Noncatalyzed Stereoselective Allylation of Carbonyl Compounds with Allylsilacyclobutanes

Kozo Matsumoto, Koichiro Oshima,* and Kiitiro Utimoto*

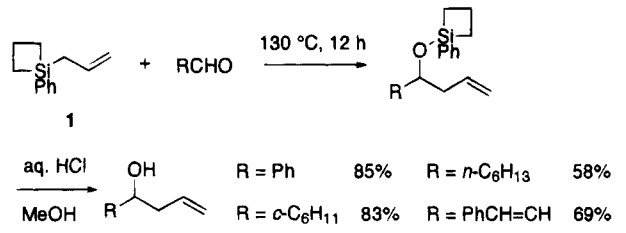
Division of Material Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Yoshida, Kyoto 606-01 Japan

Received August 26, 1994

Lewis acid-promoted allylation of carbonyl compounds with allylic trimethylsilanes proceeds with high regioselectivity to give rearranged homoallylic alcohols.[1] Recently, an uncatalyzed regio- and stereoselective allylation of aldehydes with pentacoordinate allylsilicate was reported.[2] In the course of our studies[3] on the use of silacyclobutane in organic synthesis, we learned that silacyclobutane is readily attacked by a nucleophile to give pentacoordinate silicate; in other words, silacyclobutane is a stronger Lewis acid than the corresponding tetraalkylsilanes. We conjectured that, if allylsilacyclobutane is a strong enough Lewis acid to activate a carbonyl compound, then the allylation reaction should proceed without catalyst to give a homoallylic alcohol with high regio- and stereoselectivity.[4] Indeed, heating a mixture of 1-allyl-1-phenylsilacyclobutane (**1**) and benzaldehyde at 130 °C for 12 h under argon in a sealed tube provided 1-phenyl-3-buten-1-ol in 85% yield, after workup with 1 M HCl followed by silica gel column chromatography (Scheme 1). On the other hand, the use of allyldimethylphenylsilane instead of allylsilacyclobutane resulted in the recovery of starting benzaldehyde and allylsilane, after heating at 160 °C for 24 h. Thus, the Lewis acidity of silacyclobutane is critical for the successful allylation of aldehydes. The use of heptanal or cyclohexanecarbaldehyde gave the corresponding allylated products. Reaction with cinnamaldehyde afforded the 1,2-adduct exclusively. Reaction with ketones such as cyclohexanone, did not proceed under the same reaction conditions and ketone was recovered unchanged.

Stereochemical control in the addition of 1-(2-alkenyl)-silacyclobutane to aldehydes was examined. (*E*)-1-(2-Hexenyl)silacyclobutane (**2**)[5] provided *anti* homoallylic alcohol **3** with high regio- and stereoselectivity upon treatment with various aldehydes. In contrast, (*Z*)-1-(2-alkenyl)silacyclobutane (**4**) gave *syn* allylation products selectively. (*E*)-1-Cinnamylsilacyclobutane (**5**) also provided *anti* adducts with high stereoselectivity (Table 1).

Scheme 1



The present reaction can be rationalized by the combined acid–base attack[6] of allylsilacyclobutane on aldehyde. The silicon Lewis acid center of silacyclobutane binds the substrate and subsequently the allylic group, excited by the coordination, attacks the aldehyde. Allylation proceeds through a six-membered chairlike transition state to give the adduct stereoselectively (Scheme 2).

