Silicon−Carbon Unsaturated Compounds. 57. Photolysis of *meso*- and *racemic*-1,2-Diethyl-1,2-dimethyldiphenyldisilane, Direct Evidence for a Concerted 1,3-Silyl Shift to *ortho*-Carbon in the Phenyl Ring

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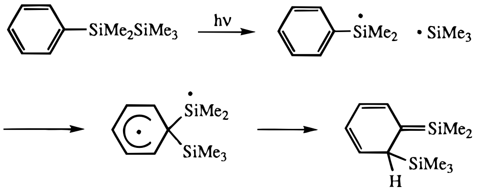
Received February 12, 1996⊗

Abstract: *meso*- and *racemic*-1,2-diethyl-1,2-dimethyldiphenyldisilane (**2a**) and (**2b**) were synthesized respectively by hydrogenation of *meso*- and *racemic*-1,2-diethynyl-1,2-dimethyldiphenyldisilane in the presence of a IrCl(CO)-$(PPh_3)_2$ catalyst. Irradiation of **2a** with a low-pressure mercury lamp in the presence of isobutene in hexane proceeded with high diastereospecificity to give (*R,S*)- and (*S,R*)-2-(isobutylethylmethylsilyl)-1-(ethylmethylphenylsilyl)benzene in 77% yield. Similar irradiation of **2b** with isobutene produced (*R,R*)- and (*S,S*)-isomer. The photolysis of **2a** and **2b** in the presence of 1,1-diphenylethylene also proceeded diastereospecifically to give the respective adducts. With 2,3-dimethylbutadiene, **2a** and **2b** produced the corresponding adducts, whose spectrometric analysis showed the presence of two diastereomers. Results on theoretical studies which were carried out using $PhSiH_2SiH_3$ as a model have also been reported.

Introduction

In 1975, we found that when phenyl- and *p*-tolylpentamethyldisilane are photolyzed at 254 nm in benzene, photochemical isomerization takes place to give a silene arising from a 1,3-trimethylsilyl shift to an ortho carbon atom in the aryl ring.[1a] In the photolysis of pentamethyl-*p*-tolyldisilane, two other reactions are observed to occur slightly.[1b,c] One involves homolytic scission of a silicon−silicon bond, followed by disproportionation of the resulting silyl radicals leading to 1-methyl-1-*p*-tolylsilene, while the other comprises extrusion of dimethylsilylene from the starting disilane. Introduction of sterically bulky substituents and also radical stabilizing substituents such as phenyl groups on the silicon atoms[2] and substitution to the ortho position in the aryl ring[3] seem to facilitate the formation of silyl radicals.

The formation of the rearranged silenes is remarkably general for the photolysis of the benzenoid aryldisilanes that have less bulky substituents, such as a methyl or ethyl group on the silicon atoms.[1c] The silenes thus formed react with various trapping agents to give addition products.[1−4] Although chemical behavior of the rearranged silenes has been extensively investigated, the mechanism for the formation of the silenes has not been fully elucidated. In 1980, a mechanism involving homolytic scission of the silicon−silicon bond of aryldisilanes, followed by addition of the silyl radical to the ipso position of the phenylsilyl group, and then a 1,2-silyl shift to give the rearranged silenes was reported by Sakurai et al.[5] However, we concluded that a concerted pathway for the formation of the rearranged silenes is more favorable than the radical mechanism on the basis of the following results. Firstly, the photolysis of 2,2,2-trimethyl(phenyl)bis(trimethylsiloxy)disilane that proceeds with homolytic scission of the silicon−silicon bond to give silyl radicals affords no rearranged silene.[6] Secondly, picosecond flash photolysis experiments on pentamethylphenyldisilane indicated that the rearranged silene is formed with a buildup time of 30 ps after excitation, which is equal to the decay time of the fluorescence of the disilane.[7] These results obviously support the concerted mechanism derived from a singlet excited state.



Recently, Leigh and Sluggett have investigated the nanosecond flash photolysis of 1,1,1-trimethyltriphenyldisilane and found that the corresponding rearranged silene was produced within a time scale shorter than the duration of the excitation pulse (ca. 10 ns).[2b] They also demonstrated that the rearranged silene from the photolysis of 1,1,1-trimethyltriphenyldisilane is

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) (a) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155. (c) Ishikawa, M.; Kumada, M. *Adv. Orgenomet. Chem.* **1981**, *19*, 51.

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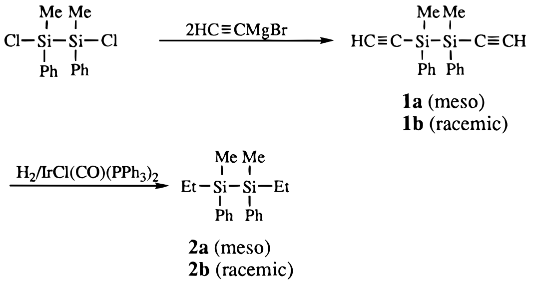
S0002-7863(96)00458-1 CCC: $12.00

Scheme 1



1a (meso)
1b (racemic)

2a (meso)
2b (racemic)

derived largely from an excited singlet state of the disilane and free silyl radicals do not play a crucial role in the formation of the silene.[2d,8] Thus, the presence of a triplet quencher in the photolysis of 1,1,1-trimethyltriphenyldisilane does not lead to the decrease in the yields of the products originating from the rearranged silene but suppresses the silyl radical formation. Furthermore, the photolysis of the aryldisilane affords the products derived from the rearranged silene in almost the same yields in the presence of the radical trapping reagent as in the absence of the radical trapping agent.[2c] These results also suggest the concerted mechanism for the formation of the rearranged silenes.

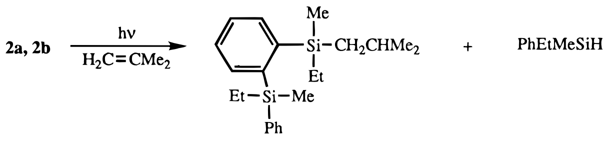
In order to get more direct evidence for the concerted mechanism, we investigated the stereochemistry of the photolysis of aryldisilanes. In this paper, we report the diastereospecific formation of the rearranged silenes in the photolysis of *meso*- and *racemic*-1,2-diethyl-1,2-dimethyldiphenyldisilane. We also report the results of MO calculations for $PhSiH_2SiH_3$ and the rearranged silene as model compounds.

