Generation of 2-Lithio-2-(trimethylsilyl)silacyclopentane and 2-Lithio-2-(phenylthio)silacyclopentane and Their Use for the Synthesis of 1,4-Butanediols and γ-Hydroxy Ketones

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(Received January 17, 1994)

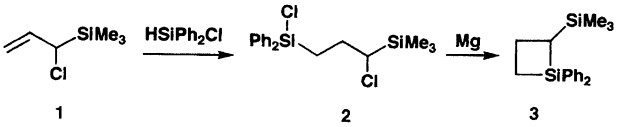
Treatment of 2-(trimethylsilyl)silacyclopentane with *t*-butyllithium in THF–HMPA gave 2-lithio-2-(trimethylsilyl)silacyclopentane in good yield. An addition of alkyl iodides to the lithium compound provided 2-alkyl-2-(trimethylsilyl)silacyclopentanes which were converted into 1-alkyl-1,4-butanediols upon treatment with H_2O_2–KF and successively with *n*-Bu_4NF. Reaction of 2-lithio-2-(trimethylsilyl)silacyclopentane with aldehydes gave 2-alkylidenesilacyclopentanes, which were transformed into γ-hydroxy ketones by oxidative cleavage of carbon–silicon bonds. 2-Lithio-2-(phenylthio)silacyclopentane, derived from 2-(phenylthio)silacyclopentane and *t*-butyllithium, afforded alkenyl sulfides having silylalkyl substituent upon treatment with aldehydes. Oxidative cleavage of carbon–silicon bonds followed by hydrolysis of alkenyl sulfide moiety also provided γ-hydroxy ketones.

It is important to have many ways to construct carbon–carbon bond in a predictable fashion. Organosilicon-based reagents have been widely used to make carbon–carbon bonds in a controlled and predictable way that is useful to synthetic organic chemists. α-Metallated organosilanes play a fundamental role in preparative organosilicon chemistry.[1] A wide range of variously functionalized organosilanes has been deprotonated α to silicon to give useful synthetic precursors. Among them, bis(trimethylsilyl)methyllithium[2] and phenylthio(trimethylsilyl)methyllithium[3] have been reported as effective reagents for the formation of alkenylsilanes and alkenyl sulfides. Here we wish to report a preparation of 2-lithio-2-(trimethylsilyl)silacyclopentane and 2-lithio-2-(phenylthio)silacyclopentane and their use in organic synthesis.[4]

(1) Generation of 2-Lithio-2-(trimethylsilyl)-silacyclobutane and 2-Lithio-2-(trimethylsilyl)-silacyclopentane and their Use in Organic Synthesis

In our study to develop new synthetic method using silacyclobutanes as a C_3 unit, we have attempted to obtain 2-lithiosilacyclobutane by an abstraction of α proton to silicon from 1,1-diphenylsilacyclobutane or 1,1-dimethylsilacyclobutane. However, various attempts that we have tried were unsuccessful. We then turned our attention to a generation of 2-lithio-2-(trimethylsilyl)silacyclobutane and 2-lithio-2-(trimethylsilyl)silacyclopentane which would be stabilized by two silicon atoms.

1,1-Diphenyl-2-(trimethylsilyl)silacyclobutane (**3**) and 1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (**4a**) were prepared as follows. Platinum-catalyzed hydrosilylation of 3-chloro-3-trimethylsilyl-1-propene (**1**) with chlorodiphenylsilane gave the dichloride **2**, which was converted into 2-(trimethylsilyl)silacyclobutane **3** upon treatment with magnesium (Eq. 1). 1,1-Diphenyl-2-(trimethylsilyl)silacyclopentane (**4a**) was generated by ring enlargement of 1,1-diphenylsilacyclobutane with lithium carbenoid derived from iodomethyltrimethylsilane and lithium diisopropylamide.[5] In the meantime, 1-isopropoxy-1-phenyl-2-(trimethylsilyl)silacyclopentane (**4b**) was prepared as shown in Eq. 3. Hydrosilylation of 4-chloro-4-trimethylsilyl-1-butene with dichlorophenylsilane in the presence of H_2PtCl_6 gave **5** which was treated with Mg and successively with *i*-PrOLi to afford **4b** as an isomeric mixture (*cis*:*trans*=1:1).



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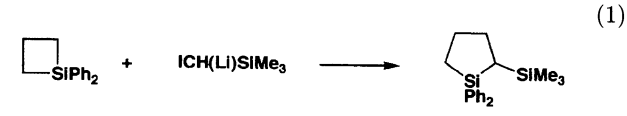
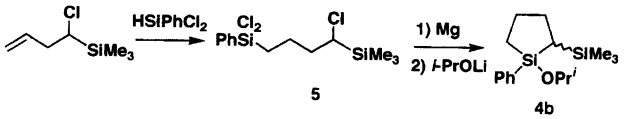


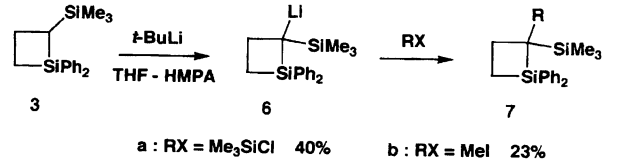
4a (2)



5 4b (3)

Generation of 2-lithio-2-(trimethylsilyl)silacyclobutane **6** was examined under various reaction conditions. Treatment of 2-(trimethylsilyl)silacyclobutane **3** with *t*-butyllithium in THF–HMPA at −78 °C followed by an addition of chlorotrimethylsilane provided 1,1-diphenyl-2,2-bis(trimethylsilyl)silacyclobutane (**7a**) in 40% yield (Eq. 4). The use of iodomethane instead of chlorotrimethylsilane gave 2-methyl-1,1-diphenyl-2-(trimethylsilyl)silacyclobutane (**7b**) in 23% yield. An attempt to obtain 2-deuterio-2-(trimethylsilyl)silacyclobutane upon treatment with D_2O resulted in failure since deuteroxide (OD^-), generated by the reaction of D_2O with 2-lithio-2-(trimethylsilyl)silacyclobutane **6**, readily attacked silicon in the four-membered ring to

give ring opening products (Eq. 5).[6] Same problem was encountered in the reaction of α-lithiosilacyclobutane **6** with carbonyl compound such as aldehyde or ketone as in the case of the reaction with D_2O. In fact, an addition of benzaldehyde to **6** afforded a complex mixture and expected adduct could not be observed in a reaction mixture. An oxide of the adduct may cause ring opening of silacyclobutane. The yield of **7** could not be improved in spite of various attempts. For instance, **3** was recovered upon treatment with *t*-butyllithium in THF or in THF–TMEDA. An addition of *s*-butyllithium to **3** in THF–HMPA resulted in the formation of a complex mixture containing ring-opened product ($Ph_2Si(s\text{-}Bu)CH_2CH_2CH_2SiMe_3$).



