Silicon−Carbon Unsaturated Compounds. 66. Photolysis of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclohexane in the Presence of Isobutene

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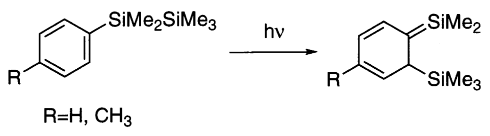
A mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a** and **1b**) was prepared by the reaction of 1,4-bis(chloromethylphenylsilyl)butane with lithium metal in the presence of a catalytic amount of dimethylphenylsilyllithium in THF. The photolysis of pure **1a** in the presence of isobutene afforded *cis*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2a**) in 63% yield, in addition to a small amount of a formal [2 + 2] cycloadduct (**3a**) with *cis*-configuration, arising from addition of the rearranged silene with isobutene. Similar photolysis of **1b** with isobutene gave a *trans*-adduct (**3b**) formed by formal [2 + 2] cycloaddition of the rearranged silene arising from **1b** to isobutene as the main product, together with a small amount of *trans*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2b**). The structure of the [2 + 2] cycloadduct **3b**, was verified by X-ray crystallography. The thermolyses of **3a** and **3b** at 150 °C for 24 h produced **2a** and **2b**, respectively, in quantitative yields.

Introduction

In 1975, we found that the photolysis of phenyl and *p*-tolylpentamethyldisilane affords the rearranged silenes, arising from the suprafacial 1,3-trimethylsilyl shift to an *ortho* carbon atom in the aryl ring as a main product.[1a] Work following this original discovery showed that the formation of the rearranged silenes is remarkably general for the photolysis of the benzenoid aryldisilanes. The silenes thus formed react with various trapping agents to give the respective adducts.[1b] Many papers concerning the photochemistry and photophysics of aryldisilanes have been published to date.[2,3] We have also investigated the stereochemistry in the photolysis of the aryldisilanes, by using *meso*- and *rac*-1,2-diethyl-1,2-dimethyldiphenyldisilane, and demonstrated that the *meso*- and *rac*-aryldisilanes rearrange diastereospecifically to give the respective silenes.[4] The reactions of the rearranged silenes thus formed with olefins, such as isobutene, 1,1-diphenylethylene, and 2,3-dimethylbutadiene, proceed with high stereospecificity to give the respective adducts arising from the ene-type reaction of the silenes with olefins.[4a] The photolysis of the *meso*- and *rac*-aryldisilane in the presence of carbonyl compounds, however, proceeds with high diastereoselectivity, but not with diastereospecificity, to give the respective adducts.[4b] Recently, we have reported the synthesis and some reactions of *cis*- and *trans*-3,4-benzo-1,2-di(*tert*-butyl)-1,2-dimethyl-1,2-disilacyclobut-3-



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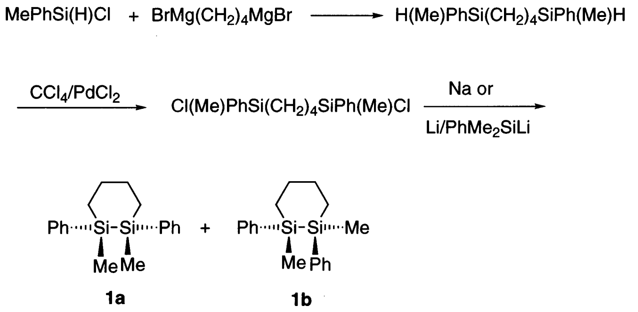
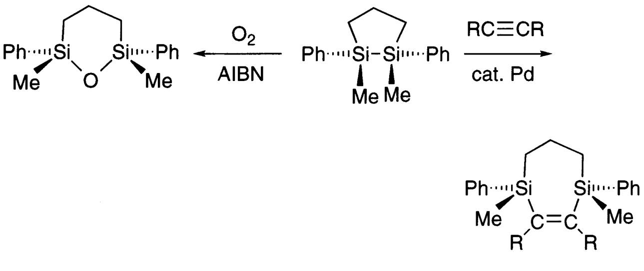
Scheme 1



ene[5] and also *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane.[6a] The reactions of *cis*- and *trans*-four-membered and five-membered cyclic compounds with molecular oxygen in the presence of AIBN proceed with high stereospecificity to give the corresponding *cis*- and *trans*-cyclic siloxanes, 4,5-benzo-2-oxa-1,3-disilacyclopent-4-enes and 2-oxa-1,3-disilcyclohexanes, respectively.



The palladium-catalyzed reactions of these compounds with alkynes also afford stereospecifically the respective *cis*- and *trans*-adducts. As part of our study concerning the stereochemistry of the organosilicon compounds, we have investigated the photolyses of *cis*- and *trans*-disilanylene-containing cyclic systems. In this paper we report the photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane.

