Facile Preparation of *Vicinal* Allylsiloxy- and Vinylsiloxyhaloalkanes and Their Radical Cyclization Reaction

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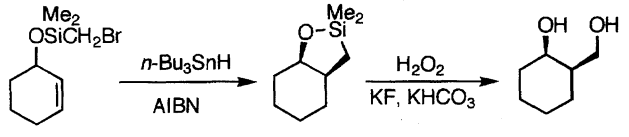
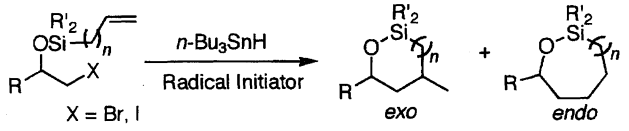
Treatment of 2-(allyldimethylsiloxy)-1,1-dibromoalkane, which was easily prepared by an addition of aldehyde to an ethereal solution of (allyldimethylsilyl)dibromomethyllithium, with tributyltin hydride in the presence of catalytic amount of triethylborane afforded 1-oxa-2-silacycloheptane derivative selectively in good yield. On the other hand, cyclization of vinyldimethylsiloxy derivative resulted in a formation of 3-methyl-1-oxa-2-silacyclopentane. An addition of allyldiphenylsilanol to ethyl vinyl ether in the presence of *N*-iodosuccinimide provided 1-(allyldiphenylsiloxy)-1-ethoxy-2-iodoethane, which was also converted into a seven-membered ring product upon treatment with tributyltin hydride.

Radical cyclization reactions developed during the last decade represent a breakthrough for a synthetic radical chemistry.[1] Among them, cyclizations of silylmethyl radicals bearing an alkenyloxy group on the silicon atom are important and there are numerous works[2] on the related system in which (bromomethyl)silyl group serves as a hydroxymethyl radical equivalent via oxidative cleavage[3] of the Si–C bond (Scheme 1). In contrast, there are few reports on cyclizations of alkyl radicals possessing an alkenylsiloxy group (Scheme 2).[4] We hope to disclose here two different methods of preparation of such radical cyclization precursors and their radical cyclizations to yield oxasilacycles which are synthetically useful intermediates.

(1) Preparation of 2-Alkenylsiloxy-1,1-dibromoalkanes by Treatment of Carbonyl Compounds with Silyldibromomethyllithiums. We have previously reported that the addition of silyldihalomethyllithium to carbonyl compounds, such as aldehydes[5] or esters,[6] provided the corresponding silyl ethers or alkyl silyl mixed acetals through the 1,3-rearrangement of silyl group from carbon to oxygen. It was anticipated that the use of allyl- or vinyl-substituted silyldibromomethyllithium (**1** or **2**) would give 2-allylsiloxy- or 2-vinylsiloxy-1,1-dibromoalkane **4** via the 1,3-rearrangement of silyl group in the adducts **3** (Scheme 3). This was indeed



Scheme 1.



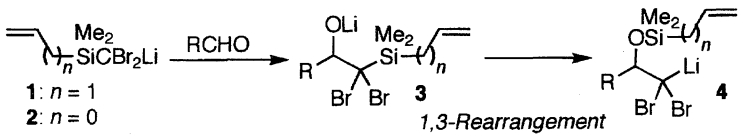
Scheme 2.

the case and an addition of carbonyl compounds to a solution of (allyldimethylsilyl)dibromomethyllithium (**1**) or (vinyldimethylsilyl)dibromomethyllithium (**2**),[7] which were derived from (allyldimethylsilyl)dibromomethane or (vinyldimethylsilyl)dibromomethane with lithium diisopropylamide at −78 °C, gave the corresponding silyl ethers or alkyl silyl mixed acetals in good yields via the 1,3-rearrangement of allyldimethylsilyl group or vinyldimethylsilyl group.

Some representative results are shown in Table 1. In method A, the reaction was quenched with methanol to give **5** or **6** (E′ = H). In method B, a three-component coupled product **7** (E′ = CH_3) was prepared by a subsequent addition of methyl iodide and HMPA before quenching with methanol. In these reactions, the increased polarity of solvent due to an addition of methanol or HMPA facilitated the rearrangement of the silyl group. Cyclization of the products is discussed in section (3).

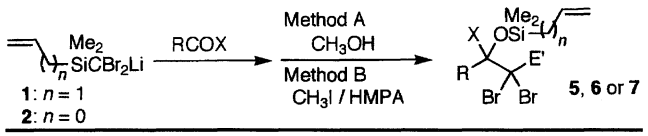
(2) Preparation of Halo Mixed Silyl Acetals by Treatment of Enol Ethers with Silanols in the Presence of *N*-Halosuccinimide. We have recently reported an iodonium ion induced intramolecular addition of silanol moiety to the carbon-carbon double bond of alkenylsilanols.[8] However, no intermolecular addition of silanol to electronically non-activated olefins, could take place, presumably because the nucleophilicity of silanol is lower than that of alcohol. Fortunately, *t*-butyldimethylsilanol proved to add intermolecularly to electron-rich olefins such as ethyl vinyl ether and to provide mixed alkyl silyl acetals **8** in good yields in the presence of *N*-iodosuccinimide (NIS) or *N*-bromosuccinimide (NBS) (Scheme 4). The reactions took about one day to complete, whereas the addition of alcohols to enol ethers generally completes within 1 h in the presence of NIS or NBS even at −78 °C.[9] The use of *N*-chlorosuccinimide in place of NIS or NBS made the reaction much slower and gave the corresponding mixed silyl acetal in an unacceptable yield (≈20%).

In similar manner, treatment of allyl(diphenyl)silanol or



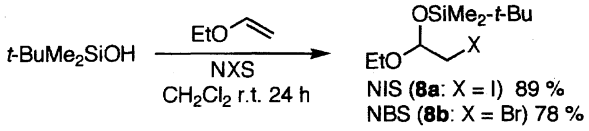
Scheme 3.

Table 1. Preparation of 2-Alkenylsiloxy-1,1-dibromoalkanes with Silyldibromomethyllithium



	n	R	X	Method[a]	E′	Yield/%
5a	1	Ph	H	A	H	80
5b	1	*n*-Hex	H	A	H	78
5c	1	Ph	OEt	A	H	72
6a	0	Ph	H	A	H	78
6b	0	*n*-Hex	H	A	H	75
7a	1	Ph	H	B	CH_3	71
7b	1	*n*-Hex	H	B	CH_3	68

a) Method A: The reaction mixture was quenched with methanol. Method B: The reaction mixture was treated with iodomethane and HMPA.



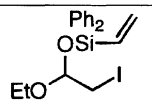
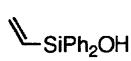
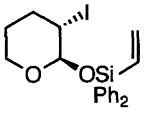
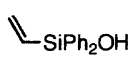
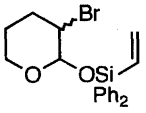
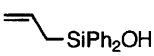
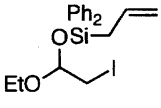
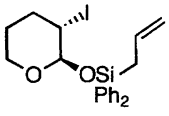
Scheme 4.

