Nucleophile-Induced Ring Enlargement of 1-(1-Iodoalkyl)silacyclobutane and 1-(1,2-Epoxyalkyl)silacyclobutane into Silacyclopentane. Application to the Syntheses of 1,4-Diol, 4-Alken-1-ol, and 1,4,5-Triol

Kozo Matsumoto, Yoshihiro Takeyama, Katsukiyo Miura, Koichiro Oshima,* and Kiitiro Utimoto*

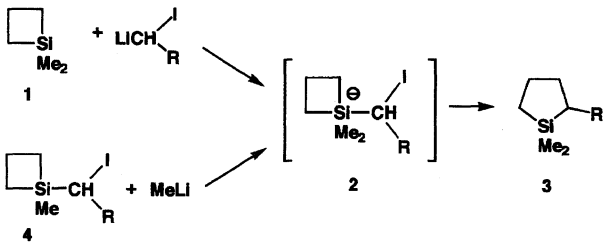
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01

(Received June 29, 1994)

Two methods for ring enlargement of silacyclobutane into silacyclopentane have been described. (1) Treatment of 1-(1-iodoalkyl)silacyclobutane with *t*-BuOK or AgOAc provided 2-alkyl-1-silacyclopentanes which were easily converted into 1,4-diols by oxidative cleavage of carbon–silicon bond. (2) An addition of *i*-PrOLi to 1-[(*Z*)-1,2-epoxyhexyl]-1-methylsilacyclobutane gave *erythro*-2-(1-hydroxypentyl)-1-isopropoxy-1-methylsilacyclopentane, which was converted into (*Z*)-4-nonen-1-ol, (*E*)-4-nonen-1-ol, or 1,4,5-nonanetriol.

Despite the advances made in the field of organosilicon chemistry and the numerous synthetic methods which rely on the properties of silicon, synthetic reactions using silacylclobutane as the C_3 unit has received little attention compared to those using allylsilanes. The large number of methods of preparation and reactions of allylsilanes have made these compounds useful synthetic tools. We thus started our research aiming to develop new synthetic usages as well as preparative methods of silacyclobutane.[1]

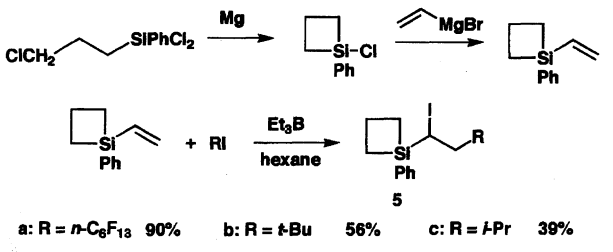
(1) Potassium *t*-Butoxide- or Silver Acetate-Induced Ring Enlargement of Silacyclobutane into Silacyclopentane. We have recently reported[2] that an addition of lithium carbenoids to 1,1-dimethylsilacyclobutane (**1**) provided silacyclopentanes **3**. The reaction might proceed via pentacoordinate silicate **2**. It then occurred to us that, if treatment of 1-(1-iodoalkyl)-1-methylsilacyclobutane **4** with a nucleophile such as methyllithium should afford the same pentacoordinate intermediate **2**, the procedure would give another route to silacyclopentanes **3** (Scheme 1).



Scheme 1.

1-(1-Iodoalkyl)-1-phenylsilacyclobutanes **5** instead of 1-(1-iodoalkyl)-1-methylsilacyclobutanes **4** were chosen as starting materials because they were easy to prepare. Treatment of dichloro(3-chloropropyl)phenylsilane with magnesium gave 1-chloro-1-phenylsilacyclobutane according to the reported procedure.[3] Addition of vinylmagnesium bromide to the solution of 1-chloro-1-phenylsilacyclobutane provided 1-phenyl-1-vinylsilacyclobutane in 90% overall yield. Triethylborane-induced radical addition of iodoalkane to 1-phenyl-1-vinylsilacyclobutane afforded 1-(1-iodoalkyl)-1-phenylsilacyclobutanes **5** in 39—90% yields (Scheme 2). Vinylsilanes were less reactive toward alkyl radicals than silylacetylene and the yields of adducts were lower than those of the reaction between silylacetylene and alkyl iodides.[4] The addition of perfluoroalkyl iodides to vinylsilane also proceeded less effectively compared with the addition to an ordinary alkene such as 1-dodecene.[5]

The reaction of **5** with nucleophile such as methyllithium or phenyllithium was examined. Contrary to



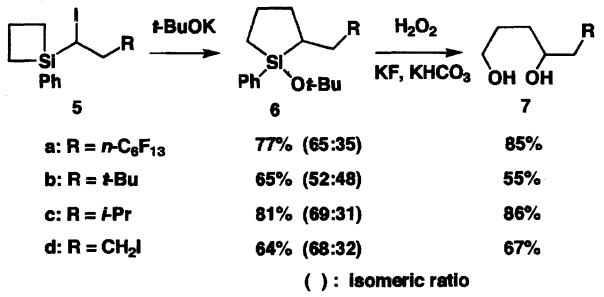
Scheme 2.

our expectation, treatment of 1-(1-iodoalkyl)-1-phenylsilacyclobutane **5a** with methyllithium or phenyllithium provided the desired silacyclopentane in only 7% or 5% yield, along with unidentified complex products. An addition of tetrabutylammonium fluoride to **5a** followed by treatment with H_2O_2[6] gave 1,4-diol **7a** in poor yield (8%). Fortunately, the use of potassium *t*-butoxide in place of alkyllithium or tetrabutylammonium fluoride resulted in clean formation of silacyclopentane **6a**.[7,8] An addition of silacyclobutane **5a** to a suspension of potassium *t*-butoxide in THF provided silacyclopentane **6a** in 77% yield. Oxidative cleavage of two carbon-silicon bonds of **6a** has been achieved by treatment with H_2O_2 to give 1,4-diol **7a** in 85% yield. Some representative results are shown in Scheme 3.

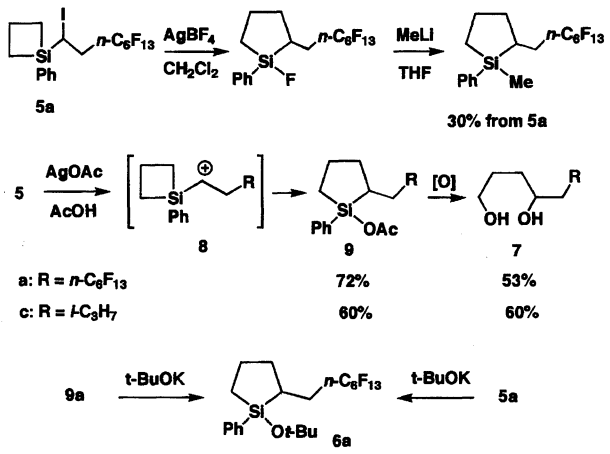
In the case of **6b**, **6c**, and **6d**, treatment with HBF_4[9] before addition of H_2O_2 was essential to obtain the corresponding diols **7b**, **7c**, and **7d** in good yields.

The rearrangement also took place upon treatment with silver tetrafluoroborate or silver acetate. Treatment of **5a** with $AgBF_4$ in dichloromethane gave 1-fluoro-1-phenyl-2-alkylsilacyclopentane, which was transformed into 1-methyl-1-phenyl-2-alkylsilacyclopentane in 30% overall yield upon treatment with methyllithium. Exposure of silacyclobutanes **5** to silver acetate in acetic acid at 25 °C provided acetoxysilacyclopentanes **9**, as shown in Scheme 4.

The reaction proceeds as follows: (1) Silver ion attacks iodine of **5** to afford silacyclobutylalkyl cation



Scheme 3.



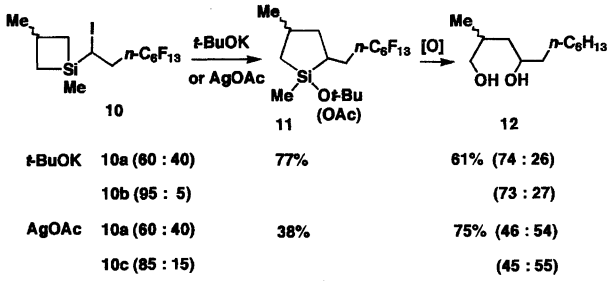
Scheme 4.

8 and (2) the attack of acetate anion on silicon of **8** causes one of carbon-silicon bonds of silacyclobutane to migrate to the α-carbon atom to give silacyclopentane **9**.[10—12] Purification of **9a** by distillation or silica-gel column chromatography caused decomposition. Thus, the compound **9a** was converted into **6a** upon treatment with *t*-BuOK in THF at 0 °C. The new compound was identified by comparison with a sample generated by the reaction of **5a** with *t*-BuOK. Treatment of **9** with H_2O_2–KF provided 1,4-diol **7** in the same way as **6**.

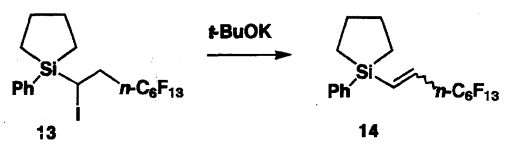
The ring enlargement of 3-methylsilacyclobutane **10** was examined. Treatment of **10a** (mixture of diastereomers, 60 : 40) with *t*-BuOK gave the corresponding silacyclopentane **11** as a mixture of four diastereomers in 77% yield. Oxidation of **11** with H_2O_2–KF provided a mixture of two diastereomeric 1,4-diols **12**, whose ratio was 74 : 26. Meantime, successive treatment of a substrate **10b** consisting of two diastereomers (95 : 5) with *t*-BuOK and H_2O_2–KF afforded another mixture of two diastereomeric 1,4-diols **12** which had a similar isomeric ratio (73 : 27). Thus, the stereochemistry of the starting material did not affect the stereochemical outcome. The reaction with silver acetate also proceeded nonstereospecifically. Exposure of **10a** or **10c** to silver acetate resulted in formation of the same isomeric mixture of two diastereomers (46 : 54 or 45 : 55) (Scheme 5).

Treatment of 1-(1-iodoalkyl)silacyclopentane **13** with *t*-BuOK provided 1-alkenylsilacyclopentane **14** exclusively; no ring-enlarged silacyclohexane could be observed in the reaction mixture. Thus, the ring strain of silacyclobutane plays a critical role for the successful ring enlargement (Scheme 6).

(2) Nucleophile-Induced Ring Enlargement of 1-(1,2-Epoxyalkyl)silacyclobutane into Silacyclopentane. Application to Stereoselective Synthesis of 4-Alken-1-ol and 1,4,5-Triol. Dialkyl cuprate reagents[13] or lithium aluminium hydride[14] attack 2-(trimethylsilyl)oxiranes nucleophilically at the carbon bearing the silyl group. Nucleophiles may



Scheme 5.



