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Regio- and Stereochemistry and Kinetics in the Addition Reactions of Alcohols to Phenyl-Substituted Disilenes[1]

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Abstract: A phenyl-substituted disilene, $PhMeSi{=}SiMe_2$, and stereoisomeric disilenes (*E*)- and (*Z*)-$PhMeSi{=}SiMePh$ were generated photochemically from newly designed precursors. These phenyl-substituted disilenes were detected spectroscopically in an argon matrix at 10 K. Introduction of the phenyl group(s) caused a large red shift in the Si=Si absorption. The reactions of these disilenes with alcohols such as *i*-PrOH, *t*-BuOH, and EtOH were examined. $PhMeSi{=}SiMe_2$ gave the addition products $PhMeHSi{-}SiMe_2OR$, regioselectively. (*E*)- and (*Z*)-$PhMeSi{=}SiMePh$ gave the corresponding alkoxyhydrodisilanes in high diastereoselectivity arising from *syn* addition of alcohols to the intermediate disilenes. A mechanism involving a four-membered intermediate is proposed for the addition reaction of alcohols to disilenes. The transient absorptions of these disilenes were also observed by laser flash photolysis, and kinetic studies revealed that disilenes were quenched by alcohols very rapidly ($k_2 = 10^7$–10^8 M^{-1} s^{-1}).

Introduction

Roark and Peddle generated tetramethyldisilene as the first silicon-silicon double bonded species in the gas phase.[2] Since then, reaction patterns of disilenes have been investigated widely.[3] Although the chemistry of disilenes has been developed considerably after the isolation of stable disilenes by West et al.,[4] rather little is known about the mechanism and the stereochemistry for the addition reactions of nucleophiles or electrophiles.[5] Addition of alcohols to (*E*)-1,2-di-*tert*-butyl-1,2-dimesityldisilene is reported to give a 1:1 mixture of two diastereomers of alkoxysilanes, suggesting a stepwise mechanism.[6] However, bulky substituents necessary to stabilize disilenes sometimes complicate the stereochemistry. In fact, theoretical calculation predicted a four-center-like transition state in a concerted-type reaction.[7] It therefore seemed worthwhile to investigate the stereochemical outcome with reactive disilenes.

Previously, we have reported that thermally generated (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilenes undergo the stereoselective Diels–Alder reaction with anthracene.[8] We report herein the diastereoselective addition of alcohols to these disilenes generated photochemically from (*E*)-2,3-bis(trifluoromethyl)-7,8-dimethyl-7,8-diphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**6a**) and (*Z*)-2,3-bis(trifluoromethyl)-7,8-dimethyl-7,8-diphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**6b**). We also describe the remarkably regioselective addition of alcohols to 1,1,2-trimethyl-2-phenyldisilene generated from 2,3-bis(trifluoromethyl)-7-phenyl-7,8,8-trimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**8**). Together with the interesting finding on the stereochemistry of alcohol addition, results of the first kinetic studies with the laser flash method and matrix isolation of the disilenes are demonstrated. The first clear evidence of substituent effects on electronic properties is also given.

Results and Discussion

Synthesis of Disilene Precursors. 7,8-Disilabicyclo[2.2.2]octa-2,5-dienes, formal adducts of disilenes to anthracene, naphthalene, and biphenyl, are well known to generate the corresponding reactive disilenes by either thermolysis[8,9] or photolysis.[10,11] However, the presence of condensed aromatic and/or polyphenyl groups sometimes causes complicated photochemical reactions which impede the observation of the reactive disilenes in matrices.[10a] For example, photolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene at 10 K in an argon matrix or at 77 K in a 3-methylpentane (3-MP) glass led to a di-π-methane-type photorearrangement instead of generating tetramethyldisilene ($Me_2Si{=}SiMe_2$).

Recently, we have reported the successful preparation of a parent, 7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**1**),[12] a formal adduct of tetramethyldisilene to benzene. Compound **1** is the parent compound of this class of masked disilenes

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(11) We have also demonstrated that these compounds can be viewed as masked disilenes for anionic polymerization to lead to high molecular weight polysilanes. See: (a) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641. (b) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, *23*, 4494.