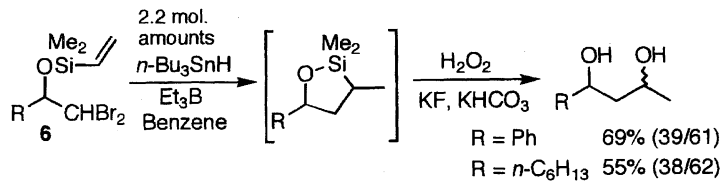
(diphenyl)vinylsilanol[10] with enol ethers in the presence of NIS or NBS afforded the corresponding allyl- or vinyl-substituted mixed silyl acetals in good yields (Table 2). Stereoselective addition of these silanols to 3,4-dihydro-2*H*-pyran was observed in the case of NIS. In contrast, the use of NBS in place of NIS resulted in a formation of stereoisomeric mixture; however, this is not a problem in the following radical cyclization reaction. In general, silanols are liable to dimerize to the corresponding disiloxanes; allyl(dimethyl)silanol, in fact, changed into 1,3-diallyl-1,1,3,3-tetramethyldisiloxane within five min along with concomitant formation of water. Allyl(diphenyl)silanol or (diphenyl)vinylsilanol, however, are stable on standing for a few months at room temperature under atmosphere and are easy to handle. The radical cyclization of iodo mixed alkenylsilyl acetals thus obtained is described in the next section.

(3) Cyclization of 3-Oxa-4-sila-5-alkenyl Radical and 3-Oxa-4-sila-6-alkenyl Radical. The radical cyclization of the precursors described in the previous two sections was performed by treatment with *n*-Bu_3SnH in the presence of a catalytic amount of triethylborane in benzene (0.017 M) (1 M = 1 mol dm^{-3}).[11] The intramolecular cyclization of 1,1-dibromo-2-vinylsiloxyalkane **6** with two molar amounts of *n*-Bu_3SnH afforded only 1-oxa-2-silacyclopentanes selectively. These compounds were not stable enough to be purified by silica-gel column chromatography, and were converted into 1,3-diols in good yields as a diastereomeric mixture via direct oxidative cleavage of the Si–C bond (Scheme 5).

The cyclization of vinylsilyl mixed acetals **9** also gave five-membered acetals exclusively upon treatment with *n*-Bu_3SnH–Et_3B. These findings obviously show that the cy-

Table 2. Preparation of Halo Mixed Silyl Acetal from Silanol

Silanol	Enol ether	*N*-Halosuccinimide	Product		Yield/%
		NIS		**9a**	78
		NIS		**9b**	81
		NBS		**9c**	75
		NIS		**10a**	61
		NIS		**10b**	50



Scheme 5.

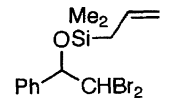
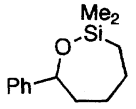
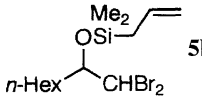
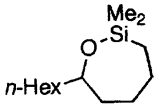
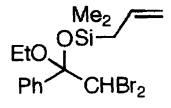
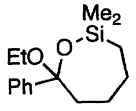
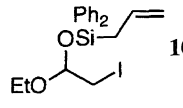
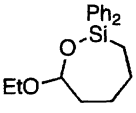
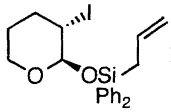
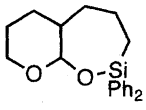
clization of 3-oxa-4-sila-5-alkenyl system predominantly proceeded in 5-*exo* mode. These cyclic silyl acetals were not stable enough to be isolated; thus they were allylated with allyltrimethylsilane[12] or reduced to ethers with triethylsilane[13] in the presence of a catalytic amount of Me_3SiOTf (Scheme 6). In the reduction with triethylsilane, **12** was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether.

In contrast to vinylsiloxy derivatives **6**, treatment of 2-allylsiloxy-1,1-dibromoalkane **5** with two molar amounts of *n*-Bu_3SnH gave 1-oxa-2-silacycloheptanes exclusively (Table 3). Similarly, the cyclization of allylsilyl mixed acetals **10** also yielded only 7-alkoxy-1-oxa-2-silacycloheptanes **13** effectively. Thus, the cyclization of 3-oxa-4-sila-6-alkenyl system shows a distinct preference for 7-*endo* mode. Interestingly, the inclination for 7-*endo* mode cyclization in these cases is coincident with that observed in the case of 3-oxa-2-sila-6-alkenyl system.[2e]

These seven-membered cyclic silyl ethers and acetals were stable and could be isolated by silica-gel column chromatography. The cyclic silyl acetals **14a** and **14b** were further converted into ethers upon treatment with silyl nucleophile such as allyltrimethylsilane and triethylsilane under the catalysis of Me_3SiOTf (Scheme 7).

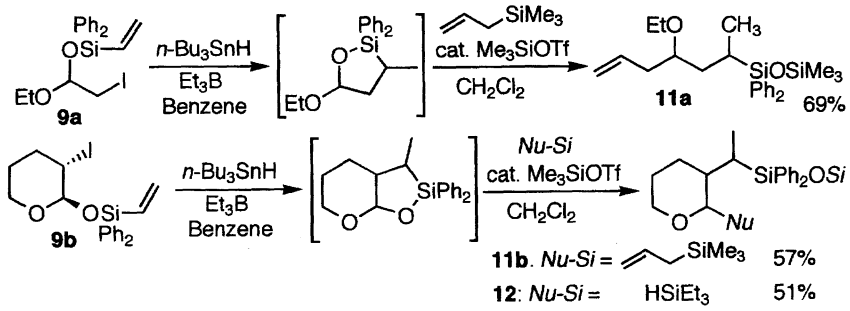
An interesting stereochemical outcome was observed in the cyclization of **7a**. Treatment of **7a** with an equimolar amount of *n*-Bu_3SnH in benzene (0.017 M) followed by the second reduction with another molar amount of tin hydride in hexane gave a stereoisomeric mixture of **17a**[14] (*cis*/*trans* = 87/13). Analysis of the reaction mixture, derived from **7a** and equimolar amount of *n*-Bu_3SnH, indicated that the products consisted of cyclic silyl ether **18a** and acyclic silyl ether **19a** (66/34) (Scheme 8). The silyl ether **19a** was isolated and treatment with *n*-Bu_3SnH–Et_3B gave **17a** nonstereoselectively (55/45). Hence it was anticipated that suppression of the formation of **19a** in the first step would improve the stereoselectivity of **17a**. In fact, the

Table 3. The Radical Cyclization of Allylsiloxy Derivatives to 1-Oxa-2-silacycloheptanes

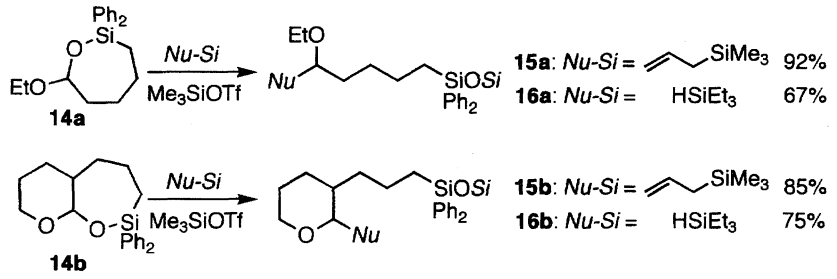
Substrate		Product		Yield/%
	**5a**[a]		**13a**	84
	**5b**[a]		**13b**	87
	**5c**[a]		**13c**	70
	**10a**[b]		**14a**	89
	**10b**[b]		**14b**	54

a) Each substrate was treated with equimolar amount of *n*-Bu_3SnH and another amount after 6 h. b) Each substrate was treated with equimolar amount of *n*-Bu_3SnH.