The reaction of 1-allyl-1-(cyclohexyloxy)silacyclobutane (**6**) with aldehydes proceeded at lower reaction temperature because of its enhanced Lewis acidity. For instance, heating a mixture of **6** and benzaldehyde at 100 °C for 12 h, and then treating it with 1 M HCl, provided 1-phenyl-3-buten-1-ol in 83% yield. The reactivity of **6** was further characterized by the diastereoselective allylation of α-hydroxy ketones.[7,8] Allylation of acetophenone with **6** did not proceed at all as was the case with 1-allyl-1-phenylsilacyclobutane (**1**) with acetophenone. However, the reaction of **6** with benzoin proceeded readily to give allylated diol **7** with high stereoselectivity (>99/1) in 84% yield (Scheme 3).[9] Thus, the replacement of a phenyl group on silicon by an alkoxy group not only enhances the Lewis acidity but also incorporates the hydroxy ketone into the allylsilacyclobutane moiety by alkoxy exchange. The facile exchange of an alkoxy group on the silicon of silacyclobutane was confirmed by the following experiments. Treatment of 1-(cyclohexyloxy)-1-phenylsilacyclobutane (**8**) with isopropyl alcohol (5 equiv) at 100 °C for 15 h provided 1-isopropoxy-1-phenylsilacyclobutane (**9**) and cyclohexanol. Only a trace of **8** was observed in the reaction mixture. The exchange reaction took place even at room temperature. A mixture of 1 equiv of isopropyl alcohol and **8** was stirred at room temperature for 10 h. Proton NMR analysis showed that the mixture contained **8**, **9**, isopropyl alcohol, and cyclohexanol in a 1:1:1:1 ratio. Meanwhile, heating a mixture of dimethylphenyl(cyclohexyloxy)silane and isopropyl alcohol at 100 °C for 10 h resulted in the complete recovery of both substrates.[10]

(1) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 97–124. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag: Berlin, 1983; pp 173–205. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Reactions using allylic metals have been reviewed: Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.

(2) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745. Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1987**, *328*, C17. Kira, M.; Kobayashi, M.; Sakurai, H. *Tetrahedron Lett.* **1987**, *28*, 4081. Hosomi, A.; Kohra, S.; Tominaga, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1517. Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599. Sakurai, H. *Synlett* **1989**, 1. Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453.

(3) Matsumoto, K.; Aoki, Y.; Oshima, K.; Utimoto, K.; Rahman, N. A. *Tetrahedron* **1993**, *49*, 8487. Matsumoto, K.; Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1991**, *32*, 4545. Matsumoto, K.; Miura, K.; Oshima, K.; Utimoto, K. *Ibid.* **1991**, *32*, 6383.

(4) Aldol reactions of enoxy silacyclobutane have been reported. Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, *114*, 7922. Denmark, S. E.; Griedel, B. D.; Coe, D. M. *J. Org. Chem.* **1993**, *58*, 988.

(5) Alkenylsilacyclobutane **2** and **4** were prepared from 1-chloro-1-phenylsilacyclobutane and 2-alkenylbarium (Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 8955. Yanagisawa, A.; Hibino, H.; Habaue, S.; Hisada, Y.; Yamamoto, H. *J. Org. Chem.* **1992**, *57*, 6386).

(6) The importance of this kind of combined acid–base attack has been reported in the reaction of R_2AlX. Takai, K.; Mori, I.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 446. Itoh, A.; Oshima, K.; Yamamoto, H.; Nozaki, H. *Ibid.* **1980**, *53*, 2050.

(7) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 6429.

(8) Chelation-controlled reactions between α-hydroxy ketone and allylic tin trihalides has been reported. Hallett, D. J.; Thomas, E. J. *Synlett* **1994**, 87. Reetz, M. T. *Acc. Chem. Res.* **1993**, *26*, 462.

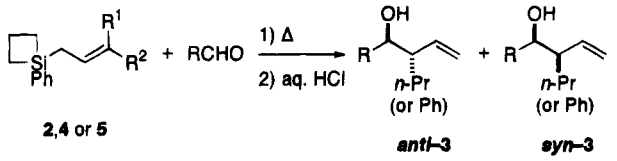
(9) Reaction of 1-allyl-1-phenylsilacyclobutane with benzoin did not take place after heating a mixture at 130 °C for 10 h.

(10) Alkoxy exchange with base such as Et_3N has been reported in the preparation of pentacoordinate siliconate. Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415.

(11) Coxon, J. M.; Eky, S. J.; Steel, P. J. *Tetrahedron* **1989**, *45*, 1029. Coxon, J. M.; Eky, S. J.; Steel, P. J.; Trenerry, V. C. *Aust. J. Chem.* **1984**, *37*, 65.