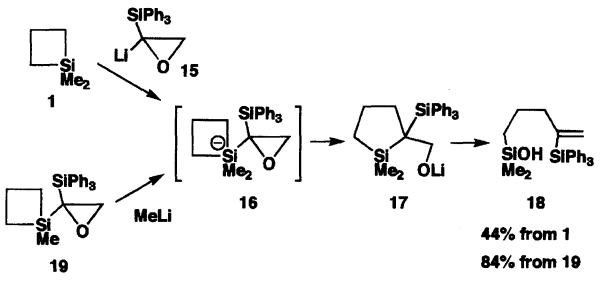
Scheme 6.

associate with vacant $3p_z$ orbitals of silicon and thus pentacoordinate reaction intermediates affect the regiochemistry.[15] In a previous report[16] we have shown that the reaction of 1,1-dimethylsilacyclobutane (**1**) with triphenylsilyl-substituted oxiranyl anion **15** gave olefinic silanol **18** (Scheme 7). We assumed the following reaction mechanism: (1) oxiranyl anion **15** attacks silicon of silacyclobutane to give pentacoordinate silicate **16**, (2) one methylene group of silacyclobutane migrates from silicon to epoxide carbon and this nucleophilic rearrangement gives silacyclopentane **17** under epoxide ring cleavage, and (3) syn elimination of Si–O^- provides **18**. Based on these assumptions, we anticipated that treatment of 1-(1,2-epoxyalkyl)silacyclobutane **19**, prepared according to Scheme 8, with nucleophile such as methyllithium would provide the same pentacoordinate intermediate **16**, which would collapse to silacyclopentane **17** and finally give olefinic silanol **18**.

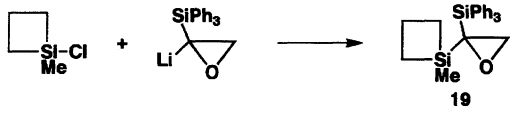
This was indeed the case, as indicated by the following experiment. An addition of methyllithium to a solution of 1-(1,2-epoxyalkyl)silacyclobutane **19** gave silanol **18** in 84% yield.

Then we examined the generality of this new reaction. In the case of the reaction of (1,2-epoxyalkyl)-silane **20** with methyllithium, the intermediary silacyclopentane derivatives could be isolated, in contrast to the reaction of **19** with methyllithium, where silanol **18** was obtained directly under the reaction conditions and an attempt to trap the intermediate **17** failed. For instance, quenching the reaction mixture of **20** and methyllithium with methanol at −78 °C provided silacyclopentane **21** (55/45 diastereomeric mixture) in 75% yield. Further treatment of **21** with potassium hydride in THF gave silanol **22** in 85% yield (Scheme 9). An addition of methyllithium to silacyclobutane **23** and successive treatment of the crude reaction mixture with potassium hydride gave silanol **24** in 71% yield.

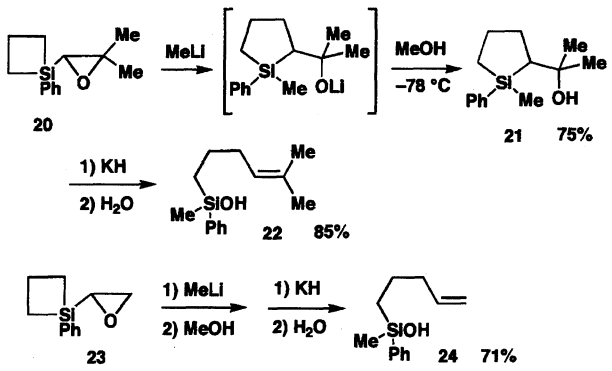
The reaction was applied to the stereoselective synthesis of 4-alken-1-ols. The starting materials, 1-[(*E*)-



Scheme 7.



Scheme 8.

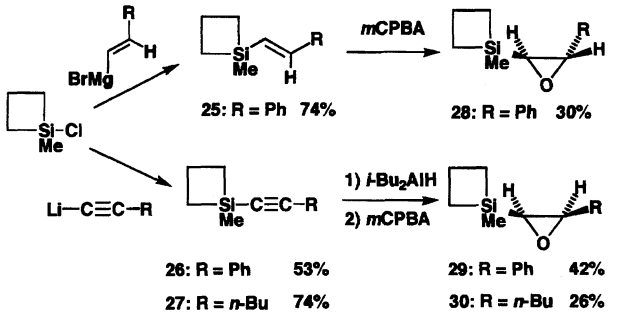


Scheme 9.

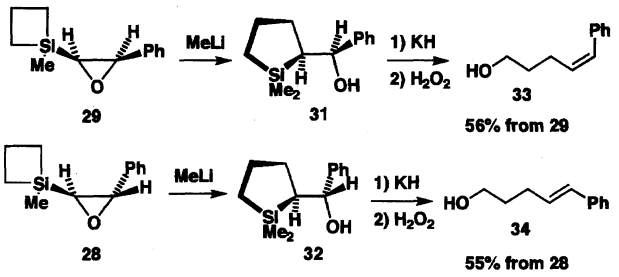
1,2-epoxyalkyl]silacyclobutanes or 1-[(*Z*)-1,2-epoxyalkyl]silacyclobutanes, were prepared as follows. An addition of (*E*)-alkenylmagnesium bromide or alkynyllithium to 1-chloro-1-methylsilacyclobutane gave (*E*)-1-alkenylsilacyclobutane or 1-alkynylsilacyclobutane in 74 or 53% yield, respectively. Hydroalumination of 1-alkynylsilacyclobutane with *i*-Bu_2AlH provided (*Z*)-1-alkenylsilacyclobutane. Epoxidation of the resulting (*E*)- or (*Z*)-1-alkenylsilacyclobutanes with *m*CPBA provided the corresponding 1-(1,2-epoxyalkyl)silacyclobutanes (Scheme 10).

An addition of methyllithium to 1-[(*Z*)-1,2-epoxy-2-phenylethyl]-1-methylsilacyclobutane (**29**) gave silacyclopentane **31** as a single stereoisomer. The reaction of the alcohol **31** with potassium hydride gave (*Z*)-$PhCH{=}CHCH_2CH_2CH_2SiMe_2OH$ which was easily converted into (*Z*)-5-phenyl-4-penten-1-ol (**33**) upon treatment with H_2O_2–KF. On the other hand, isomeric 1-[(*E*)-1,2-epoxy-2-phenylethyl]-1-methylsilacyclobutane (**28**) provided (*E*)-5-phenyl-4-penten-1-ol (**34**) selectively following the same procedure (Scheme 11) (method **A**).

Lithium alkoxide was as effective as methyllithium for the rearrangement of 1-(1,2-epoxyalkyl)silacyclobutane into silacyclopentane. Treatment of **29** or **30** with lithium isoproxide at −78 °C gave silacyclopentane derivative **35** or **36** in 88 or 77% yield, respectively. Exposure of the alcohol **35** or **36** on the one hand to (i) potassium hydride and (ii) H_2O_2–KF (method **B**) or to (i) boron trifluoride and (ii) H_2O_2–KF (method **C**) on the other led to (*Z*)-4-alken-1-ol (**33** or **37**) or (*E*)-4-



Scheme 10.



Scheme 11.

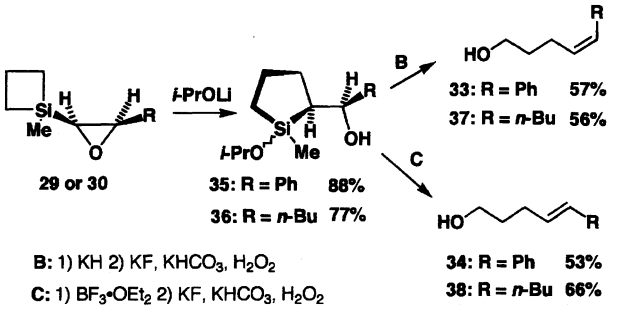
alken-1-ol (**34** or **38**), respectively. The procedure provided another route to stereoselective synthesis of (*Z*)- and (*E*)-4-alken-1-ols (Scheme 12).

The reaction was also utilized for the stereoselective synthesis of 1,4,5-triols. Oxdation of **36** with H_2O_2–KF gave 1,4,5-triol **39** in 64% yield with retention of the configuration at the carbon. In the case of the oxidation of **35**, (*E*)-5-phenyl-4-penten-1-ol (**34**) was obtained (10%) in addition of the desired triol **40** (62%) (Scheme 13).

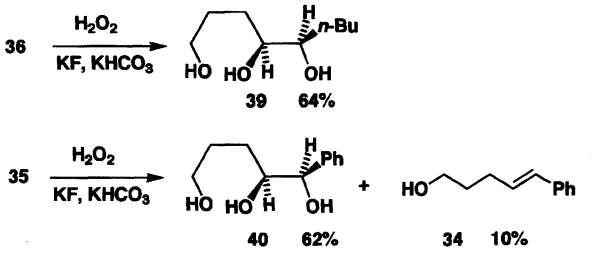
Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi); boiling points are indicated by air-bath temperature values without correction. Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. The NMR spectra (^{1}H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Preparation of 1-Ethenyl-1-phenylsilacyclobutane. To a suspension of Mg (0.80 g, 33 mmol) in THF (2.5 ml) was added 1,2-dibromoethane (0.2 ml) to activate magnesium. Then a THF (22.5 ml) solution of dichloro(3-chloropropyl)phenylsilane (5.1 ml, 25 mmol) was added dropwise over a period of 1 h. After the addition was completed, the reaction mixture was heated to reflux for 2 h. The mixture was cooled to 0 °C and a THF solution of vinylmagnesium bromide (0.92 M, 27 ml 25 mmol) was added (1 M=1 mol dm^{-3}). After being stirred for 1 h at 0 °C, the resulting mixture was poured into 1 M HCl and extracted with ethyl acetate (50 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give the title compound (3.92 g) in 90% yield: Bp 101—102 °C (bath temp, 5.0 Torr, 1 Torr=133.322 Pa); IR (neat) 3046, 2966, 2924, 1590, 1428, 1401, 1119, 1112, 1005, 956, 853, 736, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32 (t, J=8.3 Hz, 4H), 2.20 (quint, J=8.3 Hz, 2H), 5.95 (dd, J=4.2, 19.9 Hz, 1H), 6.23 (dd, J=4.2, 14.6 Hz, 1H), 6.47 (dd, J=14.6, 19.9 Hz, 1H), 7.35—7.50 (m, 3H), 7.58—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.39, 18.20, 127.93, 129.58, 134.05, 134.82, 135.65, 136.54. Found: C, 75.94; H, 8.27%. Found $C_{11}H_{14}Si$: C, 75.79; H, 8.09%.



Scheme 12.



Scheme 13.

Preparation of 1-(1-Iodoalkyl)silacyclobutane. Reaction of 1-ethenyl-1-phenylsilacyclobutane with 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl iodide is representative. Triethylborane (1.0 M hexane solution, 5.0 ml, 5.0 mmol) was added to a solution of 1-ethenyl-1-phenylsilacyclobutane (1.74 g, 10 mmol) and 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl iodide (6.40 ml, 30 mmol) in hexane (25 ml) at 25 °C under argon atmosphere. After being stirred for 10 h at 25 °C, the reaction mixture was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give 1-phenyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)silacyclobutane (**5a**, 5.60 g) in 90% yield: Bp 112—113 °C (bath temp, 0.3 Torr); IR (neat) 2928, 1430, 1355, 1240, 1206, 1146, 1123, 848, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22—1.60 (m, 4H), 1.85—2.21 (m, 2H), 2.60—2.82 (m, 2H), 3.61 (t, J=7.7 Hz, 1H), 7.38—7.52 (m, 3H), 7.68—7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=1.19, 15.47, 15.93, 17.16, 36.07 (t, J=21.5 Hz), 128.01, 130.38, 132.83, 134.71. Found: C, 33.01; H, 2.34%. Calcd for $C_{17}H_{14}F_{13}ISi$: C, 32.92; H, 2.27%.