Results and Discussion

Synthesis. A mixture of *meso*- and *racemic*-1,2-diethynyl-1,2-dimethyldiphenyldisilane was obtained by the reaction of 1,2-dichloro-1,2-dimethyldiphenyldisilane with ethynylmagnesium bromide in 94% yield, as shown in Scheme 1. NMR spectrometric analysis of the resulting product reveals that the product consists of a mixture of diastereomeric isomers in an approximate ratio of 49:51 (see Experimental Section). Fractional recrystallization of the mixture of *meso*- and *racemic*-isomer from ethanol afforded one isomer as crystals whose diastereomeric purity was determined to be more than 99% diastereomeric excess (de) by ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. The structure of this isomer was characterized by X-ray crystallographic analysis as *meso*-1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a**). Removal of the crystals of **1a** from the mixture gave *racemic*-isomer **1b** with 60% de. Treatment of the mixture with preparative GLC afforded **1b** with 78−90% de (diastereomeric ratios of **1a**/**1b** = 11/89−5/95).

Compounds **1a** (>99% de) and **1b** (78−90% de) thus obtained were converted into the respective 1,2-diethyl-1,2-dimethyldiphenyldisilanes (**2a** and **2b**) by hydrogenation in the presence of Vaska's catalyst. Compounds **2a** and **2b** were obtained as viscous liquid, and therefore, X-ray crystallographic analysis of these compounds could not be performed. However, NMR spectrometric analysis of **2a** and **2b** indicates that the hydrogenation proceeded with high diastereospecificity to give **2a** and **2b** having the same diastereomeric purity as that of the respective starting compounds **1a** and **1b** (see Experimental Section). Therefore, we identified **2a** as the *meso*-isomer and **2b** as the *racemic*-isomer.

Scheme 2



3a, 3b

Photochemical Reactions. First, we carried out the photolysis of a mixture of **2a** and **2b** in a ratio of 49:51. Thus, irradiation of the mixture in the presence of a 20-fold excess of isobutene in hexane at −78 °C with a low-pressure mercury lamp for 5 h gave 2-(isobutylethylmethylsilyl)-1-(ethylmethylphenylsilyl)benzene (**3a** and **3b**) in 85% yield, in addition to an 11% yield of ethylmethylphenylsilane and 3% of the unchanged starting compound **2** (Scheme 2). Ethylmethylphenylsilane is probably produced by homolysis of a silicon−silicon bond, followed by hydrogen abstraction by the resulting silyl radicals in the solvent cage or concerted dehydrosilation from a singlet excited state of **2** as proposed by Leigh et al.[2d]

Although GPC and GLC analysis of the adduct show a homogeneous peak, its ^{1}H NMR spectrum reveals the presence of two diastereomeric isomers in a ratio of 49:51. Interestingly, the photolysis of *meso*-isomer **2a** (>99% de) in the presence of isobutene under the same conditions produced a single isomer **3a** in 77% yield, together with a 12% yield of ethylmethylphenylsilane and 5% of the starting compound **2a**.

The structure of **3a** was confirmed by spectrometric analysis and combustion elemental analysis. The mass spectrum shows a parent ion at *m/z* 354, corresponding to the molecular weight of the isobutene adduct. The ^{1}H NMR spectrum of **3a** shows two singlets at 0.10 and 0.60 ppm ascribed to two nonequivalent methylsilyl groups, along with those of ethylsilyl, isobutyl, and aromatic ring protons. Its ^{13}C NMR spectrum reveals two signals at −1.8 and −1.7 and seven signals at 7.6, 7.7, 8.38, 8.43, 24.8, 26.1, and 26.3 (two carbons), attributed to methylsilyl carbons and ethyl and isobutyl carbons, as well as ten signals due to phenyl and phenylene ring carbons. As expected, the ^{29}Si NMR spectrum shows two signals at −4.48 and −0.15 ppm, due to two nonequivalent silicon atoms. These spectra reveal no signals due to the other diastereomer (**3b**), indicating the diasteremeric purity for **3a** is more than 99% de.

Similar irradiation of *racemic*-isomer **2b** (80% de) with isobutene in hexane at −78 °C gave adduct **3b** with 78% de and ethylmethylphenylsilane in 73% and 10% yields, along with 3% of the unchanged starting compound **2b**. For **3b**, the ^{1}H NMR spectrum shows two singlets at 0.08 and 0.60 ppm ascribed to two nonequivalent methylsilyl groups, along with those of ethylsilyl, iso-butyl, and aromatic ring protons. The ^{13}C NMR spectrum reveals methylsilyl carbon at −1.9 and −1.8 ppm and ethyl and isobutyl carbons at 7.6, 7.7, 8.38, 8.40, 24.8, 26.0, 26.2, and 26.3 ppm, along with phenyl and phenylene ring carbons. Its ^{29}Si NMR spectrum displays two signals at −4.48 and −0.18 ppm. In these spectra, signals due to **3a** with low intensities are also observed, with some overlapping with those of **3b**. The diastereomeric purity for **3b** was calculated by the integration ratio of the signals due to methylsilyl protons at 0.08 ppm for **3b** and 0.10 ppm for **3a**.

For the formation of **3a** and **3b**, if the concerted mechanism is operative, a suprafacial 1,3-silyl shift in (*R*,*R*)-1,2-diethyl-1,2-dimethyldiphenyldisilane should produce silenes **A** [(*E*)-(*S*,*S*)] and **B** [(*Z*)-(*R*,*S*)], according to paths a and b shown in Scheme 3. The silenes **A** and **B** thus formed undergo the ene reaction with isobutene to give an adduct. In this addition reaction, isobutene approaches the silicon−carbon double bond of the silenes from the opposite side of the ethylmethylphenyl-

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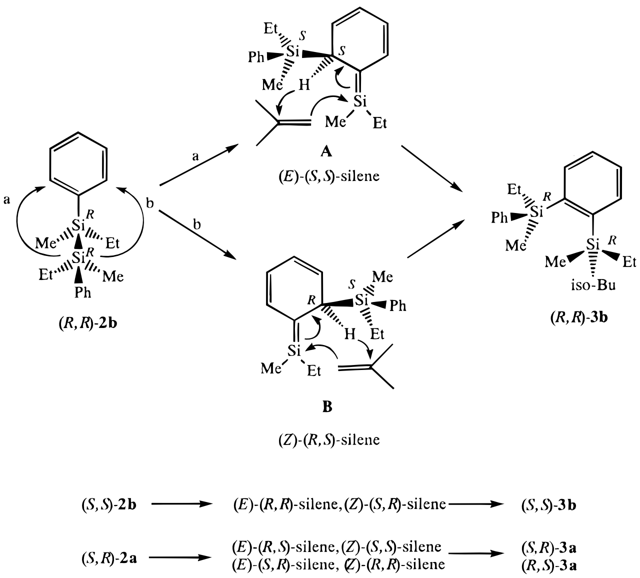
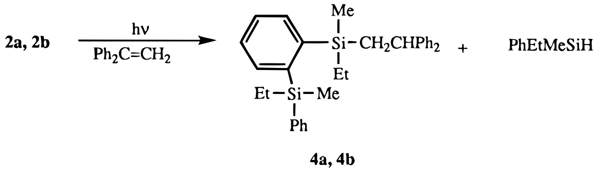
[8] Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 7531.

