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Lithium Carbenoids Induced Ring Enlargement of Silacyclobutane into 2-Halo-1-silacyclopentane and its Use in Organic Synthesis

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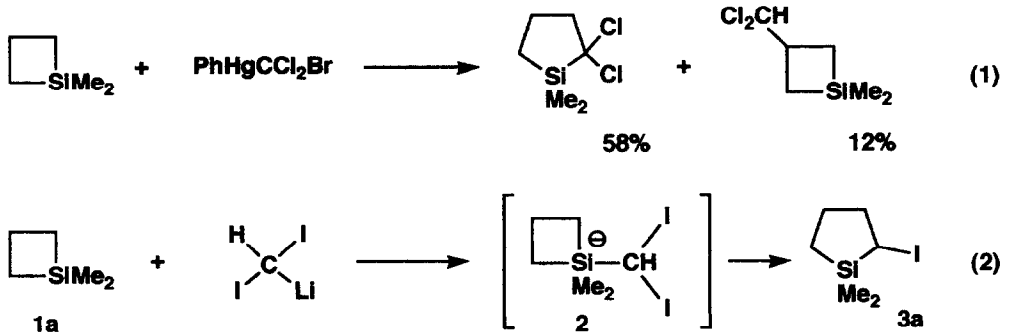
Abstract: An addition of lithium diisopropylamide to a solution of 1,1-dimethyl-1-silacyclobutane and dihalomethane such as CH_2I_2, CH_2Br_2, or CH_2Cl_2 provided the corresponding 1,1-dimethyl-2-halo-1-silacyclopentane in good yield. The reactions of 1,1,2-trimethyl-1-silacyclobutane or 1,1,3-trimethyl-1-silacyclobutane with lithium carbenoids are also described. Treatment of 2-iodo-1-silacyclopentane with *tert*-butyllithium gave 2-lithio-1-silacyclopentane which reacted with electrophiles to afford the corresponding adducts.

The silacyclobutane ring systems are considerably more reactive than the comparable acyclic systems due to the ring strain and are therefore extremely susceptible to ring opening.[1,2] In fact, nucleophiles such as water, alcohol, acetate ions, hydride ions, and organolithium derivatives easily bring about ring opening. Electrophilic cleavage is also easy and leads to ring opening in the case of acids (H_2SO_4, HCl). Ring opening and formation of linear polymers can be induced by transition metal catalysts. Gas-phase pyrolytic decomposition of silacyclobutane into silenes also has been extensively studied. However, little work has been reported on the synthetic use of silacyclobutane and we started our study to develop new synthetic method using silacyclobutanes as C3 unit.

(1) Stereoselective formation of silacyclopentanes by the reaction of silacyclobutane with lithium carbenoids

A number of ring-expansion reactions involving insertion into a Si-C ring bond of silacyclobutanes have been reported. Sulfur dioxide or sulfur trioxide reacts with silacyclobutane to afford sultine or sultone.[3] Palladium complexes catalyze the insertion of alkynes into the Si-C bonds of silacyclobutane to provide an attractive routes to silacyclohexenes.[4] Dichlorocarbene, generated from $PhHgCCl_2Br$, inserts into a Si-C ring bond to afford the silacyclopentane along with a C-H insertion product, 3-dichloromethyl-1-silacyclopentane (eq. 1).[5] Singlet methylene ($^1CH_2$), produced by the photolysis of ketene, reacts with

silacyclobutane to give a mixture of a ring insertion product and a C-H insertion product.[6] In contrast, we have found that treatment of silacyclobutane with lithium carbenoids provides silacyclopentanes exclusively (eq. 2).[7]



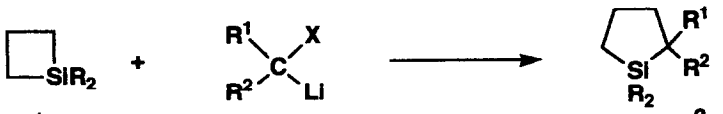
A solution of lithium diisopropylamide was added dropwise to a solution of 1,1-dimethyl-1-silacyclobutane and diiodomethane in THF over 30 min by syringe pump at -78 °C to give 2-iodo-1,1-dimethyl-1-silacyclopentane in 83% yield. The representative results are shown in Table 1. Not only dihalomethane (CH_2I_2, CH_2Br_2, CH_2Cl_2) but also benzyl bromide and iodomethyltrimethylsilane provided the corresponding 2-phenyl- and 2-trimethylsilyl-1-silacyclopentane in good yields upon treatment with lithium diisopropylamide in the presence of silacyclobutane. The substituents on silicon did not affect the reaction pathway. Thus, 1,1-diphenyl-, 1,1-dibutyl-, 1,1-di(1-hexynyl)-, and 1,1-diisopropoxy-1-silacyclobutane reacted easily with lithium carbenoids as well as 1,1-dimethyl-1-silacyclobutane. The use of trihalomethane such as CHI_3, $CHBr_3$, or $CHCl_3$ in place of dihalomethane resulted in a formation of complex mixture and desired 2,2-dihalo-1-silacyclopentanes could not be obtained.

The reaction might proceed *via* pentacoordinate silicate **2** as shown in eq. 2.[8] Analogous ring enlargement of boracyclanes *via* sequential one-carbon homologation has been reported.[9] The reaction worked stepwise, going from six-membered boracyclane to 12-membered boracyclane. In contrast, 1,1-dimethyl-1-silacyclopentane was recovered unchanged upon treatment with lithium carbenoids under the same reaction conditions. Thus, the ring strain of silacyclobutane plays an important role for the ring enlargement of silacyclobutane into silacyclopentane.

Several silacyclobutanes having substituent on four-membered ring carbon have been prepared and treated with lithium carbenoids. The reaction of 1,1,3-trimethyl-1-silacyclobutane with CHI_2Li, $CHBr_2Li$, or PhCHBrLi gave the corresponding 2,4-disubstituted 1-silacyclopentane with high stereoselectivity.[10] The ratios of *cis* and *trans* isomer (**5** : **6**) were ca 9 : 1 except for the reaction between **4b** and PhCHBrLi (Table 2).

Assignments of the products were based on the examination of the ^1H NMR spectra. All the *trans* isomers, **6a-6f**, exhibited the narrow signals for the protons (Ha) attached to carbon bearing R^1 group at lower field than those for protons in *cis* isomers **5a-5f** (See experimental part). Further support for the assignment has been given by the following transformation of **5f** and **6f** into the corresponding 1,4-diol ($HOCH_2CH(Me)CH_2CH(OH)Ph$) by the action of HBF_4 and H_2O_2 according to the reported procedure.[11]

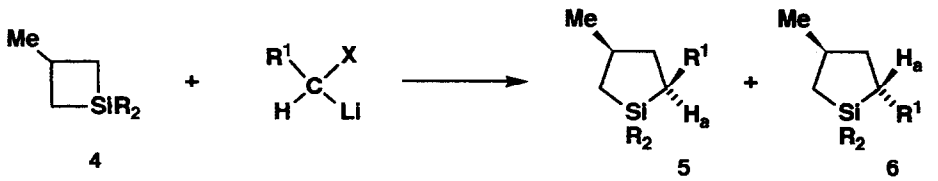
Table 1. Reaction between silacyclobutane and lithium carbenoids



1 3

Entry	Silacyclobutane 1 R	Carbenoid R^1	R^2	X	Product 3 Yield (%)
1	Me	H	I	I	83
2	Me	H	Br	Br	62
3	Me	H	Cl	Cl	49
4	Me	*n*-Bu	I	I	59
5	Me	H	Ph	Br	61
6	Me	H	Me_3Si	I	56
7	Ph	H	I	I	72
8	Ph	H	Br	Br	74
9	Ph	H	Cl	Cl	72
10	Ph	H	Ph	Br	46
11	Ph	H	Me_3Si	I	58
12	*n*-Bu	H	I	I	85
13	*n*-Bu	H	Br	Br	79
14	*n*-BuC≡C	H	I	I	88
15	O^{i}Pr	H	I	I	63

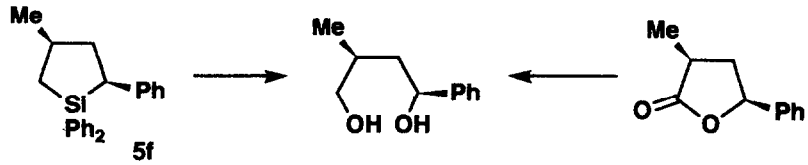
Table 2. Reaction of 3-methyl-1-silacyclobutane with lithium carbenoids



4 5 6

Entry	Silacyclobutane 4	Carbenoid R1	X	Product Yield (%)	Ratio of 5 : 6
1	**4a**: R = Me	I	I	80	**5a** : **6a** = 90 : 10
2		Br	Br	58	**5b** : **6b** = 89 : 11
3		Ph	Br	40	**5c** : **6c** = 90 : 10
4	**4b**: R = Ph	I	I	97	**5d** : **6d** = 93 : 7
5		Br	Br	88	**5e** : **6e** = 93 : 7
6		Ph	Br	58	**5f** : **6f** = 33 : 67