1-(1-Iodo-3,3-dimethylbutyl)-1-phenylsilacyclobutane (5b): Bp 127—128 °C (bath temp, 1.0 Torr); IR (neat) 2952, 2864, 1466, 1428, 1394, 1365, 1119, 848, 733, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.93 (s, 9H), 1.20—1.50 (m, 4H), 1.85—2.20 (m, 4H), 3.45 (dd, J=5.5, 6.5 Hz, 1H), 7.30—7.52 (m, 3H), 7.65—7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.20, 15.63, 16.19, 16.30, 29.46, 32.71, 47.34, 127.78, 129.85, 134.64, 134.89. Found: C, 50.40; H, 6.49%. Calcd for $C_{15}H_{23}ISi$: C, 50.28; H, 6.47%.

1-(1-Iodo-3-methylbutyl)-1-phenylsilacyclobutane (5c): Bp 92—93 °C (bath temp, 0.3 Torr); IR (neat) 3064, 2954, 2924, 2864, 1467, 1428, 1385, 1367, 1119, 850, 735, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (d, J=6.5 Hz, 3H), 0.96 (d, J=6.5 Hz, 3H), 1.22— 1.53 (m, 5H), 1.75—1.93 (m, 2H), 1.93—2.23 (m, 2H), 3.52 (dd, J=4.3, 7.3 Hz, 1H), 7.32—7.48 (m, 3H), 7.67—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.85, 14.96, 16.84, 18.36, 20.47, 22.84, 29.18, 42.11, 127.82, 129.84, 134.37, 134.98. Found: C, 49.10; H, 6.31%. Calcd for $C_{14}H_{21}ISi$: C, 48.84; H, 6.15%.

1-(1,3-Diiodopropyl)-1-phenylsilacyclobutane (5d): Bp 111—112 °C (bath temp, 0.3 Torr); IR (neat) 2962,

2920, 1428, 1206, 1164, 1119, 855, 735, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32—1.57 (m, 4H), 1.97—2.26 (m, 4H), 3.29 (ddd, J=7.7, 7.7, 9.7 Hz, 1H), 3.49 (ddd, J=5.3, 5.3, 9.7 Hz, 1H), 3.56 (dd, J=6.0, 8.9 Hz, 1H) 7.36—7.48 (m, 3H), 7.61—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=9.36, 14.69, 16.93, 19.35, 36.39, 127.97, 130.11, 134.23, 134.35. Found: C, 32.48; H, 3.57%. Calcd for $C_{12}H_{16}I_2Si$: C, 32.60; H, 3.65%.

1-Phenyl-1-(4,4,4-trifluoro-1-iodobutyl)silacyclobutane (5e): Bp 96—97 °C (bath temp, 1.0 Torr); IR (neat) 3066, 2968, 2924, 2868, 1447, 1430, 1386, 1331, 1314, 1251, 1202, 1121, 1056, 954, 846, 736, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30—1.58 (m, 4H), 1.86—2.29 (m, 5H), 2.36—2.62 (m, 1H), 3.38 (dd, J=3.7, 11.3 Hz, 1H), 7.37—7.50 (m, 3H), 7.62—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.60, 16.96, 26.19, 36.52 (q, J=28.4 Hz), 128.03, 128.52, 130.20, 134.21. Found: C, 40.90; H, 4.21%. Calcd for $C_{13}H_{16}F_3ISi$: C, 40.63; H, 4.20%.

General Procedure for *t*-BuOK-Induced Ring Enlargement of Silacyclobutane into Silacyclopentane. Ring enlargement of 1-phenyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)silacyclobutane (**5a**) with *t*-BuOK is representative. A solution of 1-phenyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)silacyclobutane (**5a**, 0.93 g, 1.5 mmol) in THF (2 ml) was added to a suspension of potassium *t*-butoxide (0.20 g, 1.8 mmol) in THF (6 ml) at −78 °C under argon atmosphere. After being stirred for 20 min at −78 °C, the dry ice–methanol bath was removed and the reaction mixture was warmed up to room temperature. The resulting mixture was poured into ice-cooled water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Distillation of the residual oil using Kugelrohr afforded 1-*t*-butoxy-1-phenyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (**6a**, 0.66 g, 65:35 diastereomeric mixture) in 77% yield. Separation of diastereomers was performed using silica-gel column chromatography.

Faster moving band (minor product): R_f=0.8 (hexane); bp 103—104 °C (bath temp, 1.0 Torr); IR (neat) 3070, 2974, 2930, 2860, 1459, 1430, 1392, 1367, 1241, 1194, 1145, 1116, 1048, 1023, 822, 734, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.74—0.96 (m, 1H), 1.05—1.61 (m, 4H), 1.24 (s, 9H), 1.88—2.26 (m, 3H), 2.33—2.69 (m, 1H), 7.35—7.54 (m, 3H), 7.59—7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.15, 18.55, 24.75, 31.07 (t, J=22.0 Hz), 31.91, 33.99, 73.23, 127.87, 129.63, 133.66, 138.06. Found: C, 44.30; H, 4.01%. Calcd for $C_{21}H_{23}F_{13}OSi$: C, 44.53; H, 4.09%.

Slower moving band (major product): R_f=0.7 (hexane); bp 103—104 °C (bath temp, 1.0 Torr); IR (neat) 3070, 2974, 2932, 2862, 1456, 1430, 1391, 1367, 1241, 1194, 1145, 1115, 1058, 1023, 811, 736, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84—1.09 (m, 2H), 1.09—1.99 (m, 5H), 1.35 (s, 9H), 1.99—2.31 (m, 2H), 7.38—7.54 (m, 3H), 7.55—7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=12.08, 20.39, 24.30, 31.29 (t, J=23.0 Hz), 31.95, 33.43, 73.46, 127.79, 129.63, 134.04. Found: C, 44.63; H, 4.07%. Calcd for $C_{21}H_{23}F_{13}OSi$: C, 44.53; H, 4.09%.

1-*t*-Butoxy-2-(2,2-dimethylpropyl)-1-phenylsilacyclopentane (6b). Faster moving band (minor product): R_f=0.8 (hexane); bp 88—89 °C (bath temp, 0.3 Torr); IR (neat) 2946, 2858, 1467, 1429, 1390, 1365, 1238, 1195, 1113, 1050, 1022, 699, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.72—0.92 (m, 2H), 0.82 (s, 9H), 1.05—1.15 (m, 1H), 1.16 (dd, J=5.7, 13.8 Hz, 1H), 1.21—1.50 (m, 2H), 1.28 (s, 9H), 1.77 (dd, J=6.4, 13.8 Hz, 1H), 1.92—2.09 (m, 2H), 7.30—7.38 (m, 3H), 7.55—7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.10, 23.45, 24.98, 29.94, 31.44, 32.09, 36.59, 44.45, 72.61, 127.53, 127.69, 128.88, 133.62. Found: C, 75.03; H, 10.76%. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59%.

Slower moving band (major product): R_f=0.6 (hexane); bp 83—85 °C (bath temp, 0.3 Torr); IR (neat) 3066, 2948, 2860, 1467, 1429, 1389, 1365, 1239, 1196, 1114, 1056, 1022, 814, 760, 736, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76—0.90 (m, 2H), 0.78 (s, 9H), 0.94—1.09 (m, 2H), 1.12—1.33 (m, 2H), 1.35 (s, 9H), 1.59 (ddddd, J=4.9, 6.8, 11.8, 11.8, 11.8 Hz, 1H), 1.95—2.14 (m, 2H), 7.30—7.38 (m, 3H), 7.52—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.53, 24.61, 25.14, 29.85, 31.35, 32.09, 36.46, 44.47, 72.87, 127.34, 128.86, 134.38, 138.14. Found: C, 75.11; H, 10.70%. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59%.

1-*t*-Butoxy-2-(2-methylpropyl)-1-phenylsilacyclopentane (6c). Faster moving band (minor product): R_f=0.8 (hexane); bp 79—81 °C (bath temp, 0.3 Torr); IR (neat) 2948, 2922, 2864, 1466, 1429, 1389, 1365, 1238, 1195, 1113, 1048, 1022, 734, 710, 698, 668 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80 (d, J=6.6 Hz, 3H), 0.85 (d, J=6.6 Hz, 3H), 0.87 (ddd, J=7.8, 7.8, 10.5 Hz, 1H), 1.16 (dddd, J=1.5, 3.0, 6.8, 10.5 Hz, 1H), 1.20—1.44 (m, 4H), 1.24 (s, 9H), 1.48 (ddd, J=6.6, 8.0, 13.3 Hz, 1H), 1.69 (ddsept, J=6.6, 6.6, 6.6 Hz, 1H), 1.88—2.04 (m, 2H), 7.30—7.38 (m, 3H), 7.56—7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.96, 22.78, 22.88, 24.74, 25.46, 27.59, 32.03, 33.99, 40.04, 72.53, 127.63, 128.96, 133.63, 140.14. Found: C, 74.58; H, 10.60%. Calcd for $C_{18}H_{30}OSi$: C, 74.41; H, 10.41%.

Slower moving band (major product): R_f=0.6 (hexane); bp 79—81 °C (bath temp, 0.3 Torr); IR (neat) 2950, 2922, 2864, 1461, 1429, 1388, 1365, 1239, 1196, 1114, 1049, 1020, 752, 736, 698, 650 cm^{-1}; ^1H NMR ($CDCl_3$)δ=0.68 (d, J=6.6 Hz, 3H), 0.79 (d, J=6.6 Hz, 3H), 0.80—1.22 (m, 6H), 1.33 (s, 9H), 1.45 (ddsept, J=6.6, 6.6, 6.6 Hz, 1H), 1.52—1.69 (m, 1H), 1.92—2.08 (m, 2H), 7.28—7.38 (m, 3H), 7.53—7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.32, 22.16, 23.06, 24.46, 26.67, 27.52, 32.06, 33.56, 39.77, 72.85, 127.37, 128.94, 134.23, 137.77. Found: C, 74.26; H, 10.42%. Calcd for $C_{18}H_{30}OSi$: C, 74.41; H, 10.41%.