Scheme 3



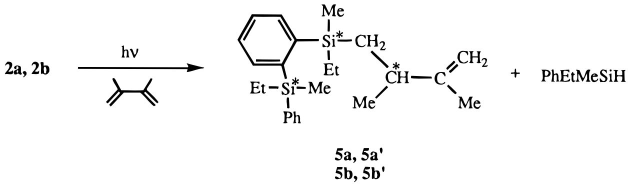
Scheme 4



silyl group on the cyclohexadienyl ring to avoid a significant steric interaction with this group.[9] Consequently, (*R*,*R*)-2-(isobutylethylmethylsilyl)-1-(ethylmethylphenylsilyl)benzene would be produced. On the basis of similar consideration, the (*S*,*S*)-isomer of **2b** should afford (*E*)-(*R*,*R*)-silene and (*Z*)-(*S*,*R*)-silene which react with isobutene to give (*S*,*S*)-2-(isobutylethylmethylsilyl)-1-(ethylmethylphenylsilyl)benzene. Similarly, (*R*,*S*)-isomer **2a** produces four types of silene by the concerted 1,3-silyl shift. The 1,3-shift of the silyl group with the *R*-configuration to the ortho phenyl carbon should produce (*E*)-(*R*,*S*)-silene and (*Z*)-(*S*,*S*)-silene, while migration of the silyl group with the *S*-configuration is expected to afford (*E*)-(*S*,*R*)-silene and (*Z*)-(*R*,*R*)-silene. The ene reaction of those four silenes with isobutene would produce (*S*,*R*)- and (*R*,*S*)-adducts. The diastereospecific reactions observed in the present photolysis are wholly consistent with the concerted mechanism, but not the radical mechanism.

We also carried out the photolysis of **2a** and **2b** in the presence of 1,1-diphenylethylene and 2,3-dimethylbutadiene. Thus, irradiation of **2a** (>99% de) in the presence of a 2.9-fold excess of 1,1-diphenylethylene in 70 mL of hexane at −78 °C for 18 h afforded 2-[ethylmethyl(2,2-diphenylethyl)silyl]-1-(ethylmethylphenylsilyl)benzene (**4a**) as a pure diastereomer, in 81% yield (Scheme 4). A 9% yield of ethylmethylphenylsilane was also produced in this reaction. No other isomer of **4a** was detected in the reaction mixture by spectrometric analysis. Similar photolysis of **2b** (80% de) in the presence of 1,1-diphenylethylene gave adduct **4b**, whose diastereomeric excess was determined to be 78% by the NMR spectrometric analysis in 85% yield, in addition to a 9% yield of ethylmethylphenylsilane. These results again indicate that the photochemical reaction of **2a** and **2b** leading to the rearranged silenes proceeds with high diastereospecificity. The structure of **4b** was determined by an X-ray diffraction study. Recrystallization of **4b** from ethanol afforded colorless crystals, whose X-ray crystallographic analysis reveals that **4b** consists of (*R*,*R*)- and (*S*,*S*)-isomers, in agreement with the mechanism proposed in Scheme 3.

Scheme 5



Next, we carried out the photolysis of **2a** and **2b** in the presence of 2,3-dimethylbutadiene to obtain further evidence for a concerted 1,3-silyl shift in the photochemical formation of the rearranged silenes. Previously, we have reported that the silenes generated photochemically from aryldisilanes react with 2,3-dimethylbutadiene to give *o*-silyl-substituted (2,3-dimethyl-3-butenylsilyl)arene as the sole product.[1b] The reaction of the silenes arising from **2a** and **2b** with 2,3-dimethylbutadiene should afford an adduct, 2-[ethylmethyl(2,3-dimethyl-3-butenyl)-silyl]-1-(ethylmethylphenylsilyl)benzene which has three chiral centers in the molecule (Scheme 5). If the photochemical formation of the silenes and the reaction of the resulting silenes with 2,3-dimethylbutadiene proceed with nonstereospecificity, four diastereomers should be detected by NMR spectrometric analysis. Thus, GPC and GLC analysis of the products obtained from the photolysis of **2a** (99% de) in the presence of 2,3-dimethylbutadiene showed a single peak, and the yield of the adduct was calculated to be 73%. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the adduct indicate the presence of two diastereomeric isomers, **5a** and **5a′**, in a ratio of 53:47, but not four diastereomers. Similar photolysis of **2b** (90% de) in the presence of 2,3-dimethylbutadiene afforded a diasrereomeric mixture of adducts **5a**, **5a′**, **5b**, and **5b′** in a ratio of 4:2:57:37 in 77% yield. Again, the results obtained can be understood in terms of a concerted 1,3-silyl shift of the aryldisilane to the ortho carbon in the aryl ring.

X-ray Crystallographic Analysis of 1a and 4b. The structures of **1a** and **4b** were verified by X-ray diffraction studies. Cell dimensions, data collections and refinement parameters, and selected bond lengths and angles for **1a** and **4b** are collected in Tables 1, 2, and 3. All unique diffraction maxima with $0 < 2\theta < 126.0°$ were recorded on a Rigaku AFC-6C automated four-circle diffractometer using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). A total of 1351 observed refractions for **1a** and 3930 for **4b** ($I > 3\sigma(I)$) were used in the least-squares refinement. The structures were solved by the Monte-Carlo direct method[10] using the MULTAN 78 program system[11] and refined by the full-matrix least-squares program.[12] Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*.[13] Anisotropic temperature factors were used for refinement of non-hydrogen atoms. Finally, R and R_w of 0.0743 and 0.0919 for **1b** and 0.0508 and 0.0525 for **4b** were obtained. ORTEP drawings of **1a** and **4b** are shown in Figures 1 and 2, along with atomic

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[12] Katayama, C.; Sakabe, N.; Sakabe, K. *Acta Crystallogr., Sect. A* **1972**, *28*, S207.

[13] *International Tables for X-ray Crystallography;* Kynoch Press: Birmingham, 1974; Vol. 4.