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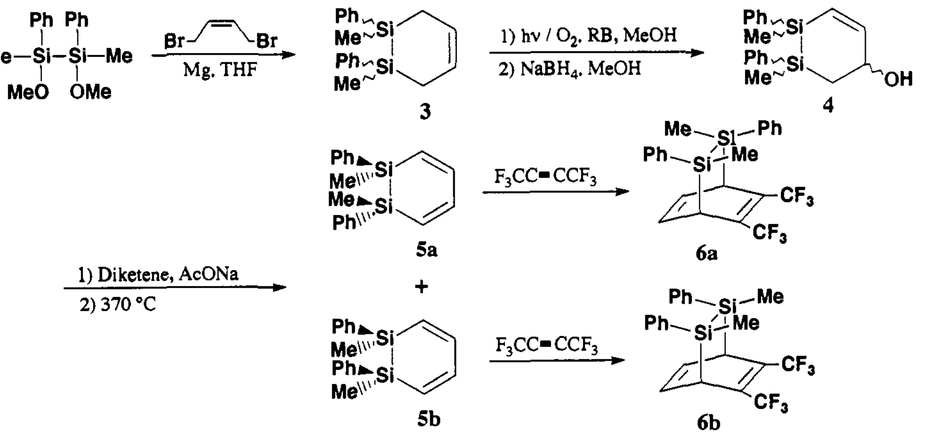
Scheme I



containing the simplest aromatics. In fact, tetramethyldisilene **2** was cleanly observed in an argon matrix by the photolysis of **1** at 10 K. However, the synthetic strategy for the preparation of **1** was based on the Diels–Alder reaction of 1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene with phenyl vinyl sulfoxide as an acetylene synthon, in which application of high pressure (10 kbar) was necessary. 2,3-Bis(trifluoromethyl)-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene gives a species with an absorption band at 344 nm attributable to tetramethyldisilene **2** upon photolysis at 77 K in a 3-MP glass and can be prepared much more easily than **1** by the reaction of 1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene and hexafluoro-2-butyne. Therefore, the bis(trifluoromethyl) derivatives of **1** are practical precursors for disilenes, although these lack the beauty of simplicity to some extent. The precursors **5a** and **5b** of the stereoisomeric disilenes **6a** and **6b** were thus prepared as outlined in Scheme I.

The reaction of 1,4-dibromo-*cis*-2-butene with 1,2-dimethoxy-1,2-dimethyl-1,2-diphenyldisilane and magnesium *in situ* gave 1,2-dimethyl-1,2-diphenyl-1,2-disila-4-cyclohexene (**3**), which was converted into an allylic alcohol, **4**, by Rose–Bengal-sensitized photooxygenation followed by reduction of the resulting peroxide. Alcohol **4** was treated with diketene, and then, gas-phase pyrolysis at 370 °C resulted in the formation of 1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexa-3,5-diene (**5**) as a stereoisomeric mixture. Separation of isomers by GC afforded pure **5a** and **5b** which were subjected to the Diels–Alder reaction with hexafluoro-2-butyne to give the disilene precursors **6a** and **6b**, respectively. The disilene precursor **8** was also prepared in a similar manner. The configurations of **6b** and **8** were determined by NOE experiments.

Matrix Isolation. The spectroscopic observations gave evidence for the photochemical generation of the stereoisomers of 1,2-dimethyl-1,2-diphenyldisilene, **7*E*** and **7*Z***, in an argon matrix (Scheme II). Argon-diluted **6a** was irradiated with 254-nm light at 10 K, which resulted in a decrease of the UV absorption at 241 nm due to **6a** with the simultaneous formation of a new band at 417 nm assignable to disilene **7*E*** (Figure 1). Disilene **7*Z*** was similarly detected by the absorption band at 423 nm during the photoreaction of the precursor **6b**. The interconversion between **7*E*** and **7*Z*** was not observed under the conditions. The absorption bands ascribed to **7*E*** and **7*Z*** were also observed in an organic glass (3-MP, EPA), the ethanol addition product being detected after annealing of the EPA matrix.

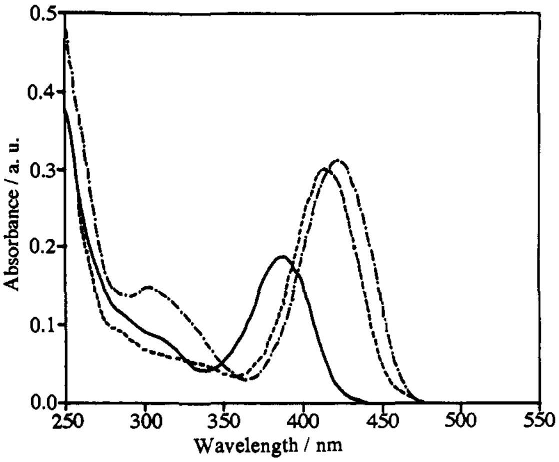
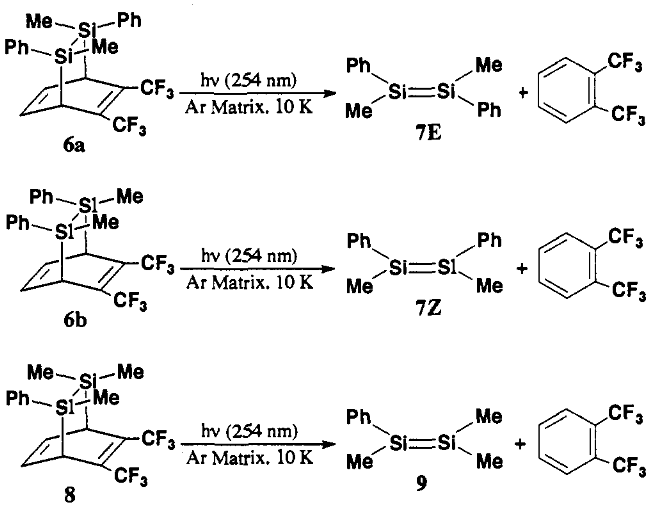


