4632 *Organometallics* **1996,** *15,* 4632−4638

Silicon−Carbon Unsaturated Compounds. 59. Stereochemistry in Addition of Carbonyl Compounds to Silenes Generated Photochemically from *meso*- and *rac*-1,2-Diethyl-1,2-dimethyldiphenyldisilane

Joji Ohshita,* Hiroyuki Niwa, and Mitsuo Ishikawa*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan

Received April 2, 1996[⊗]

Stereochemistry in ene-type addition of silenes produced photochemically from *meso*- and *rac*-1,2-diethyl-1,2-dimethyldiphenyldisilane (**1a**,**b**) to carbonyl compounds was investigated. When the *meso*-isomer **1a** was irradiated in the presence of acetone in hexane at −78 °C, a diastereomeric mixture of an adduct, 2-(ethylmethylphenylsilyl)[ethylmethyl(2-propoxy)silyl]-benzene (**3a**,**b**), in a ratio of **3a**/**3b** = 93/7 was obtained in 64% yield. Similar photolysis of a mixture consisting of **1a**/**1b** = 4/96 gave the adduct composed of **3a**/**3b** = 10/90 in 63% yield. The photolysis of **1a** with benzophenone proceeded diastereospecifically to afford an adduct, (*R*,*R*)- and (*S*,*S*)-[ethylmethyl(diphenylmethoxy)silyl]-2-(ethylmethylphenylsilyl)-benzene, in 83% yield. Irradiation of the disilane (**1a**/**1b** = 10/90) with benzophenone, under the same conditions, produced the adducts consisting of the (*R*,*R*)- and (*S*,*S*)-isomers and (*R*,*S*)- and (*S*,*R*)-isomers in a ratio of 12/88 in 86% yield. Similar photolysis of **1a** and a mixture of **1a**/**1b** = 6/94 in the presence of acetaldehyde proceeded also with high diastereoselectivity to afford the corresponding adduct with diastereomeric ratios of 96/4 and 9/91, respectively. Solvent effects on stereochemistry in the reaction of the silenes with acetone were investigated, and it was found that electron-donating solvents THF and acetonitrile led to decrease of diastereoselectivity of the reactions, while ether and toluene showed no influence for the stereochemistry. The (*R*,*S*)- and (*S*,*R*)-isomers of the adduct obtained from the photolysis of the disilane in the presence of benzophenone have been characterized by X-ray crystallography.

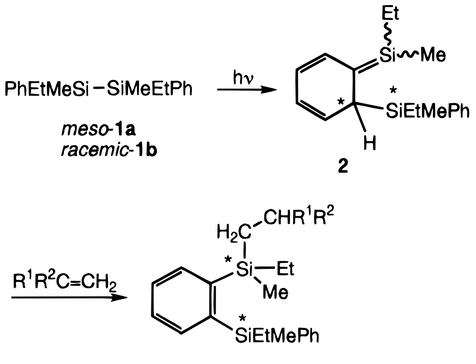
Introduction

Silenes are highly reactive unsaturated organosilicon compounds which react with a variety of reagents to give addition products.[1] The stereochemistry and the reaction mechanism for alcohol addition to silenes have been well studied, and the stepwise mechanism involving the formation of alcohol−silene complexes followed by intracomplex or intercomplex proton transfer has been proposed (Scheme 1[2]).

Besides alcohols, carbonyl compounds are often employed as efficient silene-trapping agents, and the reactions of silenes with aldehydes and ketones have been extensively investigated. In general, silenes react with carbonyl compounds in two ways.[1] If the carbonyl compounds have an enolizable proton, ene-type reactions involving proton transfer from the carbonyl compounds to the silenes giving silyl enol ethers take place mainly. With nonenolizable carbonyl compounds, silenes give formal [2 + 2] cycloadducts.

We have found that the photolysis of aryldisilanes produces the rearranged silenes arising from a 1,3-silyl shift of a terminal silyl group to the ortho position of the aryl ring,[3−6] and the silenes thus formed react with enolizable and nonenolizable carbonyl compounds to give ene adducts.[5] Recently, Leigh and his co-workers have reported the detailed mechanistic studies for the reaction of the silenes with carbonyl compounds. They proposed the concerted mechanism for the reactions of 1,1-diphenylsilene generated photochemically from 1,1-diphenylsilacyclobutane with carbonyl compounds on the basis of kinetic studies using flash-laser photolysis.[7] For the reactions of the rearranged silenes with carbonyl

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 17.

(2) (a) Wiberg, N. *J. Organomet. Chem.* **1984**, *237*, 141. (b) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986.

(3) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1985**, 5923.

(4) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1986**, *118*, 155.

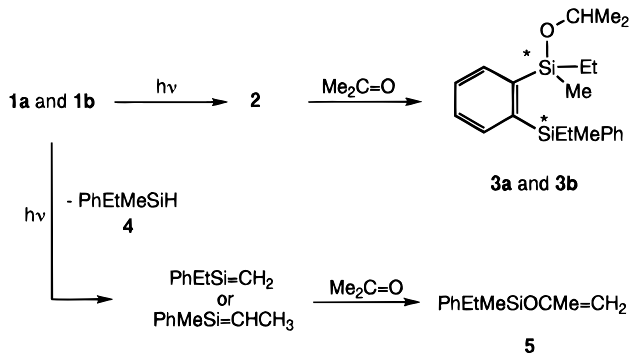
(5) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1987**, *133*, 19.

(6) Ishikawa, M.; Kumada, M. *Adv. Orgenomet. Chem.* **1981**, *19*, 51.

(7) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332.

S0276-7333(96)00259-2 CCC: $12.00

Scheme 2



compounds, however, a stepwise mechanism involving the initial formation of a biradical intermediate has been reported.[8,9]

Recently, we have demonstrated that the photolysis of *meso*- and *rac*-1,2-diethyl-1,2-dimethyldiphenyldisilane (**1a**,**b**) in the presence of olefins affords the corresponding adducts with high diastereospicifity, indicating that the formation of the respective rearranged silenes **2a**,**b** and addition of the resulting silenes **2a**,**b** to olefins proceed diastereospecifically to give ene adducts with concerted processes (Scheme 1).[10] In order to obtain direct information on the reaction mechanism for addition of the rearranged silenes to carbonyl compounds, we investigated the stereochemistry of the addition reactions of the silenes **2a**,**b** to acetone, benzophenone, and acetaldehyde. If addition of carbonyl compounds proceeds under some stereochemical control, the total reactions for the diastereospecific formation of **2** and addition of the resulting **2** to carbonyl compounds must be diastereoselective. We also studied solvent effects on the stereochemistry in the photolysis of **1a** in the presence of acetone.