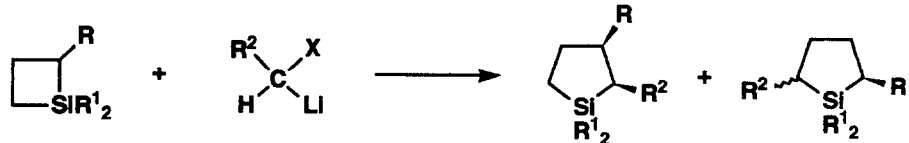
The diol (1R*,3R*) derived from **5f** was identical with a sample prepared by the reduction of *cis*-α-methyl-γ-phenyl-γ-butyrolactone[12] with $LiAlH_4$ (eq. 3). The other diol from **6f** was identical with that generated from *trans*-α-methyl-γ-phenyl-γ-butyrolactone.[12]



(3)

Cleavage of two Si-C bonds occurred in the case of 2-methyl-1-silacyclobutane (**7a** and **7c**). For instance, treatment of **7a** with diiodomethyllithium provided a mixture of *cis*-2-iodo-1,1,3-trimethyl-1-silacyclopentane (**8a**) and 2-iodo-1,1,5-trimethyl-1-silacyclopentane (**9a**) (**8a/9a** = 42/58). In contrast, one Si-C bond fission took place in the reaction of 1,1-dimethyl-2-phenyl-1-silacyclobutane **7b** with diiodomethyllithium and 2-iodo-3-phenyl-1-silacyclopentane **8d** was obtained selectively. Regioisomeric product, 2-iodo-5-phenyl-1-silacyclopentane **9d**, could not be observed in the reaction mixture. The results are summarized in Table 3. 2-Halo-3-methyl-1-silacyclopentane **8** consists of one stereoisomer (*cis*)[10] with the exception of **8d** (*cis* : *trans* = 38 : 62). The stereochemistry was confirmed by the following experiment. Treatment of **8f** with HBF_4 and H_2O_2 gave the diol (1R*,2S*) $PhCH(OH)CHMeCH_2CH_2OH$ as a single stereoisomer, which was identical with the sample prepared by the reduction of *cis*-γ-phenyl-β-methyl-γ-butyrolactone.[13] On the other hand, 2,5-disubstituted silacyclopentanes **9** are mixtures of *cis* and *trans* stereoisomers. For instance, treatment of **9f** with HBF_4 and H_2O_2 provided a 1,4-diol ($PhCH(OH)CH_2CH_2CH(Me)OH$)[14] as 2 : 1 stereoisomeric mixture.

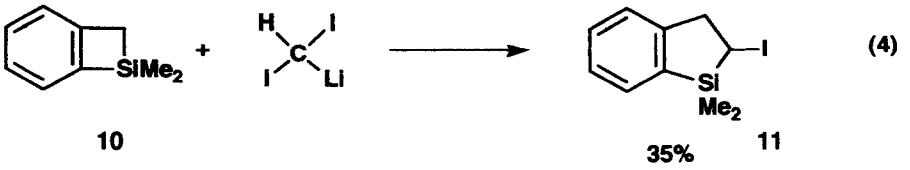
Table 3. Reaction of 2-methyl- or 2-phenyl-1-silacyclobutane with lithium carbenoids



Entry	Silacyclobutane 7			Carbenoid		Product	
		R	R^1	R^2	X	Yield (%)	Ratio of **8** : **9**
1	**7a**:	Me	Me	I	I	78	**8a** : **9a** = 42 : 58 (4 : 1)[a]
2	**7a**:	Me	Me	Br	Br	65	**8b** : **9b** = 44 : 56 (4 :1)[a]
3	**7a**:	Me	Me	Ph	Br	62	**8c** : **9c** = 36 : 64 (9 : 1)[a]
4	**7b**:	Ph	Me	I	I	53	**8d** : **9d** = 100 : 0
5	**7c**:	Me	Ph	I	I	90	**8e** : **9e** = 45 : 55 (5 : 1)[a]
6	**7c**:	Me	Ph	Ph	Br	45	**8f** : **9f** = 30 : 70 (2 : 1)[a]

a) diastereomeric ratio

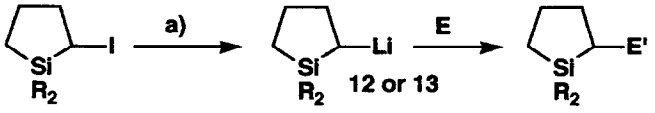
Benzosilacyclobutene (**10**)[15] afforded the corresponding silacyclopentene **11**. In this case, one of C-Si bonds was cleaved selectively (eq. 4).



10 **35%** **11** (4)

(2) Generation of 2-lithio-1-silacyclopentane from 2-iodo-1-silacyclopentane and its use for organic synthesis

α-Metallated organosilanes play a fundamental role in preparative organic chemistry. Many studies have been reported to achieve α-metallation of organosilanes. Metal-halogen exchange of α-halogenoalkylorganosilanes with either a metal or an organometallic reagent is one of reliable methods. For instance, iodomethyltrimethylsilane gives Grignard reagent upon treatment with magnesium[16] and trimethylsilylmethyllithium is formed by an addition of butyllithium.[17] Thus, we attempted to generate 2-metallated-1-silacyclopentane from 2-halo-1-silacyclopentanes. Treatment of 1,1-dimethyl-2-iodo-1-silacyclopentane with Mg in ether or *n*-BuLi in THF resulted in a formation of dimeric 2,2,2',2'-tetramethyl-2,2'-disila-1,1'-bicyclopentane in 24% or 35% yield and gave no proof of the existence of 2-metallated-1-silacyclopentane. After many experiments, the use of hexane-ether (2 : 3) instead of THF as a solvent, however, proved to be effective for the formation of 2-lithio-1-silacyclopentane with *tert*-butyllithium. An addition of *tert*-butyllithium to a solution of 1,1-diphenyl-2-iodo-1-silacyclopentane in hexane-ether at -78 °C provided **12** which gave 2-deuterio-1,1-diphenyl-1-silacyclopentane in 90% yield (90% D) upon treatment with deuterium oxide (eq. 5). 1,1-Dimethyl-2-iodo-1-silacyclopentane also provided 2-lithio compound **13** in the same way. An addition of trimethylchlorosilane to **12** or **13** afforded the corresponding 2-trimethylsilyl-1-silacyclopentane which was identical with sample derived from the reaction of silacyclobutane and iodomethyltrimethylsilane (entries 6 and 11 in Table 1).



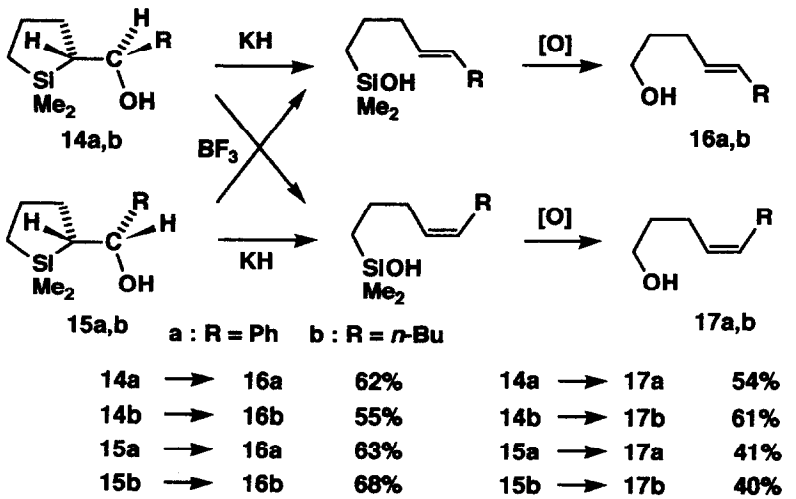
(5)

a) hexane - ether (3:2) -78°C *t*-BuLi

R = Ph E = D_2O 90% Me_3SiCl 52%

R = Me E = Me_3SiCl 63% PhCHO 55% *n*-BuCHO 68%

An addition of benzaldehyde or valeraldehyde to 2-lithio-1,1-dimethyl-1-silacyclopentane provided the adducts which are 1 : 1 mixtures of two diastereoisomers.[18] The diastereoisomers were easily separated by silica-gel column chromatography. Treatment of each stereoisomer **14** or **15** with potassium hydride[19] gave (*E*)- or (*Z*)-$RCH{=}CHCH_2CH_2CH_2SiMe_2OH$ which was converted into (*E*)- or (*Z*)-4-alken-1-ol (**16** or **17**) upon treatment with H_2O_2-KF.[20] Exposure of **14** or **15** to boron trifluoride[21] followed by oxidative cleavage of Si-C bond provided (*Z*)- or (*E*)-4-alken-1-ol (**17** or **16**), respectively (eq. 6).



(6)

EXPERIMENTAL

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

Preparation of Silacyclobutanes 1,1-Dimethyl-1-silacyclobutane and 1,1-dichloro-1-silacyclobutane were purchased from Shinetsu Silicone Chemicals and Petrarch Systems, respectively and used as derivered. 1,1-Diphenyl-1-silacyclobutane, 1,1-dibutyl-1-silacyclobutane, and 1,1-di(1-hexynyl)-1-silacyclobutane were prepared from 1,1-dichloro-1-silacyclobutane and the corresponding organometallic reagents (PhMgBr, *n*-BuLi, *n*-BuC≡CLi). 1,1,3-Trimethyl-1-silacyclobutane (**4a**) and 3-methyl-1,1-dipheny1-1-silacyclobutane (**4b**) were prepared by the treatment of $ClSi(Me_2)CH_2CH(Me)CH_2Cl$ and $ClSi(Ph_2)CH_2CH(Me)CH_2Cl$[4] with magnesium according to the reported procedure.[22] 1,1,2-Trimethyl-1-silacyclobutane (**7a**), 1,1-dimethyl-2-phenyl-1-silacyclobutane (**7b**), and 2-methyl-1,1-diphenyl-1-silacyclobutane (**7c**) were also prepared from the corresponding dichloride, $ClSi(Me_2)CH(Me)CH_2CH_2Cl$, $ClSi(Me_2)CHPhCH_2CH_2Cl$, and $ClSi(Ph_2)CH(Me)CH_2CH_2Cl$, respectively.