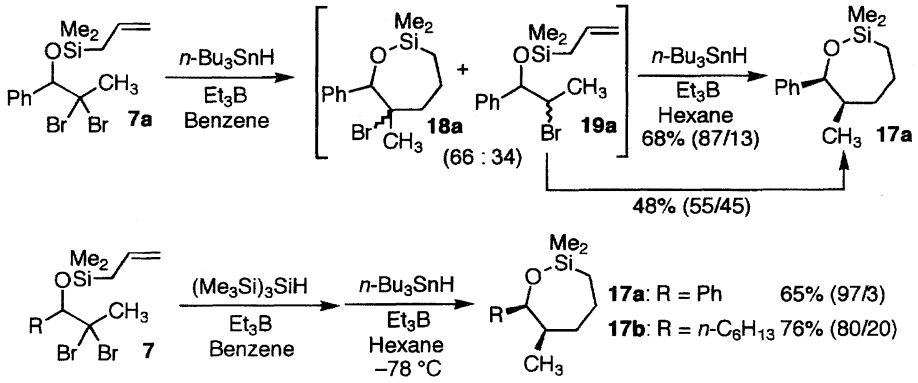
use of 1,1,1,3,3,3-hexamethyl-2-trimethylsilyltrisilane[16] in place of *n*-Bu_3SnH in the first reduction step afforded **18a** along with a trace amount of **19a** and the second reduction with *n*-Bu_3SnH at −78 °C gave **17a** in high stereoselectivity (*cis*/*trans* = 97/3). Unfortunately, the high selectivily was observed only in the case of phenyl derivative **7a**. Radical cyclization of **7b** afforded **17b** with moderate stereoselectivity (*cis*/*trans* = 80/20) under the same reaction conditions, presumably because of the flexibility of the seven-membered



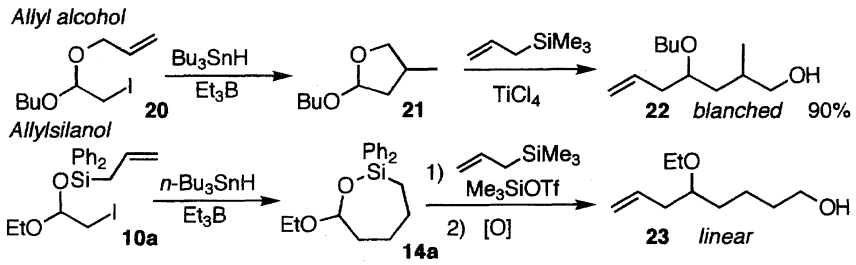
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

silyl ether ring.

Finally, we performed an experiment to compare allylsilanol with allylic alcohol, since allylsilanol can be regarded as a synthon of allyl alcohol through oxidative cleavage of Si–C bond (Scheme 9). In the case of allylic alcohol, the cyclization of **20** with *n*-Bu_3SnH–Et_3B afforded only five-membered ether **21**.[17] Treatment of the cyclic ether **21** with allyltrimethylsilane in the presence of titanium tetrachloride gave only a branched alkenol **22** selectively. In contrast, in the case of allylsilanol, cyclization of **10a** followed by subsequent treatment with allyltrimethylsilane and hydrogen peroxide provided a linear alkenol **23** exclusively. Therefore, two isomeric alkenol **22** and **23** could be prepared selectively by changing allyl alcohol and allylsilanol from alkyl vinyl ether.

Experimental

Distillation of the products was performed using Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Diethyl ether, benzene, and hexane were dried over a slice of sodium. Dichloromethane was dried by molecular sieves 4A. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl before use. Each triethylborane-catalyzed radical reaction was performed in a vessel equipped with a balloon filled with argon.

General Procedure for the Reaction of Allylsilyl- or Vinylsilyldibromomethyllithium with Carbonyl Compound (Method A). An ethereal solution of allyl(dibromomethyl)dimethylsilane (0.82 g, 3.0 mmol) was added to a solution of lithium diisopropylamide (3.6 mmol) in ether (9 ml) at −78 °C under argon atmosphere. After being stirred for 1 h at −78 °C, benzaldehyde (0.38 g, 3.6 mmol) in Et_2O (3 ml) was added and the reaction mixture was stirred for 20 min. The mixture was quenched with methanol and poured into saturated aqueous ammonium chloride and extracted with hexane (20 ml×3). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography gave 1-allyldimethylsiloxy-2,2-dibromo-1-phenylethane (**5a**, 0.91 g) in 80% yield: Bp 105 °C (0.5 Torr, 1 Torr=133.322 Pa); IR (neat) 2956, 1631, 1454, 1255, 1135, 1092, 866, 837, 756,

700, 594 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.09 (s, 3H), 0.12 (s, 3H), 1.59 (d, J = 8.1 Hz, 2H), 4.82 (m, 2H), 4.97 (d, J = 5.1 Hz, 1H), 5.64 (d, J = 5.1 Hz, 1H), 5.69 (ddt, J = 9.6, 17.7, 8.1 Hz, 1H), 7.30—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = −2.20, 24.58, 51.20, 79.87, 114.14, 127.36, 128.24, 128.74, 133.60, 139.66. Found: C, 41.23; H, 4.76%. Calcd for $C_{13}H_{18}Br_2OSi$: C, 41.29; H, 4.80%.

2-Allyldimethylsiloxy-1,1-dibromooctane (5b): Bp 110 °C (1 Torr); IR (neat) 2952, 2922, 2854, 1632, 1255, 1153, 1103, 1051, 897, 839, 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.19 (s, 3H), 0.20 (s, 3H), 0.90 (t, J = 6.8 Hz, 3H), 1.20—1.50 (m, 8H), 1.55—1.85 (m, 2H), 1.70 (d, J = 8.1 Hz, 2H), 3.84 (ddd, J = 3.6, 3.6, 7.8 Hz), 4.92 (m, 2H), 5.61 (d, J = 3.6 Hz, 1H), 5.82 (ddt, J = 9.9, 16.8, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −1.86, −1.76, 13.94, 22.46, 24.96, 25.14, 29.01, 31.60, 33.59, 51.64, 77.31, 114.21, 133.74. Found: C, 40.31; H, 6.73%. Calcd for $C_{13}H_{26}Br_2OSi$: C, 40.43; H, 6.78%.

1-Allyldimethylsiloxy-2,2-dibromo-1-ethoxy-1-phenylethane (5c): Bp 115 °C (0.5 Torr); IR (neat) 3056, 2972, 2894, 1630, 1449, 1256, 1168, 1060, 895, 837, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.25 (s, 3H), 0.30 (s, 3H), 1.20 (t, J = 6.9 Hz, 3H), 1.72 (dd, J = 13.8, 8.1 Hz, 1H), 1.82 (dd, J = 13.8, 8.1 Hz, 1H), 3.38 (dq, J = 9.0, 6.9 Hz, 1H), 3.54 (dq, J = 9.0, 6.9 Hz, 1H), 4.89 (m, 1H), 4.93 (m, 1H), 5.83 (s, 1H), 5.85 (ddt, J = 16.5, 10.2, 8.1 Hz, 1H), 7.30—7.40 (m, 3H), 7.55—7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = −0.51, −0.05, 14.82, 26.00, 52.67, 59.24, 101.02, 114.11, 127.69, 128.39, 128.92, 134.12, 138.52. Found: C, 42.54; H, 5.23%. Calcd for $C_{15}H_{22}Br_2O_2Si$: C, 42.67; H, 5.25%.