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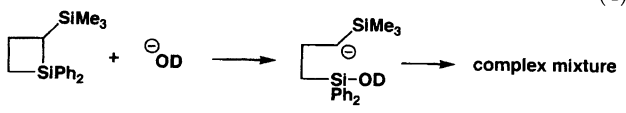
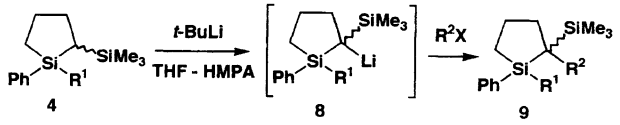


(5)

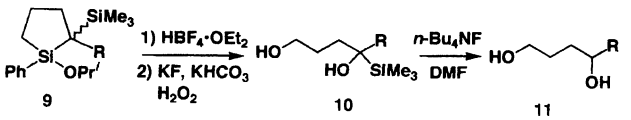
We then turned our attention to a generation of α-lithiosilacyclopentane species **8** from 2-(trimethylsilyl)-silacyclopentane **4** of which five-membered ring is stable toward base. An addition of *t*-butyllithium to a solution of **4a** in THF–HMPA at −78 °C gave dark red solution of **8a**. Treatment of the solution with iodomethane provided 2-methyl-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (**9a**) in 89% yield. The use of iodopentane or benzyl bromide gave the corresponding alkylated silacyclopentane **9b** or **9c** in 62 or 63% yield, respectively. Under the same reaction conditions, 1-isopropoxy-1-phenyl-2-(trimethylsilyl)silacyclopentane **4b** also afforded 2-lithio-2-(trimethylsilyl)silacyclopentane **8b** (orange solution) which provided the corresponding alkylated silacyclopentane **9d**, **9e**, and **9f** as 1 : 1 stereoisomeric mixtures upon treatment with alkyl halides (Scheme 1). Isomerically pure **4b** (*cis* or *trans*) as well as a 1 : 1 mixture of **4b** provided the same 1 : 1 isomeric mixtures **9d**, **9e**, and **9f**. Thus, a *cis*/*trans* mixture was used for the reaction without separation.



4a	R^1 = Ph	R^2X = MeI	**9a**	89%
4a	R^1 = Ph	R^2X = n-$C_5H_{11}I$	**9b**	62%
4a	R^1 = Ph	R^2X = $PhCH_2Br$	**9c**	63%
4b	R^1 = OPr^i	R^2X = MeI	**9d**	65%
4b	R^1 = OPr^i	R^2X = n-$C_5H_{11}I$	**9e**	43%
4b	R^1 = OPr^i	R^2X = $PhCH_2Br$	**9f**	49%

Scheme 1. Alkylation of 2-lithio-2-(trimethylsilyl)-silacyclopentane.

Treatment of the silacyclopentane **9a** with HBF_4 followed by oxidation with H_2O_2–KF–$KHCO_3$[7] gave the expected diol **10a** in only 20% yield along with unidentified complex mixtures. The oxidative cleavage of two carbon–silicon bonds of **9e** or **9f**, however, was easily performed upon treatment with HBF_4 followed by H_2O_2–KF–$KHCO_3$ to provide the corresponding silyl alcohol **10e** or **10f**. Protiodesilylation of **10** with n-Bu_4NF in DMF[8] gave 1,4-butanediol **11** (Eq. 6). Therefore, 1-isopropoxy-2-lithio-1-phenyl-2-(trimethylsilyl)silacyclopentane **8b** can be regarded as a synthon of 1-lithio-1,4-butanediol **12** (Eq. 7).

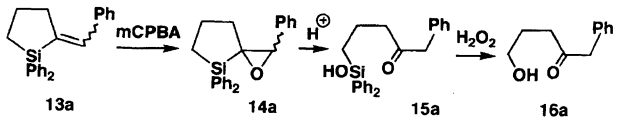


9e	R = n-C_5H_{11}	55%	75%
9f	R = CH_2Ph	79%	85%

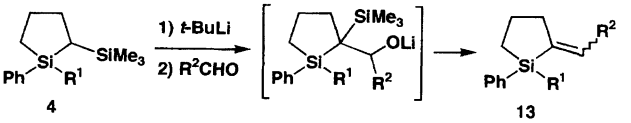
(6)

(7)

An addition of electrophile such as benzaldehyde to 2-lithio-2-(trimethylsilyl)silacyclopentane **8** afforded 2-alkylidenesilacyclopentane **13a** in moderate yield. The representative results are shown in Scheme 2. Vinylsilane **13** could be easily converted into γ-hydroxy ketone. Oxidation of **13a** with mCPBA followed by treatment of epoxide **14a** with 10% sulfuric acid in methanol[9] gave γ-silyl ketone **15a**. Oxidative cleavage of carbon–silicon bond of **15a** provided γ-hydroxy ketone **16a** in 30% overall yield from epoxysilane **14a** (Eq. 8). Isopropoxysilacyclopentane **13c** and **13d** could be converted into γ-hydroxy ketones **16a** and **16d** in a single step upon treatment with H_2O_2 (Eq. 9).

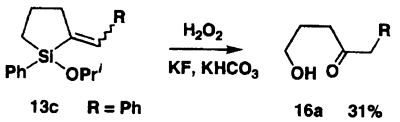


(8)



4a	R^1 = Ph	R^2 = Ph	**13a**	57%
4a	R^1 = Ph	R^2 = n-C_4H_9	**13b**	25%
4b	R^1 = OPr^i	R^2 = Ph	**13c**	49%
4b	R^1 = OPr^i	R^2 = t-Bu	**13d**	35%

Scheme 2. Reaction of 2-lithio-2-(trimethylsilyl)silacyclopentane with aldehyde.

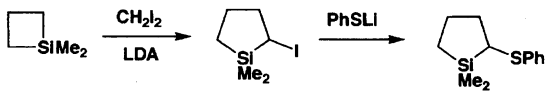


13c R = Ph 16a 31%
13d R = *t*-Bu 16d 72%

(9)

(2) Generation of 2-Lithio-2-(phenylthio)silacyclopentane and Its Use in Organic Synthesis

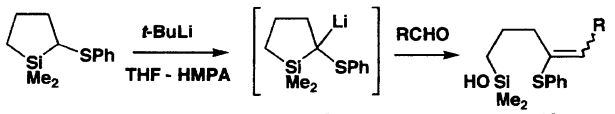
1,1-Dimethyl-2-(phenylthio)silacyclopentane (**17**) was prepared as follows. Ring enlargement of 1,1-dimethylsilacyclobutane with lithium carbenoid (CH_2(Li)I) gave 2-iodosilacyclopentane.[5] An addition of lithium benzenethiolate to 2-iodosilacyclopentane provided 1,1-dimethyl-2-(phenylthio)silacyclopentane (**17**) (Eq. 10).