Results and Discussion

Synthesis of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclohexane. A mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a** and **1b**) was prepared according to Scheme 1. A mixture of *meso*- and *rac*-1,4-bis(methylphenylsilyl)butane, readily obtained by the reaction of the di-Grignard reagent of 1,4-dibromobutane with chloromethylphenylsilane, was used as the starting material. Treatment of 1,4-bis(methylphenylsilyl)butane with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride afforded a mixture of *meso*- and *rac*-1,4-bis(chloromethylphenylsilyl)butane in a ratio of 1:1 in 98% yield.

The reaction of 1,4-bis(chloromethylphenylsilyl)butane with sodium dispersion in refluxing toluene produced a mixture of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane in a ratio of ca. 1:1 in 17% yield, together with a large amount of polymeric substances, which could readily be transformed into the starting bis(chlorosilyl)butane by treatment with chlorine gas in carbon tetrachloride in 76% yield.

In an effort to obtain much better yields of *cis*- and *trans*-disilacyclohexane **1a** and **1b**, we carried out the reaction of bis(chloromethylphenylsilyl)butane with lithium metal in the presence of a silyllithium catalyst in THF as reported recently.[6b] Thus, treatment of the bis(chlorosilyl)butane with finely cut lithium metal in the presence of a catalytic amount of dimethylphenylsilyllithium in THF produced a mixture of **1a** and **1b** in 49% yield. In this reaction, scission of the silicon−silicon bonds in the polymeric condensation products by dimethylphenylsilyllithium and also by lithium metal to afford the silyllithium derivatives is probably involved,[6c,d] as shown in Scheme 2. The silyllithium derivatives thus formed undergo a cyclization reaction to give **1a** and **1b** in higher yield than in the sodium condensation reaction. In contrast to the sodium condensation reaction, the ratio of **1a** and **1b** in this reaction was calculated to be 4:6 by GLC analysis of the mixture. Pure **1a** and **1b** could readily be obtained by fractional distillation of the mixture, using a spinning band distillation column with 50 theoretical plates. All spectral data for **1a** and **1b** were identical with those of the authentic samples reported previously.[7]

Photolysis of 1a and 1b. We carried out the photolysis of **1a** and **1b** in the presence of isobutene as a trapping agent in a hexane solution. Thus, irradiation of *cis*-isomer **1a** with a low-pressure mercury lamp in the presence of ca. 5-fold excess of isobutene gave an adduct, arising from the ene-type reaction of the rearranged silene (**A**) formed from **1a** with isobutene, *cis*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2a**) with high stereospecificity in 63% isolated yield, along with a 10% yield of the unchanged starting compound **1a** (Scheme 3). No *trans*-isomer was detected in the reaction mixture. However, a small amount of an isomer of **2a**, presumably, a formal [2 + 2] cycloadduct (**3a**, ca. 1% yield), was detected by ^{1}H NMR spectrometric analysis of the mixture, together with a trace amount of other products (see below).

The structure of **2a** was confirmed by spectrometric analysis, as well as by elemental analysis. The mass spectrum of **2a** shows a parent ion at *m*/*z* 352, corresponding to the molecular weight of the isobutene adduct. The ^{13}C NMR spectrum of **2a** shows nine resonances due to saturated carbons and 10 resonances attributed to the sp^2-hybridized carbon atoms. The ^{29}Si NMR spectrum shows two resonances at δ −3.9 and −1.2 ppm as expected. The *cis*-configuration of **2a** was verified by NOE-FID difference experiments at 500 MHz. Thus, irradiation of a resonance at 0.38 ppm due to methyl protons on the silicon atom bearing an isobutyl group reveals a strong enhancement of the resonance at 0.55 ppm attributed to the methyl protons on the silicon atom attached to a phenyl group, as well as methyl protons of the isobutyl group. These results clearly indicate that two methyl groups on the different