1,1-Dibromo-2-dimethyl(vinyl)siloxy-2-phenylethane (6a): Bp 90 °C (0.5 Torr); IR (neat) 3048, 3030, 2956, 1595, 1495, 1407, 1254, 1134, 1090, 1073, 1007, 964, 862, 838, 786, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.14 (s, 3H), 0.21 (s, 3H), 4.97 (d, J = 5.1 Hz, 1H), 5.66 (d, J = 5.1 Hz, 1H), 5.76 (dd, J = 5.7, 18.6 Hz, 1H), 5.99 (dd, J = 5.7, 14.7 Hz, 1H), 6.08 (dd, J = 14.7, 18.6 Hz, 1H), 7.30—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = −1.83, −1.67, 51.19, 79.82, 127.42, 128.20, 128.68, 134.08, 136.76, 139.68. Found: C, 39.62; H, 4.46%. Calcd for $C_{12}H_{16}Br_2OSi$: C, 39.58; H, 4.43%.

1,1-Dibromo-2-dimethyl(vinyl)siloxyoctane (6b): Bp 75 °C (0.5 Torr); IR (neat) 2952, 2924, 2854, 1595, 1466, 1407, 1253, 1103, 1051, 1008, 959, 897, 837, 785, 703, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.266 (s, 3H), 0.274 (s, 3H), 0.90 (t, J = 6.9 Hz, 3H), 1.20—1.50 (m, 8H), 1.58—1.84 (m, 2H), 3.83 (ddd, J = 3.6, 3.6, 8.1 Hz, 1H), 5.61 (d, J = 3.6 Hz, 1H), 5.84 (dd, J = 19.5, 4.8 Hz, 1H), 6.07 (dd, J = 14.7, 4.8 Hz, 1H), 6.20 (dd, J = 19.5, 14.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −1.55, −1.45, 13.96, 22.47, 25.17, 28.99, 31.61, 33.45, 51.69, 77.24, 134.06, 137.19. Found: C, 39.06; H, 6.50%. Calcd for $C_{12}H_{24}Br_2OSi$: C, 38.72; H, 6.50%.

General Procedure for the Reaction of Allylsilyl- or Vinylsilyldibromomethyllithium with Carbonyl Compound (Method B). An ethereal solution of allyl(dibromomethyl)dimethylsilane (0.27 g, 1.0 mmol) was added to a solution of lithium diisopropylamide (1.2 mmol) in ether (3 ml) at −78 °C under argon atmosphere. After being stirred for 1 h at −78 °C, benzaldehyde (0.13 g, 1.2 mmol) in Et_2O (1 ml) was added and the reaction mixture was stirred for 20 min. To the mixture was added iodomethane (0.21 g, 1.5 mmol) followed by HMPA (0.22 g, 1.2 mmol) and whole mixture was allowed to warm to ambient temperature for 5 h. Extractive workup and purification by silica-gel column chromatography gave 1-allyldimethylsiloxy-2,2-dibromo-1-phenylpropane (**7a**, 0.28 g) in 71% yield: Bp 105 °C (0.5 Torr); IR (neat) 3062, 3028, 2956, 1630, 1453, 1255, 1153, 1098, 1071, 865, 754, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.04 (s, 3H), 0.10 (s, 3H), 1.57 (d, J = 8.1 Hz, 2H), 2.39 (s, 3H), 4.83 (m, 2H), 4.95 (s, 1H), 5.69 (ddt, J = 9.3, 17.4, 8.1 Hz, 1H), 7.30—7.36 (m, 3H), 7.48—7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = −2.32, −2.26, 24.56, 35.39, 72.52, 83.82, 114.02, 127.55, 128.63, 129.21, 133.70, 138.49. Found: C, 42.68; H, 5.13 %. Calcd for $C_{14}H_{20}Br_2OSi$: C, 42.87; H, 5.14%.

3-Allyldimethylsiloxy-2,2-dibromononane (7b): Bp 95 °C (0.5 Torr); IR (neat) 2954, 2924, 2854, 1632, 1442, 1375, 1255, 1103, 1061, 896, 840, 664 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.20 (s, 3H), 0.22 (s, 3H), 0.89 (t, J = 6.8 Hz, 3H), 1.20—1.40 (m, 6H), 1.20—1.60 (m, 3H), 1.72 (d, J = 8.1 Hz, 2H), 2.02 (m, 1H), 2.40 (s, 3H), 3.80 (dd, J = 8.7, 2.1 Hz, 1H), 4.84—4.95 (m, 2H), 5.80 (ddt, J = 17.1, 10.2, 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −1.53, −1.33, 13.95, 22.50, 25.41, 26.78, 29.09, 31.62, 33.97, 35.97, 74.40, 82.91, 114.07, 134.05. Found: C, 41.81; H, 6.94%. Calcd for $C_{14}H_{28}Br_2OSi$: C, 42.01; H, 7.05%.

General Procedure for the Reaction of Silanols with Enol Ethers. The reaction of *t*-butyldimethylsilanol with ethyl vinyl ether is representative. To a stirred solution of *t*-butyldimethylsilanol (0.13 g, 1.0 mmol) and ethyl vinyl ether (0.11 g, 1.5 mmol) in dichloromethane (3 ml) was added *N*-iodosuccinimide (0.25 g, 1.1 mmol) at 0 °C. To the reaction mixture which had been stirred for 24 h, was added hexane (10 ml) and a white precipitate was formed. The whole mixture was filtered through a short alumina layer. The filtrate was concentrated in vacuo and purification of the residual oil by silica-gel column chromatography gave 1-(*t*-butyldimethylsiloxy)-1-ethoxy-2-iodoethane (**8a**, 0.29 g) in 89% yield: Bp 90 °C (1 Torr); IR (neat) 2950, 2928, 2884, 2854, 1464, 1414, 1253, 1182, 1127, 1034, 867, 836, 777, 673 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.11 (s, 3H), 0.12 (s, 3H), 0.90 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H), 3.14 (dd, J = 10.2, 3.9 Hz, 1H), 3.21 (dd, J = 10.2, 5.7 Hz, 1H), 3.47 (dq, J = 9.0, 7.1 Hz, 1H), 3.67 (dq, J = 9.0, 7.1 Hz, 1H), 4.80 (dq, J = 5.7, 3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = −4.72, −4.43, 9.45, 14.91, 17.90, 25.58, 62.03, 96.46. Found: C, 36.10; H, 7.18%. Calcd for $C_{10}H_{23}IO_2Si$: C, 36.37; H, 7.02%.

1-Bromo-2-(*t*-butyldimethylsiloxy)-2-ethoxyethane (8b): Bp 70 °C (1 Torr); IR (neat) 2952, 2928, 2886, 2856, 1464, 1254, 1123, 1035, 920, 837, 777, 681 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.12 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H), 3.27 (dd, J = 10.5, 4.2 Hz, 1H), 3.35 (dd, J = 10.5, 6.0 Hz, 1H), 3.50 (dq, J = 9.0, 7.1 Hz, 1H), 3.69 (dq, J = 9.0, 7.1 Hz, 1H), 4.91 (dq, J = 6.0, 4.2 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ = −4.69, −4.44, 14.97, 17.90, 25.55, 34.71, 62.18, 91.44, 96.53. Found: C, 42.36; H, 8.47%. Calcd for $C_{10}H_{23}BrO_2Si$: C, 42.40; H, 8.18%.