Results and Discussion

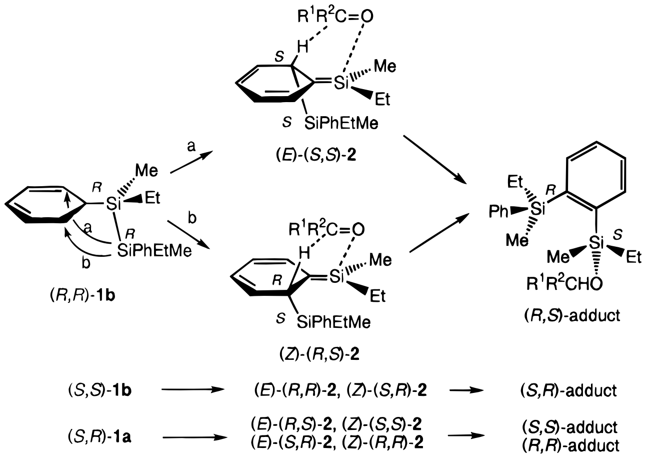
Photolysis of 1a,b with Acetone. First, we carried out the photolysis of a 1:1 mixture of *meso*- and *rac*-1,2-diethyl-1,2-dimethyldiphenyldisilane (**1a**,**b**) in the presence of acetone. Thus, when a hexane solution of a 1:1 mixture of **1a**,**b** in the presence of a 25-fold excess of acetone was irradiated with a low-pressure mercury lamp bearing a Vycor filter at −78 °C for 6 h, 2-(ethylmethylphenylsilyl)[ethylmethyl(2-propoxy)silyl]benzene (**3a**,**b**) was obtained in 70% yield. In this reaction, ethylmethylphenylsilane (**4**) and ethylmethylphenyl(2-propenoxy)silane (**5**) were also obtained in 14% and 10% yields, in addition to a 7% yield of the unreacted starting disilane as shown in Scheme 2 (see also Table 1, run 1). Although GLC and HPLC analyses of the adduct using a variety of columns always show a homogeneous peak, its ^{1}H, ^{13}C, and ^{29}Si NMR spectra reveal the presence of two diastereomers **3a**,**b** in a ratio of 1:1. Products **4** and **5** were probably derived from homolytic scission of an Si−Si bond, followed by proton abstraction by the resulting silyl radical or a concerted 1,2-proton shift from the singlet excited state of the disilane, as proposed by Leigh et al.[8]

Table 1. Photolysis of 1a,b in the Presence of Acetone

			product yield, %[a]		
run	disilane	solvent	adduct (**3a**/**3b**)	**4**	**5**
1	**1a**/**1b** = 50/50	hexane	70 (50/50)	14	10
2	**1a**	hexane	64 (93/7)	14	14
3[b]	**1a**	hexane	41 (90/10)	17	18
4	**1a**/**1b** = 4/96	hexane	63 (10/90)	14	15
5[c]	**1a**	toluene	39 (93/7)	4	3
6[d]	**1a**	toluene	60 (91/9)	7	8
7	**1a**	Et_2O	59 (91/9)	12	10
8	**1a**	THF	28 (80/20)	11	7
9[e]	**1a**	CH_3CN	58 (78/22)	3	19
10	**1a**	acetone/hexane = 1/1	52 (93/7)	10	13

[a] Determined by GLC, based on the starting disilane consumed. [b] At 68 °C. [c] *p*-, *m*-, and *o*-tolylethylmethylphenylsilanes were obtained in 14%, 8%, and 6% yields, respectively. [d] In the presence of piperylene. [e] At −43 °C.

Scheme 3



The photolysis of diastereomerically pure *meso*-isomer **1a** under the same conditions gave a mixture of **3a**,**b** in a ratio of **3a**/**3b** = 93/7 in 64% yield, together with **4**, **5**, and the unreacted starting disilane in 14%, 14%, and 1% yields, respectively, as shown in Table 1 (run 2). The diastereomeric ratio of the adduct was calculated on the basis of the integral ratio of MeSi signals at 0.28 ppm for **3a** and 0.25 ppm for **3b** in the ^{1}H NMR spectrum. Irradiation of **1a** at 68 °C afforded almost the same yields of the products, but the diastereomeric ratio of the adduct was determined to be **3a**/**3b** = 90/10, which was slightly less stereoselective than that at −78 °C (Table 1, run 3). Similarly, the photolysis of a mixture **1a**/**1b** = 4/96 with acetone proceeded diastereoselectively to afford an adduct **3a**/**3b** = 10/90 in 63% yield (Table 1, run 4).

As demonstrated previously, disilanes **1a**,**b** rearrange via a concerted suprafacial 1,3-silyl shift under the photochemical conditions to produce the respective silenes diastereospecifically.[10] Thus, **1b** gives silenes (*E*)-(*S*,*S*)-, (*Z*)-(*R*,*S*)-, (*E*)-(*R*,*R*)-, and (*Z*)-(*S*,*R*)-**2**, while **1a** affords (*E*)-(*R*,*S*)-, (*Z*)-(*S*,*S*)-, (*E*)-(*S*,*R*)-, and (*Z*)-(*R*,*R*)-**2**, as shown in Scheme 3. If the addition of acetone to the silenes proceeds with an ene-type concerted mechanism via a six-membered ring transition state, acetone must add to the silene from the opposite side of an ethylmethylphenylsilyl group with respect to the dihydrobenzene ring. Consequently, (*R*,*R*)- and (*S*,*S*)-isomers from **1a** and (*R*,*S*)- and (*S*,*R*)-isomers from **1b** would be produced with diastereospecificity, as observed for addition of olefins to silenes **2a**,**b** (Scheme 3).[10]

---

[8] (a) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269. (b) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 1005. (c) Toltl, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554.

[9] Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1994**, *116*, 10468.

[10] Ohshita, J.; Niwa, H.; Ishikawa, M.; Yamabe, T.; Yoshii, T.; Nakamura, K. *J. Am. Chem. Soc.* **1996**, *118*, 6853.