Figure 1. Absorption spectra of disilenes **7*E***(– – –), **7*Z***(· – ·), and **9** (—) produced by photolyses of the precursors **6a**, **6b**, and **8** with 254-nm light in an Ar matrix at 10 K.

Scheme II



Irradiation of **8** in an argon matrix at 10 K gave rise to an absorption band at 386 nm assignable to 1,1,2-trimethyl-2-phenyldisilene (**9**). Table I lists the absorption maxima of these disilenes together with the parent tetramethyldisilene in an argon matrix. It is now clear that introduction of the phenyl group(s) onto the Si═Si double bond causes a large red shift of the λ_{max} of the Si═Si absorption (Table I). Evidently, appreciable conjugation between the Si═Si chromophore and the phenyl group(s) exists. The *Z*-isomer absorbs at slightly lower energy than the *E*-isomer. A similar tendency was recently reported for the silyl-substituted isolable disilenes.[13]

Laser Flash Photolysis (LFP). The photochemical generation of the transient disilenes in solution was confirmed by laser flash photolyses of **6a**, **6b**, and **8**. Figures 2 and 3 show the transient absorption spectrum and decay profiles obtained in the photolysis of **8**. A very fast rise of a peak at 380 nm was observed, which

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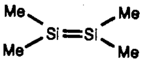
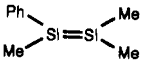
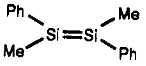
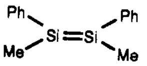
[13] Archibald, R. S.; Winkel, Y.; Millevolte, A. J.; Desper, J. M.; West, R. *Organometallics* **1992**, *11*, 3276.

Table I. Absorption Maxima of Disilenes in an Argon Matrix

disilene	λ_{max} (nm)[a]	$\Delta\tilde{\nu}$,[b] (cm^{-1})
 (2)	344	
 (9)	386	3200
 (7E)	417	5100
 (7Z)	423	5500

[a] In an argon matrix at 10 K. [b] $\Delta\tilde{\nu} = \tilde{\nu}(2) - \tilde{\nu}(7 \text{ or } 9)$.

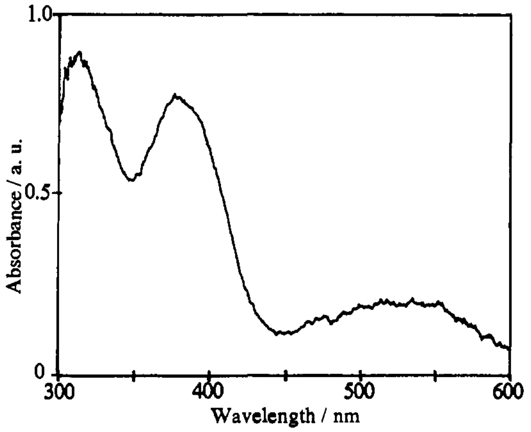


Figure 2. Transient spectrum of disilene **9** produced by LFP of the precursor **8** in degassed methylcyclohexane at 293 K. The broad band around 530 nm is due to a problem with the instrument.

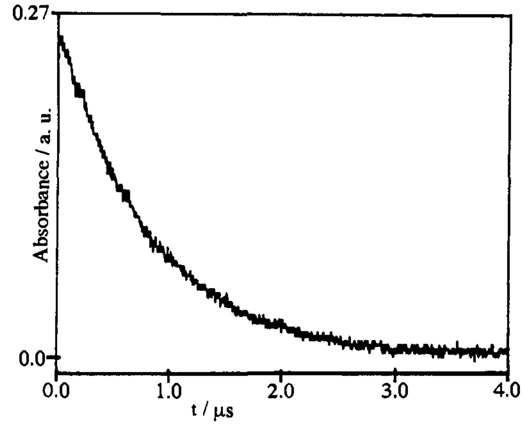


Figure 3. Decay profile of the transient absorption at 380 nm obtained by LFP of the precursor **8** in degassed methylcyclohexane at 293 K.

reached maximum intensity at ca. 10 ns after the excitation and then started to decrease. The half-life of the species was ca. 700 ns. The absorption band at 380 nm in the laser photolysis is assigned to disilene **9** since the precursor **8** gives the absorption peak at 386 nm in an argon matrix at 10 K.