1-(Diphenyl)vinylsiloxy-1-ethoxy-2-iodoethane (9a): Bp 146 °C (0.5 Torr); IR (neat) 3066, 2972, 2880, 1592, 1429, 1405, 1374, 1348, 1332, 1182, 1113, 998, 853, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.08 (t, J = 7.1 Hz, 3H), 3.19 (dd, J = 4.2, 10.2 Hz, 1H), 3.24 (dd, J = 6.2, 10.2 Hz, 1H), 3.36 (dq, J = 9.3, 7.1 Hz, 1H), 3.57 (dq, J = 9.3, 7.1 Hz, 1H), 4.90 (dq, J = 4.2, 6.0 Hz, 1H), 5.91 (dd, J = 3.6, 20.1 Hz, 1H), 6.31 (dd, J = 3.6, 14.7 Hz, 1H), 6.54 (dd, J = 14.7, 20.1 Hz, 1H), 7.35—7.50 (m, 6H), 7.60—7.70 (m, 4H), ^{13}C NMR ($CDCl_3$) δ = 9.26, 14.65, 63.22, 97.00, 127.95, 127.99, 130.31, 130.32, 133.40, 133.62, 135.20, 135.23, 137.93. Found: C, 50.84; H, 4.95%. Calcd for $C_{18}H_{21}IO_2Si$: C, 50.95; H, 4.99%.

2-(Diphenyl)vinylsiloxy-3-iodo-1-oxacyclohexane (9b): Bp 150 °C (0.5 Torr); IR (neat) 3064, 3046, 2942, 2850, 1592, 1429, 1383, 1172, 1143, 1119, 1068, 1023, 993, 816, 713, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.50—1.75 (m, 2H), 2.00 (ddt, J = 18.5, 8.4, 4.2 Hz, 1H), 2.43 (m, 1H), 3.47 (ddd, J = 11.4, 7.5, 3.6 Hz, 1H), 4.03 (m, 1H), 4.13 (ddd, J = 8.4, 5.4, 3.9 Hz, 1H), 4.99 (d, J = 5.4 Hz, 1H), 5.93 (dd, J = 20.4, 3.9 Hz, 1H), 6.29 (dd, J = 14.7, 3.9 Hz, 1H), 6.52 (dd, J = 20.4, 14.7 Hz, 1H), 7.35—7.50 (m, 6H), 7.60—7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 25.61, 32.26, 32.63, 63.89, 98.00, 127.86, 127.89, 130.19, 130.23, 133.34, 133.42, 133.45,

135.32, 135.35, 137.66. Found: C, 52.58; H, 4.98%. Calcd for $C_{19}H_{21}IO_2Si$: C, 52.30; H, 4.85%.

3- Bromo- 2- (diphenyl)vinylsiloxy- 1- oxacyclohexane (9c, 56 : 44 Diastereomeric Mixture): Bp 140 °C (0.5 Torr); IR (neat) 3046, 2942, 2848, 1591, 1430, 1388, 1156, 1119, 1020, 990, 820, 712, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.45—2.00 (m, 4H), 2.46 (ddd, J = 4.2, 8.7, 18.6 Hz, 0.56H), 3.47 (m, 1H), 3.99 (m, 1.44H), 4.97 (d, J = 5.6 Hz, 0.56H), 5.06 (dd, J = 3.0, 4.8 Hz, 0.44H), 5.90 (m, 1H), 6.28 (m, 1H), 6.52 (m, 1H), 7.35—7.50 (m, 6H), 7.60—7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 19.28, 23.57, 25.23, 30.08, 32.85, 51.72, 62.72, 63.04, 94.34, 96.73, 127.80, 127.83, 127.88, 127.91, 129.98, 130.01, 130.21, 130.25, 133.25, 133.36, 133.41, 133.95, 134.18, 134.22, 135.14, 135.19, 135.22, 135.26, 137.05, 137.71. Found: C, 58.56; H, 5.41%. Calcd for $C_{19}H_{21}BrO_2Si$: C, 58.61; H, 5.44%.

1-Allyldiphenylsiloxy-1-ethoxy-2-iodoethane (10a): Bp 150 °C (0.5 Torr); IR (neat) 3066, 2972, 2876, 1631, 1429, 1157, 1115, 1016, 997, 899, 769, 736, 699, 593 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.07 (d, J = 6.9 Hz, 3H), 2.25 (dd, J = 1.5, 8.1 Hz, 2H), 3.16 (dd, J = 4.2, 10.5 Hz, 1H), 3.21 (dd, J = 5.4, 10.5 Hz, 1H), 3.32 (dq, J = 9.3, 6.9 Hz, 1H), 3.52 (dq, J = 9.3, 6.9 Hz, 1H), 4.84 (dd, J = 4.2, 5.4 Hz, 1H), 4.94 (m, 2H), 5.82 (ddt, J = 9.9, 17.1, 8.1 Hz, 1H), 7.35—7.50 (m, 6H), 7.60—7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 9.27, 14.71, 22.27, 63.03, 96.89, 115.66, 127.96, 127.98, 130.33, 132.67, 133.71, 133.83, 135.03, 135.06. Found: C, 52.21; H, 5.23%. Calcd for $C_{19}H_{23}IO_2Si$: C, 52.06; H, 5.29%.

2-Allyldiphenylsiloxy-3-iodo-1-oxacyclohexane (10b): Bp 165 °C (0.5 Torr); IR (neat) 3066, 2944, 2848, 1631, 1429, 1383, 1173, 1143, 1111, 1066, 1022, 993, 816, 736, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.50—1.74 (m, 2H), 1.99 (ddt, J = 13.8, 4.8, 8.4 Hz, 1H), 2.26 (dd, J = 1.2, 7.8 Hz, 2H), 2.42 (m, 1H), 3.47 (ddd, J = 11.7, 8.1, 3.9 Hz, 1H), 4.06 (m, 2H), 4.94 (m, 2H), 4.95 (d, J = 5.7 Hz, 1H), 5.85 (ddt, J = 17.1, 10.2, 7.8 Hz, 1H), 7.35—7.47 (m, 6H), 7.62—7.68 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 22.18, 25.70, 32.24, 32.72, 63.93, 98.00, 115.38, 127.82, 127.86, 130.14, 130.17, 132.93, 133.73, 133.83, 135.04, 135.06. Found: C, 53.12; H, 5.22%. Calcd for $C_{20}H_{23}IO_2Si$: C, 53.34; H, 5.15%.

General Procedure for the Radical Cyclization of 1,1-Dibromo-2-(dimethyl)vinylsiloxyalkanes and the Successive Oxidation. To a solution of 1,1-dibromo-2-(dimethyl)vinylsiloxy-2-phenylethane (**6a**, 0.18 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After this was stirred for 6 h, more tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added and the mixture was stirred for another 3 h. The mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the whole mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. The residual oil was diluted with THF (2 ml) and MeOH (2 ml). Potassium fluoride (0.23 g, 4 mmol), $KHCO_3$ (1.0 g, 10 mmol), and H_2O_2 (30%, 1.1 g, 10 mmol) were added, and the mixture was stirred for 10 h at room temperature; then aqueous $NaHSO_3$ was added carefully. Extractive workup and purification by silica-gel column chromatography gave 1-phenyl-1, 3-butanediol (57 mg, 69% yield).