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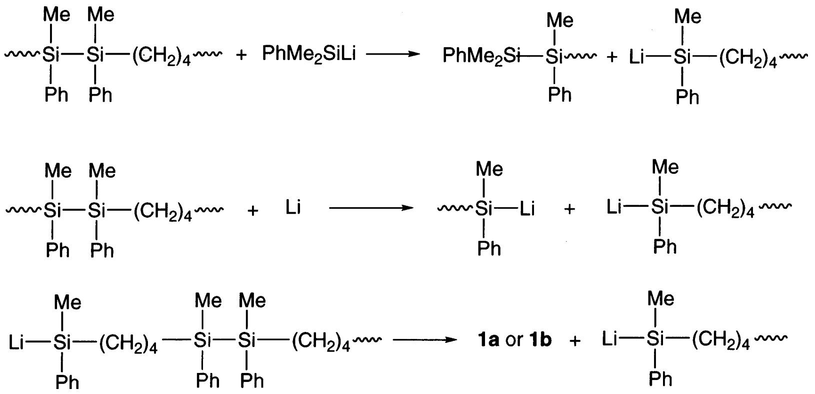
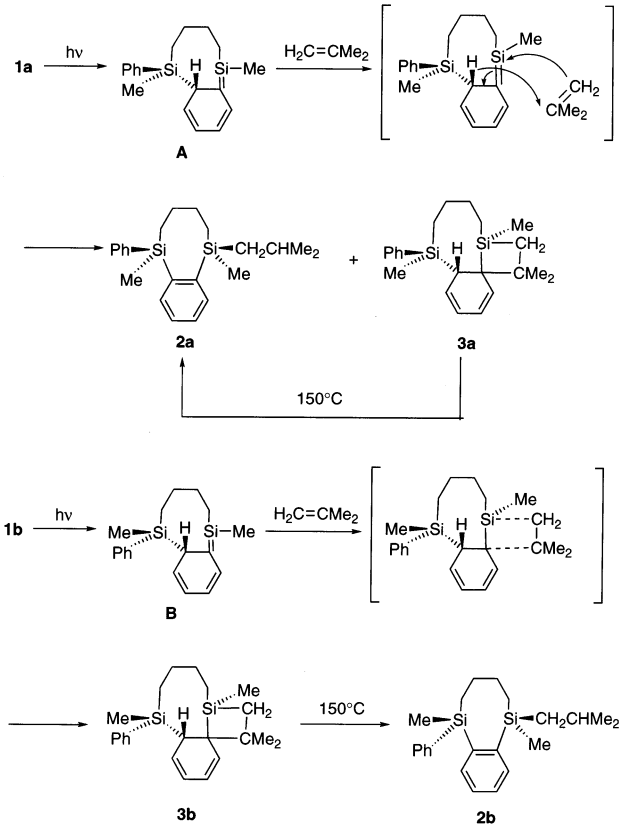
Scheme 2



Scheme 3



silicon atoms in **2a** are located *cis* to each other and also show that the photolysis of **1a** proceeds with high stereospecificity to give the *cis*-isomer **2a**. In the addition reaction of isobutene to the rearranged silene **A**, an isobutene molecule approaches the silicon–carbon double bond of **A** from the side opposite the methylphenylsilyl group in the 1,4-disilacyclooct-1-ene ring to avoid a significant steric interaction with this group. Consequently, only *cis*-isomer **2a** is produced as a single isomer.

In contrast to **1a**, similar photolysis of *trans*-isomer **1b** in the presence of isobutene gave a product consisting of a three-fused ring system, *trans*-7-phenyl-7,12,14,14-tetramethyl-7,12-disilatricyclo[8.4.0.0^{1,12}]-tetradeca-2,4-diene (**3b**), in 39% isolated yield, as the main product. In this photolysis, *trans*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2b**) was obtained in 7% yield, in addition to 32% of the unchanged starting compound **1b**. No other isomers were detected in the photolysis mixture, indicating that the photolysis of **1b** also proceeded with retention of the configuration. In this addition reaction, again, isobutene approaches the silicon–carbon double bond of the silene **B** from the opposite side of the methylphenylsilyl group in the 1,4-disilacyclooct-2-ene ring to retain the *trans*-configuration of the product **3b**. The structure of the main product **3b** was confirmed to be a [2 + 2] cycloadduct arising from addition of the rearranged silene **B** to isobutene by X-ray crystallographic analysis, as well as spectrometric analysis.

Isolation of the adduct **3b** is the first example of [2 + 2] cycloaddition in the reactions of the rearranged silenes with alkenes and dienes. All reactions of the rearranged silenes with the trapping agents reported so far afford the products derived from the ene-type reaction, although isolation of the [2 + 2] cycloadduct in the photolysis of phenyldisilanes in the presence of acetone has been reported.[3e,8a] We have also demonstrated the intermediary formation of the [2 + 2] cycloadducts in the cophotolysis of 2,6- and 2,7-bis(pentamethyldisilanyl)naphthalene with acetone and isobutene.[8b]

For the mechanism concerning the reactions of the silenes with olefins and dienes, [2 + 2] and [2 + 4] cycloadditions involving a concerted process have been proposed so far.[9] However, Yoshizawa et al. have recently reported that [2 + 2] cycloaddition of the silene formed from the acylpolysilane with acetylene under thermal conditions proceeds in a two-step manner to give the silacyclobutene.[10] We believe that the present addition reaction also proceeds in a stepwise fashion to give two different types of products. In the first step of the reaction, isobutene adds to the silene to give diradical species **C**, as shown in Scheme 4. Radical–radical coupling in **C** thus formed may produce four-membered cyclic systems **3a** and **3b**. On the other hand, a shift of hydrogen on the sp^3-carbon in the cyclohexa-

