Reaction of α,α-Bis(trimethylsilyl)phenylthiomethyllithium with (Chloromethyl)oxiranes. Synthesis of 1-Alkyl-3-phenylthio-3-trimethylsilyl-1-trimethylsiloxycyclobutanes

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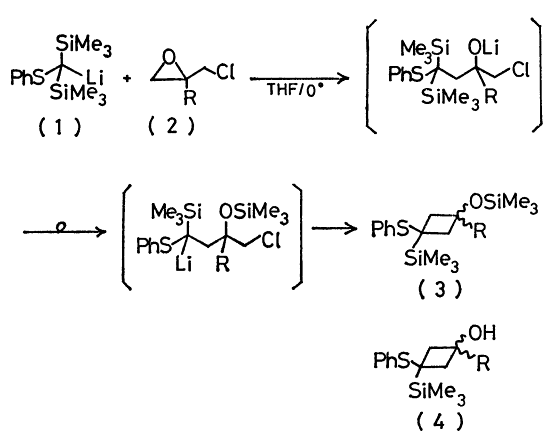
Synopsis. The cyclobutanes of the title are produced in good yields by means of the reaction of the title.

Recently many rearrangement reactions with migration of organosilyl group have been studied and a variety of useful methods for the synthesis of carbonyl compounds and silyl enol ethers have been reported.[1] Although the 1,4-silyl group shift from carbon to oxygen is especially an interesting process and would be utilized for the preparation of various γ-trimethylsiloxy carbanions, only a few examples such as reactions of oxiranes with lithium enolate of *N*,*N*-dimethyl-2-trimethylsilylacetamide,[2] lithium salt of trimethylsilylacetonitrile,[3] and α-(trimethylsilyl)phenylsulfonylmethyllithium[4] have so far been reported.

In the course of our study on reactions using α-thio carbanions, it was found that the cyclobutane derivatives (**3**) were selectively produced by a reaction of the α,α-bis(trimethylsilyl)carbanion (**1**) with (chloromethyl)oxiranes (**2**)[5] which involves the process of 1,4-silyl group shift.

When α,α-bis(trimethylsilyl)phenylthiomethyllithium (**1**) prepared from the corresponding sulfide with butyllithium at 0 °C was allowed to react with **2** in THF at the same temperature, 1-phenylthio-1-trimethylsilyl-3-trimethylsiloxycyclobutanes (**3**) and 3-phenylthio-3-trimethylsilyl-1-cyclobutanols (**4**) were obtained in good yields (Table 1). This reaction may proceed by the initial addition of the anion (**1**) at the less substituted site to the oxirane (**2**), followed by the 1,4-migration of silicon and cyclization, as shown in the following scheme:



Scheme 1.

Experimental

Table 1.

Entry	R	Yield/% 3	Yield/% 4
a	H	37	41
b	CH_3	73	—
c	CH_3CH_2	58	—
d	$CH_3(CH_2)_3$	53	—
e	$Ph(CH_2)_2$	74	—
f [a]	Ph	30	5

a) Acetophenone and phenyl 1-(trimethylsilyl)vinyl sulfide were isolated as by-products.

Reaction of Epichlorohydrin (2) with α,α-Bis(trimethylsilyl)phenylthiomethyllithium (1). To a THF (6 ml) solution of bis(trimethylsilyl)methyl phenyl sulfide (537 mg, 2 mmol) was added a hexane solution of butyllithium (2.2 mmol) at 0 °C. After stirring for 30 min, THF (2 ml) solution of epichlorohydrin (204 mg, 2.2 mmol) was added to the reaction mixture and stirred for 2 h. The reaction was quenched with a phosphate buffer solution (pH 7) and subjected to extraction with dichloromethane. The extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (AcOEt–hexane) and trimethylsiloxycyclobutane (**3a**) (238 mg, 37%) and cyclobutanol (**4a**) (205 mg, 41%) were isolated. **3a**: viscous oil; IR (neat) 2950, 1580, 1471, 1248, 1128, 841, 747, and 692 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=-0.08$ (s, 9H), 0.07 (s, 9H), 1.73—2.65 (m, 5H), 3.57—4.13 (m, 1H), and 7.13—7.66 (m, 5H). **4a**: viscous oil; IR (neat) 3330, 2950, 1580, 1472, 1248, 1117, 840, 748, and 692 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=0.04$ and 0.08 (2s, 9H), 1.73—2.70 (m, 4H), 2.70—2.93 (br s, 1H), 3.65—4.11 (m, 1H), and 7.09—7.65 (m, 5H). Found: C, 61.91; H, 8.05; S, 12.76%. Calcd for $C_{13}H_{20}OSSi$: C, 61.85; H, 7.99; S, 12.70%.

By a similar procedure, the cyclobutanes (**3b**—**f** and **4f**) were obtained. **3b**: viscous oil; IR (neat) 2960, 1584, 1474, 1249, 1173, 840, 748, and 693 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=$ 0.05 (s, 18H), 1.02 (s, 3H), 2.03—2.67 (m, 4H), and 6.97—7.52 (m, 5H). Found: C, 60.38; H, 8.94; S, 9.48%. Calcd for $C_{17}H_{30}OSSi_2$: C, 60.29; H, 8.93; S, 9.47%. **3c**: viscous oil; IR (neat) 2955, 1582, 1437, 1248, 1162, 837, 747, and 692 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=0.05$ (s, 18H), 0.48—0.84 (m, 3H), 0.96—1.38 (m, 2H), 2.02—2.59 (m, 4H), and 7.02—7.48 (m, 5H). Found: C, 61.37; H, 8.87; S, 8.94%. Calcd for $C_{18}H_{32}OSSi_2$: C, 61.30; H, 9.15; S, 9.09%. **3d**: viscous oil; IR (neat) 2955, 1581, 1438, 1249, 1137, 838, 748, and 693 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=0.04$ (s, 18H), 0.62—1.38 (m, 9H), 1.99—2.62 (m, 4H), and 7.01—7.47 (m, 5H). **3e**: viscous oil; IR (neat) 2955, 1583, 1439, 1250, 1134, 843, 749, and 697 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=0.08$ and 0.12 (2s, 18H), 1.21—1.75 (m, 4H), 2.05—2.78 (m, 6H), and 6.71—7.57 (m, 10H). **3f**: viscous oil; IR (neat) 2950, 1582, 1438, 1249, 1129, 845, 745, and 694 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=-0.32$ (s, 9H), 0.16 (s, 9H), 2.82 (s, 4H), and 6.60—7.36 (m, 10H). **4f**: mp 107—108 °C (hexane–benzene); IR (KBr) 3460, 2960, 1571, 1253, 1127, 851, 752, and 700 cm^{-1}; ^{1}H NMR (CCl_4) $\delta=0.17$ (s, 9H), 1.58 (s, 1H), 2.72 (s, 4H), and 6.57—7.49 (m, 10H). Found: C, 69.48; H, 7.40; S, 9.68%. Calcd for $C_{19}H_{24}OSSi$: C, 69.46; H, 7.36; S, 9.76%.

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