The quenching experiments gave information on the assignment of the absorption at 380 nm and the fate of the disilene. The addition of ethanol resulted in a significant decrease of the half-lives: 230 ns at 1.0 × 10^{-2} M, 165 ns at 1.8 × 10^{-2} M, 133 ns at 2.5 × 10^{-2} M, 96 ns at 3.3 × 10^{-2} M, and 80 ns at 4.0 × 10^{-2} M. Quenching rate constants k_{obs} for the disilenes were determined from the change in the half-lives in the presence of alcohols. Assuming pseudo-first-order decay, we plotted k_{obs} *vs* [ROH] as shown in Figure 4, and the second-order rate constants k_2 of **9** with various alcohols are summarized in Table II.

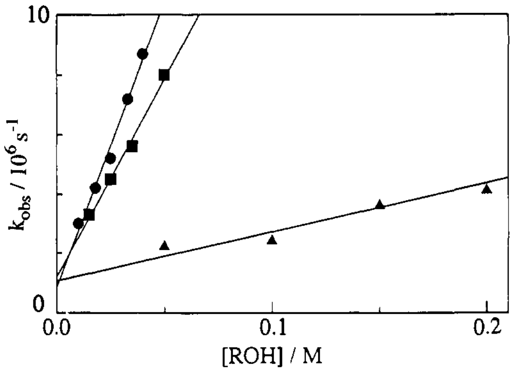


Figure 4. Plots of k_{obs} *vs* [ROH]: EtOH (●), *i*-PrOH (■), and *t*-BuOH (▲). The value of k_{obs} denotes the decay rate of disilene **9** monitored at 380 nm produced by LFP of the precursor **8** in degassed methylcyclohexane at 293 K.

Table II. Rate Constants for Quenching of Disilenes by Alcohols[a]

	k_2, (M^{-1} s^{-1})		
trapping agent	PhMeSi=SiMe$_2$ (**9**)	(*E*)-PhMeSi=SiMePh (**7E**)	(*Z*)-PhMeSi=SiMePh (**7Z**)
EtOH	1.9 × 10^8	1.7 × 10^8	1.9 × 10^8
EtOD	1.8 × 10^8	1.7 × 10^8	1.7 × 10^8
i-PrOH	1.3 × 10^8	1.2 × 10^8	1.2 × 10^8
t-BuOH	1.6 × 10^7	0.9 × 10^7	1.1 × 10^7

[a] In degassed methylcyclohexane at 293 K.

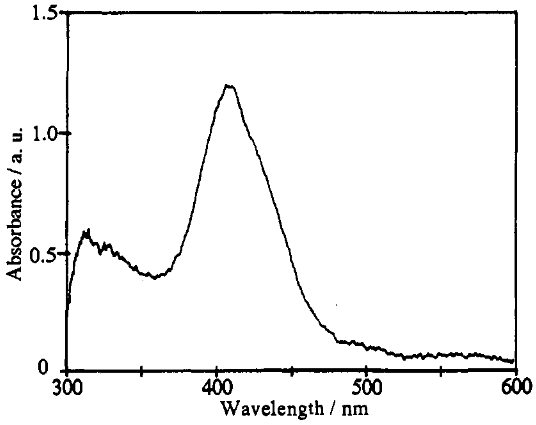


Figure 5. Transient spectrum of disilene **7*E*** produced by LFP of the precursor **6a** in degassed methylcyclohexane at 293 K.

The laser flash photolyses of the disilene precursors **6a** and **6b** gave 415-nm peaks as transient species assignable to **7*E*** and **7*Z*** (Figures 5 and 6 for **6a** and Figures 7 and 8 for **6b**). The addition of alcohols resulted in significant decreases of the half-lives, the quenching rate constants for these disilenes being also listed in Table II.

Several interesting points are mentioned. First, the addition reaction of alcohols to the disilenes is indeed a quite rapid process. The relative reactivity of disilenes is in the order of **9** > **7*E*** ≃ **7*Z***. Second, the relative rate decreases in the order of EtOH > *i*-PrOH > *t*-BuOH, consistent with the steric bulkiness of the alcohols. Third, no significant deuterium isotope effect is found when ethanol-d_1 is used, suggesting that the nucleophilic attack of the alcoholic oxygen to the coordinatively unsaturated silicon center occurs in the rate-determining step of the addition reaction.