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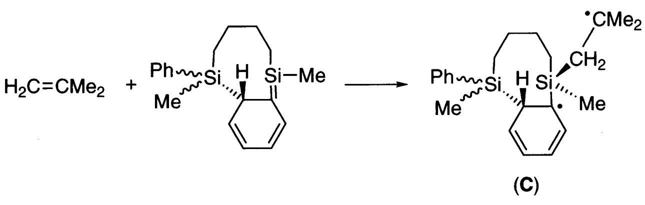
Scheme 4



dienyl ring to a carbon radical center in the isobutyl group, reproducing the aromaticity of the ring, probably affords the ene-type products **2a** and **2b**.

Thermal Reactions. The product **3b** is stable at room temperature in air. However, when **3b** was heated at 150 °C under nitrogen atmosphere for 24 h, compound **2b**, arising from opening of the four-membered ring in **3b**, was produced as a single isomer in almost quantitative yield. This shows that the thermolysis of **3b** proceeds with high stereospecificity to give **2b**.

The photolysis of **1a** with isobutene produced the product **2a** as the main product, in addition to a small amount of **3a**. All attempts to isolate **3a** in pure form using recycling preparative GPC were unsuccessful. Therefore, we used the mixture of **2a**, **3a**, and the starting compound **1a** for the thermal reaction. Thus, heating of the mixture consisting of **2a**, **3a**, and the starting compound **1a**, in a ratio of 1:4:2 (which was isolated by column chromatography of the photolysis mixture), at 150 °C for 24 h afforded the mixture involving **2a** and **1a** in ca. 5:2 ratio. No *trans*-isomer **2b** was detected in the thermolysis mixture. The result indicates that **3a** is completely transformed into **2a** with high stereospecificity.

As can be seen from the result of the X-ray crystallographic analysis of **3b**, the carbon–carbon bond in the silacyclobutane ring is quite long, compared with the normal carbon–carbon bond. In the thermal ring-opening reactions for **3a** and **3b**, these bonds would be broken to give the diradical intermediates **C**, in which a carbon radical in the isobutyl group abstracts hydrogen from the sp^3-carbon atom in the cyclohexadienyl ring to give **2a** and **2b**, respectively.

X-ray Crystallographic Analysis. The crystal structure of **3b** was determined by an X-ray diffraction study, and the ORTEP drawing is depicted in Figure 1. Cell dimensions, data collection and refinement parameters, and selected bond distances and angles are given in Tables 1 and 2. Since compound **3b** was labile toward exposure to X-ray radiation and underwent rapid decomposition during the data collection, we could obtain the structure only with rather large residuals ($R = 0.139$ and $R_w = 0.212$). However, all bond distances and angles were acceptable values, indicating that the structure was sufficiently solved for a rough discussion.

The structure has a tricyclic core with the strained silacyclobutane ring in a puckered form with a dihedral angle of 30.19° between planes defined by Si1, C1, and C3, and C1, C2, and C3, respectively, similar to the 1,1-dimethylsilacyclobutane structure determined by electron diffraction.[11] The C1–Si1–C3 angle is 77.0(4)°, smaller than the other inner-ring angles of C1–C3 in the four-membered ring system (88.4(5)–95.8(7)°), reflecting the more flexible nature of silicon bonding to adopt higher distortion, relative to carbon. The C4–Si1–C15 angle, on the other hand, is 111.1(4)°, close to the ideal sp^3 angle. Interestingly, the C1–C2 bond (1.64(1) Å) is elongated as compared with C2–C3 (1.58(1) Å). This is in accord with the fact that the thermolysis occurs by cleavage of the C1–C2 bond. It is also noted that Si2–C8 in the eight-membered ring is 2.00(1) Å, much longer the standard Si–C bond length, e.g., Si2–C16 = 1.90 (1) Å and Si1–C15 = 1.91(1) Å. Since there are no significant steric contacts between substituents around this bond, the long bond distance of Si2–C8 seems to indicate that the ring strain exists also in the eight-membered ring to some extent.

In conclusion, the photolysis of *cis*-isomer **1a** in the presence of isobutene afforded the ene-adduct **2a** with *cis*-configuration as the main product, in addition to a small amount of **3a**. Similar photolysis of *trans*-**1b** with isobutene gave a formal [2 + 2] cycloadduct **3b**, which was verified as *trans*-configured by X-ray crystallography. The thermolyses of **3a** and **3b** proceeded with high stereospecificity to give **2a** and **2b**, respectively, in quantitative yields.