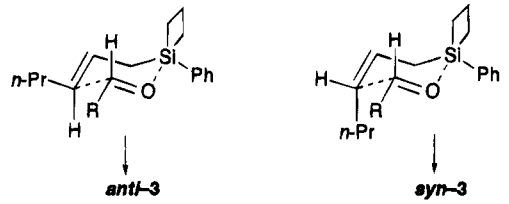
0022-3263/94/1959-7152$04.50/0

Table 1. Addition of 1-(2-Alkenyl)silacyclobutane to Aldehyde

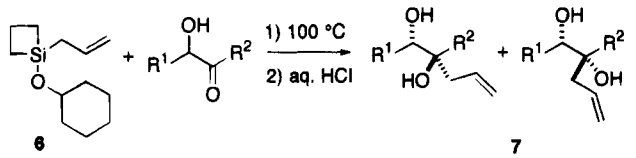


silacyclobutane			aldehyde,	reaction conditions		product	
	R^1	R^2	R	temp (°C)	time (h)	yield (%)	*anti*/*syn*
2	H	*n*-Pr	Ph	130	24	68	95/5
2	H	*n*-Pr	*n*-C_6H_{13}	160	48	59	90/10
2	H	*n*-Pr	*c*-C_6H_{11}	160	48	44	>99/1
4	*n*-Pr	H	Ph	130	24	66	5/95
4	*n*-Pr	H	*n*-C_6H_{13}	160	48	60	20/80
5	H	Ph	Ph	130	24	63	92/8
5	H	Ph	*n*-C_6H_{13}	130	48	72	97/3
5	H	Ph	*c*-C_6H_{11}	130	48	57	>99/1

Scheme 2

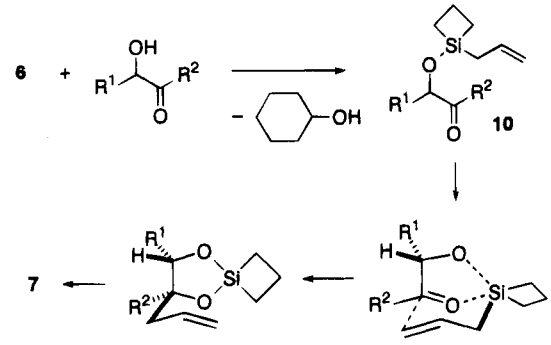


Scheme 3



R^1 = Ph	R^2 = Ph	84%	>99 / 1
R^1 = *n*-Bu	R^2 = Ph	85%	98 / 2
R^1 = Ph	R^2 = Me	84%	85 / 15

Scheme 4



On the basis of these facts, we suggest the following mechanism for the reaction between **6** and benzoin: (1) alkoxy exchange to give **10**, (2) coordination of the carbonyl oxygen to silicon, affording a five-membered chelate, and (3) intramolecular delivery of the allyl group from the silicon to the carbonyl group to give chelation-controlled product **7** stereoselectively (Scheme 4).

Experimental Section

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 (^1H 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-Phenyl-1-(2-propenyl)silacyclobutane (1). A solution of 2-propenylmagnesium chloride (0.59 M THF solution, 18.3 mL, 10.8 mmol) was added slowly to a solution of 1-chloro-1-phenylsilacyclobutane (2.19 g, 12.0 mmol) in THF (24 mL) at −78 °C under argon atmosphere. The reaction mixture was stirred for 1 h at −78 °C. Then the cooling bath was removed and the reaction mixture was allowed to come to room temperature. The resulting mixture was poured into 1 M HCl and extracted with ethyl acetate (30 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 (1.95 g, 10.04 mmol) in 96% yield: bp 101−103 °C (bath temperature, 18 Torr); IR (neat) 3068, 2964, 2918, 1630, 1428, 1151, 1119, 1113, 896, 857, 730, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 8.2 Hz, 4H), 2.03 (dt, J = 1.1, 7.9 Hz, 2H), 2.16 (quintet, J = 8.2 Hz, 2H), 4.94 (ddt, J = 1.6, 10.0, 1.1 Hz, 1H), 4.99 (ddt, J = 1.6, 16.9, 1.1 Hz, 1H), 5.90 (ddt, J = 10.0, 16.9, 8.1 Hz, 1H), 7.37−7.43 (m, 3H), 7.58−7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.66, 18.16, 22.76, 114.10, 127.90, 129.51, 133.56, 133.63, 137.19. Anal. Found: C, 76.61; H, 8.57. Calcd for $C_{12}H_{16}Si$: C, 76.52; H, 8.57.