Scheme 4

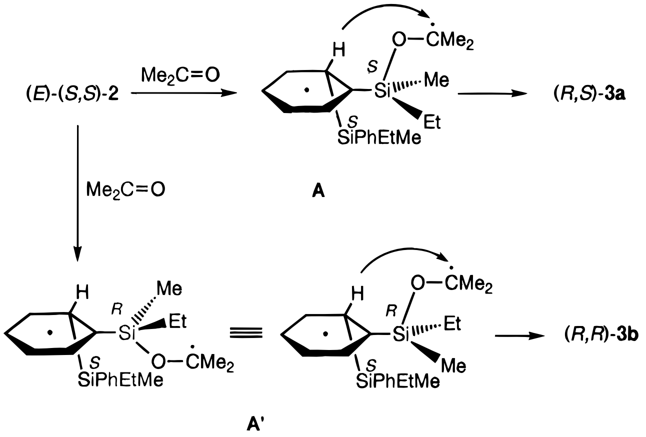
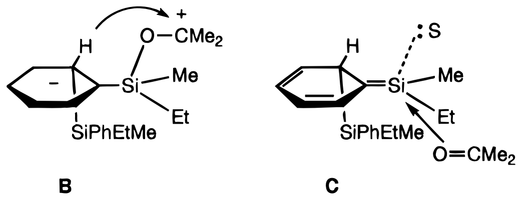


Chart 1



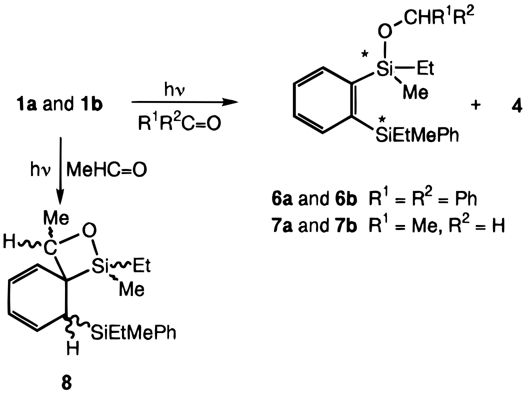
The photolysis of **1a**,**b** in the presence of acetone proceeded with high diastereoselectivity but not with diastereospecificity. A slight decrease of diastereomeric ratios in the ene adducts relative to those in the starting disilane was observed, in contrast to the reactions of silenes **2a**,**b** with olefins.[10] These results suggest that a stepwise process is involved in the reaction of the silenes with acetone. Scheme 4 illustrates mechanistic interpretation for the stepwise process, using silene (*E*)-(*S*,*S*)-**2** as an example, which involves biradical intermediates **A** and **A′**. As can be seen in Scheme 4, the formation of an intermediate **A** which gives the same adduct as that obtained from the concerted ene reaction seems to be more favorable than that of **A′**, due to steric hindrance.

In order to learn more about the mechanism for addition of acetone to the rearranged silene **2**, we investigated the solvent effects on the diastereoselectivities of the reactions. As shown in Table 1 (runs 5 and 7), the photolysis of **1a** and acetone in toluene and ether resulted in the formation of **3a**/**3b** with almost the same diastereomeric ratios as that obtained from the photolysis in hexane, indicating that a zwitter ionic intermediate **B** (Chart 1) plays little role in these addition reactions, compatible to the results reported by Leigh and Sluggett.[8]

In the photolysis of **1a** in a toluene solution, *p*-, *m*-, and *o*-tolylethylmethylphenylsilanes were also obtained in 14%, 8%, and 6% yields, respectively. These tolylsilanes may be derived from the reactions of the ethylmethylphenylsilyl radical with toluene. It seems likely that energy transfer from toluene in the triplet excited state to the disilane, leading to disilane triplets which cleave to give the silyl radicals, is involved in this reaction. In fact, when a similar reaction was carried out in the presence of piperylene as a triplet quenching agent, the formation of ethylmethylphenyltolylsilanes was completely suppressed (Table 1, run 6).

Interestingly, the photolysis of **1a** in the electron-donating solvents, acetonitrile and THF, gave the adducts with diastereomeric ratios of **3a**/**3b** = 10/80 and 22/78, respectively, lower diastereoselectivity than that in hexane, ether, and toluene (Table 1, runs 8 and 9). The low yield of the adduct in the photolysis in a THF solution may be ascribed to the formation of many products in less than 5% yields. Mass spectra of some of the byproducts reveal their parent ion at *m*/*z* 370, corresponding to the 1:1 adduct of **2** and THF. In the photolysis of **1a** in the electron-donating solvents, the solvent molecule would coordinate to the resulting silenes from the less hindered side and prevent the approach of acetone from this side. Consequently the coordinated solvent molecule facilitates the addition of acetone from the more hindered side (**C**). That the THF molecule coordinates to the rearranged silene produced by the photolysis of the aryldisilane has been previously reported by Leigh and Sluggett.[8a]

Scheme 5



Recently, Kira et al. have reported that the concentration of alcohol used as a trapping agent significantly affects the stereochemistry in the reaction with a cyclic silene.[2b] In our case, however, no such influence was observed in the present system (Table 1, run 10).

For the formation of compounds **4** and **5**, it might be considered that energy transfer from acetone in the triplet excited state to the disilane, producing disilane triplets, is involved in this reaction. Disilane triplets, thus formed, may undergo homolysis of the Si−Si bond to give silyl radicals. The concentration of acetone, however, did not exert unambiguous effects on the product distributions (Table 1, runs 2 and 10). Moreover, when we carried out the photolysis of **1a** in the absence of acetone under the same conditions, compound **4** was obtained as the sole volatile product in 15% yield, which was almost the same yield as that in the presence of acetone. These facts clearly indicate that the triplet energy transfer from acetone to the disilane plays little role in the formation of the ethylmethylphenylsilyl radical, even if it is involved.

Photolysis with Benzophenone and Acetaldehyde. The photolysis of **1a**,**b** also proceeded with high diastereoselectivity in the presence of benzophenone and acetaldehyde to give the corresponding adducts, as shown in Scheme 5 and in Table 2. Especially with benzophenone, the reactions proceed with diastereospecificity to give the adducts with diastereomeric ratios almost identical with those of the starting disilanes. Thus, when diastereomerically pure **1a** was irradiated in the presence of benzophenone in hexane at −78 °C for 10 h, (*R*,*R*)- and (*S*,*S*)-[ethylmethyl(diphenylmethoxy)silyl]-2-(ethylmethylphenylsilyl)benzene (**6a**) was ob-

Table 2. Photolysis of 1a,b in the Presence of Benzophenone and Acetaldehyde

run	disilane	carbonyl compd	product yield, %[a]	
			adduct	**4**
1	**1a**	Ph_2CO	83 (**6a**)	13
2	**1a**/**1b** = 10/90	Ph_2CO	83 (**6a**/**6b** = 12/88)	12
3[b]	**1a**	Ph_2CO	56 (**6a**)	25
4	**1a**	MeCHO	29 (**7a**/**7b** = 96/4)	11
5	**1a**/**1b** = 6/94	MeCHO	34 (**7a**/**7b** = 9/91)	11

[a] Determined by GLC on the basis of the starting disilane consumed. [b] At 68 °C.