1-*t*-Butoxy-2-(2-iodoethyl)-1-phenylsilacyclopentane (6d). Faster moving band (minor product): R_f=0.5 (hexane); bp 92—93 °C (bath temp, 0.3 Torr); IR (neat) 3064, 2968, 2852, 1428, 1365, 1238, 1193, 1114, 1044, 1021, 818, 698, 665 cm^{-1}; ^1H NNR ($CDCl_3$) δ=0.86 (ddd, J=8.1, 10.7, 15.1 Hz, 1H), 0.93 (ddd, J=7.7, 7.9, 10.5 Hz, 1H), 1.20 (dddd, J=1.5, 3.3, 6.8, 15.1 Hz, 1H), 1.24 (s, 9H), 1.25—1.33 (m, 1H), 1.36—1.52 (m, 1H), 1.90—2.04 (m, 3H), 2.19 (dddd, J=6.4, 7.9, 9.1, 14.0 Hz, 1H), 3.26 (ddd, J=6.0, 9.1, 9.1 Hz, 1H), 3.33 (ddd, J=6.4, 9.1, 9.1 Hz, 1H), 7.31—7.43 (m, 3H), 7.55—7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.36, 13.45, 24.48, 29.00, 31.97, 32.79, 35.68, 73.01, 127.80, 129.34, 133.64, 134.00. Found: C, 49.61; H, 6.61%. Calcd for $C_{16}H_{25}IOSi$: C, 49.48; H, 6.49%.

Slower moving band (major product): R_f=0.3 (hexane); bp 92—93 °C (bath temp, 0.3 Torr); IR (neat) 3064, 2968, 2922, 2854, 1452, 1428, 1365, 1240, 1195, 1113, 1054, 1021, 815, 737, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—1.30 (m, 4H), 1.34 (s, 9H), 1.40—1.82 (m, 3H), 1.95—2.08 (m, 2H), 3.04 (ddd, J=7.7, 7.7, 9.4 Hz, 1H), 3.14 (ddd, J=5.9, 8.2, 9.4

Hz, 1H), 7.32—7.42 (m, 3H), 7.51—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=8.73, 12.85, 24.22, 29.96, 32.16, 34.91, 73.23, 127.67, 129.37, 134.02, 136.79. Found: C, 49.20; H, 6.40%. Calcd for $C_{16}H_{25}IOSi$: C, 49.48; H, 6.49%.

Oxidative Cleavage of 1-*t*-Butoxy-1-phenyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (6a) into 6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoro-1,4-undecanediol (7a). Potassium fluoride (44 mg, 0.75 mmol), $KHCO_3$ (400 mg, 4.0 mmol), and H_2O_2 (30%, 450 mg, 4 mmol) were added to a solution of **6a** (214 mg, 0.38 mmol) in THF (4 ml) and MeOH (4 ml). The mixture was stirred for 20 h at 25 °C and poured into aqueous $NaHSO_3$. Extraction with ethyl acetate (20 ml×3) followed by concentration of dried organic layers (Na_2SO_4) provided a residual oil, which was submitted to silica-gel column chromatography to give **7a** (136 mg) in 85% yield: Mp 59.5—60.5 °C; IR (nujol) 3252, 1241, 1219, 1188, 1141, 1056, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48—1.66 (m, 4H), 1.97—2.38 (m, 4H), 3.44—3.79 (m, 2H), 4.06—4.26 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=28.41, 34.97, 38.00 (t, J=21.0 Hz), 62.63, 65.15. Found: C, 31.35; H, 2.57%. Calcd for $C_{11}H_{11}F_{13}O_2$: C, 31.29; H, 2.63%.

Oxidative Cleavage of Silacyclopentanes 6b, 6c, and 6d into the Corresponding Diols 7b, 7c, and 7d. We describe a typical procedure for the transformation of **6b** into **7b**. Diethyl ether–tetrafluoroboric acid (1/1) (Et_2O·HBF_4, 85%, 0.30 ml, 1.9 mmol) was added to a solution of silacyclopentane **6b** (243 mg, 0.79 mmol) in CH_2Cl_2 (3 ml) at 0 °C under argon atmosphere; the mixture was stirred for 1 h at 0°C and for 3 h at room temperature. The resulting mixture was concentrated in vacuo to give a residual oil, which was dissolved in THF (5 ml) and MeOH (5 ml). Potassium fluoride (92 mg, 1.9 mmol) and $KHCO_3$ (790 mg, 7.9 mmol) were added to the solution and then H_2O_2 (30%, 1.08 g, 9.5 mmol) was added. The mixture was stirred for another 10 h at 40 °C and then poured into aqueous $NaHSO_3$. Extraction with ethyl acetate (20 ml×3) followed by concentration of dried organic layers (Na_2SO_4) provided a residual oil, which was submitted to silica-gel column chromatography to give 6,6-dimethyl-1,4-heptanediol (**7b**, 70 mg) in 55% yield: Bp 92—93 °C (bath temp, 0.3 Torr); IR (neat) 3296 (broad), 2946, 2866, 1475, 1467, 1365, 1058, 1015, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (s, 9H), 1.31—1.41 (m, 2H), 1.42—1.62 (m, 2H), 1.68 (tt, J=6.0, 6.6 Hz, 2H), 3.06 (bs, 2H, OH), 3.62 (dt, J=10.5, 6.0 Hz, 1H), 3.68 (dt, J=10.5, 6.0 Hz, 1H), 3.78 (dddd, J=3.6, 3.6, 7.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=28.93, 30.08, 30.21, 36.58, 51.17, 62.71, 69.33. Found: C, 67.19; H, 12.52%. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58%.

6-Methyl-1,4-heptanediol (7c): Bp 86—87 °C (bath temp, 0.3 Torr); IR (neat) 3294 (broad), 2950, 2866, 1468, 1384, 1368, 1143, 1051, 1018 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 0.91 (d, J=6.5 Hz, 3H), 0.92 (d, J=6.6 Hz, 3H), 1.16—1.33 (m, 2H), 1.36—1.53 (m, 2H), 1.55—1.84 (m, 3H), 3.50—3.75 (m, 5H including 2OH); ^{13}C NMR ($CDCl_3$) δ=22.09, 23.32, 24.54, 28.99, 34.92, 46.66, 62.66, 69.58. Found: C, 65.43; H, 12.30%. Calcd for $C_8H_{18}O_2$: C, 65.71; H, 12.41%.

6-Iodo-1,4-hexanediol (7d): Bp 85—87 °C (bath temp, 0.3 Torr); IR (neat) 3276 (broad), 2934, 1430, 1333, 1233, 1138, 1048, 1014, 882, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.42—1.78 (m, 4H), 1.80—2.06 (m, 2H) 3.27 (t, J=7.5 Hz, 1H), 3.28 (t, J=6.8 Hz, 1H), 3.45 (bs, 2H OH), 3.56—3.76 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=3.38, 28.78, 34.27, 40.73, 62.66, 71.31. Found: C, 29.66; H, 5.47%. Calcd for $C_6H_{13}IO$: C, 29.53; H, 5.37%.

$AgBF_4$-Induced Ring Enlargement of Silacyclobutane 5a into Silacyclopentane. A CH_2Cl_2 (1 ml) solution of silacyclobutane **5a** (310 mg, 0.5 mmol) was added to a suspension of $AgBF_4$ (195 mg, 1.0 mmol) in CH_2Cl_2 (2 ml) at 25 °C under argon atmosphere. After the mixture was stirred for 3 h at room temperature, the resulting precipitate was filtered through Celite 545. The filtrate was concentrated in vacuo. The residual oil was dissolved in THF (2 ml). Methyllithium (1.1 M diethyl ether solution, 1.8 ml, 2.0 mmol) was added at 0 °C under argon atmosphere. Then the whole was stirred for 1 h at 0 °C and for 8 h at room temperature. The resulting mixture was poured into ice-cooled water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the product by silica-gel column chromatography provided 1-methyl-1-phenyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (78 mg, 31/69 diastereomeric mixture) in 31% yield:

Faster moving band (minor product): R_f=0.8 (hexane); bp 89—90 °C (bath temp, 1.0 Torr); IR (neat) 2930, 2856, 1430, 1364, 1239, 1145, 1113, 788, 767, 732, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$ δ=0.33 (s, 3H), 0.78—1.23 (m, 4H), 1.23—2.45 (m, 5H), 7.40—7.90 (m, 5H); ^{13}C NMR ($CDCl_3$) δ= −5.87, 12.77, 17.58, 25.77, 31.60 (t, J=22.4 Hz), 35.16, 127.95, 129.40, 133.72, 137.08. Found: C, 42.42; H, 3.44%. Calcd for $C_{18}H_{17}F_{13}Si$: C, 42.52; H, 3.37%.

Slower moving band: R_f=0.7 (hexane); bp 89—90 °C (bath temp, 1.0 Torr); IR (neat) 3068, 2926, 2856, 1453, 1430, 1364, 1234, 1205, 1145, 1113, 1074, 1048, 787, 732, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.36 (s, 3H), 0.70 (ddd, J=8.5, 11.8 14.9 Hz, 1H), 1.11 (dddd, J=2.0, 2.0, 7.2, 14.9 Hz, 1H), 1.29 (dddd, J=4.4, 12.1, 12.1, 12.1 Hz, 1H), 1.41—1.62 (m, 2H), 1.95—2.42 (m, 4H), 7.32—7.45 (m, 3H), 7.48—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−5.90, 12.75, 18.52, 25.80, 31.49 (t, J=22.9 Hz), 34.72, 127.92, 129.36, 133.72, 137.12. Found: C, 42.55; H, 3.38%. Calcd for $C_{18}H_{17}F_{13}Si$: C, 42.52; H, 3.37%.

AgOAc-Induced Ring Enlargement of Silacyclobutanes into Silacyclopentanes. The reaction of **5a** is representative. A solution of silacyclobutane **5a** (1.86 g, 3.0 mmol) in acetic acid (3 ml) was added to a suspension of AgOAc (517 mg, 3.1 mmol) in acetic acid (9 ml) at 25 °C under argon atmosphere. After the mixture was stirred for 1 h at room temperature, the resulting precipitate was filtered through Celite 545. The filtrate was concentrated in vacuo. Distillation of the residual oil using Kugelrohr afforded 1-acetoxy-1-phenyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (**9a**, 6/4 diastereomeric mixture, 1.19 g) in 72% yield: Bp 122—123 °C (bath temp, 2.0 Torr); IR (neat) 3072, 2936, 2862, 1729, 1431, 1373, 1241, 1145, 1119, 1076, 1048, 1019, 936, 733, 717, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89—2.73 (m, 10H), (2.15(s)+2.20(s) total 3H), 7.40—7.73 (m, 5H); ^{13}C NMR ($CDCl_3$) sets of 6:4 peaks δ= (10.68, 11.70), (18.38, 18.77), (23.38, 24.32), (δ=30.81 (t, J=23.0 Hz), 30.86 (t, J=23.0 Hz)), (33.64, 33.83), (128.12, 128.21), (130.17, 130.47), (130.57, 130.65), (133.81, 133.98), (171.80, 172.02). Purification by silica-gel column chromatography caused decomposition. Distillation was not effective for the preparation of analytically pure

sample. Thus, the compound **9a** was converted into **6a** upon treatment with *t*-BuOK. Potassium *t*-butoxide (170 mg, 1.5 mmol) was added to a solution of **9a** (762 mg, 1.4 mmol) in THF (3 ml) at 0 °C under argon atmosphere. The mixture was stirred for 1.5 h at 0 °C, and then poured into water. Extraction with ethyl acetate (20 ml×3) and concentration of the combined organic layers gave an oil. Distillation of the residual oil using Kugelrohr afforded **6a** (288 mg, 6/4 diastereomeric mixture) in 27% yield. Oxidative cleavage of silacyclopentane **9a** was performed as follows. Potassium fluoride (89 mg, 1.5 mmol), $KHCO_3$ (760 mg, 7.6 mmol), and H_2O_2 (30%, 868 mg, 7.6 mmol) were added to a solution of silacyclopentane **9a** (6/4 diastereomeric mixture, 420 mg, 0.76 mmol) in THF (4 ml) and MeOH (4 ml) at 25 °C. After this was stirred for 24 h at room temperature, the resulting mixture was poured into aqueous $NaHSO_3$ and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give **7a** (169 mg) in 53% yield.