1,1-Diphenyl-3-methyl-1-silacyclobutane (4b): Bp 70-72 °C (1.3 Torr, bath temperature); IR (neat) 3064, 3046, 2950, 2856, 1428, 1130, 1114, 953, 805, 735, 719, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.06-1.20 (m, 2H), 1.24 (d, *J* = 9.0 Hz, 3H), 1.63-1.83 (m, 2H), 2.59 (ttq, *J* = 6.5, 8.5, 9.0 Hz, 1H), 7.33-7.48 (m, 6H), 7.52-7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.38, 27.63, 28.05, 127.93, 129.57, 134.47, 134.72, 135.83, 137.04. Found: C, 80.67; H, 7.76%. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61%.

1,1-Diphenyl-2-methyl-1-silacyclobutane (7c): Bp 70-72 °C (1.0 Torr, bath temperature); IR (neat) 3064, 3046, 3012, 2922, 2858, 1450, 1428, 1114, 838, 734, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (d, *J* = 7.4 Hz, 3H), 1.32 (ddd, *J* = 14.4, 9.7, 9.3 Hz, 1H), 1.54 (ddd, *J* = 14.4, 9.4, 3.6 Hz, 1H), 1.76 (dddd, *J* = 12.2, 9.4, 9.3, 9.2 Hz, 1H),

2.01 (ddq, J = 9.7, 9.2, 7.4 Hz, 1H) 2.55 (ddt, J = 12.2, 3.6, 9.7 Hz, 1H), 7.32-7.47 (m, 6H), 7.52-7.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 10.18, 16.17, 23.24, 27.83, 127.91, 129.57, 133.84, 134.43, 135.11, 136.91. Found: C, 80.20; H, 7.82%. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61%.

General Procedure for Ring Enlargement of Silacyclobutane with Lithium Carbenoids Reaction of 1,1-dimethyl-1-silacyclobutane with diiodomethyllithium is representative. Butyllithium (1.6 *M* hexane solution, 12.5 ml, 20 mmol) was added to a solution of diisopropylamine (2.0 g, 20 mmol) in THF (20 ml) at 0 °C. The resulting solution of lithium diisopropylamide was added dropwise to a solution of 1,1-dimethyl-1-silacyclobutane (1.5 g, 15 mmol) and diiodomethane (5.4 g, 20 mmol) in THF (30 ml) over 30 min by syringe pump at -78 °C under an argon atmosphere. The resulting mixture was stirred at -78 °C for another 30 min after completion of the addition. Then cold bath was removed and the reaction mixture was allowed to come to room temperature. The reaction mixture was poured into saturated NH_4Cl and extracted with ethyl acetate (30 ml x 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 2-iodo-1,1-dimethyl-1-silacyclopentane (3.0 g) in 83% yield: Bp 73-75 °C (20 Torr, bath temperature); IR (neat) 2932, 1250, 1049, 840, 812, 783 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.32 (s, 3H), 0.60 (dd, J = 7.5, 7.5 Hz, 1H), 0.61 (dd, J = 7.0, 7.0 Hz, 1H), 1.48-1.73 (m, 1H), 1.68-2.16 (m, 3H), 3.18 (dd, J = 6.1, 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -2.7, -2.5, 11.1, 13.0, 25.3, 39.6. Found: C, 29.96; H, 5.58%. Calcd for $C_6H_{13}ISi$: C, 30.00; H, 5.46%.

2-Bromo-1,1-dimethyl-1-silacyclopentane: Bp 62-64 °C (60 Torr, bath temperature); IR (neat) 2934, 2858, 1251, 1070, 1057, 866, 842, 812, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.31 (s, 3H), 0.58 (dt, J = 14.9, 8.1 Hz, 1H), 0.73 (ddd, J = 14.9, 8.1, 5.1 Hz, 1H), 1.61-1.75 (m, 1H), 1.77-1.93 (m, 1H), 2.03 (dt, J = 7.0, 5.4 Hz, 2H), 3.42 (t, J = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -2.11, -2.03, 11.19, 23.62, 38.39, 39.38. Found: C, 37.07; H, 6.85%. Calcd for $C_6H_{13}BrSi$: C, 37.31; H, 6.78%.

2-Chloro-1,1-dimethyl-1-silacyclopentane: Bp 63-65 °C (82 Torr, bath temperature); IR (neat) 2936, 2860, 1252, 1079, 1058, 873, 842, 815, 784 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 3H), 0.25 (s, 3H), 0.55 (dt, J = 15.0, 8.2 Hz, 1H), 0.74 (ddd, J = 15.0, 7.3, 5.4 Hz, 1H), 1.59-1.76 (m, 1H), 1.77-1.88 (m, 1H), 1.94 (dt, J = 7.5, 5.2 Hz, 2H), 3.44 (t, J = 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.76, -2.19, 11.32, 22.87, 38.11, 48.27. Found: C, 48.20; H, 9.08%. Calcd for $C_6H_{13}ClSi$: C, 48.46; H, 8.81%.

2-Butyl-2-iodo-1,1-dimethyl-1-silacyclopentane: Bp 81-82 °C (4.0 Torr, bath temperature); IR (neat) 2952, 2926, 2870, 1458, 1434, 1249, 1128, 1025, 955, 843, 805, 783 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.38 (s, 3H), 0.49 (dt, J = 15.2, 9.7 Hz, 1H), 0.76 (dddd, J = 15.2, 9.1, 2.8, 2.2 Hz, 1H), 0.93 (t, J = 7.1 Hz, 3H), 1.22-1.50 (m, 4H), 1.57-1.78 (m, 2H), 1.81-2.03 (m, 3H), 2.15-2.26 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -3.23, 3.07, 10.25, 14.11, 22.71, 23.75, 32.86, 42.27, 46.69, 56.23. Found: C, 40.53; H, 6.88%. Calcd for $C_{10}H_{21}ISi$: C; 40.54; H, 7.15%.

1,1-Dimethyl-2-phenyl-1-silacyclopentane: Bp 89-90 °C (18 Torr, bath temperature); IR (neat) 3018, 2930, 2852, 1600, 1495, 1450, 1247, 894, 843, 830, 810, 783, 757, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.20 (s, 3H), 0.23 (s, 3H), 0.65 (ddd, J = 14.5, 11.2, 7.8 Hz, 1H), 0.88 (ddt, J = 14.5, 7.3, 1.9 Hz, 1H), 0.38-0.65 (m,1H), 0.81 (dq, J = 4.4, 11.1 Hz, 1H), 2.00-2.24 (m, 2H), 2.28 (dd, J = 11.3, 6.4 Hz, 1H), 7.05-7.20 (m, 3H), 7.23-7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.50, -1.88, 13.18, 25.38, 33.30, 36.84, 123.72, 126.37, 128.11, 144.96. Found: C, 75.98; H, 9.67%. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53%.

1,1-Dimethyl-2-trimethylsilyl-1-silacyclopentane: Bp 64-65°C (18 Torr, bath tempetrature); IR (neat) 2948, 2918, 2848, 1060, 1036, 1017, 894, 838, 809, 779, 684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.29 (dd, J = 12.1, 6.5 Hz, 1H), -0.04 (s, 9H), 0.05 (s, 6H), 0.37 (ddd, J = 14.5, 11.2, 7.8 Hz, 1H), 0.71 (ddt, J = 14.5, 7.0, 1.8 Hz, 1H), 1.06-1.40 (m,

2H), 1.80-2.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.79, -0.69, -0.25, 13.84, 15.64, 28.27, 29.71. Found: C, 57.83; H, 12.08%. Calcd for $C_9H_{22}Si_2$: C, 58.00; H, 11.90%.

2-Iodo-1,1-diphenyl-1-silacyclopentane: Bp 96-98 °C (0.3 Torr, bath temperature); IR (neat) 3064, 3044, 2930, 2854, 1428, 1114, 1047, 754, 733, 697, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (ddd, J = 15.2, 8.0, 6.3 Hz, 1H), 1.35 (ddd, J = 15.0, 8.0, 6.5 Hz, 1H), 1.68-1.93 (m, 1H), 2.00-2.43 (m, 3H), 3.64 (t, J = 6.7 Hz, 1H), 7.35-7.54 (m, 6H), 7.54-7.70 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 9.09, 9.36, 25.66, 40.27, 127.63, 128.17, 129.86, 130.00, 134.37, 134.65, 134.71, 135.76. Found: C, 52.90; H, 4.75%. Calcd for $C_{16}H_{17}ISi$: C, 52.75; H, 4.71%.

2-Bromo-1,1-diphenyl-1-silacyclopentane: Mp 68.0-69.0 °C; IR (nujol) 1429, 1107, 1075, 1019, 740, 726, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (dt, J = 15.2, 7.8 Hz, 1H), 1.41 (ddd, J = 14.0, 7.8, 6.2 Hz, 1H), 1.53-2.00 (m, 1H), 2.04-2.38 (m, 3H), 3.88 (t, J = 5.7 Hz, 1H), 7.35-7.53 (m, 6H), 7.53-7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 9.34, 23.91, 36.46, 38.95, 127.65, 128.16, 129.86, 129.97, 133.08, 134.45, 134.66, 135.81.
Found: C, 60.33; H, 5.17%. Calcd for $C_{16}H_{17}BrSi$: C, 60.56; H, 5.40%.