tained in 83% yield as a single diastereomer, in addition to a 13% yield of **4**. The structure of **6a** was verified by spectrometric and elemental analysis (see Experimental Section). Diastereomeric purity of **6a** was determined by ^{1}H and ^{13}C NMR spectrometry, and no signals due to the other diastereomer (**6b**) were observed in these spectra. In contrast to the photolysis of **1a** with acetone, the stereochemistry in the reaction with benzophenone was not influenced by the reaction temperature. Thus, the photolysis of **1a** in the presence of benzophenone at 68 °C again afforded **6a** as the single isomer. Similar photolysis of a mixture of **1a**/**1b** = 10/90 with benzophenone gave adduct **6a**/**6b** = 12/88 in 83% yield, together with a 12% yield of **4**. The structure of compound **6b** was determined by spectrometric and elemental analysis, and X-ray crystallographic analysis shows that compound **6b** consists of (*R*,*S*)- and (*S*,*R*)-isomers, in accord with the proposed reaction mechanism shown in Scheme 3 (see below).

The photolysis of **1a**,**b** in the presence of acetaldehyde proceeded again with high diastereoselectivity to give the respective adduct (ethoxyethylmethylsilyl)-2-(ethylmethylphenylsilyl)benzene (**7a**,**b**) in 29% and 34% yields, as shown in Table 2 (runs 3 and 4). The lower yields of **7a**,**b** than those of **3a**,**b** and **6a**,**b** may be ascribed to the formation of byproducts. In fact, when a solution of **1a** and acetaldehyde in benzene-d_6 was irradiated in an NMR tube at −78 °C for 7 h and the resulting mixture was directly analyzed by ^{1}H NMR spectroscopy, multiplet signals at 4−6 ppm, presumably attributed to dihydrobenzene ring protons of siloxetane **8**, were observed in addition to the signals due to compounds **7a**/**7b**, **4**, and **1a** (Scheme 5). These signals, however, disappeared and were converted into unsolved broad signals upon standing the mixture overnight in air at room temperature. The formation of the siloxetane in the photolysis of mono-, di-, and triphenyldisilane with acetone has been reported by Leigh and Sluggett.[8] When acetone and benzophenone were used as the silene trapping agents, siloxetanes analogous to **8** could not be detected in the present system.

High diastereoselectivities in the reactions of silene **2** with benzophenone, which has a higher steric requirement as compared with acetone and acetaldehyde, is in good agreement with the stepwise mechanism. Whether or not the concerted mechanism competes the stepwise mechanism in the present reactions is still unclear. However, high diastereoselectivity of the reactions even during photolysis in the presence of acetaldehyde, which seems to possess no significant steric demand, indicates that the concerted mechanism, which involves addition of carbonyl compound to the silene from the opposite side of an ethylmethylphenylsilyl group with respect to the silylenedihydrobenzene ring, might be operative to some extent.

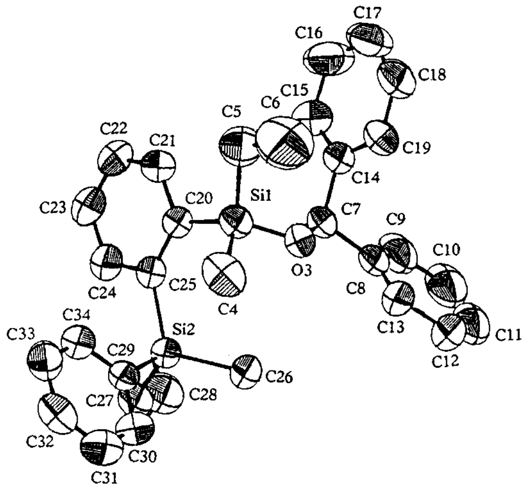


Figure 1. ORTEP drawing of **6b** with the atomic numbering scheme.

Table 3. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 6b

mol formula	$C_{31}H_{36}OSi_2$
mol wt	480.80
space group	$P\bar{1}$
cell dimens	
a, Å	16.94(2)
b, Å	17.27(2)
c, Å	9.644(2)
α, deg	96.63(6)
β, deg	92.10(6)
γ, deg	148.7(3)
V, Å^3	1405(3)
D_{calcd}, Mg/m^3	1.137
Z	2
cryst size, mm^3	0.5 × 0.4 × 0.3
cryst color	colorless
μ, mm^{-1}	1.19
diffractometer	Rigaku AFC-6C
temp, K	298
wavelength, Å	1.5418 (Cu Kα)
monochrometer	graphite crystal
scan type	$\omega-2\theta$
scan speed, deg/min	4
scan width, deg	$0 < 2\theta < 126$
diffraction geometry	symmetrical A
range of *h*,*k*,*l*	
h	$-20 \leq h \leq 20$
k	$-20 \leq k \leq 20$
l	$0 \leq l \leq 11$
no. of unique reflns	4520
no. of obsd reflns ($\lvert F_o\rvert \geq 3\sigma(F_o)$)	3846
R	0.054
R_w[a]	0.056

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

Crystal Structure of Compound 6b. Figure 1 shows an ORTEP view of compound **6b**. Cell dimensions, data collection and refinement parameters, and bond lengths and angles for **6b** are collected in Tables 3 and 4. Atomic coordinates and equivalent isotropic thermal parameters for **6b** are found in the Supporting Information. Compound **6b** has an *ortho*-phenylene ring system substituted by two silyl groups. The C20−C25 bond length (1.425(9) Å) is significantly longer than the remaining C−C bonds in the *ortho*-phenylene ring (1.388 Å (average)), presumably due to the steric repulsion between two bulky silyl groups. The larger Si1−C20−C25 (127.8(2)°) and Si2−C25−C20 (128.2(3)°) angles compared to the Si1−C20−C21 (115.5(5)°) and

Table 4. Bond Lengths (Å) and Angles (deg) for 6b with Their Esd's in Parentheses

Bond Lengths

Si1−O3	1.651(1)	Si1−C4	1.847(4)	Si1−C5	1.86(1)
Si1−C20	1.887(5)	Si2−C25	1.894(4)	Si2−C26	1.875(4)
Si2−C27	1.884(9)	Si2−C29	1.874(2)	O3−C7	1.420(3)
C5−C6	1.56(2)	C7−C8	1.511(4)	C7−C14	1.514(8)
C8−C9	1.401(5)	C8−C13	1.364(5)	C9−C10	1.384(8)
C10−C11	1.34(1)	C11−C12	1.35(1)	C12−C13	1.399(7)
C14−C15	1.376(5)	C14−C19	1.38(1)	C15−C16	1.40(1)
C16−C17	1.35(2)	C17−C18	1.366(9)	C18−C19	1.40(1)
C20−C21	1.406(5)	C20−C25	1.425(9)	C21−C22	1.376(9)
C22−C23	1.37(1)	C23−C24	1.383(6)	C24−C25	1.406(7)
C27−C28	1.518(5)	C29−C30	1.390(5)	C29−C34	1.380(4)
C30−C31	1.376(4)	C31−C32	1.359(6)	C32−C33	1.369(6)
C33−C34	1.388(3)				