General Procedure for the Radical Cyclization of 1-(Diphenyl)vinylsiloxy-2-iodoalkanes and the Successive Transformation into Ethers. To a solution of 1-(diphenyl)vinylsiloxy-1-ethoxy-2-iodoethane (**9a**, 0.21 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After being stirred for 6 h, the mixture was concentrated in vacuo and CH_2Cl_2 (5 ml) and allyltrimethylsilane (0.11 g, 1.0 mmol) was added. This mixture was cooled to −78 °C and trimethylsilyl triflate (1.0 M, 0.1 ml, 0.1 mmol) was added; the whole mixture was stirred for 1 h. The mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (10 ml×5). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residual oil was diluted with ethyl acetate (20 ml); potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and this mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 4-ethoxy-6-(trimethylsiloxy)diphenylsilyl-1-heptane (**11a**, 0.14 g, 50 : 50 diastereomeric mixture) in 69% yield: Bp 130 °C (0.5 Torr); IR (neat) 3066, 2952, 2864, 1640, 1429, 1251, 1114, 1082, 840, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.06 (s, 9H), 0.98 (d, J = 7.1 Hz, 1.5H), 1.01 (d, J = 7.1 Hz, 1.5H), 1.12 (t, J = 6.9 Hz, 1.5H), 1.17 (t, J = 6.9 Hz, 1.5H), 1.30—1.45 (m, 1H), 1.50—1.80 (m, 2H), 2.13 (ddd, J = 6.9, 6.9, 13.5 Hz, 1H), 2.27 (ddd, J = 6.9, 6.9, 13.5 Hz, 1H), 3.25—3.60 (m, 3H), 5.00 (m, 2H), 5.77 (m, 1H), 7.25—7.40 (m, 6H), 7.50—7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 1.89, 1.92, 13.46, 14.20, 14.44, 15.48, 15.56, 15.92, 35.17, 35.58, 37.60, 39.13, 63.91, 64.12, 76.39, 78.19, 116.63, 116.68, 127.70, 127.74, 129.44, 129.47, 129.53, 129.56, 134.66, 134.69, 135.23, 135.44, 136.04, 136.27. Found: C, 69.76; H, 8.74%. Calcd for $C_{24}H_{36}O_2Si_2$: C, 69.85; H, 8.79%.

2-Allyl-3-{1-[(trimethylsiloxy)diphenylsilyl]ethyl}-1-oxacyclohexane (11b, 65 : 35 Diastereomeric Mixture): Bp 165 °C (0.5 Torr); IR (neat) 3068, 2950, 2846, 1639, 1429, 1253, 1109, 1027, 909, 840, 752, 702, 602 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.07 (s, 3.15H), 0.11 (s, 5.85H), 1.02 (d, J = 7.8 Hz, 1.95H), 1.09 (d, J = 7.8 Hz, 1.05H), 1.30—1.80 (m, 6H), 2.19 (m, 1H), 2.48 (m, 1H), 3.10—3.50 (m, 2H), 3.86 (m, 1H), 5.07 (m, 1H), 5.76 (dddd, J = 6.0, 7.8, 10.5, 16.5 Hz, 0.35H), 5.89 (dddd, J = 6.3, 7.5, 9.9, 17.4 Hz, 0.65H), 7.28—7.42 (m, 6H), 7.47—7.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 1.96, 7.96, 14.63, 20.15, 20.89, 26.18, 26.62, 27.03, 27.89, 37.32, 37.78, 39.56, 46.41, 68.27, 68.46, 79.50, 79.72, 116.25, 116.38, 127.73, 127.75, 127.81, 127.88, 129.46, 129.56, 129.71, 134.32, 134.53, 134.81, 135.68, 135.75, 136.61, 136.89, 137.74. Found: C, 70.91; H, 8.74%. Calcd for $C_{25}H_{36}O_2Si_2$: C, 70.70; H, 8.54%.

Synthesis of 1- (1- Oxa- 3- cyclohexyl)ethyldiphenylsilanol. The use of triethylsilane in place of allyltrimethylsilane in the above reaction afforded **12**, which was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether. They were converted into 1-(1-oxa-3-cyclohexyl)ethyldiphenylsilanol (58 : 42 diastereomeric mixture) in 90% yield upon treatment with tetrabutylammonium fluoride in THF: Bp 160 °C (0.5 Torr); IR (neat) 3306, 3064, 2936, 2846, 1428, 1111, 1082, 908, 855, 738, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.02 (d, J = 7.5 Hz, 1.26H), 1.03 (d, J = 7.5 Hz, 1.74H), 1.20—1.58 (m, 3.58H), 1.66—1.90 (m, 2.42H), 2.86 (bs, 0.42H), 2.97 (bs, 0.58H), 3.13 (t, J = 10.8 Hz, 0.42H), 3.18—3.27 (m, 1H), 3.32 (t, J = 9.9 Hz, 0.58H), 3.77 (m, 1.58H), 3.93 (ddd, J = 2.1, 3.9, 11.1 Hz, 0.42H), 7.30—7.45 (m, 6H), 7.55—7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 10.77, 10.97, 21.21, 22.65, 25.84, 26.32, 27.33, 29.95, 37.00, 37.50, 68.15, 68.21, 72.16, 73.22, 127.93, 127.97, 127.99, 129.78, 129.83, 134.35, 134.37, 134.42, 134.46, 135.88, 136.02, 136.15, 136.28. Found: C, 72:95; H, 7.75%. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74%.

General Procedure for the Radical Cyclization of 1-Allyldimethylsiloxy-2,2-dibromoalkanes. To a solution of 1-allyldimethylsiloxy-2,2-dibromo-1-phenylethane (**5a**, 0.19 g, 0.5 mmol)

and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After this had been stirred for 6 h, more tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) were added and the mixture was stirred for another 3 h. This mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 2,2-dimethyl-7-phenyl-1-oxa-2-silacycloheptane (**13a**, 93 mg) in 84 % yield: Bp 100 °C (1 Torr); IR (neat) 2952, 2908, 2850, 1493, 1452, 1356, 1251, 1091, 1070, 999, 948, 895, 838, 822, 789, 741, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.15 (s, 3H), 0.21 (s, 3H), 0.74 (ddd, J = 3.0, 11.7, 15.0 Hz, 1H), 0.86 (m, 1H), 1.40—1.65 (m, 2H), 1.75 (m, 1H), 1.84—2.10 (m, 3H), 4.81 (dd, J = 1.2, 9.0 Hz, 1H), 7.18—7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = −0.67, −0.60, 17.70, 23.26, 30.26, 40.99, 76.65, 125.44, 126.70, 128.15, 146.28. Found: C, 70.70; H, 9.36%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

7-Hexyl-2,2-dimethyl-1-oxa-2-silacycloheptane (13b): Bp 75 °C (1 Torr); IR (neat) 2908, 2852, 1457, 1250, 1087, 997, 836, 790, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.08 (s, 3H), 0.11 (s, 3H), 0.64 (ddd, J = 2.7, 12.0, 15.0 Hz, 1H), 0.78 (m, 1H), 0.88 (t, J = 6.8 Hz, 3H), 1.20—1.54 (m, 13H), 1.66—1.92 (m, 3H), 3.60 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = −0.86, 14.00, 17.63, 22.56, 23.15, 25.99, 29.18, 30.33, 31.85, 38.62, 38.89, 74.57. Found: C, 68.35; H, 12.62%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