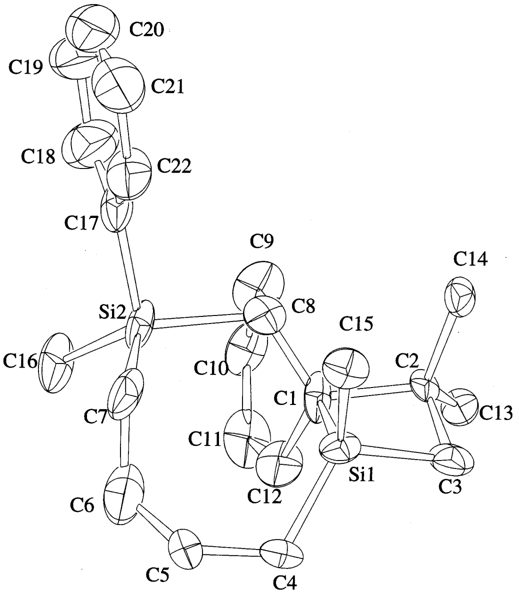


Figure 1. ORTEP diagram for **3b** showing thermal ellipsoids at the 50% level; hydrogen atoms were omitted for clarity.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 3b

mol formula	$C_{22}H_{32}Si_2$
mol wt	352.67
space group	$P2_1/a$ (#14)
temp, K	200
cell dimens	
a, Å	10.786(4)
b, Å	11.772(4)
c, Å	17.204(7)
β, deg	106.29(2)
V, Å^3	2096(1)
Z	4
D_{cacld}, Mg/m^3	1.098
F_{000}	744.00
cryst size, mm^3	0.5 × 0.5 × 0.4
cryst color	colorless
μ, cm^{-1}	1.69 (Mo Kα)
no. of obsd reflns	2058 ($\lvert F_o\rvert \geq 3\sigma(F_o)$)
corrections	Lorentz–polarization
reflns/params	9.48
R	0.139
R_w[a]	0.212

[a] Weighting scheme is $(\sigma(F_o)^2 + 0.0004\lvert F_o\rvert^2)^{-1}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3b

Si(1)	C(1)	1.92(1)	C(2)	C(3)	1.58(1)
Si(1)	C(3)	1.91(1)	C(2)	C(13)	1.54(1)
Si(1)	C(4)	1.882(9)	C(2)	C(14)	1.52(1)
Si(1)	C(15)	1.91(1)	C(4)	C(5)	1.53(1)
Si(2)	C(7)	1.85(1)	C(5)	C(6)	1.52(2)
Si(2)	C(8)	2.00(1)	C(6)	C(7)	1.53(2)
Si(2)	C(16)	1.90(1)	C(8)	C(9)	1.50(1)
Si(2)	C(17)	1.87(1)	C(9)	C(10)	1.34(2)
C(1)	C(2)	1.64(1)	C(10)	C(11)	1.43(2)
C(1)	C(8)	1.49(1)	C(11)	C(12)	1.32(1)
C(1)	C(12)	1.52(1)			

C(1)	Si(1)	C(3)	77.0(4)	C(1)	C(2)	C(3)	95.8(7)
C(1)	Si(1)	C(4)	118.8(4)	C(1)	C(2)	C(13)	115.1(7)
C(1)	Si(1)	C(15)	117.1(4)	C(1)	C(2)	C(14)	113.9(7)
C(3)	Si(1)	C(4)	116.3(4)	C(3)	C(2)	C(13)	111.1(7)
C(3)	Si(1)	C(15)	112.6(4)	C(3)	C(2)	C(14)	110.8(7)
C(4)	Si(1)	C(15)	111.1(4)	C(13)	C(2)	C(14)	109.4(8)
C(7)	Si(2)	C(8)	115.7(4)	Si(1)	C(3)	C(2)	90.6(6)
C(7)	Si(2)	C(16)	108.2(5)	Si(1)	C(4)	C(5)	118.9(7)
C(7)	Si(2)	C(17)	110.8(5)	C(4)	C(5)	C(6)	113.9(9)
C(8)	Si(2)	C(16)	113.7(4)	C(5)	C(6)	C(7)	117(1)
C(8)	Si(2)	C(17)	99.9(4)	Si(2)	C(7)	C(6)	116.6(9)
C(16)	Si(2)	C(17)	108.2(5)	Si(2)	C(8)	C(1)	113.6(7)
Si(1)	C(1)	C(2)	88.4(5)	Si(2)	C(8)	C(9)	107.1(7)
Si(1)	C(1)	C(8)	120.9(6)	C(1)	C(8)	C(9)	111.0(8)
Si(1)	C(1)	C(12)	112.8(8)	C(8)	C(9)	C(10)	120(1)
C(2)	C(1)	C(8)	115.3(8)	C(9)	C(10)	C(11)	118.0(9)
C(2)	C(1)	C(12)	111.2(7)	C(10)	C(11)	C(12)	121.1(9)
C(8)	C(1)	C(12)	107.3(7)	C(1)	C(12)	C(11)	121(1)

Experimental Section

General Procedure. All photolyses were carried out under an atmosphere of dry argon. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low- and high-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane were separated by a TSA-SB2 spinning band-type distillation column (Taika Kogyo). The melting point was measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Gel permeation chromatographic separation was carried out with the use of a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd.). Tetrahydrofuran, ether, and toluene, used as solvents, were dried over sodium benzophenone ketyl under a nitrogen atmosphere and distilled just before use. Carbon tetrachloride was dried over diphosphorus pentoxide and distilled before use.