1-Acetoxy-2-(2-methylpropyl)-1-phenylsilacyclopentane (9b, 6/4 Diastereomeric Mixture): Bp 94—95 °C (bath temp, 0.3 Torr); IR (neat) 2950, 2926, 2868, 1727, 1429, 1370, 1249, 1117, 1018, 736, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.68—2.20 (m, 10H), (0.72 (d, J=6.6 Hz)+0.84(d, J=6.5 Hz) total 3H), (0.80 (d, J=6.6 Hz)+0.86 (d, J=6.5 Hz) total 3H), (2.13(s)+2.16(s) total 3H), 7.32—7.46 (m, 3H), 7.50—7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.65, 11.94, 21.93, 22.28, 22.67, 22.72, 22.93, 23.10, 23.90, 24.36, 24.49, 24.86, 27.60, 27.74, 33.31, 33.80, 38.93, 39.11, 127.83, 127.95, 130.03, 130.07, 132.85, 133.79, 134.09, 134.57, 171.65, 171.75. The compound **9b** was converted into **6b** upon treatment with *t*-BuOK in THF at 0 °C and this was identified by comparison with a sample generated by the reaction of **5b** with *t*-BuOK.

Preparation of 1,3-Dimethyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)silacyclobutane (10a 40/60 Diastereometic Mixture). 1,2-Dibromoethane (0.2 ml) was added to magnesium (1.90 g, 78 mmol) in THF (5 ml) under argon atmosphere. The mixture was heated using a heat gun, to initiate an exothermic reaction. A solution of dichloro(3-chloro-2-methylpropyl)methylsilane (13.4 g, 65 mmol), which was prepared by hydrosilation of 3-chloro-2-methyl-1-propene with dichloromethylsilane, in THF (60 ml) was added dropwise to the activated Mg over a period of 1 h. After being stirred for 3 h at 50 °C, the reaction mixture was cooled to 0 °C. A vinylmagnesium bromide (1.0 M, THF solution, 65 ml, 65 mmol) was added and the whole was stirred for another 2 h at 0 °C. The resulting mixture was poured into 1 M HCl and extracted with ether (40 ml×2). The combined organic layers were dried over anhydrous Na_2SO_4. Distillation of the organic layers gave a mixture of 1-ethenyl-1,3-dimethylsilacyclobutane and THF (44/56), (72—79 °C, 760 Torr, 40/60 diastereomeric mixture, 2.46 g) in 34% yield. ^1H NMR ($CDCl_3$) δ=(0.32(s)+0.33(s) total 3H), 0.58—0.80 (m, 2H), (1.14 (d, J=6.6 Hz)+1.15 (d, J=6.6 Hz) total 3H), 1.18—1.36 (m, 2H), 2.30—2.50 (m, 1H), (5.78 (dd, J=3.8, 20.1 Hz)+5.84 (dd, J=3.8, 20.1 Hz) total 1H), (6.04 (dd, J=3.8, 14.6 Hz)+6.05 (dd, J=3.8, 14.6 Hz) total 1H), (6.29 (dd, J=14.6, 20.1 Hz)+6.33 (dd, J=14.6, 20.1 Hz) total 1H). Hexane (33 ml) and 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl iodide (4.3 ml, 20 mmol) were added to the above mixture (1.23 g), and Et_3B (1.0 M, hexane solution, 5.5 ml, 5.5 mmol) was successively added at 25 °C under argon atmosphere. After being stirred for 10 h at room temperature, the resulting mixture was concentrated and the residual oil was submitted to silica-gel column chromatography to give the title compound (40/60 diastereomeric mixture, 4.93 g) in 80% yield:

Faster moving band (minor compound): Bp 102—103 °C (bath temp, 15 Torr); IR (neat) 2952, 2918, 2862, 1452, 1354, 1316, 1239, 1145, 1071, 1045, 955, 825, 795, 706, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.39 (s, 3H), 0.66—0.87 (m, 2H), 1.16 (d, J=6.4 Hz, 3H), 1.33—1.46 (m, 2H), 2.13—2.28 (m, 1H), 2.60—2.90 (m, 2H), 3.39 (dd, J=7.9, 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−5.65, 3.94, 24.73, 26.14, 27.08, 36.78 (t, J=20.5 Hz). Found: C, 27.35; H, 2.56%. Calcd for $C_{13}H_{14}F_{13}ISi$: C, 27.29; H, 2.47%.

Slower moving band (major compound): Bp 102—103 °C (bath temp, 15 Torr); IR (neat) 2950, 2914, 2862, 1452, 1353, 1316, 1240, 1144, 1048, 955, 837, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.44 (s, 3H), 0.66—0.87 (m, 2H), 1.17 (d, J=6.6 Hz, 3H), 1.31—1.46 (m, 2H), 2.26—2.42 (m, 1H), 2.60—2.90 (m, 2H), 3.46 (dd, J=7.7, 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−2.31, 1.94, 23.85, 25.78, 26.66, 26.93, 36.17 (t, J=21.3 Hz). Found: C, 27.22; H, 2.46%. Calcd for $C_{13}H_{14}F_{13}ISi$: C, 27.29; H, 2.47%.

1-*t*-Butoxy-1,4-dimethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (Diastereomeric Mixture): Bp 105—106 °C (bath temp, 20 Torr); IR (neat) 2972, 2870, 1459, 1366, 1240, 1195, 1145, 1055, 829, 776, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ=(0.16(s)+0.19(s)+0.25(s)+0.31(s) total 3H), 0.62—2.50 (m, 8H), (0.94 (d, J=6.7 Hz)+1.02 (d, J=6.8 Hz)+1.03 (d, J=6.4 Hz)+1.04 (d, J=6.4 Hz) total 3H). This diastereomeric mixture was converted into 2-methyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-1,4-undecanediol (**12**, 74/26 diastereomeric mixture) upon treatment with H_2O_2, KF, and $KHCO_3$.

2-Methyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-1,4-undecanediol (12): Faster moving band (major product): R_f=0.5 (hexane/AcOEt=1/1); mp 53.0—54.0 °C; IR (neat before crystallization) 3304 (broad), 2958, 2930, 1366, 1319, 1238, 1197, 1145, 1034, 732, 707, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (d, J=7.0 Hz, 3H), 1.60 (ddd, J=4.0, 8.0, 14.5 Hz, 1H), 1.65 (ddd, J=4.6, 7.7, 14.5 Hz, 1H), 1.88—2.04 (m, 1H), 2.05—2.45 (m, 2H), 3.47 (dd, J=7.4, 10.6 Hz, 1H), 3.60 (dd, J=4.2, 10.6 Hz, 1H), 3.62—3.75 (bs, 2H, 2OH), 4.33 (dddd, J=4.0, 4.6, 7.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=17.23, 31.70, 37.63 (t, J=20.6 Hz), 42.68, 62.75, 67.61. Found: C, 32.90; H, 2.86%. Calcd for $C_{12}H_{13}F_{13}O_2$: C, 33.04; H, 3.00%.

Slower moving band (minor product): R_f=0.4 (hexane/AcOEt=1/1); mp 76.0—77.0 °C; IR (nujol) 3234 (broad), 1243, 1211, 1187, 1141, 1071, 1042, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (d, J=6.8 Hz, 3H), 1.50 (ddd, J=2.3, 5.8, 14.5 Hz, 1H), 1.66 (ddd, J=6.9, 10.1, 14.5 Hz, 1H), 1.84—1.97 (m, 1H), 2.04—2.80 (m, 4H including 2OH), 3.44 (dd, J=7.6, 10.5 Hz, 1H), 3.66 (dd, J=4.4, 10.5 Hz, 1H), 4.19—4.29 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=17.65, 34.05, 38.79 (t, J=20.2 Hz), 43.46, 64.48, 68.52. Found: C, 32.87; H, 3.05%. Calcd for $C_{12}H_{13}F_{13}O_2$: C, 33.04; H, 3.00%.

1-Acetoxy-1,4-dimethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)silacyclopentane (Diastereomeric Mixture): Bp 93—94 °C (bath temp, 2.0

Torr); IR (neat) 2952, 2868, 1724, 1373, 1206, 1051, 810, 793, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08—2.75 (m, 8H), (0.33(s)+0.35(s)+0.46(s)+0.47(s) total 3H), (0.94 (d, J=7.0 Hz)+1.00 (d, J=6.6 Hz)+1.08 (d, J=6.8 Hz)+1.16 (d, J=6.8 Hz) total 3H), (2.06(s)+2.07(s)+2.08(s)+2.09(s) total 3H). Purification by silica-gel column chromatography caused decomposition. Thus, this compound was converted into **12** (46/54 diastereomeric mixture) upon treatment with H_2O_2, KF, $KHCO_3$ in THF–MeOH at 25 °C.

1-Phenyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl)silacyclopentane (13): Bp 95—96 °C (bath temp, 0.3 Torr); IR (neat) 2934, 2854, 1429, 1364, 1240, 1209, 1145, 1115, 1078, 1021, 809, 735, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93—1.18 (m, 4H), 1.64—1.90 (m, 4H), 2.43—2.85 (m, 2H), 3.47 (dd, J=4.4, 9.3 Hz, 1H), 7.33—7.50 (m, 3H), 7.58—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.20, 11.35, 11.90, 26.91, 27.16, 35.76 (t, J=21.7 Hz), 128.06, 130.07, 133.38, 134.87. Found: C, 33.94; H, 2.53%. Calcd for $C_{18}H_{16}F_{13}SiI$: C, 34.08; H, 2.54%.

1-Phenyl-1-[(*E*)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octenyl]silacyclopentane (14): Bp 76—78 °C (bath temp, 0.3 Torr); IR (neat) 2936, 2856, 1430, 1365, 1240, 1201, 1145, 1114, 1077, 989, 809, 735, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90—1.15 (m, 4H), 1.65—1.90 (m, 4H), 6.12 (dt, J=18.9, 11.1 Hz, 1H), 6.93 (dt, J=18.9, 4.6 Hz, 1H), 7.32—7.48 (m, 3H), 7.50—7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.15, 27.31, 127.87, 128.15, 129.84, 131.93 (t, J=24.2 Hz), 134.33, 140.52. Found: C, 42.41; H, 2.86%. Calcd for $C_{18}H_{15}F_{13}Si$: C, 42.69; H, 2.99%.