2-Chloro-1,1-diphenyl-1-silacyclopentane: Mp 56.5-57.0 °C; IR (nujol) 1429, 1112, 1075, 1025, 728, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (dt, J = 15.5, 7.8 Hz, 1H), 1.41 (ddd, J = 16.0, 7.8, 5.8 Hz, 1H), 1.78-1.99 (m, 1H), 1.99-2.23 (m, 3H), 3.93 (t, J = 5.4 Hz, 1H), 7.45-7.53 (m, 6H), 7.53-7.70 (m, 4H). Found: C, 70.70; H, 6.33%. Calcd for $C_{16}H_{17}ClSi$: C, 70.43; H, 6.28%.

1,1,2-Triphenyl-1-silacyclopentane: Mp 88.5-89.5 °C; IR ($CHCl_3$) 3066, 3022, 3010, 2928, 2856, 1599, 1490, 1428, 1111, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35-1.43 (m, 2H), 1.63-1.81 (m, 1H), 1.97 (dq, J = 5.0, 12.6 Hz, 1H), 2.23-2.38 (m, 2H), 2.87 (dd, J = 12.6, 6.2 Hz, 1H), 6.92-7.03 (m, 3H), 7.03-7.19 (m, 6H), 7.21-7.28 (m, 1H), 7.32-7.44 (m, 3H), 7.57-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.52, 25.56, 34.47, 37.04, 124.10, 127.16, 127.36, 127.94, 127.96, 129.14, 129.39, 133.73, 134.85, 135.42, 136.43, 143.47. Found: C, 84.27; H, 6.87%. Calcd for $C_{22}H_{22}Si$: C, 84.02; H, 7.05%.

1,1-Diphenyl-2-trimethylsilyl-1-silacyclopentane: Bp 115-116 °C (0.5 Torr, bath temperature); IR (neat) 3064, 2942, 2918, 2846, 1428, 1247, 1112, 885, 833, 733, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H), 0.54 (dd, J = 5.9, 3.4 Hz, 1H), 1.18-1.29 (m, 2H), 1.36-1.63 (m, 2H), 2.11-2.29 (m, 2H), 7.28-7.50 (m, 6H), 7.50-7.60 (m, 2H), 7.63-7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.80, 12.72, 13.96, 28.19, 30.60, 127.64, 129.09, 135.03, 135.63, 135.76, 135.85, 136.65, 137.10. Found: C, 73.26; H, 8.45%. Calcd for $C_{19}H_{26}Si_2$: C, 73.47; H, 8.44%.

1,1-Dibutyl-2-iodo-1-silacyclopentane: Bp 86-88 °C (4 Torr, bath temperature); IR (neat) 2952, 2920, 2854, 1459, 1406, 1082, 1049, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.61 (t, J = 7.3 Hz, 2H), 0.62 (t, J = 7.3 Hz, 2H), 0.78-0.88 (m, 2H), 0.89 (t, J = 6.8 Hz, 3H), 0.91 (t, J = 6.9 Hz, 3H), 1.23-1.44 (m, 8H), 1.46-1.60 (m, 1H), 1.74-1.86 (m, 1H), 1.87-2.00 (m, 1H), 2.02-2.14 (m, 1H), 3.19 (t, J = 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.51, 10.76, 12.52, 13.75, 13.80, 15.07, 25.54, 26.08, 26.17, 26.47, 26.55, 40.18. Found: C, 44.32; H, 7.97%. Calcd for $C_{12}H_{25}ISi$: C, 44.44; H, 7.77%.

2-Bromo-1,1-dibutyl-1-silacyclopentane: Bp 59-60 °C (0.3 Torr, bath temperature); IR (neat) 2952, 2920, 2856, 1407, 1080, 885, 787, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.52-0.78 (m, 4H), 0.78-0.88 (m, 2H), 0.89 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), 1.22-1.46 (m, 8H), 1.64 (dtt, J = 11.0, 7.9, 5.5 Hz, 1H), 1.84 (ddq, J = 13.3, 5.5, 7.9 Hz, 1H), 1.93-2.12 (m, 2H), 3.45 (t, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.58, 12.61, 12.66, 13.79, 23.84, 26.04, 26.16, 26.51, 38.10, 38.98. Found: C, 51.73; H, 9.20%. Calcd for $C_{12}H_{25}BrSi$: C, 51.97; H, 9.09%.

1,1-Di(1-hexynyl)-2-iodo-1-silacyclopentane: Bp 108-110 °C (0.6 Torr, bath temperature); IR (neat) 2952, 2930, 2860, 2176, 1459, 1069, 1046, 954, 860, 752, 719, 687 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.83 (dt, *J* = 15.4, 7.2 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 H, 3H), 0.89-0.98 (m, 1H), 1.30-1.41 (m, 8H), 1.65-1.79 (m, 1H), 1.79-1.93 (m, 1H), 1.99-2.07 (m, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.32 (t, *J* = 7.0 Hz, 2H), 3.29 (t, *J* = 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.37, 12.17, 13.56, 19.80, 21.91, 24.47, 30.22, 38.57, 78.80, 79.95, 110.95, 112.70. Found: C, 51.48; H, 6.83%. Calcd for $C_{16}H_{25}ISi$: C, 51.61; H, 6.77%.

2-Iodo-1,1-diisopropoxy-1-silacyclopentane: Bp 68-70 °C (3.0 Torr, bath temperature); IR (neat) 2968, 2930, 2870, 1452, 1382, 1370, 1173, 1121, 1052, 879, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (dt, *J* = 15.5, 7.6 Hz, 1H), 0.67 (ddd, *J* = 15.5, 8.7, 5.7 Hz, 1H), 1.20 (d, *J* = 6.1 Hz, 6H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.30 (d, *J* = 5.9 Hz, 3H), 1.60-1.74 (m, 1H), 1.75-1.90 (m, 1H), 1.94-2.04 (m, 2H), 3.14 (t, *J* = 5.9 Hz, 1H), 4.18 (septet, *J* = 6.1 Hz, 1H), 4.35 (septet, *J* = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 6.77, 7.75, 22.76, 25.38, 25.53, 25.61, 37.13, 65.95, 66.92. Found: C, 36.78; H, 6.31%. Calcd for $C_{10}H_{21}IO_2Si$: C, 36.59; H, 6.45%.

Reaction of 3-Methyl-1-silacyclobutane or 2-Methyl-1-silacyclobutane with Lithium Carbenoid. Reactions were performed following the procedure described for the reaction of 1,1-dimethyl-1-silacyclobutane with diiodomethyllithium. Analytically pure samples of *cis*-2,4-disubstituted silacyclopentanes **5** were obtained by silica-gel column chromatography. Minor *trans* isomers **6** could not be obtained in pure form and thus only ^1H NMR and ^{13}C NMR spectral data were shown. The separation of **8** from **9** was also performed by silica-gel column chromatography.

cis-*2-Iodo-1,1,4-trimethyl-1-silacyclopentane (**5a**)*: Bp 79-81 °C (17 Torr, bath temperature); IR (neat) 2948, 2922, 2862, 1454, 1251, 1182, 1115, 1064, 842, 813, 794 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.23 (dd, *J* = 14.7, 11.4 Hz, 1H), 0.28 (s, 3H), 0.94 (ddd, *J* = 14.7, 6.1, 2.0 Hz, 1H), 1.05 (d, *J* = 6.2 Hz, 3H), 1.49 (q, *J* = 12.4 Hz, 1H), 1.53-1.68 (m, 1H), 2.39 (dddd, *J* = 12.4, 7.6, 3.9, 2.0 Hz, 1H), 2.92 (dd, *J* = 12.4, 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.13, 0.32, 8.31, 21.33, 23.10, 35.81, 48.56. Found: C, 33.06; H, 6.01%. Calcd for $C_7H_{15}ISi$: C, 33.07; H, 5.95%.

trans-*2-Iodo-1,1,4-trimethy-1-silacyclopentane (**6a**)*: ^1H NMR ($CDCl_3$) δ 0.13 (s, 3H), 0.16 (dd, *J* = 14.6, 9.8 Hz, 1H), 0.35 (s, 3H), 0.89 (ddd, *J* = 14.6, 7.1, 2.3 Hz, 1H), 1.05 (d, *J* = 6.5 Hz, 3H), 2.09 (ddt, *J* = 2.9, 2.3, 2.6 Hz, 1H), 2.12-2.27 (m, 2H), 3.39 (dd, *J* = 5.7, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.36, 2.13, 15.01, 21.08, 22.62, 32.94, 47.32.

cis-*2-Bromo-1,1,4-trimethyl-1-silacyclopentane (**5b**)*: Bp 72-74 °C (67 Torr, bath temperature); IR (neat) 2948, 2924, 2864, 1455, 1251, 1183, 1105, 1069, 1046, 845, 815, 795, 752, 646 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 3H), 0.25 (s, 3H), 0.27 (dd, *J* = 14.7, 11.4 Hz, 1H), 0.93 (ddd, *J* = 14.7, 6.2, 2.2 Hz, 1H), 1.44 (q, *J* = 12.1 Hz, 1H), 1.54-1.71 (m, 1H), 2.39 (dddd, *J* = 12.1, 7.8, 4.0, 2.2 Hz, 1H), 3.18 (dd, *J* = 12.1, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -2.85, -2.21, 21.84, 23.44, 33.46, 36.08, 47.18. Found: C, 40.29; H, 7.51%. Calcd for $C_7H_{15}BrSi$: C, 40.58; H, 7.30%.