Diastereoselectivity for the Addition Reaction. The time-resolved studies indicate that the addition reaction of alcohols to disilenes is a very rapid process ($k_2 = 10^7$–10^8 M^{-1} s^{-1}). Therefore,

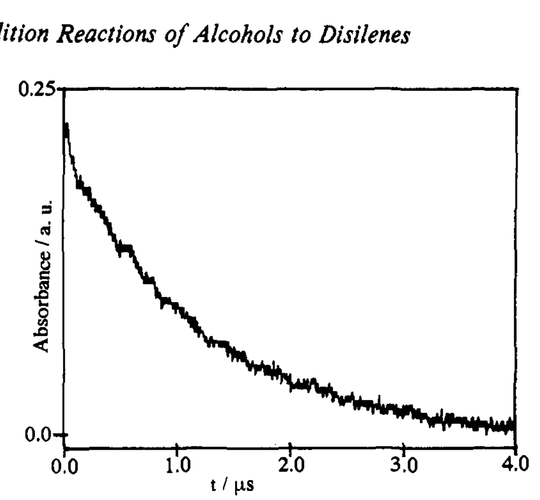


Figure 6. Decay profile of the transient absorption at 415 nm obtained by LFP of the precursor **6a** in degassed methylcyclohexane at 293 K.

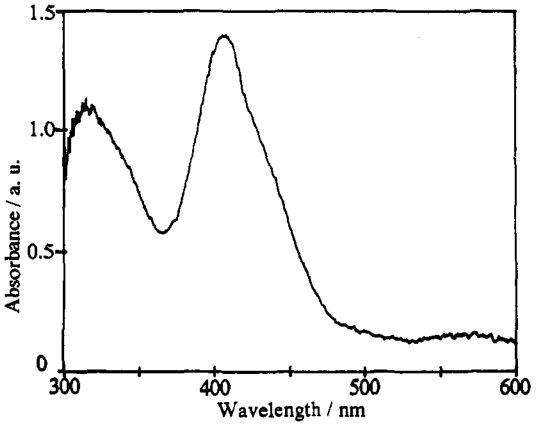


Figure 7. Transient spectrum of disilene **7*Z*** produced by LFP of the precursor **6b** in degassed methylcyclohexane at 293 K.

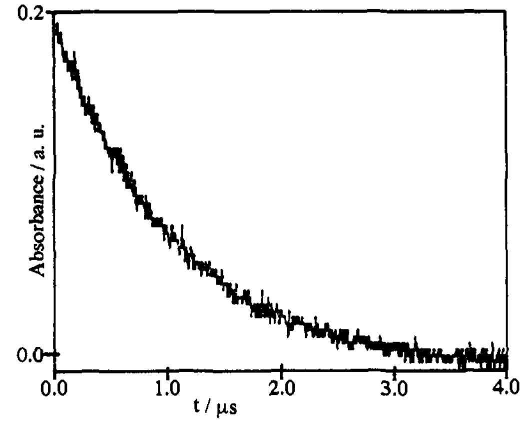


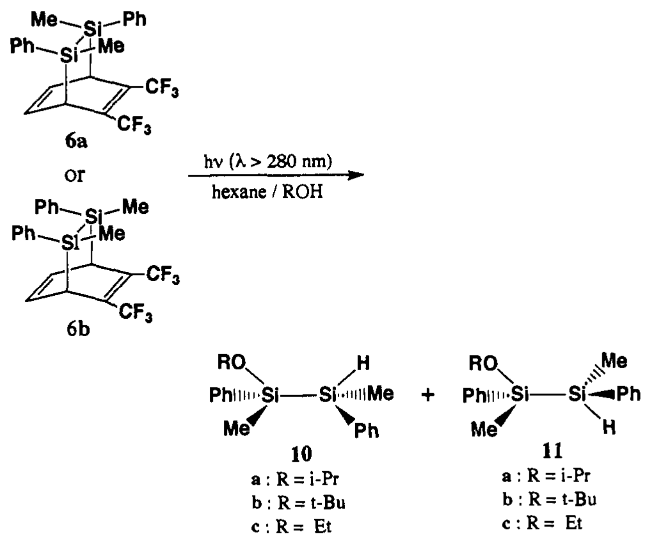
Figure 8. Decay profile of the transient absorption at 415 nm obtained by LFP of the precursor **6b** in degassed methylcyclohexane at 293 K.

the diastereoselective addition of alcohols to disilenes is highly anticipated if the intramolecular proton transfer occurs prior to the rotation of the Si–Si bond and no *E*–*Z* isomerization is involved.