Preparation of 1-(1,2-Epoxy-1-triphenylsilylethyl)-1-methylsilacyclobutane (19): *s*-BuLi (1.08 M, cyclohexane solution, 4.4 ml, 4.8 mmol) was added to a solution of (1,2-epoxyethyl)triphenylsilane (1.51 g, 5.0 mmol) at −78 °C under argon atmosphere. The mixture was stirred for 1 h at −78 °C and then was added to a solution of 1-chloro-1-methylsilacyclobutane (7 mmol), which had been prepared according to the reported procedure,[3] in THF (7 ml) at −78 °C under argon atmosphere. After being stirred for 30 min at −78 °C, the resulting mixture was poured into brine and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give the title compound **19** (454 mg) in 24%: Mp 117—119 °C; IR (Nujol) 1428, 1111, 876, 792, 761, 740, 709, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.02 (s, 3H), 0.71—1.10 (m, 4H), 1.77—2.01 (m, 2H), 2.92 (d, J=5.9 Hz, 1H), 3.02 (d, J=5.9 Hz, 1H), 7.35—7.50 (m, 9H), 7.58—7.70 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=−2.71, 12.56, 14.12, 17.69, 43.35, 48.94, 127.84, 129.84, 132.69, 136.16. Found: C, 74.05; H, 6.67%. Calcd for $C_{24}H_{26}Si_2O$: C, 74.55; H, 6.78%.

Preparation of 1-(1,2-Epoxy-2-methylpropyl)-1-phenylsilacyclobutane (20) and 1-(1,2-Epoxyethyl)-1-phenylsilacyclobutane (23). The preparation of **20** is representative. 2-Methyl-1-propenylmagnesium bromide (2.0 M, THF solution, 30 ml, 60 mmol) is added to a solution of 1-chloro-1-phenylsilacyclobutane (11.0 g, 60 mmol) in THF (60 ml) at 0 °C under argon atmosphere. After being stirred for 3 h at 0 °C, the resulting mixture was poured into 1 M HCl and extracted with ethyl acetate (50 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to a silica-gel column chromatography to give 1-(2-methyl-1-propenyl)-1-phenylsilacyclobutane (2.90 g) in 48% yield: Bp 58—60 °C (bath temp, 0.3 Torr); IR (neat) 2964, 2926, 1618, 1437, 1427, 1118, 1109, 857, 731, 698, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25—1.41 (m, 4H), 1.80 (s, 3H), 1.94 (s, 3H), 2.09—2.34 (m, 2H), 5.50 (s, 1H), 7.32—7.42 (m, 3H), 7.60—7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.76, 15.48, 18.77, 23.82, 29.25, 120.45, 127.86, 129.10, 134.02, 138.28, 155.10. Found: C, 77.08; H, 9.15%. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.96%. *m*CPBA (80% purity, 3.09 g, 14.4 mmol) was added to a solution of 1-(2-methyl-1-propenyl)-1-phenylsilacyclobutane (2.90 g, 14.3 mmol) in $CHCl_3$ (35 ml) at 0 °C under argon atmosphere. After being stirred for 1 h at 0 °C and for 2 h at room temperature, the resulting mixture was poured into saturated $NaHCO_3$ and extracted with hexane (50 ml×3). The combined organic layers were concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to provide 1-(1,2-epoxy-2-methylpropyl)-1-phenylsilacyclobutane (**20**, 2.10 g) in 67% yield: Bp 65—66 °C (bath temp, 0.3 Torr); IR (neat) 2962, 2922, 1449, 1427, 1376, 1113, 851, 832, 697, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20—1.57 (m, 4H), 1.34 (s, 3H), 1.44 (s, 3H), 2.09—2.39 (m, 2H), 2.47 (s, 1H), 7.37—7.48 (m, 3H), 7.62—7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.28, 13.54, 18.85, 22.04, 26.28, 57.30, 59.14, 128.14, 129.95, 133.99, 135.26. Found: C, 71.49; H, 8.48%. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31%.

1-(1,2-Epoxyethyl)-1-phenylsilacyclobutane (23): Bp 97—98 °C (bath temp, 3.0 Torr); IR (neat) 2968, 2922, 1429, 1230, 1120, 874, 851, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21—1.30 (m, 2H), 1.32—1.42 (m, 2H), 2.20 (tt, J=8.3, 8.3 Hz, 2H), 2.62 (dd, J=4.0, 5.5 Hz, 1H), 2.74 (dd, J=4.0, 5.9 Hz, 1H), 3.07 (dd, J=5.5, 5.9 Hz, 1H), 7.36—7.48 (m, 3H), 7.62—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.32, 11.90, 18.46, 42.39, 44.66, 128.09, 130.10, 133.94, 134.49. Found: C, 69.45; H, 7.43%. Calcd for $C_{11}H_{14}OSi$: C, 69.42; H, 7.41%.

General Procedure for Reaction of 19 and 20 with Methyllithium. Methyllithium (1.05 M, diethyl ether solution, 0.49 ml, 0.52 mmol) was added to a solution of silacyclobutane **19** (100 mg, 0.26 mmol) at −78 °C under argon atmosphere. After this mixture was stirred for 2 h at −78 °C, MeOH (1 ml) was added at −78 °C and the whole was stirred for 5 min. The resulting mixture was poured into saturated aqueous NH_4Cl and extracted with ethyl acetate (20 ml×3). The combined organic layers were concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give dimethyl(4-triphenylsilyl-4-pentenyl)silanol (**18**, 91 mg) in 84% yield: Bp 136—137 °C (bath temp, 0.3 Torr); IR (neat) 3246 (broad), 3064, 3046, 2950, 2920, 1428, 1252, 1108, 933, 863, 772, 739, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (s, 6H), 0.43—0.52 (m, 2H), 1.28—1.42 (m, 2H), 1.44 (bs, 1H, OH), 2.27 (dt, J=1.5, 5.5 Hz, 2H), 5.55 (d, J=2.7 Hz, 1H), 5.98 (dt, J=2.7, 1.5 Hz, 1H), 7.31—7.44 (m, 9H), 7.52—7.59 (m, 6H); ^{13}C NMR ($CDCl_3$) δ=−0.39, 17.53, 22.59, 40.12, 127.76, 129.44, 130.57, 134.12, 136.24, 146.34. Found: C, 74.51; H, 7.50%. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51%.

2-(1-Hydroxy-1-methylethyl)-1-methyl-1-phenylsilacyclopentane (21): Faster moving band (major product); R_f=0.5 (hexane/AcOEt=10/1); Bp 105—110 °C (bath temp, 1.0 Torr); IR (neat) 3395 (broad), 2960, 2924,

2852, 1428, 1252, 1111, 806, 783, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.49 (s, 3H), 0.55—0.80 (m, 1H), 0.90—1.70 (m, 4H), 1.25 (s, 3H), 1.29 (s, 3H), 1.95—2.25 (m, 3H including OH), 7.30—7.73 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−2.90, 13.71, 25.58, 29.95, 30.59, 30.67, 43.34, 73.10, 127.81, 128.88, 133.86, 139.46. Found: C, 71.75; H, 9.52%. Calcd for $C_{14}H_{22}OSi$: C, 71.74; H, 9.46%. Slower moving band (minor product); R_f=0.4 (hexane/AcOEt=10/1); Bp 107—110 °C (bath temp, 1.0 Torr); IR (neat) 3230 (broad), 2960, 2920, 2854, 1428, 1253, 1116, 1069, 790, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.47 (s, 3H), 0.88—1.75 (m, 5H), 1.04 (s, 3H), 1.11 (s, 3H), 1.95—2.28 (m, 3H including OH), 7.33—7.75 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−2.58, 12.24, 30.01, 30.14, 30.41, 45.23, 72.80, 128.06, 129.49, 134.96, 137.33. Found: C, 71.69; H, 9.48%. Calcd for $C_{14}H_{22}OSi$: C, 71.74; H, 9.46%.

Conversion of 2-(1-Hydroxy-1-methylethyl)-1-methyl-1-phenylsilacyclopentane (21) into Methyl(5-methyl-4-hexenyl)phenylsilanol (22). Excess potassium hydride (35 wt%, dispersion in mineral oil) was added to a solution of silacyclopentane **21** (216 mg, 0.92 mmol) in THF (4 ml) at 0 °C under argon atmosphere. After being stirred for 1 h at 0 °C and 1 h at room temperature, the resulting mixture was poured into brine and extracted with ethyl acetate (20 ml×3). The combined organic layers were concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give methyl(5-methyl-4-hexenyl)phenylsilanol (**22**, 183 mg) in 85% yield: Bp 103—104 °C (bath temp, 0.3 Torr); IR (neat) 3272 (broad), 2960, 2922, 2856, 1449, 1429, 1254, 1117, 848, 792, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.38 (s, 3H), 0.75—0.95 (m, 2H), 1.33—1.58 (m, 2H), 1.58 (s, 3H), 1.68 (s, 3H), 1.83—2.15 (m, 3H including OH), 5.03—5.20 (m, 1H), 7.25—7.73 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−1.67, 16.24, 17.72, 23.32, 25.71, 31.56, 124.42, 127.84, 129.54, 131.73, 133.23, 138.46. Found: C, 71.45; H, 9.49%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

Methyl(4-pentenyl)phenylsilanol (24): Bp 81—82 °C (bath temp, 0.3 Torr); IR (neat) 3326 (broad), 3070, 2924, 1639, 1427, 1252, 1114, 909, 847, 733, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.38 (s, 3H), 0.81—0.90 (m, 2H), 1.42—1.56 (m, 2H), 1.60—2.00 (bs, 1H, OH), 2.08 (dtt, J=6.8, 1.2, 7.1 Hz, 2H), 4.94 (ddt, J=2.2, 10.2, 1.2 Hz, 1H), 4.98 (ddt, J=2.2, 18.2, 1.2 Hz, 1H), 5.77 (ddt, J=10.2, 18.2, 6.8 Hz, 1H), 7.32—7.43 (m, 3H), 7.52—7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.71, 16.02, 22.49, 37.24, 114.72, 127.86, 129.58, 133.21, 138.33, 138.64. Found: C, 69.56; H, 8.74%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%.

Preparation of 1-[(*E*)-1,2-Epoxy-2-phenylethyl]-1-methylsilacyclobutane (28). The title compound was prepared by the same procedure as **20**.

1-Methyl-1-[(*E*)-2-phenylethenyl]silacyclobutane (25): Bp 88—89 °C (bath temp, 3.0 Torr); IR (neat) 3020, 2958, 2922, 2854, 1603, 1573, 1494, 1447, 1249, 1119, 987, 902, 879, 772, 731, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.43 (s, 3H), 1.01—1.26 (m, 4H), 2.14 (tt, J=8.3, 8.3 Hz, 2H), 6.62 (d, J=19.1 Hz, 1H), 7.02 (d, J=19.1 Hz, 1H), 7.21—7.38 (m, 3H), 7.45—7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.78, 14.32, 18.17, 126.54, 127.28, 128.25, 128.55, 138.05, 145.18. Found: C, 76.26; H, 8.73%. Calcd for $C_{12}H_{16}Si$: C, 76.52; H, 8.56%.