Table 1. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for Compounds 1a and 4b

	1a	**4b**
chem formula	$C_{18}H_{18}Si_2$	$C_{32}H_{38}Si_2$
fw	290.51	478.82
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
cell dimens		
a (Å)	12.164(2)	16.773(5)
b (Å)	10.349(1)	17.260(5)
c (Å)	6.885(1)	9.605(2)
α (deg)	90.00	95.54(3)
β (deg)	83.49(1)	92.77(3)
γ (deg)	90.00	147.92(1)
V (Å^3)	861.1(2)	1424.6(9)
Z	2	2
D_{calcd} (g/cm^3)	1.121	1.117
cryst dimens (mm^3)	0.60 × 0.58 × 0.33	0.53 × 0.30 × 0.09
crystal color	colorless	colorless
μ (cm^{-1})	1.64	1.14
diffractmeter	Rigaku AFC-6C	Rigaku AFC-6C
T (K)	293	293
λ (Cu Kα) (Å)	1.5418	1.5418
monochrometer	graphite crystal	graphite crystal
scan type	$\omega-2\theta$	$\omega-2\theta$
scan speed (deg/min)	4	4
scan width	$0 < 2\theta < 126$	$0 < 2\theta < 126$
diffraction geometry	symmetrical A	symmetrical A
range of *h, k, l*		
h	$-14 < h < 14$	$-19 < h < 19$
k	$0 \leq k \leq 12$	$-20 \leq k \leq 20$
l	$0 \leq l \leq 8$	$0 \leq l \leq 11$
no. of measd rflns	1609	5066
no. of unique rflns obsd	1563	4599
no. of obsd rflns ($I > 3\sigma(I)$)	1351	3930
R	0.0743	0.0508
Rw^a	0.0919	0.0525

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

Table 2. Bond Distances (Å) and Angles (deg) for Compound **1a** with Their Esd's in Parantheses

Si1−Si1′	2.344(2)	Si1-C2	1.864(5)	Si1-C3	1.841(3)
Si1−C5	1.869(3)	C3−C4	1.175(5)	C5−C6	1.387(5)
C5−C20	1.389(6)	C6−C7	1.381(6)	C7−C8	1.345(8)
C8−C9	1.353(7)	C9−C20	1.380(7)		

Si1′−Si1−C2	110.7(2)	Si1′−Si1−C3	107.3(1)
Si1′−Si1−C5	110.9(1)	C2−Si1−C3	110.4(2)
C2−Si1−C5	109.6(2)	C3−Si1−C5	108.0(2)
Si1−C3−C4	176.2(4)	Si1−C5−C6	121.6(3)
Si1−C5−C20	121.5(3)	C5−C6−C7	121.2(4)
C6−C7−C8	120.3(4)	C7−C8−C9	120.2(5)
C8−C9−C20	120.4(5)	C5−C20−C9	120.9(4)

Table 3. Bond Distances (Å) and Angles (deg) for Compound **4b** with Their Esd's in Parantheses

Si1−C3	1.868(3)	Si1−C4	1.878(4)	Si1−C6	1.879(2)
Si1−C20	1.902(5)	Si2−C25	1.900(4)	Si2−C26	1.874(4)
Si2−C27	1.875(8)	Si2−C29	1.879(2)	C4−C5	1.52(1)
C6−C7	1.529(3)	C7−C8	1.530(3)	C7−C14	1.524(7)
C8−C9	1.371(4)	C8−C13	1.393(4)	C9−C10	1.408(4)
C10−C11	1.357(6)	C11−C12	1.349(6)	C12−C13	1.378(4)
C14−C15	1.38(1)	C14−C19	1.377(4)	C15−C16	1.39(1)
C16−C17	1.362(7)	C17−C18	1.35(1)	C18−C19	1.39(1)
C20−C21	1.410(5)	C20−C25	1.428(8)	C21−C22	1.374(8)
C22−C23	1.36(1)	C23−C24	1.387(6)	C24−C25	1.396(6)
C27−C28	1.535(5)	C29−C30	1.390(4)	C29−C34	1.390(5)
C30−C31	1.379(3)	C31−C32	1.375(6)	C32−C33	1.357(6)
C33−C34	1.373(3)				

C3−Si1−C4	106.7(3)	C3−Si1−C6	108.0(2)
C3−Si1−C20	112.0(2)	C4−Si1−C6	109.2(2)
C4−Si1−C20	109.1(2)	C6−Si1−C20	111.7(2)
C25−Si2−C26	115.4(2)	C25−Si2−C27	110.1(2)
C25−Si2−C29	109.8(2)	C26−Si2−C27	105.8(3)
C26−Si2−C29	109.4(1)	C27−Si2−C29	105.8(2)
Si1−C4−C5	113.1(5)	Si1−C6−C7	118.1(2)
C6−C7−C8	115.1(2)	C6−C7−C14	111.9(4)
C8−C7−C14	109.3(3)	C7−C8−C9	124.1(3)
C7−C8−C13	117.8(3)	C9−C8−C13	118.1(3)
C8−C9−C10	119.7(3)	C9−C10−C11	120.7(3)
C10−C11−C12	120.0(3)	C11−C12−C13	120.4(4)
C8−C13−C12	121.1(3)	C7−C14−C15	120.6(3)
C7−C14−C19	121.1(5)	C15−C14−C19	118.2(5)
C14−C15−C16	120.6(4)	C15−C16−C17	119.8(9)
C16−C17−C18	120.4(8)	C17−C18−C19	120.5(5)
C14−C19−C18	120.5(6)	Si1−C20−C21	114.4(5)
Si1−C20−C25	128.7(2)	C21−C20−C25	116.9(4)
C20−C21−C22	123.2(6)	C21−C22−C23	119.9(4)
C22−C23−C24	118.8(5)	C23−C24−C25	123.3(7)
Si2−C25−C20	129.4(3)	Si2−C25−C24	112.8(4)
C20−C25−C24	117.8(4)	Si2−C27−C28	117.6(5)
Si2−C29−C30	122.5(2)	Si2−C29−C34	121.3(2)
C30−C29−C34	116.1(2)	C29−C30−C31	121.9(4)
C30−C31−C32	120.0(3)	C31−C32−C33	119.4(3)
C32−C33−C34	120.5(4)	C29−C34−C33	122.1(3)

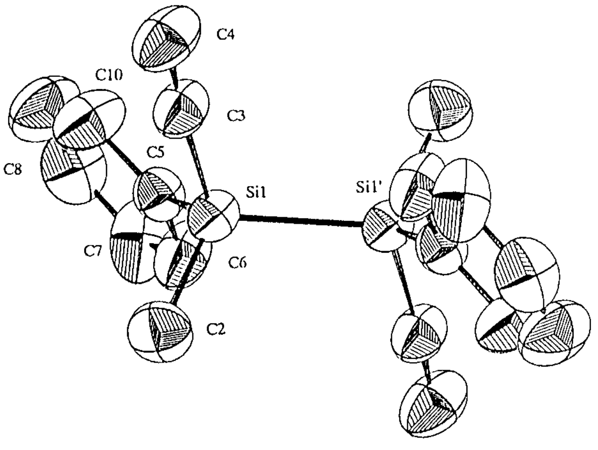

Figure 1. ORTEP drawing of **1a** showing the atom-numbering scheme.