trans-*2-Bromo-1,1,4-trimethyl-1-silacyclopentane (**6b**)*: ^1H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.15 (dd, *J* = 16.2, 8.6 Hz, 1H), 0.31 (s, 3H), 0.88 (ddd, *J* = 16.2, 6.3, 2.5 Hz, 1H), 1.05 (d, *J* = 6.4 Hz, 3H), 2.12 (dq, *J* = 2.5, 2.2 Hz, 1H), 2.15-2.28 (m, 2H), 3.54 (dd, *J* = 5.4, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -1.39, -1.27, 21.16, 22.83, 32.08, 40.72, 46.56.

cis-*1,1,4-Trimethyl-2-phenyl-1-silacyclopentane (**5c**)*: Bp 91-93 °C (20 Torr, bath temperature); IR (neat) 3020, 2946, 2918, 2862, 1601, 1495, 1452, 1248, 1076, 866, 842, 814, 797, 759, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.23 (s, 3H), 0.20 (s, 3H), 0.26 (dd, *J* = 14.6, 11.7 Hz, 1H), 1.03 (ddd, *J* = 14.6, 6.5, 2.4 Hz, 1H), 1.13 (d, *J* = 6.4 Hz, 3H),

1.48 (dt, J = 13.3, 12.2 Hz, 1H), 1.73-1.89 (m, 1H), 2.10 (dddd, J = 12.2, 6.2, 4.0, 2.4 Hz, 1H), 2.34 (dd, J = 13.3, 6.5 Hz, 1H), 7.02-7.09 (m, 3H), 7.18-7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -3.30, -1.60, 23.00, 23.73, 34.04, 37.68, 41.77, 123.73, 126.32, 128.11, 144.66. Found: C, 76.13; H, 9.80%. Calcd for $C_{13}H_{20}Si$: C, 76.39; H, 9.86%.

trans-*1,1,4-Trimethyl-2-phenyl-1-silacyclopentane (6c)*: ^{1}H NMR ($CDCl_3$) δ -0.30 (s, 3H), 0.25 (s, 3H), 0.42 (dd, J = 14.4, 7.1 Hz, 1H), 0.93 (ddd, J = 14.4, 6.8, 1.1 Hz, 1H), 1.06 (d, J = 6.8 Hz, 3H), 1.69-1.85 (m, 1H), 2.02-2.12 (m, 2H), 2.56 (t, J = 7.8 Hz, 1H), 7.02-7.08 (m, 3H), 7.20-7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.66, -0.01, 22.43, 23.24, 33.21, 37.68, 40.90, 123.59, 126.33, 128.11, 145.70.

cis-*2-Iodo-4-methyl-1,1-diphenyl-1-silacyclopentane (5d)*: Bp 119-120 °C (1.3 Torr, bath temperature); IR (neat) 3064, 2946, 2918, 2860, 1453, 1428, 1115, 729, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (dd, J = 15.0, 11.3 Hz, 1H), 1.20 (d, J = 6.0 Hz, 3H), 1.13-1.22 (m, 1H), 1.45-1.56 (m, 1H), 1.70-1.89 (m, 1H), 2.43-2.60 (m, 1H), 3.42 (dd, J = 12.6, 7.4 Hz, 1H), 7.34-7.68 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 4.58, 19.79, 23.11, 36.06, 49.11, 127.59, 127.66, 128.18, 129.74, 130.00, 134.51, 134.65, 135.70. Found: C, 53.95; H, 5.21%. Calcd for $C_{17}H_{19}ISi$: C, 53.97; H, 5.06%.

trans-*2-Iodo-4-methyl-1,1-diphenyl-1-silacyclopentane (6d)*: ^{1}H NMR ($CDCl_3$) δ 0.77 (dd, J = 15.0, 9.0 Hz, 1H), 0.84-0.95 (m, 1H), 1.17 (d, J = 6.6 Hz, 3H), 1.52-1.63 (m, 1H), 1.70-1.89 (m, 1H), 2.28-2.38 (m, 1H), 3.89 (dd, J = 5.7, 3.3 Hz, 1H), 7.34-7.68 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.52, 19.02, 22.60, 33.48, 48.01 (Phenyl ring carbons could not be determined because of its low content).

cis-*2-Bromo-4-methyl-1,1-diphenyl-1-silacyclopentane (5e)*: Bp 109-111 °C (1.3 Torr, bath temperature); IR (neat) 3064, 2946, 2922, 2862, 1736, 1454, 1429, 1116, 1068, 905, 730, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (dd, J = 15.3, 11.6 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H), 1.52 (ddd, J = 15.1, 6.2, 2.3 Hz, 1H), 1.72 (q, J = 12.3 Hz, 1H), 1.78-1.93 (m, 1H), 2.58 (dddd, J = 11.6, 7.3, 3.6, 2.3 Hz, 1H), 3.67 (dd, J = 12.3, 7.7 Hz, 1H), 7.33-7.48 (m, 6H), 7.52-7.59 (m, 2H), 7.61-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.21, 23.41, 33.32, 33.65, 47.68, 127.67, 128.17, 129.78, 132.97, 133.73, 134.66, 135.75. Found: C, 61.91; H, 5.88%. Calcd for $C_{17}H_{19}BrSi$: C, 61.62; H, 5.78%.

trans-*2-Bromo-4-methyl-1,1-diphenyl-1-silacyclopentane (6e)*: ^{1}H NMR ($CDCl_3$) δ 0.75 (dd, J = 15.2, 10.5 Hz, 1H), 1.17 (d, J = 6.3 Hz, 3H), 1.57-1.63 (m, 1H), 2.29-2.34 (m, 1H), 2.34-2.39 (m, 1H), 2.45-2.55 (m, 1H), 4.01 (dd, J = 4.6, 2.3 Hz, 1H), 7.33-7.48 (m, 6H), 7.52-7.59 (m, 2H), 7.61-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.94, 22.81, 32.56, 37.81, 47.06 (Phenyl ring carbons could not be determined).

cis-*4-Methyl-1,1,2-triphenyl-1-silacyclopentane (5f)*: Mp 57-58 °C; IR (neat before crystallization) 3064, 3018, 2946, 2912, 2860, 1600, 1492, 1451, 1428, 1112, 1075, 770, 730, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (dd, J = 15.0, 11.7 Hz, 1H), 1.26 (d, J = 6.4 Hz, 3H), 1.53 (ddd, J = 15.0, 6.2, 2.0 Hz, 1H), 1.70 (dt, J = 13.5, 12.8 Hz, 1H), 2.02-2.15 (m, 1H), 2.21-2.34 (m, 1H), 2.98 (dd, J = 13.5, 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.21, 23.66, 34.27, 37.68, 42.87, 124.11, 127.36, 127.61, 127.70, 127.96, 129.14, 129.38, 133.80, 134.79., 135.41, 143.24. Found: C, 84.03; H, 7.34%. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36%.

trans-*4-Methyl-1,1,2-triphenyl-1-silacyclopentane (6f)*: Mp 62-63 °C; IR (neat before crystallization) 3064, 3018, 2946, 2912, 1601, 1492, 1451, 1428, 1111, 1071, 770, 730, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (dd, J = 14.8, 6.2 Hz, 1H), 1.17 (d, J = 6.8 Hz, 3H), 1.67 (dd, J = 14.8, 7.2 Hz, 1H), 1.95 (ddd, J = 13.3, 7.8, 7.5 Hz, 1H), 2.27 (ddd, J = 13.3, 7.8, 5.7 Hz, 1H), 2.60 (ddddq, J = 7.5, 7.2, 6.2, 5.7, 6.8 Hz, 1H), 3.18 (t, J = 7.8 Hz, 1H), 6.90-7.68 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 20.42, 23.43, 33.15, 33.42, 41.95, 123.92, 127.11, 127.28, 127.93, 128.98, 129.38, 133.87, 134.82, 135.22, 135.41, 136.66, 144.23. Found: C, 83.81; H, 7.35%. Calcd for $C_{23}H_{24}Si$: C, 84.09; H,

7.36%.

cis-*2-Iodo-1,1,3-trimethyl-1-silacyclopentane (**8a**)*: Bp 75-77 °C (38 Torr, bath temperature); IR (neat) 2948, 2920, 2860, 1454, 1250, 1067, 1045, 844, 812, 792, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3H), 0.26 (s, 3H), 0.55 (ddd, *J* = 14.8, 12.1, 8.4 Hz, 1H), 0.77 (ddd, *J* = 14.8, 7.2, 1.8 Hz, 1H), 1.00 (ddt, *J* = 13.1, 7.1, 11.9 Hz, 1H), 1.08 (d, *J* = 6.4 Hz, 3H), 1.68-1.85 (m, 1H), 1.93 (dddd, *J* = 13.1, 8.4, 4.9, 1.8 Hz, 1H), 2.46 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.08, 0.53, 11.39, 20.81, 20.86, 33.29, 45.37. Found: C, 33.35; H, 5.76%. Calcd for $C_7H_{15}ISi$: C, 33.07; H, 5.95%.