Preparation of (*E*)-1-(2-Hexenyl)-1-phenylsilacyclobutane (2) and (*Z*)-1-(2-Hexenyl)-1-phenylsilacyclobutane (4). The reaction of (*E*)-1-chloro-2-hexene with 1-chloro-1-phenylsilacyclobutane is representative. To a suspension of anhydrous BaI_2 (2.35 g, 6.0 mmol) in THF (5 mL) was added at room temperature a preformed lithium biphenylide, prepared from freshly cut lithium (83 mg, 12.0 mmol) and biphenyl (1.85 g, 12.0 mmol) in THF (25 mL), and the reaction mixture was stirred for 30 min at room temperature. To the resulting brown suspension of barium powder in THF was slowly added a solution of (*E*)-1-chloro-2-hexene (640 mg, 5.4 mmol) in THF (4 mL) at −78 °C. After being stirred for 30 min, the mixture was treated with a solution of 1-chloro-1-phenylsilacyclobutane (1.37 g, 7.5 mmol) in THF (2 mL) at −78 °C and stirred for another 30 min at this temperature. The resulting mixture was poured into 1 M HCl and extracted with ethyl acetate (25 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel to afford (*E*)-1-(2-hexenyl)-1-phenylsilacyclobutane (**2**, 570 mg, 2.5 mmol) in 46% yield: bp 94−96 °C (bath temperature, 5.0 Torr); IR (neat) 2956, 2922, 2868, 1428, 1119, 1113, 962, 856, 731, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H), 1.25 (t, J = 8.3 Hz, 4H), 1.35 (tq, J = 7.3, 7.3 Hz, 2H), 1.92 (dd, J = 0.9, 7.4 Hz, 2H), 1.97 (ddt, J = 1.0, 6.5, 7.3 Hz, 2H), 2.15 (quintet, J = 8.3 Hz, 2H), 5.38 (ddt, J = 0.9, 15.1, 6.5 Hz, 1H), 5.49 (ddt, J = 1.0, 15.1, 7.4 Hz, 1H), 7.35−7.43 (m, 3H), 7.57−7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.70, 13.61, 18.13, 20.73, 23.00, 34.95, 124.34, 127.84, 129.39, 130.43, 133.67, 137.59. Anal. Found: C, 78.42; H, 9.83. Calcd for $C_{15}H_{22}Si$: C, 78.18; H, 9.63.

(*Z*)-1-(2-Hexenyl)-1-phenylsilacyclobutane (4): bp 91−93 °C (bath temperature, 4.0 Torr); IR (neat) 3004, 2956, 2924, 2866, 1429, 1147, 1119, 1112, 857, 731, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 1.25 (t, J = 8.2 Hz, 4H), 1.34 (tq, J = 7.4, 7.3 Hz, 2H), 1.98 (d, J = 8.6 Hz, 2H), 1.99 (dt, J = 7.5, 7.4 Hz, 2H), 2.90−2.25 (m, 2H), 5.37 (dt, J = 10.5, 7.5 Hz, 1H), 5.56 (dt, J = 10.5, 8.6 Hz, 1H), 7.35−7.45 (m, 3H), 7.60−7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.94, 13.91, 16.93, 18.34, 22.85, 29.28, 123.62, 127.87, 129.00, 129.43, 133.60, 137.59. Anal. Found: C, 78.22; H, 9.54. Calcd for $C_{15}H_{22}Si$: C, 78.42; H, 9.63.