Bond Angles

O3−Si1−C4	104.3(2)	O3−Si1−C5	110.6(2)
O3−Si1−C20	110.1(2)	C4−Si1−C5	107.7(3)
C4−Si1−C20	114.6(3)	C5−Si1−C20	109.4(3)
C25−Si2−C26	114.0(3)	C25−Si2−C27	110.7(2)
C25−Si2−C29	108.8(2)	C26−Si2−C27	106.3(3)
C26−Si2−C29	111.9(2)	C27−Si2−C29	104.8(2)
Si1−O3−C7	126.1(2)	Si1−C5−C6	113.4(6)
O3−C7−C8	109.3(2)	O3−C7−C14	111.3(4)
C8−C7−C14	110.8(4)	C7−C8−C9	117.8(3)
C7−C8−C13	122.7(3)	C9−C8−C13	119.4(3)
C8−C9−C10	119.2(5)	C9−C10−C11	120.9(6)
C10−C11−C12	120.4(6)	C11−C12−C13	120.8(5)
C8−C13−C12	119.3(5)	C7−C14−C15	120.4(6)
C7−C14−C19	120.0(4)	C15−C14−C19	119.6(6)
C14−C15−C16	119.5(8)	C15−C16−C17	120.7(6)
C16−C17−C18	121(1)	C17−C18−C19	120(1)
C14−C19−C18	119.7(5)	Si1−C20−C21	115.5(5)
Si1−C20−C25	127.8(2)	C21−C20−C25	116.7(5)
C20−C21−C22	123.6(8)	C21−C22−C23	119.5(5)
C22−C23−C24	119.2(6)	C23−C24−C25	122.8(7)
Si2−C25−C20	128.2(3)	Si2−C25−C24	113.6(5)
C20−C25−C24	118.2(4)	Si2−C27−C28	117.8(5)
Si2−C29−C30	121.4(2)	Si2−C29−C34	121.9(2)
C30−C29−C34	116.5(2)	C29−C30−C31	121.7(3)
C30−C31−C32	120.3(4)	C31−C32−C33	120.2(3)
C32−C33−C34	119.2(3)	C29−C34−C33	122.1(3)

Si2−C25−C24 (113.6(5)°) angles would also result from the steric repulsion of the silyl groups. There are no unusual bond lengths and angles in the ethylmethylphenylsilyl and ethylmethyl(diphenylmethoxy)silyl fragments.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of purified argon. NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer. Exact mass spectra were measured on a Hitachi M-80B spectrometer.

Materials. Hexane, ether, toluene, and THF were dried over sodium−potassium alloy and distilled just before use. Acetonitrile and acetone were distilled from P_2O_5 or CaH_2 just before use. Compounds **1a**,**b** were prepared as reported in the literature.[10]

Photolysis of 1a in the Presence of Acetone. A mixture of 0.345 g (1.15 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of hexane was placed in a reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter. The mixture was cooled down to −78 °C and irradiated for 6 h. After evaporation of the solvent, the residue was analyzed by GLC, using 15 mg (0.067 mmol) of pentadecane as an internal standard, as consisting of **3a**/**3b** (64% yield), **4** (14%), and **5** (14%), in addition to 1% of **1a**. Product **3a**/**3b** and compounds **4** and **5** were separated from the mixture by preparative GLC. The diastereomeric ratio of product **3a**/**3b** was determined to be 93/7 by ^{1}H NMR spectrometry. All spectral data obtained for **4** are identical with those reported in the literature.[10] All spectra data obtained for **5** are identical with those of an authentic sample. Data for **3a**: MS *m/z* 356 (M$^+$); IR ν_{Si-O} 1016 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.28 (s, 3H, MeSi), 0.64 (s, 3H, MeSi), 0.65−0.79 (m, 2H, CH$_3$*CH$_2$Si*), 0.83 (t, 3H, *CH$_3$*CH$_2$Si, *J* = 7.7 Hz), 0.97 (t, 3H, *CH$_3$*CH$_2$Si, *J* = 7.8 Hz), 1.03 (d, 3H, *Me$_2$*CH, *J* = 6.6 Hz), 1.06 (d, 3H, *Me$_2$*CH, *J* = 6.6 Hz), 1.10 (dq, 1H, CH$_3$*CH$_2$*Si, *J* = 8.0, 15.1 Hz), 1.25 (dq, 1H, CH$_3$*CH$_2$*Si, *J* = 7.9, 14.9 Hz), 3.99 (septet, 1H, Me$_2$*CH*, *J* = 6.6 Hz), 7.27−7.37 (m, 5H, Ph), 7.44−7.47 (m, 2H, phenylene), 7.56 (dd, 1H, phenylene, *J* = 7.6, 1.2 Hz), 7.66 (dd, 1H, phenylene, *J* = 7.6, 1.2 Hz); ^{13}C NMR (δ in CDCl$_3$) −2.3, −1.3, 7.2, 7.7, 7.8, 9.0, 25.43, 25.44, 65.5, 127.5, 127.7, 127.9, 128.4, 134.7, 135.2, 136.9, 139.8, 143.0, 144.8; ^{29}Si NMR (δ in CDCl$_3$) −3.22, 6.08. Anal. Calcd for $C_{21}H_{32}Si_2O$: C, 70.72; H, 9.04. Found: C, 70.65; H, 8.98 (as a 1:1 mixture with **3b**). Data for **3b**: MS *m/z* 356 (M$^+$); IR ν_{Si-O} 1016 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.25 (s, 3H, MeSi), 0.64 (s, 3H, MeSi), 0.67−0.75 (m, 2H, CH$_3$*CH$_2$*Si), 0.86 (t, 3H, *CH$_3$*CH$_2$Si, *J* = 7.5 Hz), 0.96 (t, 3H, *CH$_3$*CH$_2$Si, *J* = 7.7 Hz), 0.98 (d, 3H, *Me$_2$*CH, *J* = 6.0 Hz), 1.06 (d, 3H, *Me$_2$*CH, *J* = 6.2 Hz), 1.08 (dq, 1H, CH$_3$*CH$_2$*Si, *J* = 7.9, 14.8 Hz), 1.25 (dq, 1H, CH$_3$*CH$_2$*Si, *J* = 7.8, 14.8 Hz), 3.98 (septet, 1H, Me$_2$*CH*, *J* = 6.1 Hz), 7.29−7.35 (m, 5H, Ph), 7.44−7.46 (m, 2H, phenylene), 7.55−7.59 (m, 1H, phenylene), 7.65−7.67 (m, 1H, phenylene); ^{13}C NMR (δ in CDCl$_3$) −2.4, −1.2, 7.2, 7.8 (2 carbons), 9.0, 25.4 (2 carbons), 65.5, 127.4, 127.7, 127.9, 128.4, 134.7, 135.1, 136.9, 139.8, 143.0, 144.8; ^{29}Si NMR (δ in CDCl$_3$) −3.23, 5.98.