Preparation of 1,4-Bis(methylphenylsilyl)butane. In a 2 L four-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed a 1,4-di-Grignard reagent prepared from 22.5 g (0.93 mol) of magnesium and 76.7 g (0.36 mol) of 1,4-dibromobutane in 750 mL of dry ether. To this was added 112.9 g (0.72 mol) of chloromethylphenylsilane with ice-cooling. The mixture was heated to reflux for 10 h and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvent ether was evaporated, and the residue was distilled under reduced pressure to give 70.9 g (67% yield) of 1,4-bis(methylphenylsilyl)butane: bp 132−134/1 Torr; MS *m/z* 298 (M^+); ^{1}H NMR δ ($CDCl_3$) 0.34 (d, 6H, MeSi, $J = 3.7$ Hz), 0.81−0.89 (m, 4H, CH_2), 1.45 (t, 4H, CH_2, $J = 7.3$ Hz), 4.35 (q, 2H, SiH, $J = 3.7$ Hz), 7.35−7.41 (m, 6H, phenyl ring protons), 7.53−7.55 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −5.70 (MeSi), 13.05, 27.82 (CH_2), 127.80, 129.13, 134.27, 136.67 (phenyl ring carbons); ^{29}Si NMR δ($CDCl_3$) −13.5. Anal. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78. Found: C, 72.48; H, 8.96.

Preparation of 1,4-Bis(chloromethylphenylsilyl)butane. In a 500 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 0.005 g (0.28 mmol) of a palladium dichloride catalyst in 200 mL of dry carbon tetrachloride. To this solution was added 96.6 g (0.32 mol) of 1,4-bis(methylphenylsilyl)butane at room temperature over a period of 30 min. After the mixture was heated to reflux for 10 h, carbon tetrachloride and the resulting chloroform were distilled off and the residue was distilled under reduced pressure to give 116.3 g (98%) of 1,4-bis(chloromethylphenylsilyl)butane: bp 161−164 °C/1 Torr; MS *m/z* 366 (M^+); ^{1}H NMR δ ($CDCl_3$) 0.64 (s, 6H, MeSi), 1.00−1.05 (m, 4H, CH_2), 1.48−1.54 (m, 4H, CH_2), 7.37−7.45 (m, 6H, phenyl ring protons), 7.57−7.61 (m, 4H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) 0.26 (MeSi), 17.68, 26.24 (CH_2), 128.05, 130.28, 133.28, 135.34 (phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) 20.8. Anal. Calcd for $C_{18}H_{24}Si_2Cl_2$: C, 58.83; H, 6.58. Found: C, 58.47; H, 6.69.

Reaction of 1,4-Bis(chloromethylphenylsilyl)butane with Sodium Metal. In a 500 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel were placed 6.8 g (0.29 mol) of sodium and 200 mL of dry toluene. To the sodium dispersion prepared by stirring in refluxing toluene was added 41.5 g (0.11 mol) of 1,4-bis(chloromethylphenylsilyl)butane in 50 mL of toluene at 100 °C over a period of 2 h. The resulting mixture was heated at 100−105 °C for 10 h. At this stage, GLC analysis of the mixture showed the presence of only the *cis*- and *trans*-isomer as a volatile product. No other products were detected by GLC. The mixture was hydrolyzed with EtOH−H_2O, and the organic layer was separated, washed three times with water, and dried over calcium chloride. Toluene was distilled off and the residue was distilled under reduced pressure to give 5.4 g (17% yield) of a mixture of **1a** and **1b** (bp 125−134 °C/1 Torr) and 27.4 g of viscous polymeric materials as the residue. All spectral data for **1a** and **1b** were identical with the authentic samples.[7]

Conversion of Polymeric Materials to 1,4-Bis(chloromethylphenylsilyl)butane. In a 200 mL two-necked flask was placed 27.4 g (0.092 mmol) of polymeric substances obtained from Wurtz coupling reaction of 1,4-bis(chloromethylphenylsilyl)butane in 150 mL of carbon tetrachloride. To this was introduced chlorine gas with ice-cooling until the solution showed a yellow color of chlorine at room temperature. The solvent carbon tetrachloride was distilled off, and the residue was distilled under reduced pressure to give 25.6 g (76% yield) of 1,4-bis(chloromethylphenylsilyl)butane. All spectral data for 1,4-bis(chlorosilyl)butane were identical with those of the authentic samples obtained from the above reaction.