Preparation of 1-Phenyl-1-[(*E*)-3-phenyl-2-propenyl]-silacyclobutane (5). Ethyl bromide (0.05 mL) and iodine (20 mg) were added to magnesium turnings (290 mg, 12 mmol) in THF (5 mL) at room temperature under an argon atmosphere. After the brown solution turned colorless, 1-chloro-1-phenylsilacyclobutane (1.28 g, 7.0 mmol) was added at 0 °C. Then a solution of (*E*)-3-chloro-1-phenyl-1-propene (0.84 mL, 6.0 mmol) was slowly added over a period of 1 h at 0 °C. After completion of the addition, the reaction mixture was stirred for 30 min at

(12) Krepski, L. R.; Heilmann, S. M.; Rasmussen, J. K. *Tetrahedron Lett.* **1983**, *24*, 4075.

0 °C and for another 30 min at room temperature. The resulting mixture was poured into 1 M HCl and extracted with ethyl acetate (25 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 (**5**, 1.18 g, 4.5 mmol) in 78% yield: mp 29.0 °C; IR (neat before crystallization) 3062, 3018, 2962, 2920, 2868, 1641, 1495, 1428, 1395, 1145, 1112, 960, 862, 731, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7.8 Hz, 4H), 2.17 (quintet, J = 7.8 Hz, 2H), 2.18 (d, J = 6.6 Hz, 2H), 6.32 (dt, J = 15.8, 6.6 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 7.12–7.22 (m, 1H), 7.23–7.32 (m, 4H), 7.32–7.43 (m, 3H), 7.58–7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.87, 18.15, 22.08, 125.60, 125.89, 126.42, 128.00, 128.45, 129.51, 129.59, 133.62, 137.12, 138.17. Anal. Found: C, 81.50; H, 7.65. Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62.

General Procedure for Allylation of Aldehydes with 1-(2-Alkenyl)-1-phenylsilacyclobutanes. The reaction of benzaldehyde with 1-phenyl-1-(2-propenyl)silacyclobutane (**1**) is representative. A mixture of benzaldehyde (0.31 mL, 3.0 mmol) and 1-phenyl-1-(2-propenyl)silacyclobutane (**1**, 94 mg, 0.5 mmol) was heated to 130 °C in a sealed tube under an argon atmosphere. After being stirred for 12 h at 130 °C, the reaction mixture was diluted in methanol (3.0 mL), and a few drops of 1 M HCl were added. The mixture was stirred for 3 h at room temperature. The resulting 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. Purification by silica gel column chromatography provided 1-phenyl-3-buten-1-ol (63 mg, 0.43 mmol) in 85% yield. Physical data of 1,2-diphenyl-3-buten-1-ol are available in the literature,[11] and those of others are shown below.

***threo*-1-Phenyl-2-ethenyl-1-pentanol (*anti*-3):** bp 63–65 °C (bath temperature, 0.3 Torr); IR (neat) 3400 (broad), 2954, 2928, 2868, 1641, 1455, 1118, 1049, 1029, 913, 763, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (t, J = 7.0 Hz, 3H), 1.05–1.21 (m, 2H), 1.22–1.52 (m, 2H), 2.19 (d, J = 2.0 Hz, 1H, OH), 2.25–2.37 (m, 1H), 4.38 (dd, J = 2.0, 8.0 Hz, 1H), 5.20 (dd, J = 2.0, 17.0 Hz, 1H), 5.26 (dd, J = 2.0, 10.3 Hz, 1H), 5.66 (ddd, J = 9.2, 10.3, 17.0 Hz, 1H), 7.23–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.85, 20.25, 32.49, 52.49, 76.59, 118.65, 126.93, 127.55, 128.17, 139.35, 142.46. Anal. Found: C, 81.83; H, 9.41. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53.

***erythro*-1-Phenyl-2-ethenyl-1-pentanol (*syn*-3):** bp 63–65 °C (bath temperature, 0.3 Torr); IR (neat) 3366 (broad), 3064, 3026, 2954, 2926, 2868, 1640, 1494, 1466, 1455, 1118, 1028, 1000, 913, 763, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.1 Hz, 3H), 1.10–1.62 (m, 4H), 2.04 (d, J = 4.4 Hz, 1H, OH), 2.37–2.49 (m, 1H), 4.63 (dd, J = 4.4, 5.1 Hz, 1H), 5.01 (ddd, J = 0.8, 2.0, 17.0 Hz, 1H), 5.07 (dd, J = 2.0, 10.3 Hz, 1H), 5.50 (ddd, J = 9.1, 10.3, 17.0 Hz, 1H), 7.22–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.03, 20.35, 31.81, 51.16, 76.86, 117.27, 126.70, 127.92, 138.48, 142.45. Anal. Found: C, 82.03; H, 9.50. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53.