*2-Iodo-1,1,5-trimethyl-1-silacyclopentane (**9a**, 4 : 1 diastereomeric mixture)*: Bp 77-79 °C (38 Torr, bath temperature); IR (neat) 2928, 2858, 1450, 1250, 1068, 1044, 844, 795, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.27 (s, 3H), 0.76-1.12 (m, 2H), 1.00 (d, *J* = 5.0 Hz, 3H), 1.75-1.88 (m, 1H), 1.89-2.01 (m, 1H), 2.25 (ddt, *J* = 12.8, 6.8, 4.1 Hz, 1H), 3.00 (dd, *J* = 9.5, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -6.13, -0.01, 10.61, 15.18, 18.68, 35.91, 38.20. Found: C, 33.29; H, 6.10%. Calcd for $C_7H_{15}ISi$: C; 33.07; H, 5.95%.

cis-*2-Bromo-1,1,3-trimethyl-1-silacyclopentane (**8b**)*: Bp 74-76 °C (72 Torr, bath temperature); IR (neat) 2950, 2920, 2866, 1455, 1250, 1072, 847, 817, 794 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 3H), 0.25 (s, 3H), 0.60 (ddd, *J* = 14.9, 11.6, 8.5 Hz, 1H), 0.78 (ddd, *J* = 14.9, 7.2, 2.3 Hz, 1H), 1.02-1.15 (m, 1H), 1.11 (d, *J* = 6.4 Hz, 3H), 1.77-1.93 (m, 1H), 1.99 (dddd, *J* = 15.6, 8.5, 4.8, 2.3 Hz, 1H), 2.71 (d, *J* = 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -2.72, -2.00, 11.07, 19.67, 32.35, 44.80, 45.65. Found: C, 40.78; H, 7.19%. Calcd for $C_7H_{15}BrSi$: C, 40.58; H, 7.30%.

*2-Bromo-1,1,5-trimethyl-1-silacyclopentane (**9b**, 4 : 1 diastereomeric mixture)* : Bp 78-80 °C (76 Torr, bath temperature); IR (neat) 2932, 2860, 1460, 1452, 1251, 1071, 846, 799, 777, 768 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.25 (s, 3H), 0.95-1.19 (m, 2H), 0.99 (d, *J* = 1.9 Hz, 3H), 1.83 (ddt, *J* = 13.5, 4.8, 9.3 Hz, 1H), 1.97-2.10 (m, 1H), 2.27 (dddd, *J* = 13.2, 6.8, 6.1, 4.8 Hz, 1H), 3.29 (dd, *J* = 8.2, 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -5.80, -2.64, 15.25, 18.60, 33.89, 36.79, 38.03. Found: C, 40.79; H, 7.58%. Calcd for $C_7H_{15}BrSi$: C, 40.58; H, 7.30%.

cis-*1,1,3-Trimethyl-2-phenyl-silacyclopentane (**8c**)*: Bp 91-93 °C (20 Torr, bath temperature); IR (neat) 3018, 2946, 2920, 2862, 1599, 1496, 1450, 1248, 1076, 1058, 898, 846, 796, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.21 (s, 3H), 0.15 (s, 3H), 0.63 (ddd, *J* = 14.8, 12.6, 8.0 Hz, 1H), 0.86 (ddd, *J* = 14.8, 7.2, 0.9 Hz, 1H), 0.95 (d, *J* = 6.0 Hz, 3H), 1.18 (ddt, *J* = 13.7, 7.2, 12.6 Hz, 1H), 1.73 (d, *J* = 11.8Hz, 1H), 1.95-2.18 (m, 2H), 6.96-7.08 (m, 3H), 7.20-7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.96, -1.88, 12.36, 20.35, 34.49, 40.31, 45.66, 123.67, 126.92, 128.13, 143.87. Found: C, 76.48; H, 9.96%. Calcd for $C_{13}H_{20}Si$: C, 76.39; H, 9.86%.

*1,1,5-Trimethyl-2-phenyl-1-silacyclopentane (**9c**, 9 : 1 diastereomeric mixture)*: Bp 92-94 °C (20 Torr, bath temperature); IR (neat) 3018, 2922, 2858, 1601, 1496, 1449, 1247, 1077, 851, 833, 796, 768, 749, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.26 (s, 3H), 0.12 (s, 3H), 0.92-1.04 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 1H), 1.16 (ddt, *J* = 12.5, 4.4, 12.1 Hz, 1H), 1.76 (dq, *J* = 12.1, 4.4 Hz, 1H), 2.08-2.18 (m, 2H), 2.28 (dd, *J* = 12.5, 6.7 Hz, 1H), 7.00-7.08 (m, 3H), 7.18-7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -4.77, -4.06, 15.36, 21.09, 31.78, 35.53, 37.30, 123.73, 126.38, 128.12, 145.01. Found: C, 76.14; H, 10.08%. Calcd for $C_{13}H_{20}Si$: C, 76.39; H, 9.86%.

cis-*2-Iodo-1,1-dimethyl-3-phenyl-1-silacyclopentane* (cis-***8d***): Bp 85-86°C (1.0 Torr, bath temperature); IR (neat) 3020, 2948, 2918, 2870, 1489, 1453, 1248, 1172, 1063, 1013, 876, 848, 803, 784, 697, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 3H), 0.41 (s, 3H), 0.75 (ddd, *J* = 15.0, 12.6, 8.6 Hz, 1H), 1.00 (ddd, *J* = 15.0, 7.3, 1.2 Hz, 1H), 1.55 (ddt, *J* = 12.4, 10.9, 7.3 Hz, 1H), 2.15 (dddd, *J* = 10.9, 8.7, 4.8, 1.3 Hz, 1H), 2.91 (dt, *J* = 12.4, 4.8 Hz, 1H), 3.00 (d, *J* = 12.4 Hz, 1H), 7.13-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.25, 0.55, 11.90, 18.05, 34.53, 56.39, 126.68,

126.91, 128.36, 143.66. Found: C, 45.52; H, 5.66%. Calcd for $C_{12}H_{17}ISi$: C, 45.57; H, 5.42%.

trans-*2-Iodo-1,1-dimethyl-3-phenyl-1-silacyclopentane* (trans-***8d***): Bp 85-86 °C (1.0 Torr, bath temperature); ^1H NMR ($CDCl_3$) δ 0.29 (s, 3H), 0.48 (s, 3H), 0.63-0.73 (m, 1H), 0.88-1.01 (m, 1H), 1.90-2.09 (m, 2H), 2.48 (dt, *J* = 11.3, 4.2 Hz, 1H), 3.58 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.18-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -0.62, 2.39, 10.60, 27.81, 28.73, 49.44, 126.45, 127.46, 127.88, 143.85.

*2-Iodo-3-methyl-1,1-diphenyl-1-silacyclopentane (**8e**)*: Bp 103-105 °C (0.5 Torr, bath temperature); IR (neat) 3064, 3044, 2950, 2910, 2852, 1453, 1425, 1113, 1065, 733, 713, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz, 3H), 1.22-1.45 (m, 3H), 1.97-2.33 (m, 2H), 2.98 (d, *J* = 11.7 Hz, 1H), 7.30-7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 10.03, 17.17, 20.89, 33.46, 45.86, 127.64, 128.02, 128.20, 129.88, 129.99, 134.70, 135.39, 135.71. Found: C, 54.26; H, 5.09%. Calcd for $C_{17}H_{19}ISi$: C, 53.97; H, 5.06%.

*2-Iodo-5-methyl-1,1-diphenyl-1-silacyclopentane (**9e**, 5 : 1 diastereomeric mixture)*: Bp 103-105 °C (0.5 Torr, bath temperature); IR (neat) 3064, 3010, 2918, 2858, 1428, 1113, 734, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (d, *J* = 7.5 Hz, 3H), 1.19-1.38 (m, 1H), 1.98-2.26 (m, 2H), 2.50-2.61 (ddt, *J* = 13.0, 7.0, 3.6 Hz, 1H), 3.69 (dd, *J* = 10.3, 7.3 Hz, 1H), 7.33-7.70 (m, 10H), ^{13}C NMR ($CDCl_3$) δ 6.07, 16.05, 18.47, 36.55, 38.85, 127.08, 128.01, 129.87, 130.08, 131.74, 134.23, 135.38, 135.97. Found: C, 53.75; H, 5.04%. Calcd for $C_{17}H_{19}ISi$: C, 53.97; H, 5.06%.

cis-*3-Methyl-1,1,2-triphenyl-1-silacyclopentane (**8f**)*: Mp 77-78 °C; IR (neat) 3064, 3046, 3018, 1428, 1112, 759, 738, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (d, *J* = 6.9 Hz, 3H), 1.22-1.40 (m, 1H), 1.72-1.99 (m, 2H), 2.20-2.40 (m, 2H), 2.91 (d, *J* = 6.5 Hz, 1H), 6.88-7.70 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 9.29, 17.69, 33.19, 40.57, 41.27 (Phenyl ring carbons could not be determined). Found: C, 84.19; H, 7.39%. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36%.

*5-Methyl-1,1,2-triphenyl-1-silacyclopentane (**9f**, major isomer)*: Mp 80-81 °C; IR (neat before crystallization) 3064, 3018, 2920, 2858, 1428, 1111, 757, 736, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, *J* = 7.7 Hz, 3H), 1.71-1.97 (m, 2H), 2.05-2.18 (m, 1H), 2.21-2.42 (m, 2H), 2.99 (dd, *J* = 9.0, 7.6 Hz, 1H), 6.85-7.71 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 16.84, 19.66, 30.95, 35.49, 36.26, 124.11, 127.05, 127.18, 128.04, 128.12, 128.90, 129.38, 132.56, 134.89, 136.14, 136.94, 143.87. Found: C, 83.81; H, 7.31%. Calcd for $C_{23}H_{24}Si$: C, 84.09; H, 7.36%.