1-[(*E*)-1,2-Epoxy-2-phenylethyl]-1-methylsilacyclobutane (28): Bp 73—74 °C (bath temp, 0.3 Torr); IR (neat) 2962, 2924, 1457, 1396, 1251, 1121, 884, 756, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.39 (s, 3H), 0.95—1.33 (m, 4H), 2.03—2.29 (m, 2H), 2.55 (d, J=3.3 Hz, 1H), 3.81 (d, J=3.3 Hz, 1H), 7.23—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−3.51, 12.39, 12.74, 18.49, 56.04, 56.79, 125.33, 127.94, 128.47, 138.92. Found: C, 70.43; H, 7.87%. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.83%.

Preparation of 1-[(*Z*)-1,2-Epoxy-2-phenylethyl]-1-methylsilacyclobutane (29) and 1-[(*Z*)-1,2-Epoxyhexyl]-1-methylsilacyclobutane (30). The preparation of silacyclobutane **29** is representative. Butyllithium (1.52 M, 32.9 ml, 50 mmol) was added to a solution of ethynylbenzene (6.0 ml, 55 mmol), in THF (50 ml) at 0 °C under argon atmosphere. The mixture was stirred for 30 min at 0 °C and was added to a solution of 1-chloro-1-methylsilacyclobutane (50 mmol) in THF (50 ml) at 0°C under argon atmosphere. After being stirred for 30 min at 0 °C, the resulting mixture was poured into ice-cooled water. Extractive workup followed by purification by silica-gel column chromatography gave 1-methyl-1-(phenylethynyl)silacyclobutane (**26**, 4.95 g) in 53% yield: Bp 96—97 °C (bath temp, 3.0 Torr); IR (neat) 2966, 2024, 2152, 1488, 1250, 1220, 1121, 878, 773, 755, 720, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.51 (s, 3H), 1.05—1.18 (m, 2H), 1.24—1.37 (m, 2H), 2.03—2.32 (m, 2H), 7.26—7.35 (m, 3H), 7.42—7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.09, 15.41, 18.38, 92.37, 107.06, 122.69, 128.24, 128.77, 131.98. Found: C, 77.07; H, 7.66%. Calcd for $C_{12}H_{14}Si$: C, 77.35; H, 7.57%. Diisobutylaluminum hydride (5.7 ml, 32 mmol) was added to a solution of **26** (4.95 g, 26.6 mmol) in hexane (36 ml) and ether (18 ml) at 0 °C under argon atmosphere. The mixture was stirred for 2 h at 0 °C and 8 h at room temperature, and diluted with CH_2Cl_2 (50 ml). First NaF (9.5 g) was added and then H_2O (8.6 ml) was added and the whole was stirred for 3 h. The resulting precipitate was filtered, and the filtrate was concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give 1-methyl-1-[(*Z*)-2-phenylethenyl]silacyclobutane (3.62 g) in 72% yield: Bp 92—93 °C (bath temp, 3.0 Torr); IR (neat) 3056, 3020, 2958, 2924, 2868, 1591, 1493, 1445, 1396, 1249, 1120, 868, 780, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.32 (s, 3H), 1.05 (t, J=8.2 Hz, 4H), 1.93—2.11 (m, 2H), 6.01 (d, J=14.9 Hz, 1H), 7.20—7.35 (m, 5H), 7.36 (d, J=14.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−1.22, 15.49, 17.86, 127.56, 128.02, 131.12, 139.35, 146.75. Found: C, 76.62; H, 8.70%. Calcd for $C_{12}H_{16}Si$: C, 76.52; H, 8.56%. *m*CPBA (80% purity, 8.28 g, 38.4 mmol) was added to a solution of 1-methyl-1-[(*Z*)-2-phenylethenyl]silacyclobutane (3.61 g, 19.2 mmol) in $CHCl_3$ (60 ml) at 0 °C under argon atmosphere. After being stirred for 5 min at 0 °C and 1 h at room temperature, the resulting mixture was poured into saturated $NaHCO_3$ and extracted with hexane (60 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give 1-[(*Z*)-1,2-epoxy-2-phenylethyl]-1-methylsilacyclobutane (**29**, 2.33 g) in 59% yield: Bp 74—75 °C (bath temp, 0.3 Torr); IR (neat) 3026, 2960, 2922, 2868, 1497, 1452, 1386, 1250, 1187, 1121, 904, 869, 768, 740, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08 (s, 3H), 0.71—0.86 (m, 3H), 0.96—1.08 (m, 1H), 1.84—2.07 (m, 2H), 2.75 (d, J=5.2 Hz, 1H), 4.30 (d, J=5.2 Hz, 1H), 7.20—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−2.96, 13.56, 13.70, 18.49, 52.98, 57.04, 125.77,

127.51, 128.04, 137.63. Found: C, 70.42; H, 7.85%. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.83%.

1-(1-Hexynyl)-1-methylsilacyclobutane (27): Bp 91—92 °C (bath temp, 28 Torr); IR (neat) 2958, 2928, 2868, 2170, 1466, 1250, 1121, 870, 773, 719, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.40 (s, 3H), 0.92 (t, J=7.1 Hz, 3H), 0.96—1.09 (m, 2H), 1.12—1.25 (m, 2H), 1.35—1.60 (m, 4H), 1.96—2.23 (m, 2H), 2.28 (t, J=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ= 0.00, 13.59, 15.42, 18.20, 19.66, 21.93, 30.56, 82.79, 110.14. Found: C, 71.96; H, 10.89. Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91%.

1-[(*Z*)-1-Hexenyl]-1-methylsilacyclobutane: Bp 84—85 °C (bath temp, 28 Torr); IR (neat) 2958, 2924, 2854, 1604, 1466, 1249, 1120, 867, 774, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.36 (s, 3H), 0.90 (t, J=7.1 Hz, 3H), 0.96—1.24 (m, 4H), 1.25—1.44 (m, 4H), 1.97—2.23 (m, 4H), 5.62 (dt, J=13.8, 1.2 Hz, 1H), 6.38 (dt, J=7.4, 13.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−0.22, 13.99, 15.33, 18.44, 22.36, 31.82, 33.36, 127.58, 150.16. Found: C, 71.05; H, 11.93%. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.98%.

1-[(*Z*)-1,2-Epoxyhexyl]-1-methylsilacyclobutane (30): Bp 89—91 °C (bath temp, 5.0 Torr); IR (neat) 2956, 2926, 2858, 1467, 1414, 1251, 1122, 869, 772, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.39 (s, 3H), 0.91 (t, J=7.1 Hz, 3H), 0.95—1.10 (m, 2H), 1.12—1.30 (m, 2H), 1.30—1.59 (m, 6H), 2.00—2.26 (m, 2H), 2.41 (d, J=5.1 Hz, 1H), 3.16 (dt, J=5.1, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−2.64, 13.78, 13.96, 18.57, 22.54, 29.04, 31.25, 49.88, 57.56. Found: C, 64.88; H, 11.11%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94%.

Stereoselective Synthesis of (*Z*)-, or (*E*)-4-Alken-1-ol. Method A: The transformation of silacyclobutane **29** into (*Z*)-5-phenyl-4-penten-1-ol is representative. Methyllithium (1.1 M, diethyl ether solution, 2.0 ml, 2.2 mmol) was added to a solution of **29** (408 mg, 2.0 mmol) in THF (6 ml) at −78 °C under argon atmosphere. After being stirred for 30 min at −78 °C, the resulting mixture was poured into ice-cooled water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with THF (4 ml) and excess potassium hydride (35 wt% suspension in mineral oil) was added at 0 °C under argon atmosphere. The mixture was stirred for 1 h at 0 °C and 1 h at room temperature, poured into ice-cooled water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with THF (9 ml) and MeOH (9 ml). Potassium fluoride (128 mg, 2.2 mmol), $KHCO_3$ (1.0 g, 10 mmol), and H_2O_2 (30%, 1.13 g, 10 mmol) were added, and the whole was stirred for 5 h at room temperature. The resulting mixture was poured into saturated aqueous $NaHSO_3$ and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over aqueous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give (*Z*)-5-phenyl-4-penten-1-ol (**33**, 182 mg) in 56% yield. The spectral datum of (*Z*)-5-phenyl-4-penten-1-ol (**33**) is reported in Ref. 2. The spectral datum of (*E*)-5-Phenyl-4-penten-1-ol (**34**) has been also reported in Ref. 2.

Method B: Excess potassium hydride was added to a solution of **35** (150 mg, 0.57 mmol) at 0 °C under argon atmosphere. After being stirred for 30 min at 0 °C and 30 min at room temperature, the reaction mixture was poured into ice-cooled water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with THF (3 ml) and MeOH (3 ml). Potassium fluoride (66 mg, 1.14 mmol), $KHCO_3$ (570 mg, 5.7 mmol), and H_2O_2 (30%, 775 mg, 6.8 mmol) were added, and the whole was stirred for 5 h at room temperature. The resulting mixture was poured into saturated $NaHSO_3$ and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give (*Z*)-5-phenyl-4-penten-1-ol (**33**, 53 mg) in 57% yield. The spectral datum of (*Z*)-4-nonen-1-ol (**37**) has been reported.[2)]

Method C: The reaction of silacyclopentane **35** with trifluoroborane diethyl ether complex and successive treatment with H_2O_2 is representative. $BF_3{\cdot}OEt_2$ (0.38 ml, 3.1 mmol) was added dropwise to a solution of **35** in CH_2Cl_2 at 0 °C under argon atmosphere. After being stirred for 2 h at 0 °C, the reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude reaction mixture was diluted with THF (3 ml) and MeOH (3 ml). Potassium fluoride (36 mg, 0.62 mmol), $KHCO_3$ (310 mg, 3.1 mmol), and H_2O_2 (30%, 422 mg, 3.7 mmol) were added, and the whole was stirred for 5 h at room temperature. The mixture was poured into saturated $NaHSO_3$ and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give (*E*)-5-phenyl-4-penten-1-ol (**34**, 53 mg) in 57% yield. The spectral datum of (*E*)-4-nonen-1-ol (**38**) has been reported.[2)]

Reaction of 1-[(*Z*)-1,2-Epoxy-2-phenylethyl]-1-methylsilacyclobutane (29) or 1-[(*Z*)-1,2-Epoxyhexyl]-1-methylsilacyclobutane (30) with Lithium Isopropoxide. The reaction of silacyclobutane **29** with lithium isopropoxide is representative. Butyllithium (1.53 M, hexane solution, 0.78 ml, 1.2 mmol) was added to a solution of *i*-PrOH (0.092 ml, 1.2 mmol) in THF (2 ml) at 0 °C under argon atmosphere. The reaction mixture was stirred for 30 min and was added to a solution of silacyclobutane **29** (204 mg, 1.0 mmol) at −78 °C under argon atmosphere. After this mixture was stirred for 30 min at −78 °C, MeOH (0.3 ml) was added and the whole was stirred for another 5 min at −78 °C. The resulting mixture was poured into water and extracted with ethyl acetate (20 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography to give *erythro*-2-[1-hydroxy(phenyl)methyl]-1-isopropoxy-1-methylsilacyclopentane (**35**, 22/78 diastereomeric mixture, 171 mg) in 64% yield:

Faster moving band (minor product): R_f=0.4 (hexane/AcOEt=5/1); bp 88—89 °C (bath temp, 0.3 Torr); IR (neat) 3364 (broad), 2966, 2926, 2856, 1451, 1381, 1368, 1254, 1123, 1024, 879, 809, 783, 761, 751, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08 (s, 3H), 0.57—0.97 (m, 3H), 1.02—1.14 (m, 1H), 1.18 (d, J=6.0 Hz, 3H), 1.20 (d, J=6.0

Hz, 3H), 1.46—1.75 (m, 2H), 1.89—2.01 (m, 1H), 3.15—3.30 (bs, 1H, OH), 4.02 (sept, $J=6.0$ Hz, 1H), 5.08 (d, $J=5.7$ Hz, 1H), 7.16—7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta=-2.33$, 13.47, 23.51, 25.62, 27.62, 37.59, 66.20, 73.76, 125.82, 126.61, 127.88, 145.02. Found: C, 67.99; H, 9.14%. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15%.