17

(10)

(Phenylthiomethyl)trimethylsilane has been deprotonated by treatment with butyllithium in THF at −78 °C to give trimethylsily(phenylthio)methyllithium.[3] However, 1,1-dimethyl-2-(phenylthio)silacyclopentane (**17**) could not be deprotonated with butyllithium, *s*-butyllithium, or *t*-butyllithium in THF. It was essential to use HMPA as a cosolvent to obtain good yield of 2-lithio-2-(phenylthio)silacyclopentane **18**. *t*-Butyllithium provided the best result among three butyllithiums. Treatment of **17** with *t*-butyllithium in THF–HMPA at −78 °C gave dark orange solution of **18** which provided the corresponding alkenyl sulfides **19** in good yields as mixture of *E* and *Z* isomers upon treatment with aldehydes (Eq. 11). An addition of methanol-*d* (MeOD) provided 2-deuterio-2-phenylthio-1,1-dimethylsilacyclopentane in only 15% yield along with complex mixture containing ring-opened products which might be produced by an attack of MeOLi on 2-(phenylthio)silacyclopentane. This was confirmed by the following experiment. Treatment of **17** with *t*-BuOK in THF gave ring-opened product $SiMe_2(O\text{-}Bu^t)CH_2CH_2CH_2CH_2SPh$ in good yield.

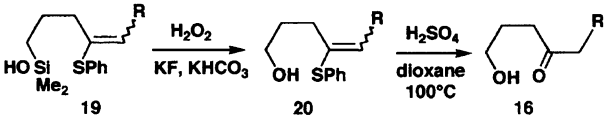


17 **18** **19**

a : R = Ph 57% b : R = *t*-Bu 40% c : R = *n*-Bu 55%

(11)

Oxidative cleavage of silicon-carbon bond of **19** followed by hydrolysis of the resulting alkenyl sulfides **20** afforded γ-hydroxy ketones **16** (Eq. 12). Hydrolysis of **19** proceeded easily at 100 °C in dioxane in the presence of trace amount of sulfuric acid.



19 **20** **16**

a: R = Ph 76% 84%
b: R = *t*-Bu 84% 83%
c: R = *n*-Bu 65% 70%

(12)

Experimental

Distillation of the products was performed using the Kugelrohr (Büchi) oven, and their boiling points were indicated by air-bath temperature 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 $CDCl_3$, and 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 1,1-Diphenyl-2-(trimethylsilyl)silacyclobutane (3). A mixture of 3-chloro-3-trimethylsilyl-1-propene[10] (5.29 g, 35.6 mmol) and chlorodiphenylsilane (7.0 ml, 35.6 mmol) was added via syringe pump to $H_2PtCl_6 \cdot 6H_2O$ (30 mg) over 1 h at 50 °C under argon atmosphere. After the completion of addition, the resulting mixture was stirred for 2 h at 50 °C. Distillation (180 °C, 1.0 Torr, 1 Torr=133.322 Pa) gave 1-chloro-3-chlorodiphenylsilyl-1-trimethylsilylpropane (**2**, 6.01 g, 16.4 mmol) in 46% yield: IR (neat) 3068, 3048, 2954, 2926, 2900, 1429, 1251, 1117, 864, 840, 737, 712, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.06 (s, 9H), 1.36 (ddd, J=3.5, 11.5, 13.5 Hz, 1H), 1.70—2.08 (m, 3H), 3.20 (dd, J=2.7, 10.0 Hz, 1H), 7.35—7.49 (m, 6H), 7.60—7.68 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−3.43, 14.91, 27.00, 54.73, 128.16, 130.62, 134.20, 134.27. Under argon atmosphere, tetrahydrofuran (THF, 2 ml) was added to magnesium (608 mg, 25 mmol). Dibromoethane (0.2 ml) was added to activate the magnesium metals and then a THF solution (15 ml) of the dichloride **2** (6.01 g, 16.4 mmol) was added via syringe pump over a 1 h period. The resulting mixture was heated at 50 °C for 2 h. The mixture was poured into 1 M HCl (1 M=1 mol dm^{-3}) and extracted with ethyl acetate (15 ml × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residual oil was submitted to silica-gel column chromatography (hexane as an eluant) to give the title compound **3** (3.15 g, 10.6 mmol) in 65% yield: Bp 88—90 °C (bath temp, 0.3 Torr); IR (neat) 3066, 3046, 2948, 2920, 1428, 1246, 1111, 864, 833, 719, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.19 (s, 9H), 1.34 (dddd, J=1.0, 1.3, 8.3, 11.6 Hz, 1H), 1.45 (dddd, J=1.3, 7.0, 10.3, 14.5 Hz, 1H), 1.71 (dddd, J=1.0, 5.5, 9.7, 14.5 Hz, 1H), 2.22 (dddd, J=7.0, 8.3, 9.7, 12.5 Hz, 1H), 2.46 (dddd, J=5.5, 10.3, 11.6, 12.5 Hz, 1H), 7.32—7.43 (m, 6H), 7.55—7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−1.26, 13.23, 16.49, 19.91, 127.83, 127.91, 129.49, 129.62, 134.27, 134.91, 136.03, 137.90. Found: C, 72.76; H, 8.36%. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16%.

Preparation of 1,1-Diphenyl-2-(trimethylsilyl)silacyclopentane (4a). The title compound was prepared following the reported procedure.[5]