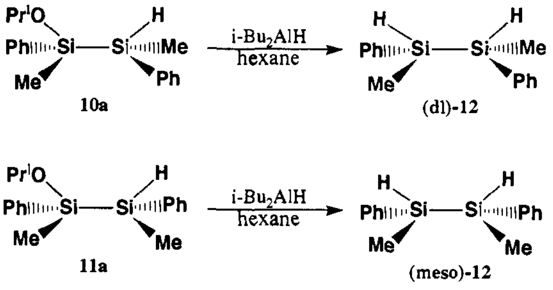
Irradiation (λ > 280 nm) of a hexane/isopropyl alcohol (9:1) solution of **6a** at room temperature afforded alkoxyhydrodisilane **10a**, which should arise from the *syn* addition of *i*-PrOH to **7*E*** together with a small amount of **11a** (**10a**/**11a**: >99/1, 62% yield). High diasteteroselectivity was also found for the photochemical reaction of **6b** (**11a**/**10a**: >99/1, 49% yield) in which disilene **7*Z*** should play a key role (Scheme III).

Since the diastereomers **10a** and **11a** could not be separated by GC, the configuration was determined after reduction of **10a** or **11a** to 1,2-dimethyl-1,2-diphenyldisilane (**12**) (Scheme IV).

Scheme III



Scheme IV



Thus, reduction of **10a** and **11a** with *i*-Bu_2AlH in hexane gave the respective single isomer exclusively, either the *d,l* or *meso* form of **12**. The *d,l* and *meso* forms of **12** were determined by ^{29}Si NMR ($CDCl_3$): $\delta = -36.23$ (*d,l*) and $\delta = -36.65$ (*meso*). The latter was independently prepared by the reduction of (*meso*)-1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane (**13**) with $LiAlH_4$ in ether. The configuration of *meso*-**13** was confirmed by X-ray diffraction. It is well established that reduction of chlorosilanes by $LiAlH_4$ proceeds with inversion of configuration, whereas reduction of alkoxysilanes with *i*-Bu_2AlH in hexane proceeds with retention.[14] Therefore, it is concluded that reduction of **10a** and **11a** proceeds with retention of configuration: *e.g.*, **10a** → *d,l*-**12**, **11a** → *meso*-**12**. These results lead to the conclusion that alkoxyhydrodisilanes **10a** and **11a** were derived by the *syn* addition of *i*-PrOH to **7*E*** and **7*Z***, respectively.

The product ratios of the photolyses of **6a** and **6b** in the presence of alcohols in hexane are summarized in Tables III and IV. Highly diastereoselective addition was also observed in the reaction with *tert*-butyl alcohol, but the diastereoselectivity decreased to some extent at high concentrations of *i*-PrOH. The diastereoselectivity in the reaction with ethanol is highly concentration dependent. At higher concentrations of ethanol, lower diastereoselectivity in the addition was observed. However, at low concentration of ethanol, the addition was highly diastereoselective.

The high diastereoselectivity suggests that *E* ⇄ *Z* photoisomerization of **7*E*** or **7*Z*** does not occur in solution at room temperature or that trapping of **7*E*** or **7*Z*** by alcohols proceeds faster than the *E* ⇄ *Z* isomerization. In addition, the results show that proton transfer in the intermediate adduct formed by the disilenes and alcohols occurs much faster than rotation of the Si–Si bond. However, in the reaction with ethanol, an appreciable

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(14) Sommer, L. H.; McLick, J.; Golino, C. M. *J. Am. Chem. Soc.* **1972**, *94*, 669. See also: Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. In *The Chemistry of Organic Silicon Compounds*, Part 1; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989.