7-Ethoxy-2,2-dimethyl-7-phenyl-1-oxa-2-silacycloheptane (13c): Bp 75 °C (0.5 Torr); IR (neat) 2928, 1447, 1253, 1173, 1140, 1044, 1014, 966, 835, 782, 753, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.22 (s, 3H), 0.31 (s, 3H), 0.73 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H), 1.10—1.30 (m, 1H), 1.50—1.72 (m, 3H), 2.06 (ddd, J = 2.4, 8.4, 15.3 Hz, 1H), 2.17 (ddd, J = 2.4, 9.3, 15.3 Hz, 1H), 3.00 (dq, J = 9.6, 7.1 Hz, 1H), 3.45 (dq, J = 9.6, 7.1 Hz, 1H), 7.20—7.37 (m, 3H), 7.43—7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = −0.43, 0.08, 15.39, 16.45, 23.30, 23.40, 43.25, 56.82, 102.41, 126.80, 127.25, 127.84, 144.48. Found: C, 68.42; H, 9.43%. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15%.

Radical Cyclization of 1-Allyldiphenylsiloxy-1-ethoxy-2-iodoalkane. To a solution of 1-allyldiphenylsiloxy-1-ethoxy-2-iodoethane (**10a**, 0.22 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature. After being stirred for 6 h, the mixture was concentrated in vacuo and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 7-ethoxy-2,2-diphenyl-1-oxa-2-silacycloheptane (**14a**, 0.14 g) in 89% yield: Bp 145 °C (0.5 Torr); IR (neat) 2922, 2856, 1429, 1376, 1135, 1119, 1059, 1035, 978, 730, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.12 (t, J = 7.1 Hz, 3H), 1.18—1.42 (m, 2H), 1.44—1.60 (m, 1H), 1.70—1.94 (m, 5H), 3.39 (dq, J = 9.6, 7.1 Hz, 1H), 3.79 (dq, J = 9.6, 7.1 Hz, 1H), 5.06 (dd, J = 5.7, 2.1 Hz, 1H), 7.30—7.45 (m, 6H), 7.55—7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 14.73, 14.89, 23.22, 25.39, 37.99, 63.13, 99.61, 127.80, 127.90, 129.72, 134.34, 134.38, 136.55. Found: C, 73.03; H, 7.88%. Calcd for $C_{19}H_{24}O_2Si$: C, 73.03; H, 7.74%.

3,3-Diphenyl-2,11-dioxa-3-silabicyclo[5.4.0]undecane (14b): Bp 155 °C (0.5 Torr); IR (neat) 2924, 2856, 1429, 1118, 1085, 1068, 1045, 1009, 996, 981, 730, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.29 (m, 2H), 1.40—1.95 (m, 9H), 3.63 (ddd, J = 11.4, 5.1, 5.1 Hz, 1H), 4.15 (ddd, J = 4.2, 9.0, 11.4 Hz, 1H), 5.28 (s, 1H), 7.30—7.43 (m, 6H), 7.60—7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 15.43, 19.37, 24.38, 25.55, 32.84, 41.60, 62.04, 96.63, 127.80, 128.08, 129.72, 129.90, 134.12, 134.24, 135.89, 136.17. Found: C, 73.84; H, 7.61%. Calcd for $C_{20}H_{24}O_2Si$: C, 74.03; H, 7.45%.

Allylation of 7-Alkoxy-1-oxa-2-silacycloheptane. To a cooled solution of 7-ethoxy-2,2-diphenyl-1-oxa-2-silacycloheptane (**14a**, 0.16 g, 0.5 mmol) and allyltrimethylsilane (0.11 g, 1.0 mmol) in dichloromethane (5 ml) at −78 °C was added trimethylsilyl triflate (1.0 M, 0.1 ml, 0.1 mmol) and the whole mixture was stirred for 1h. The mixture was poured into saturated aqueous $NaHCO_3$. Extractive workup followed by purification by silica-gel column chromatography gave 4-ethoxy-8-[diphenyl(trimethylsiloxy)silyl]-1-octene (**15a**, 0.20 g) in 92% yield: Bp 130 °C (0.5 Torr); IR (neat) 3066, 2928, 2858, 1620, 1429, 1253, 1116, 1062, 1027, 839, 754, 732, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.09 (s, 9H), 1.07 (t, J = 7.8 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.25—1.50 (m, 6H), 2.21 (ddd, J = 1.2, 5.7, 6.9 Hz, 2H), 3.22 (m, 1H), 3.40 (dq, J = 9.0, 7.2 Hz, 1H), 3.51 (dq, J = 9.0, 7.2 Hz, 1H), 5.03 (m, 2H), 5.80 (ddt, J = 17.1, 9.9, 7.2 Hz, 1H), 7.30—7.45 (m, 6H), 7.50—7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 1.87, 15.45, 15.70, 23.14, 29.23, 33.59, 38.45, 64.21, 78.81, 116.64, 127.74, 129.49, 134.21, 135.31, 137.47. Found: C, 70.21; H, 9.20%. Calcd for $C_{25}H_{38}O_2Si_2$: C, 70.36; H, 8.98%.

2-Allyl-3-[3-diphenyl(trimethylsiloxy)silylpropyl]-1-oxacyclohexane (15b, 67 : 33 Diastereomeric Mixture): Bp 155 °C (0.5 Torr); IR (neat) 3066, 3046, 2930, 2846, 1429, 1253, 1113, 1066, 860, 840, 753, 732, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.09 (s, 9H), 1.02 (m, 2H), 1.20—1.85 (m, 9H), 2.06 (m, 1H), 2.31 (m, 1H), 3.00 (ddd, J = 2.7, 7.8, 10.5 Hz, 0.67H), 3.30 (ddd, J = 3.6, 11.4, 14.7 Hz, 0.67H), 3.42 (m, 0.66H), 3.89 (m, 1H), 5.03 (m, 2H), 5.69—5.93 (m, 1H), 7.30—7.43 (m, 6H), 7.50—7.56 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 1.89, 15.71, 15.86, 19.55, 20.78, 21.62, 26.26, 26.38, 28.96, 29.23, 35.45, 35.93, 36.20, 37.53, 39.25, 67.71, 68.21, 79.88, 81.69, 116.24, 116.35, 127.77, 129.56, 134.18, 135.73, 137.32, 137.38. Found: C, 71.20; H, 8.86%. Calcd for $C_{26}H_{38}O_2Si_2$: C, 71.18; H, 8.73%.

Reduction of 7-Alkoxy-1-oxa-2-silacycloheptane. The use of triethylsilane in place of allyltrimethylsilane in the above reaction afforded ether **15** which was obtained as a mixture of trimethylsilyl ether and triethylsilyl ether. They were converted into (5-ethoxypentyl)diphenylsilanol in 93% yield upon treatment with tetrabutylammonium fluoride in THF: Bp 160 °C (0.5 Torr); IR (neat) 3348, 3064, 2972, 2926, 1429, 1113, 852, 737, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.15 (t, J = 7.8 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H), 1.34—1.60 (m, 6H), 2.20—2.60 (bs, 1H), 3.36 (t, J = 6.5 Hz, 2H), 3.43 (q, J = 7.1 Hz, 2H), 7.30—7.45 (m, 6H), 7.55—7.64 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 14.79, 15.04, 22.61, 29.01, 29.54, 66.04, 70.54, 127.94, 129.84, 134.23, 136.60. Found: C, 72.31; H, 8.58%. Calcd for $C_{19}H_{28}O_2Si$: C, 72.10; H, 8.92%.