numbering scheme. As shown in Figure 1, **1a** has a Ci center in the middle of the silicon−silicon bond. Selected bond distances and angles for compounds **1a** and **4b** shown in Tables 2 and 3 agree well with the accepted values. There are no intermolecular contacts less than the van der Waals distances.[14]

Theoretical Studies. In order to learn theoretically the stereochemistry of the suprafacial 1,3-silyl shift in 1,2-diethyl-1,2-dimethyldiphenyldisilanes **2a** and **2b**, we carried out molecular orbital (MO) calculations for phenyldisilane ($PhSiH_2$-SiH_3, **C**) and silene (**D**) arising from a 1,3-silyl shift to one of the *ortho*-carbons of a phenyl group, as models of disilanes **2a** and **2b** and silenes **A** and **B**, respectively. The *ab initio* MO calculations were carried out with the Gaussian 92 program[16] at the RHF/6-31G** level. The geometries of **C** and **D** were optimized, as shown in Figures 3 and 4. The structure **C** has C_s symmetry, and the silyl group is perpendicular to the *π*-plane of phenyl ring. In structure **D**, the Si(2)−C(3) bond length of 1.725 Å corresponds to the double bond.

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(14) All computations were performed on the HITAC M-680/180E system at the Information Processing Center of Hiroshima University using the CRYSTAN program system.[15]

(15) Katayama, C.; Honda, M. CRYSTAN, The Computer Center of Nagoya University Library Program.

(16) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Reghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

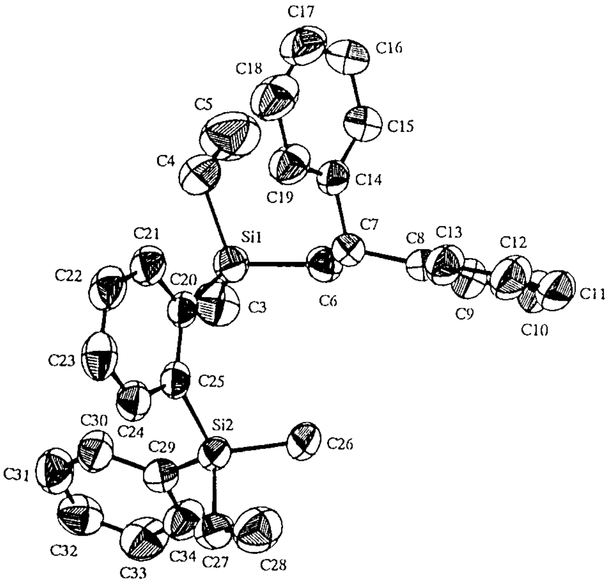
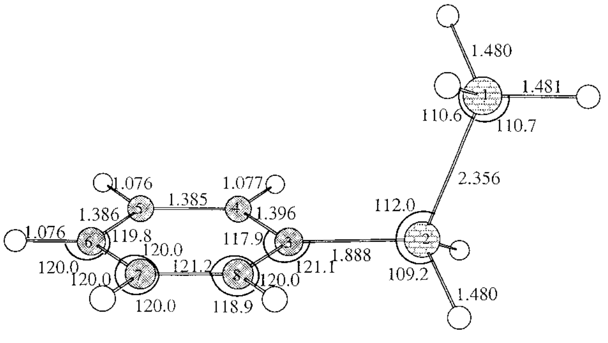
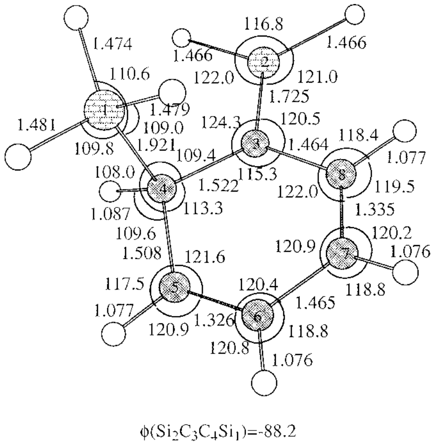


Figure 2. ORTEP drawing of **4b** showing the atom-numbering scheme.



C

Figure 3. Calculated RHF/6-31G** geometries of phenyldisilane (**C**). All bond lengths are in angstroms and all angles are in degrees.



D

Figure 4. Calculated RHF/6-31G** geometries of silene arising from a 1,3-silyl shift (**D**). All bond lengths are in angstroms and all angles are in degrees.

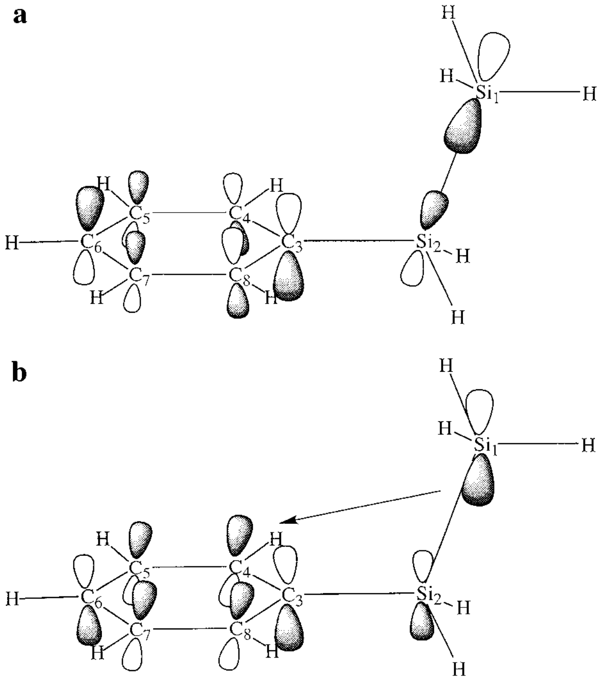


Figure 5. Frontier orbitals of phenyldisilane (**C**): (a) HOMO and (b) LUMO. The broad arrow in part b indicates the 1,3-silyl shift with retention of configuration at the migrating silicon.

The reaction mechanism of a 1,3-silyl shift is understood by using the frontier orbital theory. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **C** are displayed in Figure 5. Generally, the LUMO plays an important role in the photochemical intramolecular reaction.[17] With respect to the LUMO of phenyldisilane **C**, the Si(1)−Si(2) bond is antibonding and the C(3)−Si(2) bond is bonding so that in the excited state the Si(1)−Si(2) bond is weakened to form the new C(4)−Si(1) bond because the lobe of Si(1) toward the π-plane and the lobe of C(4) toward the perpendicular Si(1) are in the same phase. Hence, the photochemical 1,3-silyl shift in **C** is expected to occur with a preference for retention of configuration at the migrating silicon by the rules for conservation of orbital symmetry.[17] This expectation is coincident with the experimental results. On the other hand, the C(3)−Si(2) bond is strengthened to make the bonding π conjugation, leading to the product **D**.