Scheme V

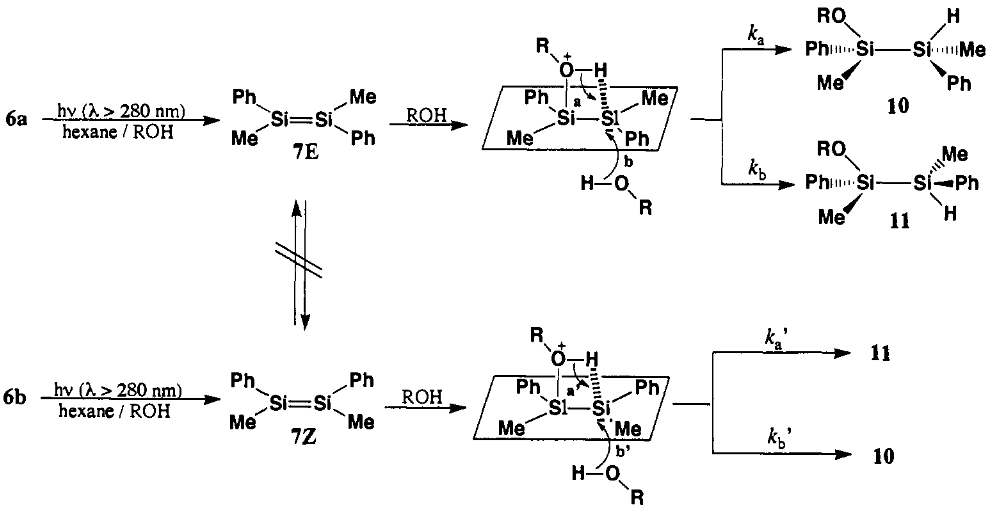


Table III. Product Ratio of the Photolysis of **6a** in Hexane/Alcohol[a]

ROH	conc (M)	10/11
EtOH	0.85	92/8
	1.26	82/18
	1.69	78/22
	2.48	70/30
	5.68	51/49
i-PrOH	1.31	>99/1
	4.33	89/11
t-BuOH	3.51	94/6

[a] A solution of **6a** (ca. 0.1 M) was irradiated in hexane/alcohol through a cutt-off filter (>280 nm) for 15–20 min.

Table IV. Product Ratio of the Photolysis of **6b** in Hexane/Alcohol[a]

ROH	conc (M)	11/10
EtOH	0.85	92/8
	1.26	75/25
	1.69	73/27
	2.48	56/44
	5.68	49/51
i-PrOH	1.31	>99/1
	4.33	91/9
t-BuOH	3.51	95/5

[a] A solution of **6b** (ca. 0.1 M) was irradiated in hexane/alcohol through a cutt-off filter (>280 nm) for 15–20 min.

amount of the *anti* addition product of ethanol was formed, and furthermore, the diastereoselectivity remarkably depended on the concentration of ethanol.

These data are best interpreted by a mechanism depicted in Scheme V involving *syn* addition of alcohol to the intermediate disilene similar to the mechanism of alcohol addition to a cyclic silene.[5f] The high diastereoselectivity suggests that the intramolecular proton transfer to the anionic silicon in the final stage of the addition reaction takes place much faster than the rotation of the Si–Si bond. The intermolecular proton transfer probably gives rise to the *anti* addition product.

The rate of intramolecular proton transfer in the intermediate adduct is expected to decrease by decreasing order of the acidity of protonated alkoxysilanes in the following order: $t\text{-BuO}^+\text{H(Si)} > i\text{-PrO}^+\text{H(Si)} \gg \text{EtO}^+\text{H(Si)}$.[15] As a result, in the reaction with ethanol, especially at high concentration, intermolecular proton transfer leading to the *anti* addition product can compete with the intramolecular one.

The product ratio is given by the equation [*syn*]/[*anti*] = (k_a/k_b)/[EtOH] if the *anti* addition product is formed by the intermolecular proton transfer only. Indeed, the plots of **10c**/**11c** for **6a** (**11c**/**10c** for **6b**) against the inverse of the ethanol concentrations gave linear relationships as shown in Figure 9. A slightly larger slope for **6a** compared to that for **6b** is probably due to the more effective intramolecular proton transfer facilitated by the geometrical factor.

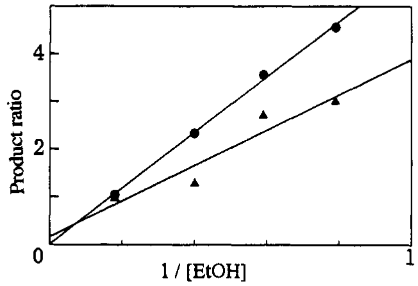
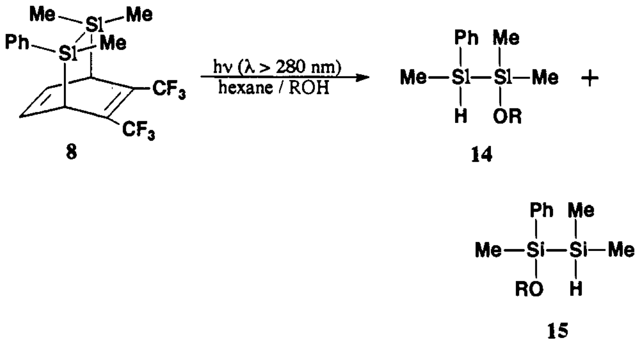


Figure 9. Plots of **10c**/**11c** *vs* 1/[EtOH] for **6a** (●) and **11c**/**10c** *vs* 1/[EtOH] for **6b** (▲).