***threo*-4-Ethenyl-5-undecanol:** bp 91–93 °C (bath temperature, 3.0 Torr); IR (neat) 3346 (broad), 3070, 2954, 2926, 2856, 1638, 1467, 1421, 1379, 1033, 1001, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H), 1.15–1.70 (m, 15H including OH), 2.01 (dddd, J = 5.2, 5.5, 9.3, 9.3 Hz, 1H), 3.44 (ddd, J = 3.6, 5.5, 8.8 Hz, 1H), 5.08 (dd, J = 2.2, 17.2 Hz, 1H), 5.17 (dd, J = 2.2, 10.3 Hz, 1H), 5.63 (ddd, J = 9.3, 10.3, 17.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 20.44, 22.62, 25.67, 29.39, 31.84, 32.92, 34.66, 50.05, 73.59, 117.68, 138.94. Anal. Found: C, 78.75; H, 13.00. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21.

***erythro*-4-Ethenyl-5-undecanol:** bp 91–93 °C (bath temperature, 3.0 Torr); IR (neat) 3336 (broad), 3070, 2954, 2924, 2856, 1639, 1467, 1123, 1032, 998, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H), 1.15–1.70 (m, 15H including OH), 2.05–2.17 (m, 1H), 3.40–3.52 (m, 1H), 5.07 (dd, J = 2.2, 16.8 Hz, 1H), 5.11 (dd, J = 2.2, 10.3 Hz, 1H), 5.60 (ddd, J = 9.3, 10.3, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, 20.49, 22.63, 26.63, 29.35, 31.84, 32.17, 33.80, 50.56, 74.79, 117.02, 139.26. Anal. Found: C, 78.75; H, 13.41. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21.

***threo*-1-Cyclohexyl-2-ethenyl-1-pentanol:** bp 81–83 °C (bath temperature, 3.0 Torr); IR (neat) 3366 (broad), 3068, 2922, 2850, 1638, 1450, 1117, 1055, 1033, 1003, 978, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 3H), 0.95–1.52 (m, 10H), 1.57–1.88 (m, 6H including OH), 2.15–2.26 (m, 1H), 3.16 (dd, J = 5.8, 5.8 Hz, 1H), 5.08 (dd, J = 2.2, 17.2 Hz, 1H), 5.16 (dd, J = 2.2, 10.3 Hz, 1H), 5.66 (ddd, J = 9.3, 10.3, 17.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.06, 20.36, 26.07, 26.36, 26.48, 27.45, 29.74, 33.18, 40.34, 46.35, 77.58, 117.38, 138.90. Anal. Found: C, 79.34; H, 12.21. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32.

***erythro*-1-Cyclohexyl-2-ethenyl-1-pentanol:** bp 81–83 °C (bath temperature, 3.0 Torr); IR (neat) 3366 (broad), 3068, 2924, 2850, 1641, 1450, 1027, 998, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.1 Hz, 3H), 0.95–1.88 (m, 16H including OH), 2.10–2.21 (m, 1H), 3.18 (dd, J = 4.8, 6.6 Hz, 1H), 5.02 (dd, J = 2.1, 17.0 Hz, 1H), 5.07 (dd, J = 2.1, 10.3 Hz, 1H), 5.61 (ddd, J = 9.2, 10.3, 17.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.16, 20.36, 26.05, 26.46, 30.24, 31.13, 40.27, 46.97, 78.79, 115.77, 140.12. Anal. Found: C, 79.55; H, 12.55. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32.

