 99 (15), 91 (97), 82 (10), 74 (8), 73 (100), 65 (7), 59 (17), 45 (8). Found: C, 68.84; H, 9.69%. Calcd for C$_{16}$H$_{26}$SSi: C, 69.00; H, 9.41%.

Preparation of an Authentic Sample of 11b: A hexane solution of triethylborane (1 M, 5.0 ml, 5.0 mmol) was added to a solution of phenylmethanethiol (0.94 g, 7.6 mmol) and methacrylaldehyde (0.6 ml, 0.51 g, 7.3 mmol) in benzene (20 ml) at 0 °C under argon atmosphere.[9] After stirring for 1 h, the reaction mixture was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give 3-benzylthio-2-methylpropanal (0.27 g) in 20% yield: ^{1}H NMR (CDCl$_3$) δ=1.15 (d, J=7.0 Hz, 3H), 2.40—2.60 (m, 2H), 2.65—2.85 (m, 1H), 3.72 (s, 2H), 7.20—7.45 (m, 5H), 9.60 (d, J=1.4 Hz, 1H). The aldehyde (72 mg, 0.37 mmol) and Me$_3$SiCHBr$_2$ (0.20 g, 0.8 mmol) were added to a suspension of CrCl$_2$ (0.39 g, 3.2 mmol) in THF (5 ml) at 25 °C under argon atmosphere and the resulting mixture was stirred at 25 °C overnight. Work-up (ethyl acetate, brine) followed by preparative tlc on silica gel gave alkenylsilane (41 mg, 42% yield) whose spectral data were identical with the sample generated from the rearrangement of **10** (R=H).

Reaction of 3-(Octylthio)allyllithium with Iodomethane. Treatment of a THF-HMPA (4 ml)-(0.71 ml, 4.1 mmol) solution of 3-octylthio-1-propene (0.38 g, 2.0 mmol) with butyllithium (1.56 M, 1.3 ml, 2.0 mmol) at −60 °C gave an orange solution. After stirring for 2 h at −50 °C, iodomethane (0.42 g, 3.0 mmol) was added to the reaction mixture. Work-up followed by purification by silica-gel column chromatography provided a mixture of 3-octylthio-1-butene (^{1}H NMR ($CDCl_3$) δ=0.80—0.95 (m, 3H), 1.20—1.50 (m, 13H including doublet at 1.33 (3H)), 1.50—1.70 (m, 2H), 2.30—2.55 (m, 2H), 3.30 (dq, J=8.7, 7.0 Hz, 1H), 4.90—5.10 (m, 2H), 5.68 (ddd, J=15.5, 10.5, 8.5 Hz, 1H) and 1-octylthio-1-butene in 64% combined yield. Only a trace amount of the rearranged product **7** (<3%) was detected in the reaction mixture by the examination of GLPC. The authentic sample of **7** was prepared according to the reported procedure.[1] Butyllithium (1.56 M, 9 ml, 17 mmol) was added to a solution of trimethyl(methylthiomethyl)silane (2.0 g, 15 mmol) in THF (15 ml) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then at 25 °C for another 1 h. Decanal (2.37 g, 15 mmol) was added to the resulting solution at −78 °C. The mixture was allowed to warm up to 25 °C and poured into sat. NH_4Cl. Extraction followed by purification gave 1-methylthio-1-undecene (1.1 g, E/Z=20/1) in 36% yield: ^{1}H NMR ($CDCl_3$) δ=0.80—0.98 (m, 3H), 1.20—1.55 (m, 14H), 2.00—2.20 (m, 2H), 2.25 (s, 3H), 5.50 (dt, J=15, 7.0 Hz, 1H), 6.00 (d, J=15 Hz, 1H).

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7) The attack of allylic anion at γ position might be unfavorable as compared to the attack at α position from the sterical point of view.

8) Obviously, an in-depth study is needed to obtain precise reaction mechanism. We are now investigating the reaction of silacyclobutane with several nucleophiles to get further information.

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