1-Isopropoxy-1-phenyl-2-(trimethylsily)silacyclopentane (4b). 4-Chloro-4-trimethylsilyl-1-butene was prepared according to the reported procedure.[11] Under argon atmosphere, *s*-butyllithium (1.13 M cyclohexane solution, 90.9 ml, 100 mmol) was added to a THF (150 ml) solution of (chloromethyl)trimethylsilane (14.0 ml, 100 mmol) at −78 °C. TMEDA (15 ml, 100 mmol) was added and the mixture was stirred at −78 °C for 5 min and then at −55 °C for 30 min. The resulting mixture was recooled to −78 °C and allyl bromide (9.52 ml, 110 mmol) was added and then stirred for 30 min at −55 °C. The cooling bath was removed and the mixture was allowed to warm up to room temperature and poured into sat. NH_4Cl. Extraction with ether (60 ml × 2) followed by concentration of the dried organic layers provided a residual oil which was submitted to silica-gel column chromatography (hexane) to give 4-chloro-4-trimethylsilyl-1-butene (7.16 g, 43.4 mmol) in 43% yield: Bp 78—79 °C (50 Torr); IR (neat) 3076, 2956, 2898, 1428, 1251, 993, 916, 861, 840, 750, 695, 644 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.13 (s, 9H), 2.38 (dddt, J=7.1, 10.7, 15.0, 1.3 Hz, 1H), 2.56 (dddt, J=3.9, 6.5, 15.0, 1.3 Hz, 1H), 3.28 (dd, J=3.9, 10.7 Hz, 1H), 5.10 (ddt, J=3.3, 10.2, 1.3 Hz, 1H), 5.12 (ddt, J=3.3, 16.9, 1.3 Hz, 1H), 5.91 (ddt, J=10.2, 16.9, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−3.38, 37.74, 50.41, 116.73, 136.14. A catalyst ($H_2PtCl_6 \cdot 6H_2O$, 20 mg) was added to 4-chloro-4-trimethylsilyl-1-butene (4.17 g, 25.6 mmol) under argon atmosphere and the mixture was heated to 50 °C. Dichlorophenylsilane (3.74 ml, 25.6 mmol) was added via syringe pump over 30 min and the resulting mixture was stirred for 2 h at 50 °C. Direct distillation of the mixture afforded 1-chloro-4-dichlorophenylsilyl-1-(trimethylsilyl)butane (6.03 g, 17.7 mmol) in 69% yield: Bp 113 °C (0.5 Torr); IR (neat) 2950, 2896, 1431, 1251, 1118, 865, 840, 758, 737, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.09 (s, 9H), 1.28 (ddd, J=5.5, 5.5, 14.9 Hz, 1H), 1.42 (ddd, J=4.8, 11.4, 14.9 Hz, 1H), 1.59—1.82 (m, 3H), 1.90—2.05 (m, 1H), 3.24 (dd, J=4.1, 10.4 Hz, 1H), 7.43—7.57 (m, 3H), 7.70—7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.60, 19.86, 20.81, 35.33, 50.75, 128.35, 131.64, 132.42, 133.34. Found: C, 45.93; H, 6.24%. Calcd for $C_{13}H_{21}Cl_3Si_2$: C, 45.94; H, 6.23%. A THF (22 ml) solution of 1-chloro-4-dichlorophenylsilyl-1-(trimethylsilyl)butane (5.50 g, 16.2 mmol) was added to a suspension of magnesium (486 mg, 20 mmol), activated by 1,2-dibromoethane (0.1 ml), via syringe pump over 1 h under argon atmosphere. The mixture was heated at 50 °C for 2 h and cooled to 0 °C. A hexane-THF solution of *i*-PrOLi (from *i*-PrOH) (1.43 ml, 18.7 mmol) and butyllithium (1.55 M hexane solution, 11.0 ml, 17.0 mmol) was added and the resulting mixture was stirred for 20 min at 0 °C and then at room temperature for 3 h. The mixture was poured into 1 M HCl and extracted with ethyl acetate (20 ml × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography (hexane) gave the isopropoxysilacyclopentane **4b** (1 : 1 diasteremomeric mixture, 2.25 g, 7.7 mmol) in 48% yield.

Faster moving band: R_f=0.7 (hexane); Bp 92 °C (bath temp, 0.5 Torr); IR (neat) 2964, 2944, 2922, 2848, 1244, 1114, 1022, 876, 834, 733, 698, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.01 (dd, J=8.0, 10.7 Hz, 1H), 0.07 (s, 9H), 0.71—0.82 (m, 1H), 1.09—1.22 (m, 1H), 1.12 (d, J=6.2 Hz, 3H), 1.14 (d, J=6.2 Hz, 3H), 1.41—1.53 (m, 2H), 1.90—2.11 (m, 2H), 4.01 (sep, J=6.2 Hz, 1H), 7.36—7.47 (m, 3H), 7.58—7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.71, 12.56, 15.64, 25.67, 27.90, 28.62, 66.06, 127.64, 127.76, 129.07, 129.20, 133.77, 138.37. Found: C, 65.59; H, 9.82%. Calcd for $C_{16}H_{28}OSi_2$: C, 65.68: H, 9.65%.

Slower moving band: R_f=0.3 (hexane); Bp 92 °C (bath temp, 0.5 Torr); IR (neat) 2966, 2946, 2924, 2850, 1247, 1118, 1039, 1019, 874, 833, 735, 699, 654 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.27 (s, 9H), 0.12 (dd, J=6.9, 12.5 Hz, 1H), 0.70—0.98 (m, 2H), 1.22 (d, J=6.0 Hz, 3H), 1.23 (d, J=6.0 Hz, 3H), 1.25—1.43 (m, 2H), 1.93—2.18 (m, 2H), 4.12 (sep, J=6.0 Hz, 1H), 7.30—7.40 (m, 3H), 7.55—7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.00, 11.65, 14.93, 25.74, 27.44, 28.64, 65.57, 127.41, 127.52, 127.58, 129.46, 134.56, 137.24. Found: C, 65.65; H, 9.85%. Calcd for $C_{16}H_{28}OSi_2$: C, 65.68; H, 9.65%.

General Procedure for the Reaction of 2-Lithio-2-(trimethylsilyl)silacyclobutane or 2-Lithio-2-(trimethylsilyl)silacyclopentane with Alkyl Halide. Reaction of 2-lithio-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (**8a**) with iodomethane is representative. *t*-Butyllithium (1.66 M pentane solution, 0.72 ml, 1.2 mmol) was added to a solution of 1,1-diphenyl-2-(trimethylsilyl)silacyclopentane **4a** (0.31 g, 1.0 mmol) in THF (3.0 ml) and HMPA (0.4 ml) at −78 °C. The solution immediately turned dark red. After stirring for 30 min at −78 °C, iodomethane (0.19 ml, 3.0 mmol) was added and the resulting mixture was warmed to room temperature over 2 h. The mixture was poured into ice-cooled water and extracted with ethyl acetate (10 ml × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The residual oil was submitted to silica-gel column chromatography to give 2-methyl-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane **9a** (0.29 g) in 89% yield: Bp 112—114 °C (bath temp, 0.5 Torr); IR (neat) 3066, 2944, 2856, 1428, 1247, 1109, 857, 833, 735, 699, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.21 (s, 9H), 0.97 (s, 3H), 1.15—1.16 (m, 3H), 1.62—2.25 (m, 3H), 7.25—7.49 (m, 6H), 7.50—7.60 (m, 2H), 7.61—7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.35, 9.71, 14.19, 19.26, 22.29, 38.94, 127.52, 127.72, 128.90, 129.07, 135.03, 135.43, 135.56, 135.75. Found: C, 74.30; H, 8.80%. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69%.

1, 1- Diphenyl- 2, 2- bis(trimethylsilyl)silacyclobutane (7a): Mp 89—90 °C; IR (Nujol) 1429, 1248, 1103, 936, 890, 833, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.10 (s, 18H), 1.74—1.82 (m, 2H), 2.50—2.59 (m, 2H), 7.32—7.38 (m, 6H), 7.58—7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=1.48, 11.63, 16.45, 23.46, 127.76, 129.22, 134.40, 138.20. Found: C, 68.36; H, 9.03%. Calcd for $C_{21}H_{32}Si_3$: C, 68.40; H, 8.75%.

2-Methyl-1,1-diphenyl-2-(trimethylsilyl)silacyclobutane (7b): Bp 85—87 °C (bath temp, 0.3 Torr); IR (neat) 3066, 2946, 2852, 1429, 1247, 1109, 878, 833, 748, 715, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.17 (s, 9H), 1.14 (s, 3H), 1.56 (ddd, J=7.7, 10.1, 14.6 Hz, 1H), 1.67 (ddd, J=5.3, 9.7, 14.6 Hz, 1H), 1.91 (ddd, J=7.7, 9.7, 12.5 Hz, 1H), 2.52 (ddd, J=5.3, 10.1, 12.5 Hz, 1H), 7.32—7.42 (m, 6H), 7.58—7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−2.84, 8.43, 20.06, 29.63, 127.81, 127.86, 129.21, 129.42, 134.40, 134.51, 135.71, 136.89. Found: C, 73.48; H, 8.57%. Calcd for $C_{19}H_{26}Si_2$: C, 73.47; H, 8.44%.