Reaction of 1,4-Bis(chloromethylphenylsilyl)butane with Lithium in the Presence of a Dimethylphenylsilyllithium Catalyst. In a 500 mL flask were placed 3.0 g (0.43 mol) of finely cut lithium, 0.5 g (2.93 mmol) of chlorodimethylphenylsilane, and 200 mL of THF. The mixture was stirred at room temperature to produce dimethylphenylsilyllithium. To this brown-colored solution was added 68.0 g (0.19 mol) of 1,4-bis(chloromethylphenylsilyl)butane in 50 mL of THF at room temperature over a period of 8 h. The resulting brown-colored solution was stirred at room temperature for 15 h and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and extracts were combined, washed with water, and dried over calcium chloride. The solvents were evaporated and the residue was distilled under reduced pressure to give 27.5 g (49% yield) of a mixture of *cis*- and *trans*-isomer, whose ratio was determined to be 4:6 by GLC analysis: bp 130−145 °C/3 Torr. Pure *cis*- and *trans*-isomer were obtained by distillation using a spinning band distillation column with 50 theoretical plates. Data for *cis*-isomer **1a**:[7] bp 132 °C/3 Torr; UV λ_{max} (cyclohexane) 235.5 nm (ϵ 16000); MS *m/z* 296 (M^+); ^{1}H NMR δ($CDCl_3$) 0.40 (s, 6H, MeSi), 0.96−1.01 (m, 2H, CH_2Si), 1.16−1.21 (m, 2H, CH_2Si), 1.74−1.81 (m, 4H, CH_2), 7.21−7.28 (m, 6H, phenyl ring protons), 7.34−7.36 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.57 (MeSi), 15.45, 26.05 (CH$_2$), 127.63, 128.51, 134.46, 137.99 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −23.7. Data for *trans*-isomer **1b**:[7] bp 142−143 °C/3 Torr; UV $\lambda_{\max}$ (cyclohexane) 237.5 nm (e 16000); MS *m*/*z* 296 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.34 (s, 6H, MeSi), 1.09−1.11 (m, 4H, CH$_2$Si), 1.59−1.65 (m, 2H, CH$_2$), 1.96−2.02 (m, 2H, CH$_2$), 7.32−7.37 (m, 6H, phenyl ring protons), 7.47−7.51 (m, 4H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −4.95 (MeSi), 15.43, 26.03 (CH$_2$), 127.83, 128.57, 134.18, 138.43 (phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −23.6.

Photolysis of 1a. A mixture of 0.532 g (1.68 mmol) of **1a** and 0.455 g (8.11 mmol) of isobutene in 60 mL of hexane was placed in a reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated for 30 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, eluting with hexane, to give 0.410 g of **2a**, including a small amount of **3a** (ca. 1%) and 0.051 g (10%) of the starting compound **1a**. Pure **2a** (0.390 g, 63% yield) was separated by recycling preparative HPLC eluting with benzene. Data for **2a**: MS *m*/*z* 352 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.38 (s, 3H, MeSi), 0.55 (s, 3H, MeSi), 0.74 (d, 3H, CH$_3$, $J = 6.6$ Hz), 0.78 (d, 3H, CH$_3$, $J = 6.6$ Hz), 0.91−1.01 (m, 2H, CH$_2$), 1.14−1.36 (m, 4H, CH$_2$), 1.52−1.85 (m, 5H, CH$_2$, CH), 7.29−7.46 (m, 7H, phenyl ring protons), 7.68−7.74 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −1.18, 1.07 (MeSi), 12.97, 13.04, 24.53, 24.77, 24.95, 25.88, 36.61, 28.00 (CH$_2$), 127.58, 127.67, 128.00, 128.65, 134.22, 135.02, 136.10, 140.41, 141.97, 147.72 (phenyl and phenylene ring carbons); ^{29}Si NMR δ (CDCl$_3$) −3.9, −1.2. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.92; H, 9.34. Data for **3a**: ^{1}H NMR δ (CDCl$_3$) 0.22 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 0.85 (br s, 1H, CH$_2$), 0.89 (br s, 1H, CH$_2$), 1.19 (s, 3H, CH$_3$), 1.30 (s, 3H, CH$_3$), 1.50−1.68 (m, 4H, CH$_2$), 1.71−1.83 (m, 2H, CH$_2$), 1.86−1.99 (m, 1H, CH$_2$), 2.12−2.23 (m, 1H, CH$_2$), 2.98 (d, 1H, CH, $J = 6.4$ Hz), 5.33−6.12 (m, 4H, cyclohexadienyl ring protons), 7.35−7.42 (m, 3H, phenyl ring protons), 7.55−7.58 (m, 2H, phenyl ring protons).