***erythro*-3-Phenyl-1-decen-4-ol:** bp 85–87 °C (bath temperature, 0.3 Torr); IR (neat) 3398 (broad), 3064, 3024, 2924, 2854, 1640, 1603, 1493, 1125, 1029, 998, 916, 758, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.10–1.52 (m, 10H), 1.79 (d, J = 2.6 Hz, 1H, OH), 3.24 (dd, J = 7.3, 9.1 Hz, 1H), 3.74–3.83 (m, 1H), 5.19 (dd, J = 1.8, 10.4 Hz, 1H), 5.21 (dd, J = 1.8, 16.8 Hz, 1H), 6.12 (ddd, J = 9.2, 10.4, 16.8 Hz, 1H), 7.17–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.56, 25.65, 29.20, 31.76, 34.35, 57.39, 73.92, 117.83, 126.59, 127.95, 128.65, 138.35, 141.67. Anal. Found: C, 82.45; H, 10.45. Calcd for $C_{16}H_{24}O$: 82.70; H, 10.41.

***erythro*-1-Cyclohexyl-2-phenyl-3-buten-1-ol:** bp 86–87 °C (bath temperature, 0.3 Torr); IR (neat) 3392 (broad), 3024, 2922, 2848, 1640, 1603, 1439, 1450, 1085, 1061, 1040, 988, 916, 757, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02–1.32 (m, 6H), 1.53–1.77 (m, 5H including OH), 1.78–1.88 (m, 1H), 3.45 (dd, J = 7.1, 9.2 Hz, 1H), 3.57 (ddd, J = 3.5, 3.5, 7.2 Hz, 1H), 5.18 (dd, J = 1.7, 17.0 Hz, 1H), 5.22 (dd, J = 1.7, 10.3 Hz, 1H), 6.14 (ddd, J = 9.1, 10.3, 17.0 Hz, 1H), 7.18–7.27 (m, 3H), 7.28–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.95, 26.30, 26.41, 26.48, 30.14, 39.47, 53.63, 78.04, 117.66, 126.48, 127,89, 128.66, 138.38, 142.02. Anal. Found: C, 83.24; H, 9.66. Calcd for $C_{16}H_{22}O$: C, 83.42; H, 9.63.

Preparation of 1-(Cyclohexyloxy)-1-(2-propenyl)silacyclobutane (6). A solution of 2-propenylmagnesium chloride (0.63 M THF solution, 15.9 mL, 10.0 mmol) was slowly added to a solution of 1,1-dichlorosilacyclobutane (1.41 g, 10.0 mmol) in hexane (20 mL) at −78 °C under an argon atmosphere. The reaction mixture was gradually warmed to room temperature over a period of 2 h. Then triethylamine (2.8 mL, 20 mmol) and cyclohexanol (1.04 mL, 10.0 mmol) were successively added. The mixture was stirred for 1 h at room temperature. The resulting precipitate was filtered through a glass filter, and the filtrate was concentrated. Distillation of the residual oil using Kugelrohr distillation afforded the title compound **6** (610 mg, 2.9 mmol) in 29% yield: bp 107–109 °C (bath temperature, 15 Torr); IR (neat) 2928, 2854, 1631, 1450, 1153, 1121, 1084, 1047, 1026, 997, 894, 866, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.42 (m, 8H), 1.42–1.63 (m, 2H), 1.65–2.10 (m, 8H), 3.77 (tt, J = 4.0, 13.4 Hz, 1H), 4.91 (ddt, J = 2.0, 10.1, 1.0 Hz, 1H), 4.97 (ddt, J = 2.0, 17.1, 2.0 Hz, 1H), 5.86 (ddt, J = 10.1, 17.1, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.41, 17.89, 23.33, 24.24, 25.45, 35.79, 71.83, 113.86, 133.21. Anal. Found: C, 68.23; H, 10.38. Calcd for $C_{12}H_{22}OSi$: C, 68.50; H, 10.54.