2-Pentyl-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (9b): Bp 120—121 °C (bath temp, 0.3 Torr); IR

(neat) 3066, 2946, 2926, 2856, 1428, 1247, 1109, 833, 754, 732, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.15 (s, 9H), 0.76 (t, J=7.1 Hz, 3H), 0.92—1.45 (m, 10H), 1.52—1.68 (m, 1H), 1.81—2.06 (m, 3H), 7.28—7.40 (m, 6H), 7.56—7.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−0.11, 9.27, 14.04, 20.23, 22.49, 22.79, 27.31, 32.93, 34.21, 35.59, 127.51, 128.73, 129.03, 135.48, 135.54, 136.38, 137.49. Found: C, 75.66; H, 9.72%. Calcd for $C_{24}H_{36}Si_2$: C, 75.71; H, 9.53%.

2-Benzyl-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (9c): Mp 73—74 °C; IR (neat before crystallization) 3064, 3024, 2944, 2846, 1494, 1454, 1427, 1247, 1109, 876, 834, 760, 732, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.33 (s, 9H), 1.37—1.45 (m, 2H), 1.88—2.18 (m, 4H), 2.70 (d, J=14.0 Hz, 1H), 2.93 (d, J=14.0 Hz, 1H), 7.02—7.08 (m, 2H), 7.08—7.17 (m, 3H), 7.28—7.40 (m, 6H), 7.62—7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−0.20, 8.63, 22.31, 22.56, 35.04, 39.09, 125.75, 127.63, 127.69, 127.84, 128.95, 129.27, 130.24, 135.55, 136.09, 136.82, 141.21. Found: C, 77.87; H, 8.07%. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05%.

1-Isopropoxy-2-methyl-1-phenyl-2-(trimethylsilyl)silacyclopentane (9d). Faster moving band: R_f=0.6 (hexane); Bp 75—76 °C (bath temp, 0.3 Torr); IR (neat) 3066, 2946, 2858, 1428, 1381, 1369, 1245, 1113, 1020, 930, 857, 835, 764, 736, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.07 (s, 9H), 0.62 (s, 3H), 0.68—0.81 (m, 1H), 0.84—1.01 (m, 1H), 1.10 (d, J=6.0 Hz, 3H), 1.11 (d, J=6.0 Hz, 3H), 1.15—1.25 (m, 1H), 1.33—1.43 (m, 1H), 1.68—1.93 (m, 2H), 3.92 (sep, J=6.0 Hz, 1H), 7.30—7.40 (m, 3H), 7.52—7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−2.46, 11.67, 12.70, 18.25, 23.44, 25.57, 25.63, 37.58, 66.23, 127.56, 129.26, 134.37, 135.89. Found: C, 66.84; H, 10.14%. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86%.

Slower moving band: R_f=0.4 (hexane); Bp 75—76 °C (bath temp, 0.3 Torr); IR (neat) 3066, 2946, 2858, 1429, 1382, 1369, 1248, 1114, 1025, 861, 834, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.35 (s, 9H), 0.85—0.99 (m, 2H), 1.08 (s, 3H), 1.15 (d, J=6.0 Hz, 3H), 1.17 (d, J=6.0 Hz, 3H), 1.47 (dddd, J=1.3, 3.4, 5.4, 13.2 Hz, 1H), 1.62 (ddd, J=6.4, 10.6, 13.2 Hz, 1H), 1.74—1.95 (m, 2H), 4.04 (sep, J=6.0 Hz, 1H), 7.28—7.39 (m, 3H), 7.57—7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−3.06, 8.80, 13.71, 16.61, 21.49, 25.53, 25.75, 35.94, 66.12, 127.47, 129.44, 134.85, 137.92. Found: C, 66.43; H, 10.06%. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86%.

1-Isopropoxy-2-pentyl-1-phenyl-2-(trimethylsilyl)-silacyclopentane: (9e): Bp 94—95 °C (bath temp, 0.3 Torr); IR (neat) 2952, 2926, 2870, 1429, 1380, 1368, 1247, 1171, 1114, 1023, 874, 834, 751, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.30 (s, 9H), 0.92 (t, J=7.0 Hz, 3H), 0.93—0.99 (m, 2H), 1.12 (d, J=6.0 Hz, 3H), 1.13 (d, J=6.0 Hz, 3H), 1.22—1.90 (m, 12H), 3.97 (sep, J=6.0 Hz, 1H), 7.30—7.38 (m, 3H), 7.56—7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.94, 9.66, 14.27, 19.50, 22.26, 22.70, 25.54, 25.70, 28.16, 33.46, 34.14, 35.22, 65.97, 127.43, 129.44, 134.97, 137.82. Found: C, 69.63; H, 10.77%. Calcd for $C_{21}H_{38}OSi_2$: C, 69.54: H, 10.56%.

2-Benzyl-1-isopropoxy-1-phenyl-2-(trimethylsilyl)silacyclopentane (9f). Faster moving band: R_f=0.5 (hexane); Bp 95—97 °C (bath temp, 0.3 Torr); IR (neat) 3062, 3024, 2966, 2924, 1453, 1428, 1381, 1368, 1245, 1112, 1020, 878, 836, 763, 736, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.03 (s, 9H), 0.75—0.92 (m, 2H), 1.12 (d, J=6.1 Hz, 3H), 1.14 (d, J=6.1 Hz, 3H), 1.76—1.92 (m, 4H), 2.39 (d, J=14.1 Hz, 1H), 2.48 (d, J=14.1 Hz, 1H), 3.94 (sep, J=6.1 Hz, 1H), 6.84—6.91 (m, 2H), 7.04—7.12 (m, 3H), 7.35—7.42 (m, 3H), 7.58—7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−0.56, 10.84, 20.78, 23.24, 25.42, 25.61, 32.88, 38.15, 66.42, 125.50, 127.48, 127.80, 129.51, 130.26, 134.66, 135.90, 141.47. Found: C, 71.96; H, 9.07%. Calcd for $C_{23}H_{34}OSi_2$: C, 72.18; H, 8.96%.