Slower moving band (major product): $R_f=0.3$ (hexane/AcOEt=5/1); bp 88—89 °C (bath temp, 0.3 Torr); IR (neat) 3362 (broad), 2966, 2930, 2858, 1453, 1381, 1368, 1251, 1123, 1054, 1020 880, 786, 765, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=0.05$ (s, 3H), 0.41 (ddd $J=8.4$, 11.6, 15.2 Hz, 1H), 0.78—0.89 (m, 1H), 0.92 (d, $J=6.1$ Hz, 3H), 0.95 (d, $J=6.1$ Hz, 3H), 1.19—1.63 (m, 3H), 1.90—2.05 (m, 2H including OH), 2.18—2.29 (m, 1H), 3.51 (sept, $J=6.1$ Hz, 1H), 4.65 (d, $J=10.1$ Hz, 1H), 7.14—7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta=-2.66$, 13.14, 23.90, 25.33, 25.44, 30.70, 36.91, 65.09, 76.91, 126.67, 127.72, 128.37, 144.82. Found: C, 67.86; H, 9.38. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15%.

***erythro*-2-(1-Hydroxypentyl)-1-isopropoxy-1-methylsilacyclopentane (36).** Faster moving band (minor product): $R_f=0.4$ (hexane/AcOEt=5/1); bp 76—77 °C (bath temp, 1.0 Torr), IR (neat) 3298 (broad), 2954, 2930, 2856, 1728, 1459, 1381, 1369, 1351, 1254, 1172, 1124, 1029, 878, 810, 782, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=0.26$ (s, 3H), 0.60 (ddd, $J=8.2$, 12.3, 14.5 Hz, 1H), 0.68—0.85 (m, 1H), 0.91 (t, $J=6.7$ Hz, 3H), 1.17 (d, $J=6.0$ Hz, 3H), 1.18 (d, $J=6.0$ Hz, 3H), 1.25—1.73 (m, 9H), 1.80—2.08 (m, 2H), 2.93 (bs, 1H, OH), 3.89—4.00 (m, 1H), 4.03 (sept, $J=6.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta=-1.67$, 13.34, 14.13, 22.79, 23.62, 25.54, 25.63, 26.84, 28.46, 34.51, 36.35, 66.19, 71.74. Found: C, 63.77; H, 11.82%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.

Slower moving band (major product): $R_f=0.3$ (hexane/AcOEt=5/1); bp 76—77 °C (bath temp, 1.0 Torr); IR (neat) 3286 (broad), 2956, 2930, 2858, 1731, 1460, 1382, 1369, 1254, 1174, 1124, 1095, 1052, 1021, 879, 786, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=0.18$ (s, 3H), 0.41 (ddd, $J=8.8$, 12.0, 15.3 Hz, 1H), 0.80—1.05 (m, 1H), 0.92 (t, $J=7.0$ Hz, 3H), 1.03—1.75 (m, 10H), 1.18 (d, $J=6.1$ Hz, 6H), 1.85—2.23 (m, 2H including OH), 3.55—3.73 (m, 1H), 4.01 (sept, $J=6.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta=-3.07$, 12.42, 14.07, 22.64, 24.19, 25.54, 25.61, 28.25, 29.76, 36.02, 38.23, 65.40, 73.74. Found: C, 63.81; H, 11.59%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.

Stereoselective Synthesis of 1,4,5-Triols. The synthesis of *erythro*-1,4,5-nonanetriol (**39**) is representative. Potassium fluoride (60 mg. 1.04 mmol), $KHCO_3$ (500 mg, 5.0 mmol), and H_2O_2 (30%, 567 mg, 5.0 mmol) were added to a solution of silacyclopentane **36** (125 mg, 0.51 mmol) in THF (3 ml) and MeOH (3 ml) at 25 °C. The mixture was stirred for 20 h at room temperature, and filtered through an anhydrous Na_2SO_4 column. The filtrate was concentrated in vacuo. A residual oil was submitted to silica-gel column chromatography to give *erythro*-1,4,5-nonanetriol (**39**, 57 mg) in 64% yield: Mp 91.7—92.2 °C; IR ($CHCl_3$) 3300 (broad), 3004, 2932, 2870, 1467, 1458, 1381, 1050, 1006 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=0.92$ (t, $J=6,8$ Hz, 3H), 1.13—1.88 (m, 10H), 2.50—3.58 (bs, 3H, 3OH), 3.55—3.85 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta=14.02$, 22.73, 28.21, 28.36, 29.43, 31.24, 62.91, 74.69, 74.76. Found: C, 61.11; H, 11.56%. Calcd for $C_9H_{20}O_3$: C, 61.33; H, 11.44%.

***erythro*-1-Phenyl-1,2,5-pentanetriol (40):** Bp 125—126 °C (bath temp, 0.3 Torr); IR (neat) 3314 (broad), 2926, 2876, 1494, 1452, 1198, 1044, 1014, 912, 758, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.29$—1.42 (m, 1H), 1.47—1.68 (m, 3H), 3.42—3.51 (m, 1H), 3.52—3.63 (m, 4H including 3OH), 3.71—3.79 (m, 1H), 4.65 (d, $J=4.2$ Hz, 1H), 7.20—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta=28.09$, 29.07, 62.58, 75.30, 76.85, 126.68, 127.61, 128.25, 140.52. The analytical sample was prepared after acetylation. Treatment of **40** with acetic anhydride in pyridine at 25 °C for 24 h gave *erythro*-1,2,5-triacetoxy-1-phenylpentane. Bp 112—113 °C (bath temp, 0.3 Torr); IR (neat) 3030, 2960, 1733, 1498, 1454, 1434, 1370, 1218, 1030, 976, 760, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=1.50$—1.75 (m, 4H), 2.01 (s, 3H), 2.02 (s, 3H), 2.13 (s, 3H), 4.00 (t, $J=5.7$ Hz, 2H), 5.17—5.26 (m, 1H), 5.93 (d, $J=4.4$ Hz, 1H), 7.26—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta=20.84$, 24.59, 25.48, 63.48, 74.30, 75.42, 126.94, 128.25, 128.28, 136.17, 169.83, 170.45, 171.01. Found: C, 63.15; H, 7.04%. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%.

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 06453135 and 06227231 from the Ministry of Education, Science and Culture. One of us (K. Matsumoto) is grateful for Research Fellowship of the Japan Society for Promotion of Science for Japanese Junior Scientists.

References

1) A. Part of this work was published in communications; K. Matsumoto, K. Miura, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **32**, 6383 (1991); K. Matsumoto, Y. Takeyama, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **32**, 4545 (1991).

2) K. Matsumoto, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **31**, 6055 (1990); K. Matsumoto, Y. Aoki, K. Oshima, K. Utimoto, and, N. A. Rahman, *Tetrahedron*, **49**, 8487 (1993).

3) J. Laane, *J. Am. Chem. Soc.*, **89**, 1144 (1967).

4) Y. Ichinose, S. Matsunaga, K. Fugami, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **30**, 3155 (1989).

5) Y. Takeyama, Y. Ichinose, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **30**, 3159 (1989).

6) K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, *Organometallics*, **2**, 1694 (1983).

7) Metal-alkoxide-induced 1,2-rearrangement reactions of chloromethylsilanes have been reported: R. L. Kreeger, P. R. Menard, E. A. Sans, and H. Schechter, *Tetrahedron Lett.*, **26**, 1115 (1985); E. A. Sans and H. Schechter, *Tetrahedron Lett.*, **26**, 1119 (1985); P. F. Hudrlik, Y. M. Abdallah, and A. M. Hudrlik, *Tetrahedron Lett.*, **33**, 6743 (1992). Fluoride-ion-induced 1,2-rearrangement reactions of chloromethylsilanes have been reported: R. Damrauer, S. E. Danahey, and V. E. Yost, *J. Am. Chem. Soc.*, **106**, 7633 (1984); J. Y. Corey, E. R. Corey, V. H. Chang, M. A. Hauser, M. A. Leiber, T. E. Reinsel, and M. E. Riva, *Organometallics*, **3**, 1051 (1984); R. Damrauer, V. E. Yost, S. E. Danahey, and B. K. O'Connell, *Organometallics*, **4**, 1779 (1985); S. L. Aprahamian and H. Shechter, *Tetrahedron Lett.*, **31**, 1089 (1990).

8) Sodium-methoxide-induced ring enlargement of 1-chloromethylsilacyclopentane has been reported : N. S.

Nametkin, E. D. Babich, T. N. Arkhipova, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1978**, 836; *Chem. Abstr.*, **69**, 77317 (1968).

9) Cleavage of Si–Ph by HBF_4 has been reported: I. Fleming, R. Henning, and H. Plaut, *J. Chem. Soc., Chem. Commun.*, **1984**, 29.

10) Aluminium-chloride-induced 1,2-rearrangement reactions of chloromethylsilanes have been reported : M. Kumada and M. Ishikawa, *J. Organomet. Chem.*, **1**, 411 (1964); R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organomet. Chem.*, **3**, 455 (1965).

11) The Wagner–Meerwein type rearrangement involving migration of an organic group from silicon to the α-carbon atom has been reported: K. Tamao, T. Nakajima, and M. Kumada, *Organometallics*, **3**, 1655 (1984).

12) Aluminium-chloride-induced ring enlargement reactions of 1-chloromethylsilacyclopentane and 1-chloromethylsilacyclohexane have been reported : V. M. Vdovin, N. S. Nametkin, K. S. Pushchevaya, and A. V. Topchiev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, **1963**, 274; *Chem. Abstr.*, **58**, 13980 (1963); R. D. Bush and C. M. Golino, *J. Am. Chem. Soc.*, **96**, 7105 (1974); N. R. Pearson and L. H. Sommer, *J. Am. Chem. Soc.*, **101**, 2419 (1979).

13) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975).

14) W. E. Fristad, T. R. Bailey, and L. A. Paquette, *J. Org. Chem.*, **45**, 3028 (1980).

15) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Veralg, Berlin (1983), Chap. 1; S. Patai, "The Chemistry of Organosilicon Compounds," Wiley, New York (1989), Chap. 2, p. 204.

16) Y. Takeyama, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **31**, 6059 (1990).