*5-Methyl-1,1,2-triphenyl-1-silacyclopentane (**9f**, minor isoer)*: ^1H NMR ($CDCl_3$) δ 1.06 (d, *J* = 7.3 Hz, 3H), 1.45 (dt, *J* = 12.0, 4.8 Hz, 1H), 1.73-1.96 (m, 2H), 2.18-2.39 (m, 2H), 3.07 (dd, *J* = 13.0, 6.8 Hz, 1H), 6.80-7.71 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.27, 20.24, 32.77, 35.90, 36.59, 124.10, 127.16, 127.36, 127.78, 127.90, 129.08, 129.18, 130.29, 135.55, 135.65, 142.15, 143.56.

*Conversion of **5f**, **6f**, **8f**, and **9f** into the Corresponding 1,4-Diol*: Transformation of **5f** to $HOCH_2CH(Me)CH_2CH(OH)Ph$ is representative. Tetrafluoroboric acid ($HBF_4 \cdot OEt_2$, 1.18 g, 6.2 mmol) was added to a solution of **5f** (424 mg, 1.3 mmol) in dichloromethane (3 ml) at 0 °C and the reaction mixture was warmed to room temperature and stirred for 1 h. The mixture was concentrated *in vacuo* and the residual oil was dissolved in THF (6 ml) and MeOH (6 ml). Potassium fluoride (0.3 g, 5.2 mmol), $KHCO_3$ (2.4 g, 24 mmol) and H_2O_2 (30%, 3.4 g, 30 mmol) were added and the whole was heated at 50 °C for 4 h. Extractive workup followed by purification by silica-gel column gave (1R*,3R*)-3-methyl-1-phenyl-1,4-butanediol (69 mg, 39%) which was identical with a sample prepared by the reduction of *cis*-α-methyl-γ-phenyl-γ-butyrolactone with $LiAlH_4$: Bp 120-122 °C (0.3 Torr, bath temperature); IR (neat) 3290, 2952, 2924, 2870, 1454, 1030, 996, 754, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, *J* = 6.8 Hz, 3H), 1.56 (ddd, *J* = 14.4, 5.3, 2.8 Hz, 1H), 1.70-1.95 (m, 2H), 3.35 (dd, *J* = 10.6, 7.7 Hz, 1H), 3.53 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.60-4.18 (bs, 2H), 4.70 (dd, *J* = 9.9, 2.8 Hz, 1H), 7.21-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.97, 34.74, 45.42, 68.46,

73.48, 125.60, 127.33, 128.35, 145.32. Found: C, 73.26; H, 9.02%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

(1R,3S*)-3-Methyl-1-phenyl-1,4-butanediol*: Bp 120-123 °C (0.3 Torr, bath temperature); IR (neat) 3320, 2954, 2926, 2872, 1454, 1036, 995, 754, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6.6 Hz, 3H), 1.66-1.86 (m, 3H), 3.17-4.02 (bs, 2H), 3.42 (dd, J = 10.8, 6.2 Hz, 1H), 3.48 (dd, J = 10.8, 4.4 Hz, 1H), 5.82 (t, J = 6.0 Hz, 1H), 7.20-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.13, 32.04, 43.54, 67.70, 71.54, 125.73, 127.18, 128.30, 144.68. C, 72.80; H, 9.03%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

(1R,2S*)-2-Methyl-1-phenyl-1,4-butanediol*: ^1H NMR ($CDCl_3$) δ 0.87 (d, J = 6.9 Hz, 3H), 1.44 (dddd, J = 14.2, 9.4, 6.4, 5.5 Hz, 1H), 1.68 (ddt, J = 14.2, 7.4, 6.0 Hz, 1H), 1.94-2.08 (m, 1H), 2.45-3.30 (bs, 2H), 3.61 (ddd, J = 10.7, 7.4, 5.7 Hz, 1H), 3.70 (ddd, J = 10.7, 6.4, 6.0 Hz, 1H), 4.64 (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 35.84, 37.57, 60.50, 77.43, 126.37, 127.12, 128.03, 143.06.

*2-Iodo-1,1-dimethyl-1-silaindan (**11**)*: Bp 74-75 °C (1.0 Torr, bath temperature); IR (neat) 3050, 2952, 2922, 1441, 1249, 1129, 1070, 846, 821, 803, 782, 740, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 3H), 0.49 (s, 3H), 3.36 (dd, J = 16.2, 6.6 Hz, 1H), 3.45 (t, J = 6.6 Hz, 1H), 3.69 (dd, J = 16.2, 6.6 Hz, 1H), 7.18-7.28 (m, 2H), 7.32 (dt, J = 7.2, 1.2 Hz, 1H), 7.55 (d, J = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.75, -0.90, 8.15, 44.64, 125.41, 126.47, 130.37, 132.32, 137.24, 150.17. Found: C, 41.70; H, 4.56%. Calcd for $C_{10}H_{13}ISi$: C, 41.67; H, 4.55%.

2,2,2',2'-Tetramethyl-2,2'-disila-1,1'-bicyclopentane (1:1 diastereomeric mixture): Butyllithium (1.5 *M*, 0.7 ml, 1.05 mmol) was added to a THF solution of 2-iodo-1,1-dimethyl-1-silacyclopentane (0.24 g, 1.0 mmol) at -78°C. The mixture was stirred at -78 °C for 30 min and 2 h at 25 °C. The resulting mixture was poured into water and extracted with ethyl acetate. Purification by silica-gel column gave the title compound (40 mg) in 35% yield: Bp 60-65 °C (1.0 Torr, bath temperature); IR (neat) 2928, 2838, 1449, 1247, 1046, 866, 839, 807, 778 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (s, 3H), 0.05 (s, 3H), 0.10 (s, 3H), 0.12 (s, 3H), 0.37-0.50 (m, 2H), 0.60-0.77 (m, 4H), 0.93-1.15 (m, 2H), 1.16-1.36 (m, 2H), 1.81-1.95 (m, 3H), 1.97-2.09 (m, 1H); ^{13}C NMR ($CDCl_3$) -4.02, -3.23, -1.13, -0.91, 13.26, 13.47, 25.08, 25.57, 28.52, 29.95, 35.50; MS (*m/e*) 227 (M^++1, 7), 226 (M^+, 32), 211 (14), 125 (6), 112 (14), 73 (27), 58 (100). Found: C, 63.73; H, 11.73%. Calcd for $C_{12}H_{26}Si_2$: C, 63.63; H, 11.57%.

Preparation of 2-Lithio-1-silacyclopentane and its Reaction with Electrophile. Reaction with deuterium oxide is representative. *tert*-Butyllithium (1.48 *M* pentane solution, 1.1 ml, 1.65 mmol) was added to a solution of 1,1-diphenyl-2-iodo-1-silacyclopentane (182 mg, 0.5 mmol) in hexane (1.5 ml) and ether (1.0 ml) at -78°C under argon atmosphere. After stirring for 10 min, deuterium oxide (0.15 ml, 7.5 mmol) was added and the resulting mixture was stirred at -78 °C for another 10 min. Cold bath was removed and the mixture was warmed to room temperature. The mixture was poured into brine and extracted with ethyl acetate (30 ml x 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 2-deuterio-1,1-diphenyl-1-silacyclopentane (111 mg) in 93% yield: Bp 77-80 °C (0.3 Torr, bath temperature); IR (neat) 3062, 2924, 2850, 1428, 1112, 781, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06-1.15 (m, 3H), 1.76-1.84 (m, 4H), 7.32-7.41 (m, 3H), 7.52-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.77 (t, J = 19.5 Hz), 12.14, 27.62, 27.71, 127.82, 129.17, 134.75, 136.87. Found: C, 80.33; H, 7.84%. Calcd for $C_{16}H_{17}DSi$: C, 80.27; H, 7.14, D, 0.84%.

threo-*2-Hydroxyphenylmethyl-1,1-dimethyl-1-silacyclopentane (**14a**)*: R_f = 0.5 (EtOAc/hexane = 1/5); Bp 74-76 °C (1.0 Torr, bath temperature); IR (neat) 3438, 2930, 2854, 1451, 1245, 1063, 1016, 840, 803, 783, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19 (s, 3H), 0.24 (s, 3H), 0.49 (ddd, J = 14.7, 11.3, 8.2 Hz, 1H), 0.76 (ddt, J = 14.7, 7.3, 1.5 Hz, 1H), 1.01 (dq, J = 4.9, 12.0 Hz, 1H), 1.15-1.39 (m, 2H), 1.75-1.86 (m, 2H), 4.53 (dd, J = 10.3, 2.6 Hz, 1H), 7.17-7.35