Slower moving band: R_f=0.4 (hexane); Bp 94—96 °C (bath temp, 0.3 Torr); IR (neat) 3062, 3024, 2964, 2926, 1453, 1428, 1381, 1368, 1248, 1114, 1020, 876, 835, 761, 736, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.46 (s, 9H), 0.85—0.97 (m, 1H), 1.03 (ddd, J=7.9, 7.9, 15.2 Hz, 1H), 1.17 (d, J=6.1 Hz, 3H), 1.18 (d, J=6.1 Hz, 3H), 1.65—1.84 (m, 3H), 1.86—1.96 (m, 1H), 3.08 (s, 2H), 4.01 (sep, J=6.1 Hz, 1H), 7.12—7.26 (m, 3H), 7.31—7.41 (m, 5H), 7.61—7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=−1.22, 9.73, 21.56, 22.18, 25.57, 25.70, 34.06, 37.19, 66.06, 125.64, 127.56, 127.63, 129.70, 130.74, 135.11, 137.11, 142.06. Found: C, 72.30; H, 9.18%. Calcd for $C_{23}H_{34}OSi_2$: C, 72.18; H, 8.96%.

Oxidative Cleavage of Silacyclopentane into 1,4-Diol. A typical experimental procedure is as follows. Diethyl ether–tetrafluoroboric acid (1/1) ($Et_2O{\cdot}HBF_4$, 85%, 0.24 ml, 1.5 mmol) was added to a solution of silacyclopentane **9f** (147 mg, 0.39 mmol) in CH_2Cl_2 (4.0 ml) at 0 °C under argon atmosphere and the mixture was stirred for 1 h at 0 °C and then at room temperature for 3 h. The resulting mixture was concentrated in vacuo to give a residual oil which was dissolved in THF (3.0 ml) and MeOH (3.0 ml). Potassium fluoride (89 mg, 1.5 mmol) and $KHCO_3$ (0.39 g, 3.9 mmol) were added to the solution and H_2O_2 (30%, 0.35 g, 3.1 mmol) was successively added. The mixture was stirred for another 5 h at room temperature 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 5-phenyl-4-trimethylsilyl-1,4-pentanediol (**10f**, 77 mg, 0.31 mmol) in 79% yield: Mp 78—79 °C; IR (Nujol) 3376 (broad), 1245, 1066, 989, 886, 865, 836, 751, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (s, 9H), 1.45—1.82 (m, 6H including OH), 2.80 (d, J=13.5 Hz, 1H), 2.92 (d, J=13.5 Hz, 1H), 3.57 (dt, J=11.0, 6.2 Hz, 1H), 3.61 (dt, J=11.0, 6.2 Hz, 1H), 7.18—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−2.97, 27.76, 34.43, 42.55, 63.40, 67.99, 126.47, 128.24, 130.59, 136.80. Found: C, 66.37; H, 9.56%. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58%.

4-Trimethylsilyl-1,4-nonanediol (10e): Bp 94—95 °C (bath temp, 0.3 Torr); IR (neat) 3336 (broad), 2952, 2930, 2860, 1459, 1248, 1056, 837, 751, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (s, 9H), 0.87 (t, J=6.8 Hz, 3H), 1.16—1.42 (m, 6H), 1.45—1.68 (m, 6H), 1.70—1.85 (bs, 2H, OH), 3.56—3.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=2.88, 14.07, 22.57, 23.68, 26.47, 32.68, 33.64, 37.86, 63.50, 68.53. Found: C, 61.82; H, 12.33%. Calcd for $C_{12}H_{28}O_2Si$: C, 62.01; H, 12.14%.

5-Phenyl-1,4-pentanediol (11f). Tetrabutylammonium fluoride (1.0 M THF solution, 0.92 ml, 0.92 mmol) was added to a solution of **10f** (77 mg, 0.31 mmol) in DMF (3 ml) at room temperature under argon atmosphere. The mixture was stirred for 48 h and poured into brine and extracted with ethyl acetate (15 ml × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. Purification of

the product by silica-gel column chromatography provided the title diol **11f** (47 mg, 0.26 mmol) in 85% yield: Bp 103—105 °C (bath temp, 0.3 Torr); IR (neat) 3304 (broad), 2922, 2868, 1454, 1007, 738, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 1.41—1.61 (m, 1H), 1.63—1.78 (m, 3H), 2.50—2.82 (bs, 2H, OH), 2.70 (dd, J=7.9, 13.4 Hz, 1H), 2.80 (dd, J=4.9, 13.4 Hz, 1H), 3.59 (dt, J=10.8, 5.4 Hz, 1H), 3.67 (dt, J=10.8, 5.5 Hz, 1H), 3.84 (dddd, J=2.7, 4.8, 8.0, 8.0 Hz, 1H), 7.17—7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=29.17, 33.74, 44.10, 62.77, 72.65, 126.42, 128.50, 129.37, 138.45. Found: C, 73.20; H, 9.09%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

General Procedure for the Reaction of 2-Lithio-2-(trimethylsilyl)silacyclopentane with Aldehyde. Reaction of 2-lithio-1,1-diphenyl-2-(trimethylsilyl)silacyclopentane (**8a**) with benzaldehyde is representative. *t*-Butyllithium (1.66 M pentane solution, 0.72 ml, 1.2 mmol) was added to a solution of 1,1-diphenyl-2-(trimethylsilyl)-silacyclopentane **4a** (0.31 g, 1.0 mmol) in THF (3.0 ml) and HMPA (0.4 ml) at −78 °C. The solution immediately turned dark red. After stirring for 30 min at −78 °C, benzaldehyde (0.21 g, 2.0 mmol) was added and the resulting mixture was warmed to room temperature over 2 h. The mixture was poured into ice-cooled water and extracted with ethyl acetate (10 ml × 3). The combined orgainc layers were dried over Na_2SO_4 and concentrated. The residual oil was submitted to silica-gel column chromatography to give 2-benzylidene-1,1-diphenylsilacyclopentane (**13a**, 0.19 g) in 57% yield as a stereoisomeric mixture:

Faster moving band (major product): R_f=0.5 (hexane); Bp 122—124 °C (bath temp, 0.3 Torr); IR (neat) 3064, 3046, 3018, 2918, 2856, 1428, 1113, 1044, 955, 768, 751, 735, 696, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (t, J=7.1 Hz, 2H), 1.89 (tt, J=6.6, 7.1 Hz, 2H), 2.74 (dt, J=1.9, 6.6 Hz, 2H), 6.96—7.06 (m, 3H), 7.14—7.21 (m, 2H), 7.23—7.38 (m, 6H), 7.41—7.44 (m, 1H), 7.48—7.56 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=16.08, 24.67, 42.90, 126.88, 127.82, 128.10, 129.34, 134.77, 135.30, 138.86, 140.35, 142.65. Found: C, 84.81; H, 6.68%. Calcd for $C_{23}H_{22}Si$: C, 84.60; H, 6.79%.

Slower moving band (minor product): R_f=0.5 (hexane); Bp 122—124 °C (bath temp, 0.3 Torr); IR (neat) 3064, 3046, 3018, 2918, 2856, 1428, 1113, 1044, 955, 768, 751, 735, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (t, J=7.2 Hz, 2H), 1.95 (tt, J=6.8, 7.2 Hz, 2H), 2.82 (dt, J=2.6, 6.8 Hz, 2H), 6.92 (t, J=2.6 Hz, 1H), 7.17—7.55 (m, 12H), 7.57—7.67 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=12.21, 25.65, 34.95, 126.90, 127.89, 128.13, 128.95, 129.49, 135.03, 135.24, 135.73, 138.31, 138.86. Found: C, 84.61; H, 6.84%. Calcd for $C_{23}H_{22}Si$: C, 84.60; H, 6.79%.