Conclusions

meso- and *racemic*-1,2-diethyl-1,2-dimethyldiphenyldisilane (**2a** and **2b**) were obtained by hydrogenation of *meso*- and *racemic*-1,2-diethynyl-1,2-dimethyldiphenyldisilane (**1a** and **1b**), respectively, which could be separated from the mixture by fractional recrystallization. The photolysis of **2a** and **2b** in the presence of isobutene, 1,1-diphenylethylene, and 2,3-dimethyl-1,3-butadiene as silene trapping reagents proceeded with high stereospecificity to give the respective adducts arising from ene reaction of the rearranged silenes with olefins.

For the photochemical 1,3-silyl shift in aryldisilanes leading to rearranged silenes, two types of mechanistic interpretation have been reported so far. One is a concerted pathway recently proposed by Leigh and Sluggett,[2,8] while the other is a stepwise mechanism via radical intermediates suggested by Sakurai et al.[5] The results described here are wholly consistent with the concerted mechanism, but not the radical process. This is the first direct evidence for a concerted 1,3-silyl shift in aryldisilanes.

Experimental Section

General. All reactions were carried out under an atomosphere of purified argon. Yields of the products from the photolysis of **2a** and **2b** were determined by GLC based on the starting compounds photolyzed. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Brucker

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[17] (a) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (b) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

AMX 400 spectrometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer.

Materials. Hexane, THF, and benzene were dried over sodium−potassium alloy and distilled just before use.

Preparation of 1,2-Diethynyl-1,2-dimethyldiphenyldisilane (1a and 1b). A 1:1 mixture of **1a** and **1b** was obtained by the reaction of 1,2-dichloro-1,2-dimethyldiphenyldisilane with ethynylmagnesium bromide as reported in the literature.[18] The mixture was recrystallized from ethanol to give **1a** (>99% de) as colorless crystals. Removal of the crystals gave a 2:8 mixture of **1a** and **1b**. The mixture was treated with preparative GLC on a silicone SE-30 column to give **1b** with 80−90% de. For **1a**: mp 88−89 °C; MS *m*/*z* 290 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.53 (s, 6H), 2.66 (s, 2H), 7.33−7.66 (m, 10H); ^{13}C NMR (δ in $CDCl_3$) −4.3, 85.5, 97.9, 128.0, 129.5, 133.4, 134.4; ^{29}Si NMR (δ in $CDCl_3$) −38.68. For **1b**: MS *m*/*z* 290 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.58 (s, 6H), 2.68 (s, 2H), 7.25−7.52 (m, 10H); ^{13}C NMR (δ in $CDCl_3$) −4.4, 85.5, 97.7, 127.9, 129.5, 133.2, 134.4; ^{29}Si NMR (δ in $CDCl_3$) −38.64.

Preparation of *meso*-1,2-Diethyl-1,2-dimethyldiphenyldisilane (2a). In a 50-mL autocleave was placed 459.1 mg (1.580 mmol) of **1a**, 13.9 mg (0.018 mmol) of $IrCl(CO)(PPh_3)_2$, and 30 mL of benzene. Into the autocleave 150 atm of hydrogen gas was indroduced and the autocleave was heated at 100 °C for 12 h. After evaporation of the solvent, the resulting mixture was chromatographed on a silica gel column eluting with hexane to give 308.7 mg (65% yield) of **2a**: MS *m*/*z* 298 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.33 (s, 6H), 0.83−0.96 (m, 10H), 7.27−7.32 (m, 6H), 7.35−7.39 (m, 4H); ^{13}C NMR (δ in $CDCl_3$) −6.4, 5.4, 7.9, 127.7, 128.3, 134.2, 138.0; ^{29}Si NMR (δ in $CDCl_3$) −18.63. Anal. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78. Found: C, 72.32; H, 8.76 (as a 49:51 mixture with **2b**).

Compound **2b** was prepared by hygrogenation of **1b** in a similar maner to that for **2a** in 68% yield: For **2b**: MS *m*/*z* 298 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.33 (s, 6H), 0.83−0.96 (m, 10H), 7.27−7.32 (m, 6H), 7.35−7.39 (m, 4H); ^{13}C NMR (δ in $CDCl_3$) −6.3, 5.5, 7.9, 127.7, 128.3, 134.2, 138.0; ^{29}Si NMR (δ in $CDCl_3$) −18.63.

Photolysis of 2a in the Presence of Isobutene. In a 75-mL reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter was placed 0.263 g (0.881 mmol) of **2a**, 2.270 g (40.46 mmol) of isobutene, 18.4 mg (0.108 mmol) of dodecane as an internal standard, and 70 mL of hexane. The vessel was cooled at −78 °C and the mixture was irradiated for 1 h. At this stage, 95% of the starting compound **2a** was photolyzed. The resulting mixture was analyzed by GLC as being compound **3a** (77% yield) and ethylmethylphenylsilane (12% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. Compound **3a** (>99% de) was isolated by MPLC on a silica gel column eluting with hexane. For **3a**: MS *m*/*z* 354 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.10 (s, 3H, MeSi), 0.60 (s, 3H, MeSi), 0.61−0.70 (m, 4H, CH$_3$*CH*$_2$Si), 0.76 (t, 3H, *CH*$_3$CH$_2$Si, *J* = 6.6 Hz), 0.77 (d, 3H, *Me*$_2$CH, *J* = 6.6 Hz), 0.78 (d, 2H, *Me*$_2$CH, *J* = 6.9 Hz), 0.97 (t, 3H, *CH*$_3$CH$_2$Si, *J* = 6.9 Hz), 1.10 (br q, 2H, CH$_3$*CH*$_2$Si, *J* = 6.6 Hz), 1.61 (nonet, CH$_2$C*H*Me$_2$, *J* = 6.6 Hz), 7.28−7.36 (m, 5H, Ph), 7.39−7.42 (m, 2H, phenylene), 7.65−7.71 (m, 2H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −1.8, −1.7, 7.6, 7.7, 8.38, 8.43, 24.8, 26.1, 26.3 (2C), 127.3, 127.6, 127.8, 128.7, 134.5, 136.2, 136.8, 139.4, 142.5, 145.9; ^{29}Si NMR (δ in $CDCl_3$) −4.48, −0.15. Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.50; H, 9.66. Found: C, 74.45; H, 9.77 (as a 49:51 mixture with **3b**).