Preparation of Ethylmethylphenyl(2-propenoxy)silane (5). To a solution of 2.20 mmol of lithium diisopropylamide in 5 mL of THF was added a mixture of 0.369 g (2.00 mmol) of chloroethylmethylphenylsilane and 0.124 g (2.13 mmol) of acetone in 2 mL of THF at −78 °C. The resulting mixture was stirred at −78 °C for 5 min and then allowed to warm to room temperature. After evaporation of the solvent, 10 mL of hexane was added to the residue to precipitate the resulting LiCl. The precipitates were filtered off, and the solvent was evaporated. The residue was treated with preparative GPC eluting with benzene to give 0.255 g (62% yield) of **5**: MS *m/z* 206 (M$^+$); IR ν_{Si-O} 1048 cm^{-1}, $\nu_{C=C-O}$ 1638 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.44 (s, 3H, MeSi), 0.85−0.96 (m, 2H, CH$_3$*CH$_2$*Si), 0.99 (t, 3H, *CH$_3$*CH$_2$, *J* = 7.2 Hz), 1.77 (s, 3H, MeC), 4.00 (s, 1H, H$_2$C=), 4.02 (s, 1H, H$_2$C=), 7.35−7.42 (m, 3H, Ph), 7.57−7.59 (m, 2H, Ph); ^{13}C NMR (δ in CDCl$_3$) −3.8, 6.6, 7.3, 22.7, 91.6, 127.8, 129.7, 133.6, 136.6, 155.9; HRMS calcd for $C_{12}H_{18}SiO$ (M$^+$) 206.1125, found 206.1161.

Photolysis of 1a in the Presence of Acetone at 68 °C. A mixture of 0.299 g (1.00 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of hexane was irradiated for 1.5 h at 68 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 36 mg (0.17 mmol) of pentadecane as an internal standard, as consisting of **3a**/**3b** (41% yield), **4** (17%), and **5** (18%), in addition to 1% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 90/10 by ^{1}H NMR spectrometry.

Photolysis of a Mixture 1a/1b = 4/96 in the Presence of Acetone. A mixture of 0.176 g (0.590 mmol) of **1a**/**1b** = 4/96, 2.0 mL (27.2 mmol) of acetone, and 70 mL of hexane was irradiated for 5.5 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 22 mg (0.10 mmol) of pentadecane as an internal standard, as consisting of **3a**/**3b** (63% yield), **4** (14%), and **5** (15%), in addition to 6% of the starting disilane. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 10/90 by ^{1}H NMR spectrometry.

Photolysis of 1a in the Presence of Acetone in Toluene. A mixture of 0.207 g (0.695 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of toluene was irradiated for 14 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 21 mg (0.10 mmol) of pentadecane, as consisting of **3a**/**3b** (39% yield), **4** (4%), **5** (3%), and *p*-, *m*-, and *o*-tolylethylmethylsilane (14%, 8%, and 6%), in addition to 12% of **1a**. Product **3a**/**3b** and a mixture of *p*-, *m*-, and *o*-tolylethylmethylsilane were separated from the mixture by preparative GLC. *p*-, *m*-, and *o*-Tolylethylmethylsilane could not be isolated and were analyzed as the mixture. All spectral data obtained for *p*-, *m*-, and *o*-tolylethylmethylsilane are identical with those of the authentic samples prepared as follows. The diasteromeric ratio was determined to be **3a**/**3b** = 93/7 by ^{1}H NMR spectrometry.

Preparation of Ethylmethylphenyltolylsilanes. To a mixture of 4−5 mmol of the respective tolylmagnesium bromide in 5 mL of THF was added a mixture of 0.9 equiv of chloroethylmethylphenylsilane at room temperature. The resulting mixture was heated to reflux for 3 h. After hydrolysis of the mixture, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled under reduced pressure.

Data for ethylmethylphenyl(*o*-tolyl)silanes: 46% yield; MS *m*/*z* 240 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.56 (s, 3H, MeSi), 1.00 (t, 3H, CH_3CH$_2$Si, $J = 6.3$ Hz), 1.10 (br q, 2H, CH$_3$$CH_2$Si, $J = 6.3$ Hz), 2.23 (s, 3H, *o*-Me), 7.14 (d, 1H, Tol, $J = 7.4$ Hz), 7.18 (d, 1H, Tol, $J = 7.4$ Hz), 7.25−7.37 (m, 4H, aromatic H), 7.45−7.51 (m, 3H, aromatic H); ^{13}C NMR (δ in CDCl$_3$) −4.0, 6.3, 7.6, 23.2, 124.9, 127.8, 128.9, 129.5, 129.9, 134.2, 135.3, 135.6, 138.1, 144.3. Anal. Calcd for C$_{16}$H$_{20}$Si: C, 79.93; H, 8.38. Found: C, 79.91; H, 8.38.

Data for ethylmethylphenyl(*m*-tolyl)silanes: 70% yield; MS *m*/*z* 240 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.52 (s, 3H, MeSi), 0.97−1.09 (m, 5H, Et), 2.33 (s, 3H, *m*-Me), 7.18 (br d, 1H, Tol, $J = 7.6$ Hz), 7.24 (t, 1H, Tol, $J = 7.5$ Hz), 7.30−7.40 (m, 5H, aromatic H), 7.50−7.53 (m, 2H, aromatic H); ^{13}C NMR (δ in CDCl$_3$) −5.0, 6.0, 7.5, 21.6, 127.7, 127.8, 129.0, 129.9, 131.6, 134.5, 135.1, 137.1 (2 carbons), 137.4. Anal. Calcd for C$_{16}$H$_{20}$Si: C, 79.93 ; H, 8.38. Found: C, 79.93; H, 8.40.