2-Pentylidene-1,1-diphenylsilacyclopentane (13b): Bp 93—95 °C (bath temp, 0.3 Torr); IR (neat) 3064, 3046, 2922, 2852, 1428, 1112, 833, 734, 698, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.66 (t, J=7.1 Hz, 3H), 0.96—1.16 (m, 4H), 1.17 (t, J=7.1 Hz, 2H), 1.86 (tt, J=6.6, 7.1 Hz, 2H), 1.97 (q, J=7.3 Hz, 2H), 2.45 (dt, J=1.6, 6.6 Hz, 2H), 6.33 (tt, J=1.6, 7.3 Hz, 1H), 7.30—7.42 (m, 6H), 7.55—7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=13.84, 14.44, 22.21, 25.54, 31.61, 34.87, 39.08, 127.09, 129.25, 135.27, 135.50, 139.56, 141.10. Found: C, 82.67; H, 8.59%. Calcd for $C_{21}H_{26}Si$: C, 82.29; H, 8.55%.

2-Benzylidene-1-isopropoxy-1-phenylsilacyclopentane (13c): Bp 102—103 °C (bath temp, 0.3 Torr); IR (neat) 2968, 2922, 2864, 1429, 1172, 1117, 1025, 878, 764, 735, 696, 657 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05 (d, J= 6.1 Hz, 3H), 1.08—1.20 (m, 2H), 1.25 (d, J=6.1 Hz, 3H), 1.79—2.01 (m, 2H), 2.62 (ddd, J=2.0, 6.4, 15.2 Hz, 1H), 2.72 (ddd, J=2.0, 6.4, 15.2 Hz, 1H), 4.10 (sep, J=6.1 Hz, 1H), 7.10—7.21 (m, 3H), 7.23—7.46 (m, 6H), 7.58—7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.39, 23.94, 25.05, 25.72, 41.61, 66.34, 127.02, 127.65, 127.88, 128.11, 129.49, 134.03, 134.42, 138.65, 140.55, 141.48. Found C, 77.63; H, 8.00%. Calcd for $C_{20}H_{24}OSi$: C, 77.86; H, 7.84%.

2-(2,2-Dimethylpropylidene)-1-isopropoxy-1-phenylsilacyclopentane (13d): Bp 81—82 °C (bath temp, 0.3 Torr); IR (neat) 2954, 2862, 1461, 1429, 1381, 1367, 1202, 1172, 1117, 1025, 878, 760, 734, 709, 697, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.78 (dt, J=15.5, 7.2 Hz, 1H), 0.83 (dt, J=15.5, 6.9 Hz, 1H), 1.13 (s, 9H), 1.20 (d, J=6.1 Hz, 3H), 1.69 (dtt, J=19.0, 6.6, 7.2 Hz, 1H), 1.88 (dtt, J=19.0, 6.6, 6.9 Hz, 1H), 2.53 (dt, J=2.6, 6.6 Hz, 2H), 4.08 (sep, J=6.1 Hz, 1H), 5.94 (t, J=2.6 Hz, 1H), 7.31—7.42 (m, 3H), 7.60—7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=11.65, 24.01, 25.58, 30.23, 31.65, 35.42, 65.75,. 127.66, 129.50, 134.43, 136.25, 150.95, 150.97. Found: C, 74.75; H, 9.97%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.

2,4,4-Triphenyl-1-oxa-4-silaspiro[2.4]heptane (14a). Faster moving band: R_f=0.4 (EtOAc/hexane=1/20); mp 108—109 °C; IR (neat before crystallization) 3064, 3044, 2940, 2856, 1453, 1428, 1114, 1026, 765, 735, 697, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20—1.40 (m, 2H), 1.42—1.56 (m, 1H), 1.67—1.83 (m, 2H), 1.92—2.07 (m, 1H), 4.08 (s, 1H), 7.21—7.38 (m, 5H), 7.39—7.50 (m, 6H), 7.53—7.61 (m, 2H), 7.72—7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=12.30, 23.20, 32.29, 61.69, 65.47, 126.20, 127.26, 127.98, 128.06, 128.20, 129.97, 130.04, 132.04, 133.74, 135.11, 135.47, 136.98. Found: C, 80.45; H, 6.52%. Calcd for $C_{23}H_{22}OSi$: C, 80.65: H, 6.48%.

Slower moving band: R_f=0.3 (EtOAc/hexane=1/20); mp 108—109 °C; IR (neat before crystalization) 3064, 3046, 2934, 2858, 1455, 1429, 1114, 1029, 910, 757, 734, 697, 656 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.21—1.36 (m, 2H), 1.75—1.85 (m, 1H), 2.01—2.19 (m, 3H), 4.10 (s, 1H), 6.82—7.08 (m, 9H), 7.14—7.23 (m, 1H), 7.32—7.46 (m, 3H), 7.58—7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.61, 23.62, 40.16, 62.21, 67.40, 125.72, 127.24, 127.43, 127.78, 127.96, 129.19, 129.76, 131.86, 133.65, 135.00, 135.58, 138.42. Found: C, 80.42; H, 6.48%. Calcd for $C_{23}H_{22}OSi$: C, 80.65; H, 6.48%.

2,2-Dimethyl-7-hydroxyl-4-heptanone (16d): Bp 84—85 °C (bath temp, 1.0 Torr); IR (neat) 3368 (broad), 2950, 2868, 1709, 1479, 1466, 1365, 1233, 1104, 1059, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (s, 9H), 1.82 (tt, J=6.2, 6.9 Hz, 2H), 1.95—2.12 (bs, 1H, OH), 2.33 (s, 2H), 2.54 (t, J=6.9 Hz, 2H), 3.64 (t, J=6.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=26.35, 29.70, 31.01, 41.86, 55.02, 62.25, 211.53. Found: C, 68.59; H, 11.72%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46%.

1,1-Dimethyl-2-(phenylthio)silacyclopentane (17). Butyllithium (1.57 M hexane solution, 0.64 ml, 1.0 mmol) was added to a solution of benzenethiol (0.21 ml, 2.0 mmol) in THF (2.0 ml) at 0 °C under argon atmosphere. After stirring for 20 min, a THF solution of 2-iodo-1,1-dimethylsilacyclopentane (0.24 g, 1.0 mmol) was added. The resulting mixture was stirred at 0 °C for 1 h and then at room temperature for 3 h. The 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 con-

centrated. The residual oil was submitted to silica-gel column chromatography to give the title compound **17** (165 mg, 0.74 mmol) in 74% yield: Bp 123—125 °C (bath temp, 16 Torr); IR (neat) 2930, 2854, 1583, 1479, 1438, 1250, 871, 842, 820, 785, 735, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.227 (s, 3H), 0.232 (s, 3H), 0.70 (t, J=14.1 Hz, 2H), 1.45—1.64 (m, 2H), 1.80—1.94 (m, 1H), 2.01—2.14 (m, 1H), 2.68 (t, J=13.8 Hz, 1H), 7.08—7.14 (m, 1H), 7.22—7.37 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−3.80, −1.70, 12.77, 24.16, 29.65, 35.32, 125.04, 127.96, 128.62, 138.52. Found: C, 64.77; H, 8.02%. Calcd for $C_{12}H_{18}SSi$: C, 64.80; H, 8.16%.