(m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.67, -1.09, 13.47, 25.28, 31.47, 37.79, 77.41, 125.94, 127.31, 128.32, 146.22. Found: C, 70.59; H, 8.94%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

erythro-*2-Hydroxyphenylmethyl-1,1-dimethyl-1-silacyclopentane (15a)*: R_f = 0.2 (EtOAc/hexane = 1/10); Bp 74-75°C (1.0 Torr, bath temperature); IR (neat) 3340, 2932, 2852, 1453, 1247, 1057, 1023, 842, 807, 784, 761, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -0.38 (s, 3H), -0.13 (s, 3H), 0.34-0.59 (m, 1H), 0.64-0.84 (m, 1H), 1.31-1.54 (m, 3H), 1.81-2.09 (m, 2H), 2.19-2.35 (m, 1H), 4.51-4.69 (d, *J* = 10.2 Hz, 1H), 7.16-7.19 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.10, -2.17, 13.09, 24.90, 32.31, 38.32, 77.70, 126.7, 127.9, 128.5, 144.8. Found: C, 70.64; H, 9.10%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

threo-*2-(1-Hydroxypentyl)-1,1-dimethyl-1-silacyclopentane (14b)*: R_f = 0.5 (EtOAc/hexane = 1/10); Bp 58-61 °C (0.5 Torr, bath temperature); IR (neat) 3404, 2952, 2928, 2854, 1246, 1118, 1058, 840, 813, 783 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 3H), 0.15 (s, 3H), 0.43 (ddd, *J* = 14.6, 11.9, 8.3 Hz, 1H), 0.73 (ddt, *J* = 14.6, 7.1, 2.0 Hz, 1H), 0.85 (ddd, *J* = 12.0, 8.9, 7.0 Hz, 1H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.10 (dq, *J* = 12.6, 4.7 Hz, 1H), 1.22-1.53 (m, 7H), 1.53-1.70 (m, 1H), 1.74-1.83 (m, 1H), 1.85-1.98 (m, 1H), 3.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -3.07, -0.87, 13.24, 14.13, 22.80, 25.43, 27.73, 31.22, 36.68, 38.11, 74.38. Found: C, 65.63; H, 12.30%. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07%.

erythro-*2-(1-Hydroxypentyl)-1,1-dimethyl-1-silacyclopentane (15b)*: R_f = 0.2 (EtOAc/hexane = 1/10); Bp 59-62 °C (0.5 torr, bath temperature); IR (neat) 3320, 2952, 2854, 1452, 1249, 1097, 1055, 1021, 839, 812, 783 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.13 (s, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 1.12-1.65 (m, 10H), 1.91-2.00 (m, 1H), 2.03-2.13 (m, 1H), 3.59 (t, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.60, -1.27, 13.20, 14.10, 22.68, 24.96, 28.07, 31.63, 37.30, 38.25, 74.16. Found: C, 65.92; H, 12.14%. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07%.

*Conversion of **14** (or **15**) into **16** (or **17**).* Transformation of **14a** into **16a** is representative. Potassium hydride (excess) was added to a solution of **14a** (66 mg, 0.3 mmol) in THF (2 ml) at 0 °C under argon atmosphere and the mixture was stirred for 1 h. The resulting mixture was poured into cold water and extracted with ethyl acetate (10 ml x 3). The combined organic layers were dried and concentrated in vacuo. The residual oil was dissolved in THF (3 ml) and MeOH (3 ml). Potassium fluoride (35 mg, 0.6 mmol), $KHCO_3$ (120 mg, 1.2 mmol) and H_2O_2 (30%, 204 mg) were added and the resulting mixture was stirred for 5 h at room temperature. Extractive workup followed by purification by silica-gel column chromatography gave (*E*)-5-phenyl-4-penten-1-ol **16a** (30 mg, 0.19 mmol) in 62% yield: Bp 70-75 °C (0.25 Torr, bath temperature); IR (neat) 3312, 3026, 2932, 2872, 1493, 1446, 1057, 964, 740, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56-1.65 (bs, 1H), 1.75 (tt, *J* = 6.9, 6.4 Hz, 2H), 2.30 (dq, *J* = 1.2, 6.9 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 6.22 (dt, *J* = 15.8, 6.9 Hz, 1H), 6.42 (dt, *J* = 15.8, 1.2 Hz, 1H), 7.15-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 29.28, 32.17, 62.34, 125.84, 126.91, 128.46, 129.99, 130.30, 137.53. Found: C, 81.20; H, 8.62%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

(Z)-*5-Phenyl-4-penten-1-ol*: Bp 75-79 °C (0.3 Torr, bath temperature); IR (neat) 3314, 3008, 2932, 2870, 1494, 1446, 1051, 1024, 766, 732, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.57-1.70 (bs, 1H), 1.72 (tt, *J* = 7.5, 6.6 HZ, 2H), 2.42 (dq, *J* = 1.8, 7.5 Hz, 1H), 3.65 (t, *J* = 6.6 Hz, 2H), 5.67 (dt, *J* = 11.5, 7.3 Hz, 1H), 6.45 (dt, *J* = 11.5, 1.8 Hz, 1H), 7.18-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.81, 32.72, 62.27, 126.53, 128.11, 128.65, 129.37, 131.99, 137.40. Found: C, 81.43; H, 8.83%. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70%.

(E)-*4-Nonen-1-ol*: Bp 85-87 °C (28 Torr, bath temperature); IR (neat) 3300, 2952, 2924, 2856, 1466, 1124, 1059, 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.25-1.48 (m, 5H), 1.63 (tt, *J* = 7.5, 6.5 Hz, 2H), 1.98 (q, *J* = 6.6 Hz, 2H), 2.08 (q, *J* = 7.2 Hz, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 5.40 (dt, *J* = 15.3, 6.0 Hz, 1H), 5.46 (dt, *J* =

15.3, 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.18, 28.91, 31.70, 32.22, 32.41, 62.57, 129.33, 131.22. Found: C, 75.98; H, 12.98%. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75%.

(Z)-*4-Nonen-1-ol*: Bp 69-72 °C (15 Torr, bath temperature); IR (neat) 3320, 2952, 2926, 2858, 1459, 1124, 1061, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.1 Hz, 3H), 1.27-1.30 (m, 4H), 1.45-1.57 (bs, 1H), 1.64 (tt, J = 7.6, 6.6 Hz, 2H), 1.95-2.09 (m, 2H), 2.13 (q, J = 6.6 Hz, 2H), 3.66 (t, J = 6.6 Hz, 2H), 5.36 (dt, J =10.9, 6.2 Hz, 1H), 5.42 (dt, J = 10.9, 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.32, 23.55, 26.88, 31.85, 32.60, 62.64, 128.78, 130.74. Found: C, 75.76; H, 12.96%. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75%.

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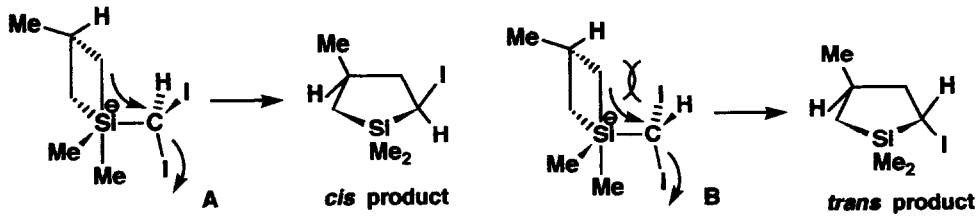
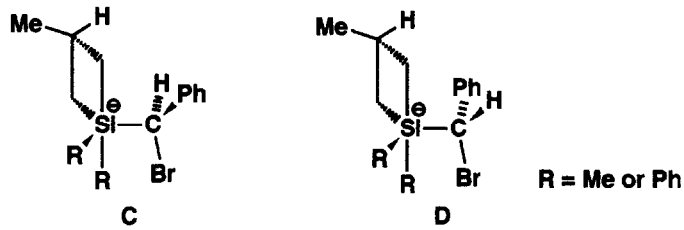
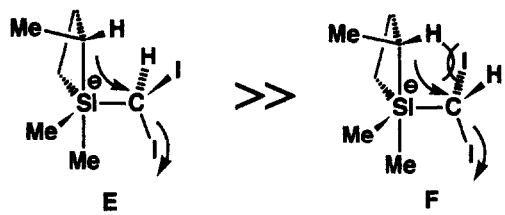
10. Selective formation of *cis*-2-iodo-1,1,4-trimethyl-1-silacyclopentane **5a** might be explained as follows. In a pentacoordinate silicate transition state, C-3 methyl group keeps away from bulky diiodomethyl group and occupies the same side as equatrial methyl group on silicon (A or B). Transition state A, in which hydrogen of diiodomethyl group occupies inside position, is favorable as compared to B because of steric interaction and affords major *cis* isomer by the migration of carbon from silicon to carbon bearing iodine as depicted below. Selective formation of **5b**, **5d**, and **5e** (Entries 2, 4, and 5 in Table 2) is explained in the same way. In contrast, stereochemical outcome of the reaction of **4a** and **4b** with PhCHBrLi (Entries 3 and 6) might be explainable by different way. Carbenoid PhCHBrLi attacks silicon to give two pentacoordinate silicates C and D which collapse to *cis*-silacyclopentane **5** and *trans*-isomer **6**, respectively. The product ratio (**5c** : **6c** or **5f** : **6f**) is determined by the attacking step and independent from energy difference between C and D. The steric interaction between methyl group on silicon (**4a**) (or phenyl group on silicon (**4b**)) and phenyl or bromine of carbenoid determines the ratio of the formation of C and D.





The stereochemical results of **9a**, **9b**, and **9e** (Entries 1, 2, and 4 in Table 3, diastereomeric ratio = 4:1–5:1) might be explained along the same line as in the case of the reaction of **4** with CHI_2Li or $CHBr_2Li$. Meantime, exclusive formation of *cis*-silacyclopentane **8** might be explained as follows. Repulsion between methyl group on carbon and equatrial methyl group (or phenyl group) on silicon forces silacyclobutane ring to bend toward CHI_2 group. Thus, transition state E is much more favorable as compared to F and provides *cis*-silacyclopentane as a single isomer.



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