Data for ethylmethylphenyl(*p*-tolyl)silanes: 72% yield; MS *m*/*z* 240 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.51 (s, 3H, MeSi), 0.97−1.08 (m, 5H, Et), 2.35 (s, 3H, *p*-Me), 7.17, 7.41 (2d, 2H × 2, Tol, $J = 7.6$ Hz), 7.31−7.36 (m, 3H, Ph), 7.49−7.51 (m, 2H, Ph); ^{13}C NMR (δ in CDCl$_3$) −4.9, 6.0, 7.5, 21.5, 127.7, 128.6, 129.0, 133.5, 134.5, 134.6, 137.5, 139.0. Anal. Calcd for C$_{16}$H$_{20}$Si: C, 79.93; H, 8.38. Found: C, 79.86; H, 8.30.

Photolysis of 1a in the Presence of Acetone and Piperylene in Toluene. A mixture of 0.167 g (0.561 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, 0.758 g (11.1 mmol) of piperylene, and 70 mL of toluene was irradiated for 90 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 19 mg (0.091 mmol) of pentadecane, as consisting of **3a**/**3b** (60% yield), **4** (7%), and **5** (8%), in addition to 6% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 91/9 by ^{1}H NMR spectrometry.

Photolysis of 1a in the Presence of Acetone in Ether. A mixture of 0.294 g (0.983 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of ether was irradiated for 6 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 22 mg (0.11 mmol) of pentadecane, as consisting of **3a**/**3b** (59% yield), 4 (12%), and **5** (10%), in addition to 7% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 91/9 by ^{1}H NMR spectrometry.

Photolysis of 1a in the Presence of Acetone in THF. A mixture of 0.296 g (0.990 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of THF was irradiated for 12 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 21 mg (0.097 mmol) of pentadecane, as consisting of **3a**/**3b** (28% yield), **4** (11%), and **5** (7%), in addition to 7% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 80/20 by ^{1}H NMR spectrometry.

Photolysis of 1a in the Presence of Acetone in Acetonitrile. A mixture of 0.191 g (0.561 mmol) of **1a**, 2.0 mL (27.2 mmol) of acetone, and 70 mL of acetonitrile was irradiated for 6 h at −43 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 17 mg (0.079 mmol) of pentadecane, as consisting of **3a**/**3b** (58% yield), **4** (3%), and **5** (19%), in addition to 3% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 78/22 by ^{1}H NMR spectrometry.

Photolysis of 1a in Acetone/Hexane = 1/1. A mixture of 0.206 g (0.690 mmol) of **1a**, 35 mL (27.2 mmol) of acetone, and 35 mL of hexane was irradiated for 10 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 23 mg (0.108 mmol) of pentadecane, as consisting of **3a**/**3b** (52% yield), **4** (10%) and **5** (13%), in addition to 14% of **1a**. Product **3a**/**3b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **3a**/**3b** = 93/7 by ^{1}H NMR spectrometry.

Photolysis of 1a in the Presence of Benzophenone. A mixture of 0.148 g (0.495 mmol) of **1a**, 0.470 g (2.49 mmol) of benzophenone, and 70 mL of hexane was irradiated for 10 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 19 mg (0.091 mmol) of pentadecane, as consisting of **6a** (83% yield) and **4** (13%), in addition to 9% of **1a**. Compound **6a** was isolated from the mixture by MPLC on a silica gel column eluting with hexane/ethyl acetate = 10/1 as the single isomer: MS *m*/*z* 480 (M$^+$); IR $\nu_{\mathrm{Si-O}}$ 1077 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.06 (s, 3H, MeSi), 0.49 (s, 3H, MeSi), 0.54−0.67 (m, 2H, CH$_3$$CH_2$Si), 0.48 (t, 3H, CH_3CH$_2$Si, $J = 7.5$ Hz), 0.85 (t, 3H, CH_3CH$_2$Si, $J = 7.7$ Hz), 1.00 (dq, 1H, CH$_3$$CH_2$Si, $J = 7.7$, 14.7 Hz), 1.01 (dq, 1H, CH$_3$$CH_2$Si, $J = 7.8$, 14.8 Hz), 5.68 (s, 1H, Ph$_2$$CH$OSi), 7.15−7.35 (m, 17H, Ph and phenylene), 7.62−7.64 (m, 1H, phenylene), 7.72−7.74 (m, 1H, phenylene); ^{13}C NMR (δ in CDCl$_3$) −2.6, −1.3, 7.0, 7.7, 7.9, 9.1, 77.2, 126.7, 126.8, 126.9, 127.0, 127.6, 127.8, 128.0, 128.1, 128.2, 128.7, 134.6, 136.1, 136.8, 139.3, 142.8, 143.5, 144.4, 144.5; ^{29}Si NMR (δ in CDCl$_3$) −4.00, 10.14. Anal. Calcd for C$_{31}$H$_{36}$Si$_2$O: C, 77.44; H, 7.55. Found: C, 77.30; H, 7.55 (as a 1:1 mixture with **6b**).

Photolysis of 1a in the Presence of Benzophenone at 68 °C. A mixture of 0.268 g (0.897 mmol) of **1a**, 0.341 g (1.87 mmol) of benzophenone, and 70 mL of hexane was irradiated for 3 h at 68 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 24 mg (0.14 mmol) of pentadecane, as consisting of **6a** (56% yield) and **4** (25%), in addition to 11% of **1a**. Compound **6a** was isolated from the mixture by MPLC on a silica gel column eluting with hexane/ethyl acetate = 10/1 as the single isomer.

Photolysis of a Mixture 1a/1b = 10/90 in the Presence of Benzophenone. A mixture of 0.155 g (0.517 mmol) of **1a**/**1b** = 10/90, 0.313 g (1.72 mmol) of benzophenone, and 70 mL of hexane was irradiated for 9 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 15 mg (0.088 mmol) of pentadecane, as consisting of **6a**/**6b** (83% yield) and **4** (12%), in addition to 10% of the starting disilane. Product **6a**/**6b** was separated from the mixture by MPLC on a silica gel column eluting with hexane/ethyl acetate = 10/1, and the diastereomeric ratio was determined to be **6a**/**6b** = 12/88 by ^{1}H NMR spectrometry. Data for **6b**: Mp 89 °C; MS *m*/*z* 480 (M$^+$); IR $\nu_{\mathrm{Si-O}}$ 1077 cm^{-1}; ^{1}H NMR (δ in CDCl$_3$) 0.07 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 0.59 (br q, 2H, CH$_3$$CH_2$Si, $J = 7.3$ Hz), 0.74 (t, 3H, CH_3CH$_2$Si, $J = 7.4$ Hz), 0.85 (t, 3H, CH_3CH$_2$Si, $J = 7.7$ Hz), 0.98 (dq, 1H, CH$_3$$CH_2$Si, $J = 7.7$, 15.0 Hz), 1.08 (dq, 1H, CH$_3$$CH_2$Si, $J = 7.7$, 15.2 Hz), 5.70 (s, 1H, Ph$_2$$CH$OSi), 7.14−7.36 (m, 17H, Ph and phenylene), 7.63−7.65 (m, 1H, phenylene), 7.73−7.76 (m, 1H, phenylene); ^{13}C NMR (δ in CDCl$_3$) −2.5, −1.1, 7.1, 7.7, 7.9, 9.0, 77.3, 126.6, 126.9 (2 carbons), 127.0, 127.6, 127.8, 128.0, 128.1, 128.2, 128.7, 134.6, 136.1, 136.9, 139.2, 142.3, 143.5, 144.5 (2 carbons); ^{29}Si NMR (δ in CDCl$_3$) −3.84, 10.10.