3-(1-Oxa-3-cyclohexyl)propyldiphenylsilanol: Bp 165 °C (0.5 Torr); IR (neat) 3336, 3064, 2920, 2846, 1429, 1117, 1082, 856, 731, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.90—1.25 (m, 5H), 1.30—1.56 (m, 5H), 1.75 (m, 1H), 2.94 (t, J = 10.5 Hz, 1H), 3.03 (bs, 1H), 3.27 (m, 1H), 3.74 (ddd, J = 1.8, 3.9, 11.4 Hz, 1H), 3.80 (m, 1H), 7.30—7.45 (m, 6H), 7.55—7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 15.18, 19.89, 25.66, 29.70, 35.45, 36.05, 68.37, 73.33, 127.93, 129.86, 134.21, 136.49. Found: C, 73.81; H, 8.23%. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03%.

Cyclization of 1-Allyldimethylsiloxy-2,2-dibromoalkane into 2,2,6-Trimethyl-1-oxa-2-silacycloheptane. To a solution of 1-allyldimethylsiloxy-2,2-dibromo-1-phenylpropane (**7a**, 0.20 g, 0.5

mmol) and 1,1,1,3,3,3-hexamethyl-2-trimethylsilyltrisilane (0.14 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature under argon atmosphere. After being stirred for 6 h, the mixture was concentrated in vacuo and the residual oil was diluted with hexane (5 ml). Then tributyltin hydride (0.16 g, 0.55 mmol) and triethylborane (1.0 M, hexane solution, 0.1 ml, 0.1 mmol) were added successively at −78 °C and the mixture was stirred for another 2 h. The mixture was concentrated and the residual oil was diluted with ethyl acetate (20 ml). Potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 2,2,6-trimethyl-7-phenyl-1-oxa-2-silacycloheptane (**17a**, 97 : 3 diastereomeric mixture) in 68% yield: Bp 60 °C (0.5 Torr); IR (neat) 2958, 2910, 2854, 1450, 1251, 1097, 1041, 911, 848, 835, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.08 (s, 2.91H), 0.12 (s, 0.09H), 0.15 (s, 0.09H), 0.19 (s, 2.91H), 0.53 (d, J = 6.9 Hz, 0.09H), 0.65—0.76 (m, 1H), 0.73 (d, J = 6.9 Hz, 2.91H), 0.79—0.90 (m, 1H), 1.60—2.05 (m, 4H), 2.11 (m, 1H), 4.26 (d, J = 9.3 Hz, 0.03H), 4.93 (s, 0.97H), 7.16—7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = −1.55, −0.90, 10.95, 17.58, 17.81, 38.12, 40.24, 77.02, 125.80, 126.29, 127.68, 145.05. Found: C, 71.51; H, 9.43%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

7-Hexyl-2,2,6-trimethyl-1-oxa-2-silacycloheptane (17b, 80 : 20 Diastereomeric Mixture): Bp 80 °C (1 Torr); IR (neat) 2922, 2852, 1460, 1380, 1250, 1160, 1088, 1034, 906, 834, 797, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.04 (s, 2.4H), 0.06 (s, 0.6H), 0.08 (s, 2.4H), 0.09 (s, 0.6H), 0.54—0.76 (m, 2H), 0.80—0.90 (m, 6H), 1.10—1.80 (m, 15H), 3.31 (ddd, J = 2.7, 8.1, 8.1 Hz, 0.2H), 3.65 (dd, J = 2.4, 9.3 Hz, 0.8H); ^{13}C NMR ($CDCl_3$) δ = −1.41, −0.94, −0.89, −0.49, 12.16, 14.00, 17.37, 17.55, 17.90, 18.66, 20.54, 22.57, 22.59, 25.99, 26.65, 29.24, 29.35, 31.90, 36.02, 38.05, 38.12, 40.93, 76.19, 78.21. Found: C, 69.38; H, 12.52%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

Synthesis of 4-Butoxy-2-methyl-6-hepten-1-ol (22). To a solution of 1-allyloxy-1-butoxy-2-iodoethane (**20**, 0.14 g, 0.5 mmol) and tributyltin hydride (0.16 g, 0.55 mmol) in benzene (30 ml) was added triethylborane (1.0 M hexane solution, 0.1 ml, 0.1 mmol) at room temperature. After being stirred for 6 h, the mixture was concentrated and CH_2Cl_2 (5 ml) and allyltrimethylsilane (0.11 g, 1.0 mmol) was added. Then titanium tetrachloride (1.0 M, 1 ml, 1.0 mmol) was added at −78 °C and stirred for 1 h. The mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (10 ml×5). The organic layer was dried and concentrated. The residual oil was diluted with ethyl acetate (20 ml); then potassium fluoride (1 g) and saturated aqueous KF (2 ml) were added and the mixture was stirred for 5 h. The resulting precipitate was filtered off and the filtrate was concentrated. Purification by silica-gel column chromatography gave 4-butoxy-2-methyl-6-hepten-1-ol (**22**, 70 : 30 diastereomeric mixture) in 90% yield: Bp 110°C (5 Torr); IR (neat) 3370, 3072, 2956, 2926, 1642, 1460, 1437, 1378, 1348, 1091, 1042, 994, 912 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92 (m, 6H), 1.37 (m, 2H), 1.46—1.68 (m, 4H), 1.80 (m, 0.3H), 1.92 (m, 0.7H), 2.31 (m, 2H), 2.72 (s, 0.3H), 3.03 (s, 0.7H), 3.30—3.65 (m, 5H), 5.08 (m, 2H), 5.79 (ddt, J = 9.9, 17.1, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.75, 17.51, 17.79, 19.25, 31.99, 33.85, 37.75, 37.93, 38.30, 39.03, 68.02, 68.46, 68.64, 68.77, 77.05, 77.99, 117.10, 117.32, 134.52, 134.81. Found: C, 71.83; H, 12.23%. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%.

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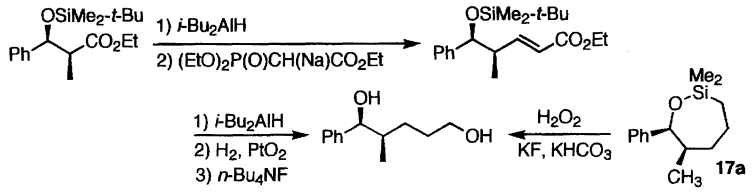

Scheme 10.

H_2O_2 oxidation (Scheme 10). Physical data of 2-methyl-1-phenyl-1,5-pentanediol: Bp 120 °C (1 Torr); IR (neat) 3268, 2932, 2870, 1459, 1377, 1030, 762, 700 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.93$ (d, $J = 6.9$ Hz, 3H), 1.05—1.21 (m, 1H), 1.38—1.75 (m, 5H), 1.75—1.87 (m, 1H), 3.59 (t, $J = 6.5$ Hz, 2H), 4.57 (d, $J = 5.4$ Hz, 1H), 7.20—7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 14.28$, 28.85, 30.08, 39.77, 62.81, 77.65, 126.39, 127.24, 128.17, 143.63. Found: C, 73.93; H, 9.24%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.

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