Photolysis of 1b. A mixture of 0.499 g (1.68 mmol) of **1a** and 0.376 g (6.70 mmol) of isobutene in 60 mL of hexane was placed in a reaction vessel. The mixture was irradiated for 30 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, eluting with hexane, to give 0.041 g (7% yield) of **2b**, 0.230 g (39% yield) of **3b**, and 0.164 g (32%) of the starting compound **1b**. Data for **2b**: MS *m*/*z* 352 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.22 (s, 3H, MeSi), 0.55 (s, 3H, MeSi), 0.90−0.94 (m, 4H, CH$_2$), 0.94 (d, 3H, CH$_3$, $J = 6.6$ Hz), 0.99 (d, 3H, CH$_3$, $J = 6.6$ Hz), 1.22−1.24 (m, 2H, CH$_2$), 1.61−1.71 (m, 4H, CH$_2$, CH), 1.88 (sep, 1H, CH, $J = 6.8$ Hz), 7.29−7.48 (m, 7H, phenyl ring protons), 7.54 (d, 1H, $J = 7.3$ Hz, phenyl ring protons), 7.68 (d, 1H, $J = 7.3$ Hz, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) 0.27, 0.68 (MeSi), 13.26, 13.77, 24.77, 24.95, 25.09, 26.18, 26.87, 27.39 (CH$_2$), 127.44, 127.66, 127.95, 128.71, 134.46, 134.94, 136.38, 139.90, 142.95, 147.10 (phenyl and phenylene ring carbons); ^{29}Si NMR δ(CDCl$_3$) −3.8, −1.3. Exact MS calcd for $C_{22}H_{32}Si_2$: 352.2043. Found: 352.2033. Data for **3b**: mp 103−104 °C; MS *m*/*z* 352 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.09 (s, 3H, MeSi), 0.61 (s, 3H, MeSi), 0.80 (br s, 1H, CH$_2$), 0.85 (br s, 1H, CH$_2$), 1.04−1.28 (m, 4H, CH$_2$), 1.12 (s, 3H, Me), 1.16 (s, 3H, Me), 1.40−1.48 (m, 2H, CH$_2$), 1.60−1.75 (m, 1H, CH$_2$), 2.07−2.15 (m, 1H, CH$_2$), 2.65 (d, 1H, CH, $J = 6.6$ Hz), 5.63−5.69 (m, 1H, CH), 5.87−5.92 (m, 1H, CH), 6.08−6.09 (m, 2H, CH), 7.31−7.37 (m, 3H, phenyl ring protons), 7.46−7.49 (m, 2H, phenyl ring protons); ^{13}C NMR δ (CDCl$_3$) −5.27, 0.71 (MeSi), 11.85, 15.36, 21.30, 26.48, 26.80, 29.83, 31.06, 31.85, 37.26, 43.85 (CH$_3$, CH$_2$, CH, *C*Me$_2$, *C*Si), 123.87, 125.41, 126.65, 127.76, 128.55, 131.10, 133.28, 141.48 (cyclohexadienyl and phenyl ring carbons); ^{29}Si NMR δ (CDCl$_3$) −2.4, 12.0. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 75.16; H, 9.00.

Thermolysis of 3a. A mixture of 0.387 g consisting of **2a**, **3a**, and **1a** in a ratio of 1:4:2 was heated in a sealed glass tube at 150 °C for 24 h. The mixture was chromatographed on a short silica gel column, eluting with hexane, to give 0.264 g (68%) of the product. The ^{1}H NMR spectrometric analysis indicated the presence of **2a** and **1a** in a ratio of 5:2.

Thermolysis of 3b. In a sealed glass tube was placed 0.0706 g (0.20 mmol) of **3b**. The glass tube was heated to 150 °C for 24 h. The product was chromatographed on a short silica gel column, eluting with hexane, to give 0.051 g (72% yield) of **2b**. All spectral data for **2b** are identical with those of an authentic sample.

X-ray Crystallographic Analysis. Data collection was performed on a MacScience DIP2030 imaging plate system at 200 K. Unit cell parameters for the crystal were determined by the program DENZO,[12] and the data were processed by using SCALEPACK.[13] The structure was solved by the SIR92 direct method[13] and expanded using DIRDIF94 Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_{calc};[16] the values for $\Delta f'$ and $\Delta f'$ were those of Creagh and McAuley.[17] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[18] All calculations were performed using the teXsan[19] crystallographic software package.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, bond lengths and angles, and anisotropic thermal parameters for **3b**. An X-ray crystallographic file in CIF format is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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