Photolysis of 1a in the Presence of Acetaldehyde. A mixture of 0.177 g (0.591 mmol) of **1a**, 0.47 g (11 mmol) of acetaldehyde, and 70 mL of hexane was irradiated for 3 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 15 mg (0.067 mmol) of hexadecane, as consisting of **7a**/**7b** (29% yield) and **4** (11%), in addition to 3% of **1a**. Product **7a**/**7b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **7a**/**7b** = 96/4 by ^{1}H NMR spectrometry. Data for **7a**: MS *m*/*z* 327 ($M^+ - Me$); IR ν_{Si-O} 1076 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.22 (s, 3H, MeSi), 0.60 (s, 3H, MeSi), 0.61 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 8.0$, 14.9 Hz), 0.70 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J =$ 7.9, 15.0 Hz), 0.83 (t, 3H, $\mathit{CH_3}\mathrm{CH_2Si}$, $J = 7.9$ Hz), 0.96 (t, 3H, $\mathit{CH_3}\mathrm{CH_2Si}$, $J = 7.7$ Hz), 1.05 (t, 3H, $\mathit{CH_3}\mathrm{CH_2O}$, $J = 7.0$ Hz), 1.09 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 7.7$, 14.7 Hz), 1.22 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 7.6$, 14.7 Hz), 3.47 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{O}$, $J = 7.0$, 14.0 Hz), 3.48 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{O}$, $J = 7.0$, 14.0 Hz), 7.28−7.36 (m, 5H, Ph), 7.43−7.46 (m, 2H, phenylene), 7.59−7.62 (m, 2H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −2.5, −2.1, 7.1, 7.6, 7.9, 8.3, 18.1, 58.2, 127.4, 127.7, 128.0, 128.4, 134.5, 134.9, 136.8, 139.9, 143.2, 144.6; ^{29}Si NMR (δ in $CDCl_3$) −3.48, 7.96. Anal. Calcd for $C_{20}H_{30}Si_2O$: C, 70.11; H, 8.83. Found: C, 70.05; H, 8.80 (as a 1:1 mixture with **7b**). Data for **7b**: MS *m*/*z* 327 ($M^+ - Me$); IR ν_{Si-O} 1078 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.19 (s, 3H, MeSi), 0.61 (s, 3H, MeSi), 0.70 (dq, 2H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 7.8$, 14.5 Hz), 0.86 (t, 3H, $\mathit{CH_3}\mathrm{CH_2Si}$, $J = 7.9$ Hz), 0.96 (t, 3H, $\mathit{CH_3}\mathrm{CH_2Si}$, $J = 7.7$ Hz), 1.04 (t, 3H, $\mathit{CH_3}\mathrm{CH_2O}$, $J = 7.0$ Hz), 1.08 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 7.7$, 15.1 Hz), 1.19 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{Si}$, $J = 7.6$, 15.0 Hz), 3.40 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{O}$, $J = 7.0$, 10.0 Hz), 3.46 (dq, 1H, $\mathrm{CH_3}\mathit{CH_2}\mathrm{O}$, $J = 7.0$, 10.0 Hz), 7.26−7.38 (m, 5H, Ph), 7.43−7.45 (m, 2H, phenylene), 7.59−7.61 (m, 2H, phenylene); ^{13}C NMR (δ in $CDCl_3$) −2.6, −2.1, 7.1, 7.7, 7.9, 8.4, 18.1, 58.1, 127.4, 127.8, 128.0, 128.4, 134.5, 134.9, 136.8, 139.8, 143.2, 144.6; ^{29}Si NMR (δ in $CDCl_3$) −3.57, 7.82.

Photolysis of 1a/1b = 6/94 in the Presence of Acetaldehyde. A mixture of 0.176 g (0.591 mmol) of **1a**/**1b** = 6/94, 0.47 g (11 mmol) of acetaldehyde, and 70 mL of hexane was irradiated for 6 h at −78 °C. After evaporation of the solvent, the residue was analyzed by GLC, using 28 mg (0.124 mmol) of hexadecane, as consisting of **7a**/**7b** (34% yield) and **4** (11%), in addition to 10% of the starting disilane. Product **7a**/**7b** was separated from the mixture by preparative GLC, and the diasteromeric ratio was determined to be **7a**/**7b** = 9/91 by ^{1}H NMR spectrometry.

X-ray Analysis of Compound 6b. Compound **6b** crystallizes in the space group $P\bar{1}$. 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 3846 observed reflections for **6b** ($I > 3\sigma(I)$) were used in the least-squares refinement. The structures were solved by Monte-Carlo direct methods[11] using the MULTAN 78 program system[12] and refined by a full-matrix least-squares program.[13] Atomic scattering factors were taken from ref 14. Anisotropic temperature factors were used for refinement of non-hydrogen atoms. 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] Finally, $R = 0.054$ and $R_w = 0.056$, where the weighting scheme was $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$, were obtained.

Acknowledgment. We thank the JSPS Program for supporting University-Industry Cooperative Research Project, Shin-Etsu Chemical Co. Ltd., Toshiba Silicone Co. Ltd., Kaneka Corp., Sumitomo Electric Industry, and Mitsubishi Electric Corp. for financial support. We also thank Dr. Yoshio Aso for assistance in the single-crystal X-ray analysis for compound **6b**.

Supporting Information Available: Tables of anisotropic thermal parameters and positional and *B* values for **6b** (2 pages). Ordering information is given on any current masthead page.

OM960259J

---

[11] Furusaki, A. *Acta Crystallogr., Sect. A* **1979**, *35*, 220.

[12] Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declarcq, J.-P.; Woolfson, M. MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Univ. of York, England, and Louvain, Belgium, 1978.

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

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

[15] Katayama, C.; Honda, M. *CRYSTAN*, The Computer Center of Nagoya University Library Program.