Preparation of 2-Hydroxy-1-phenyl-1-hexanone and 1-Hydroxy-1-phenyl-2-propanone. These compounds were prepared according to a reported procedure.[12]

***erythro*-4-Phenyl-1-nonene-4,5-diol:** mp 63.0–63.5 °C; IR (Nujol) 3432 (broad), 1640, 1221, 1129, 1067, 1029, 944, 917, 884, 760, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (t, J = 6.8 Hz, 3H), 1.09–1.52 (m, 6H), 1.90 (d, J = 8.0 Hz, 1H, OH), 2.44 (s, 1H, OH), 2.79 (d, J = 7.2 Hz, 2H), 3.70 (ddd, J = 3.2, 8.0, 8.0 Hz, 1H), 5.10 (dd, J = 2.2, 10.0 Hz, 1H), 5.16 (dd, J = 2.2, 17.2 Hz, 1H), 5.50 (ddt, J = 10.0, 17.2, 7.2 Hz, 1H), 7.21–7.29 (m, 1H), 7.30–7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.44, 28.46, 30.96, 43.58, 77.42, 77.98, 119.79, 125.61, 126.77, 128.14, 133.43, 143.04. Anal. Found: C, 76.77; H, 9.61. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.47.

***threo*-2-Methyl-1-phenyl-4-pentene-1,2-diol:** bp 80–81 °C (bath temperature, 0.3 Torr); IR (neat) 3380 (broad), 3066, 3028, 2974, 2928, 1640, 1494, 1454, 1377, 1039, 1026, 914, 750, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 3H), 2.00–2.90 (bs, 2H, OH), 2.27 (dd, J = 7.4, 13.8 Hz, 1H), 2.35 (dd, J = 7.4, 13.8 Hz, 1H), 4.55 (s, 1H), 5.16 (dd, J = 2.0, 17.2 Hz, 1H), 5.19 (dd, J = 2.0,

10.3 Hz, 1H), 5.94 (dddd, J = 7.4, 7.4, 10.3, 17.1 Hz, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.60, 43.39, 74.72, 79.00, 119.01, 127.54, 127.77, 127.93, 133.52, 140.16. Anal. Found: C, 74.74; H, 8.56. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.38.

Preparation of 1-(Alkyloxy)-1-phenylsilacyclobutanes 8 and 9. The reaction of cyclohexanol with 1-chloro-1-phenylsilacyclobutane is representative. Cyclohexanol (0.62 mL, 6.0 mmol) was added to a solution of 1-chloro-1-phenylsilacyclobutane (910 mg, 5.0 mmol) and pyridine (0.49 mL, 6.0 mmol) in benzene (10 mL) at room temperature under an argon atmosphere. After being stirred for 24 h at room temperature, the resulting precipitate was filtered through a glass filter and the filtrate was concentrated *in vacuo*. Distillation of the residue using Kugelrohr distillation gave 1-(cyclohexyloxy)-1-phenylsilacyclobutane (**8**, 550 mg, 2.2 mmol) in 45% yield: bp 93–95 °C (bath temperature, 0.3 Torr); IR (neat) 3064, 2928, 2852, 1450, 1429, 1123, 1080, 1047, 1025, 997, 863, 849, 738, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10–1.60 (m, 10H), 1.60–1.79 (m, 3H), 1.80–1.92 (m, 2H), 2.02–2.19 (m, 1H), 3.86 (tt, J = 3.7, 8.7 Hz, 1H), 7.35–7.48 (m, 3H), 7.63–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.74, 18.50, 24.13, 25.48, 35.74, 71.93, 127.88, 129.89, 133.56, 136.33. Anal. Found: C, 72.83; H, 8.95. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00.

1-Isopropoxy-1-phenylsilacyclobutane (9): bp 91–92 °C (bath temperature, 5.0 Torr); IR (neat) 3066, 2964, 2926, 2870, 1429, 1382, 1370, 1173, 1118, 1026, 851, 736, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 6.1 Hz, 6H), 1.38–1.85 (m, 5H), 2.00–2.28 (m, 1H), 4.24 (septet, J = 6.1 Hz, 1H), 7.35–7.58 (m, 3H), 7.68–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.70, 18.35, 25.69, 66.18, 127.91, 129.95, 133.57, 136.18. Anal. Found: C, 69.99; H, 8.99. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79.

Acknowledgment. Financial support by the Grant-in-Aid for Scientific Research on Priority Area of Relative Organometallics (No. 06227231) from the Ministry of Education, Science and Culture, Japan, is acknowledged.