General Procedure for the Reaction of 2-Lithio-1,1-dimethyl-2-(phenylthio)silacyclopentane 18 with Aldehyde. *t*-Butyllithium (1.6 M pentane solution, 0.7 ml, 1.1 mmol) was added to a solution of 1,1-dimethyl-2-(phenylthio)silacyclopentane **17** (0.24 g, 1.1 mmol) in THF (6.0 ml) and HMPA (0.8 ml) at −78 °C under argon atmosphere. The solution immediately turned dark orange. After stirring for 15 min at −78 °C, benzaldehyde (106 mg, 1.0 mmol) was added and the resulting mixture was stirred at −78 °C for 15 min and then at 0 °C for another 15 min. The mixture was poured into water and extracted with ethyl acetate (10 ml × 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The residual oil was submitted to silica-gel column chromatography to give alkenylsilanol **19a** (0.19 g) in 57% yield. Oxidative cleavage of silicon–carbon bond of **19a** (0.19 g) was performed as described above with H_2O_2 (30%, 0.33 g, 3.0 mmol) in MeOH (3 ml) and THF (3 ml) containing KF (70 mg, 1.1 mmol) and $KHCO_3$ (0.24 g, 2.2 mmol) to afford 5-phenyl-4-phenylthio-4-penten-1-ol (**20a**, 0.12 g) in 76% yield.

Faster moving band: R_f=0.25 (EtOAc/hexane=1/3); bp 117—118 °C (bath temp, 0.3 Torr); IR (neat) 3320 (braod), 3052, 3018, 2940, 2870, 1582, 1475, 1439, 1067, 1024, 746, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25—1.45 (broad s, 1H), 1.88 (tt, J=6.3, 7.6 Hz, 2H), 2.53 (t, J=7.6 Hz, 2H), 3.58 (t, J=6.3 Hz, 2H), 6.70 (s, 1H), 7.20—7.38 (m, 8H), 7.41—7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=27.71, 31.59, 62.08, 126.96, 127.40, 128.33, 128.40, 129.13, 131.71, 131.91, 133.80, 136.78, 138.43. Found: C, 74.97; H, 6.58%. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71%.

Slower moving band: R_f=0.20 (EtOAc/hexane=1/3); bp 118—120 °C (bath temp, 0.3 Torr), IR (neat) 3564 (broad), 3292, 3052, 2928, 2866, 1582, 1475, 1438, 1068, 1024, 742, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30—1.58 (broad s, 1H), 1.81 (tt, J=6.9, 7.4 Hz, 2H), 2.39 (t, J=7.4 Hz, 2H), 3.59 (t, J=6.9 Hz, 2H), 6.84 (s, 1H), 7.12—7.38 (m, 8H), 7.52—7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=31.69, 34.34, 61.82, 126.79, 127.26, 127.97, 128.92, 129.16, 130.89, 132.77, 133.94, 134.94, 136.40. Found: C, 75.46; H, 6.79%. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71%.

6,6-Dimethyl-4-phenylthio-4-hepten-1-ol (20b, 8 : 2 Isomeric Mixture): Bp 100—102 °C (bath temp, 0.3 Torr), IR (neat) 3306 (broad), 2954, 2866, 1702, 1478, 1439, 1363, 1195, 1067, 1025, 739, 690 cm^{-1}; ^1H NMR ($CDCl_3$) for major product δ=1.99 (s, 9H), 1.50—1.70 (broad s, 1H, OH), 1.75—1.90 (m, 2H), 2.35—2.45 (m, 2H), 3.61 (t, J= 6.4 Hz, 2H), 6.07 (s, 1H), 7.15—7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=28.15, 30.93, 32.14, 34.17, 62.49, 126.03, 128.87, 129.12, 132.47, 136.20, 149.15. minor product δ=1.25 (s, 9H), 1.50—1.70 (broad s, 1H, OH), 1.65—1.75 (m, 2H), 2.10—2.20 (m, 2H), 3.56 (t, J=6.4 Hz, 2H), 5.99 (s, 1H), 7.15—7.35 (m, 5H). Found: C, 71.81; H, 8.89%. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86%.

4-Phenylthio-4-nonen-1-ol (20c). Faster moving band: R_f=0.35 (EtOAc/hexane=1/3); bp 105—107 °C (bath temp, 0.3 Torr), IR (neat) 3330 (broad), 3056, 2930, 2870, 1581, 1473, 1437, 1066, 1023, 745, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (t, J=7.1 Hz, 3H), 1.22—1.42 (m, 4H), 1.53—1.73 (broad s, 1H), 1.76 (tt, J=6.4, 7.5 Hz, 2H), 2.16 (q, J=7.4 Hz, 2H), 2.29 (t, J=7.5 Hz, 2H), 3.61 (t, J=6.4 Hz, 2H), 5.92 (t, J=7.4 Hz, 1H), 7.12—7.21 (m, 1H), 7.21—7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=13.96, 22.37, 27.19, 28.89, 31.43, 31.56, 62.10, 126.29, 128.88, 129.31, 129.81, 132.45, 138.17.

Slower moving band: R_f=0.30 (EtOAc/hexane=1/3); bp 105—107 °C (bath temp, 0.3 Torr), IR (neat) 3318 (broad), 3052, 2938, 2870, 1581, 1492, 1476, 1440, 1069, 1024, 741, 690, cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, J=7.1 Hz, 3H), 1.22—1.44 (m, 4H), 1.58—1.68 (broad s, 1H, OH), 1.76 (tt, J=6.4, 7.5 Hz, 2H), 2.25 (t, J=7.5 Hz, 2H), 2.35 (q, J=7.2 Hz, 2H), 3.58 (t, J=6.4 Hz, 2H), 5.94 (t, J=7.2 Hz, 1H), 7.11—7.21 (m, 1H), 7.21—7.39 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=13.97, 22.32, 29.62, 31.44, 31.54, 33.57, 62.02, 125.80, 125.88, 128.82, 129.31, 135.28, 137.42. Found: C, 71.45; H, 9.12%. Calcd $C_{15}H_{22}OS$: C, 71.95; H, 8.86%.

Financial supports by the Ministry of Education, Science and Culture of Japan (Grant-in-Aid for Scientific Research in Priority Areas No. 05650877) and JSPS Cooperation Programmes with Southeast Asian Countries under the core university system are acknowledged.

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