Preparation of Ethylmethylphenylsilane. To a solution of 13.4 mmol of ethylmagnesium bromide in 15 mL of THF was added dropwise 1.56 g (9.96 mmol) of chloromethylphenylsilane at room temperature. The resulting mixture was stirred for 15 h at room temperature and hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water. After evaporation of the solvent, the residue was distilled under atmospheric pressure and a fraction boiling in a range of 153−154 °C was collected (0.800 g, 53% yield): MS *m*/*z* 150 (M$^+$); IR $\nu_{\mathrm{Si-H}}$ 2114 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.35 (d, 3H, *J* = 3.8 Hz), 0.80−0.88 (m, 2H), 1.03 (t, 3H, *J* = 8.2 Hz), 4.34 (sept, 1H, *J* = 3.5 Hz), 7.36−7.41 (m, 3H), 7.55−7.57 (m, 2H); ^{13}C NMR (δ in $CDCl_3$) −6.18, 5.25, 7.90, 127.81, 129.16, 134.31, 136.50; ^{29}Si NMR (δ in $CDCl_3$) −11.40. Anal. Calcd for $C_9H_{14}Si$: C, 71.92; H, 9.39. Found: C, 71.63; H, 9.42.

Photolysis of 2b in the Presence of Isobutene. A mixture of 0.263 g (0.882 mmol) of **2b** (80% de), 2.27 g (40.47 mmol) of isobutene, 15.2 mg (0.0892 mmol) of dodecane as an internal standard, and 70 mL of hexane was irradiated internally with a low-presure mercury lamp at −78 °C for 3.5 h. At this stage, 97% of the starting compound **2b** was photolyzed. The resulting mixture was analyzed by GLC as being **3b** (73% yield) and ethylmethylphenylsilane (10% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. Compound **3b** (78% de) was isolated by MPLC on a silica gel column eluting with hexane. For **3b**: MS *m*/*z* 354 (M$^+$); ^{1}H NMR (δ in $CDCl_3$) 0.08 (s, 3H, MeSi), 0.60 (s, 3H, MeSi), 0.62 −0.69 (m, 4H, *CH*$_2$CH and CH$_3$*CH*$_2$Si), 0.75 (d, 3H, *Me*$_2$CH, *J* = 6.6 Hz), 0.78 (d, 3H, *Me*$_2$CH, *J* = 6.4 Hz), 0.79 (t, 3H, C*H*$_2$CH$_2$, *J* = 6.8 Hz), 0.97 (t, 3H, *CH*$_3$CH$_2$Si, *J* = 7.3 Hz), 1.61 (nonet, CH$_2$C*H*Me$_2$, *J* = 6.6 Hz), 7.26−7.35 (m, 5H, Ph), 7.39−7.41 (m, 2H, phenylene), 7.66−7.70 (m, 2H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −1.9, −1.8, 7.6, 7.7, 8.38, 8.40, 24.8, 26.0, 26.2, 26.3, 127.3, 127.6, 127.8, 128.7, 134.5, 136.1, 136.8, 139.4, 142.5, 145.9; ^{29}Si NMR (δ in $CDCl_3$) −4.48, −0.18.

Photolysis of 2a in the Presence of 1,1-Diphenylethylene. A mixture of 0.268 g (0.898 mmol) of **2a** (>99% de), 0.470 g (2.609 mmol) of 1,1-diphenylethylene, 15.6 mg (0.0916 mmol) of dodecane as an internal standard, and 70 mL of hexane was irradiated internally with a low-presure mercury lamp at −78 °C for 18 h. At this stage, 90% of the starting compound **2a** was photolyzed. The resulting mixture was analyzed by GLC as being compound **4a** (81% yield) and ethylmethylphenylsilane (9% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. Compound **4a** (>99% de) was isolated by preparative TLC on silica gel. For **4a**: MS *m*/*z* 449 (M$^+$ − Et); ^{1}H NMR (δ in $CDCl_3$) −0.17 (s, 3H), 0.38 (dq, 1H, *J* = 14.8, 7.2 Hz), 0.50 (dq, 1H, *J* = 14.9, 7.1 Hz), 0.55 (s, 3H), 0.64 (t, 2H, *J* = 7.3 Hz), 0.94 (t, 3H, *J* = 7.6 Hz), 1.05 (br q, 2H, *J* = 7.7 Hz), 1.37 (dd, 1H, *J* = 14.6, 7.7 Hz), 1.45 (dd, 1H, *J* = 14.7, 7.8 Hz), 3.88 (t, 1H, *J* = 7.6 Hz), 7.08−7.19 (m, 10H), 7.21−7.36 (m, 5H), 7.36−7.39 (m, 2H), 7.51 (dd, 1H, *J* = 5.6, 1.7 Hz), 7.71 (dd, 1H, *J* = 5.6, 1.7 Hz); ^{13}C NMR (δ in $CDCl_3$) −2.14, −1.81, 7.42, 7.60, 7.73, 8.43, 22.77, 47.24, 125.84, 127.24, 127.55, 127.67, 127.85, 127.94, 128.18, 128.52, 128.82, 129.08, 134.54, 136.42, 136.80, 139.14, 142.57, 144.87, 146.90, 146.97; ^{29}Si NMR (δ in $CDCl_3$) −4.52, 0.61. Anal. Calcd for $C_{32}H_{38}Si_2$: C, 80.27; H, 8.00. Found: C, 80.09; H, 8.04 (as a 1:1 mixture with **4b**).

Photolysis of 2b in the Presence of 1,1-Diphenylethylene. A mixture of 0.210 g (0.706 mmol) of **2b** (80% de), 0.684 g (3.79 mmol) of 1,1-diphenylethylene, 14.3 mg (0.084 mmol) of dodecane as an internal standard, and 70 mL of hexane was irradiated internally with a low-presure mercury lamp at −78 °C for 30 h. At this stage, 93% of the starting compound **2b** was photolyzed. The resulting mixture was analyzed by GLC as being compound **4b** (85% yield) and ethylmethylphenylsilane (9% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. Compound **4b** (78% de) was isolated by prepatative TLC on silica gel. Diastereomeric pure **4b** was obtained by recrystallization from ethanol as colorless crystals. For **4b**: mp 89 °C; MS *m*/*z* 449 (M$^+$ − Et); ^{1}H NMR (δ in $CDCl_3$) −0.19 (s, 3H), 0.37 (dq, 1H, *J* = 14.8, 7.6 Hz), 0.52 (dq, 1H, *J* = 14.8, 7.6 Hz), 0.55 (s, 3H), 0.66 (t, 2H, *J* = 7.7 Hz), 0.94 (t, 3H, *J* = 7.7 Hz), 1.06 (br q, 2H, *J* = 6.0 Hz), 1.42 (d, 2H, *J* = 7.8 Hz), 3.90 (t, 1H, *J* = 7.4 Hz), 7.07−7.19 (m, 10H), 7.21−7.34 (m, 5H), 7.36−7.39 (m, 2H), 7.51 (dd, 1H, *J* = 7.1, 1.3 Hz), 7.71 (dd, 1H, *J* = 6.2, 1.3 Hz); ^{13}C NMR (δ in $CDCl_3$) −2.29, −1.85, 7.45, 7.64, 7.69, 8.39, 22.80, 47.22, 125.80, 125.84, 127.47, 127.51, 127.54, 127.65, 127.83, 128.13, 128.19, 128.79, 134.50, 136.37, 136.77, 139.17, 142.51, 144.86, 146.88, 146.94; ^{29}Si NMR (δ in $CDCl_3$) −4.54, 0.56.

Photolysis of 2a in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.152 g (0.574 mmol) of **2a** (>99% de), 0.382 g (4.65 mmol) of 2,3-dimethylbutadiene, 14.9 mg (0.086 mmol) of dodecane as an internal standard, and 70 mL of hexane was irradiated internally with a low-presure mercury lamp at −78 °C for 4 h. At this stage, 91% of the starting compound **2a** was photolyzed. The resulting mixture was

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[18] Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R.-F.; Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134.

analyzed by GLC as being **5a** and **5a′** (73% combined yield) and ethylmethylphenylsilane (14% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. After evaporation of the solvent and excess 1,3-dimethylbutadiene, the resulting mixture was treated with gel permeation chromatography eluting with chloroform to give a 53:47 mixture of **5a** and **5a′**. Products **5a** and **5a′** cannot be isolated and analyzed as the mixture: MS m/z 380 (M^+); ^{1}H NMR (δ in CDCl$_3$) 0.10 (s, 1.59H), 0.12 (s, 1.41H), 0.60 (s, 3H, MeSi), 0.61−0.71 (m, 2H), 0.72 (t, 3H, J = 9.5 Hz), 0.84 (d, 2H, J = 6.7 Hz), 0.85 (d, 3H, J = 6.8 Hz), 0.97 (t, 3H, J = 7.5 Hz), 1.09 (q, 2H, J = 7.3 Hz), 1.55 (s, 1.59H), 1.56 (s, 1.41H), 2.21 (sextet, 1H, J = 6.9 Hz), 4.52 (br s, 1H), 4.55 (s, br s, 0.47H), 4.57 (s, br s, 0.53H), 7.28−7.37 (m, 5H), 7.40 (br d, 2H, J = 6.7 Hz), 7.60−7.70 (m, 2H); ^{13}C NMR (δ in CDCl$_3$) for **5a** −1.89, −1.79, 7.56, 7.73 (overlapping with signals of **5a′**), 7.99, 8.45, 18.59, 22.30, 22.81, 37.32, 108.11, 127.41, 127.61, 127.81, 128.75, 134.51, 136.29, 136.80, 136.82, 139.29, 142.54, 145.48, 145.65, 152.44, 152.52 (overlapping with those of **5a′**); ^{13}C NMR (δ in CDCl$_3$) for **5a′** −2.12, −1.81, 8.03, 8.40, 18.54, 22.24, 22.74, 37.37, 108.16, 142.49, other signals are overlapped by those of **5a**; ^{29}Si NMR (δ in CDCl$_3$) −4.45, 0.44 (overlapping). Anal. Calcd for $C_{24}H_{36}Si_2$: C, 75.72; H, 9.53. Found: C, 75.69; H, 9.52 (as a 30:23:25:21 mixture of **5a**, **5a′**, **5b**, and **5b′**).

Photolysis of 2b in the Presence of 2,3-Dimethylbutadiene. A mixture of 0.325 g (1.09 mmol) of **2b** (90% de), 0.218 g (2.66 mmol) of 2,3-dimethylbutadiene, 26.4 mg (0.155 mmol) of dodecane as an internal standard, and 70 mL of hexane was irradiated internally with a low-presure mercury lamp at −78 °C for 3 h. At this stage, 93% of the starting compound **2b** was photolyzed. GLC analysis of the mixture showed the formation of a mixture of isomers **5a**, **5a′**, **5b**, and **5b′** (77% combined yield) and ethylmethylphenylsilane (14% yield). GLC retention time and the mass spectrum for ethylmethylphenylsilane were identical with those of the authentic sample. After evaporation of the solvent and excess 1,3-dimethylbutadiene, the resulting mixture was treated with gel permeation chromatography eluting with chloroform to give a mixture of **5a**, **5a′**, **5b**, and **5b′** in a ratio of 4:2:57:37. Products **5a**, **5a′**, **5b**, and **5b′** cannot be isolated and analyzed as the mixture. For **5b** and **5b′**: MS m/z 380 (M^+); ^{1}H NMR (δ in CDCl$_3$) 0.07 (s, 1.19H), 0.09 (s, 1.81H), 0.60 (s, 3H), 0.67 (dq, 1H, J = 6.8, 3.5 Hz), 0.70 (dq, 1H, J = 6.4, 3.5 Hz), 0.77 (t, 3H, J = 6.4 Hz), 0.82 (d, 3H, J = 6.9 Hz), 0.87 (d, 2H, J = 6.8 Hz), 0.97 (t, 3H, J = 7.4 Hz), 1.09 (q, 2H, J = 7.4 Hz), 1.55 (s, 3H), 2.21 (sextet, 1H, J = 6.9 Hz), 4.52 (br s, 1H), 4.55 (br s, 0.61H), 4.57 (br s, 0.39H), 7.26−7.37 (m, 5H), 7.41 (br d, 2H, J = 6.3 Hz), 7.66−7.70 (m, 2H); ^{13}C NMR (δ in CDCl$_3$) for **5b** −2.17, −1.83, 7.62, 7.74 (overlapping with a signal of **5b′**), 8.13, 8.44, 18.50, 22.22, 22.80 (overlapping with a signal of **5b′**), 37.45, 108.22, 127.41, 127.62, 127.82, 128.77, 134.52, 136.25, 136.82, 136.85 (overlapping with those of **5b′**), 139.33, 142.46, 145.67, 152.39; ^{13}C NMR (δ in CDCl$_3$) for **5b′** −1.93, −1.74, 8.03, 8.37, 18.65, 22.40, 37.33, 108.12, 139.39, 142.53, 145.52, 152.51, other signals are overlapped by those of **5b**; ^{29}Si NMR (δ in CDCl$_3$) −4.45, 0.40 (**5b**), −4.42, 0.36 (**5b′**).

Acknowledgment. We thank Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Asia Ltd., Toshiba Silicone Co. Ltd., Kaneka corporation, and Sumitomo Electric Industry for financial support. We also thank Dr. Yoshio Aso for assistance in the single-crystal X-ray analysis for compounds **1a** and **4b**.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic thermal parameters and anisotropic thermal parameters for **1a** and **4b** (5 pages). See any current masthead page for ordering and Internet access instructions.

JA960458U