Scheme VI



Regioselectivity in the Addition Reaction. The regioselectivity of the addition reaction of alcohols to 1,1,2-trimethyl-2-phenyldisilene (**9**) is also remarkable. Irradiation of **8** in alcohols led to the formation of alkoxyhydrodisilane **14** as a major product along with a small amount of **15** (Scheme VI). Very high regioselectivity was found; the ratios of **14**/**15** were 92/8 (MeOH), 95/5 (EtOH), 97/3 (*i*-PrOH), and >99/1 (*t*-BuOH). The regioselectivity is also explained by a mechanism involving the four-membered intermediate where stabilization of the incipient silyl anion by the phenyl group is a major factor, although a steric effect is observed to some extent. This is the first clear evidence demonstrating the importance of an electronic effect in the alcohol addition to disilenes.

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(15) For pK_a values of RO^+H_2 in H_2O; −3.8 ($t\text{-BuO}^+\text{H}_2$), −3.2 ($i\text{-PrO}^+\text{H}_2$), −2.4 (EtO^+H_2). Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

Experimental Section

General methods. ^{1}H NMR spectra were recorded on a Bruker AC 300 FT spectrometer. ^{13}C and ^{29}Si NMR spectra were collected on a Bruker AC-300 spectrometer at 75.5 and 59.6 MHz, respectively. Chemical shifts are based on the residual solvent resonances. Mass spectra and high-resolution mass spectra were obtained on Shimadzu QP-1000 and JEOL JMS D-300 mass spectrometers. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. Melting points are uncorrected. Solvents were dried and distilled from sodium benzophenone ketyl prior to use. Methylcyclohexane (Spectrosol grade, Wako) was purified by distillation over LiAlH$_4$ just before use.

1,2-Dimethyl-1,2-diphenyl-1,2-disila-4-cyclohexene (3). A mixture of 1,2-dimethoxy-1,2-diphenyl-1,2-dimethyldisilane (8.67 g, 28.7 mmol) and 1,4-dibromo-*cis*-2-butene (9.0 g, 42.0 mmol) in THF (30 mL) was added dropwise to magnesium (2.15 g, 88.5 mmol) in THF (20 mL) and was refluxed for 26 h. The mixture was then poured onto 60 mL of hydrochloric acid followed by extraction with hexane. Kugelrohr distillation gave the product (7.2 g, 24.5 mmol, 85%) as a streoisomeric mixture of **3*E*** and **3*Z***, bp 130–145 °C/0.05 mmHg. **3*E***: ^{1}H NMR (CDCl$_3$) δ 0.26 (s, 6 H), 1.68–1.78 (m, 2 H), 1.86–1.96 (m, 2 H), 5.76–5.88 (m, 2 H), 7.28–7.38 (m, 6 H), 7.44–7.54 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ –4.3, 15.8, 125.7, 127.9, 128.7, 134.2, 138.0; ^{29}Si NMR (CDCl$_3$) δ –23.2; MS *m/z* (rel. intensity) 294 (M$^+$, 36), 279 (29), 240 (47), 225 (100), 197 (82), 105 (90); HRMS calcd for $C_{18}H_{22}Si_2$ 294.1260, found 294.1249. **3*Z***: ^{1}H NMR (CDCl$_3$) δ 0.42 (s, 6 H), 1.70–1.80 (m, 2 H), 1.86–1.96 (m, 2 H), 5.76–5.84 (m, 2 H), 7.12–7.30 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ –4.4, 15.9, 125.6, 127.6, 128.6, 134.4, 137.4; ^{29}Si NMR (CDCl$_3$) δ –23.8; MS *m/z* (rel. intensity) 294 (M$^+$, 36), 279 (29), 240 (47), 225 (100), 197 (82), 105 (90); HRMS calcd for $C_{18}H_{22}Si_2$ 294.1260, found 294.1239.

1,2-Dimethyl-1,2-diphenyl-1,2-disila-3-cyclohexen-5-ol (4). A solution of **3** (4.55 g, 15.5 mmol) in methanol (150 mL) was photooxygenated with Rose–Bengal (590 mg) as a sensitizer under bubbling oxygen for 45 min. To the resulting mixture was slowly added sodium borohydride (8.1 g, 0.21 mol) at 0 °C, and the mixture was stirred for 14 h. After removal of the methanol, the mixture was extracted with hexane. Usual workup followed by Kugelrohr distillation gave **4** (4.20 g, 13.5 mmol, 87%) as a mixture of four stereoisomers, bp 155–170 °C/0.07 mmHg: ^{1}H NMR (CDCl$_3$) δ 0.21 (s, 3 H), 0.28 (s, 3 H), 0.35 (s, 3 H), 0.39 (s, 3 H), 0.44 (s, 3 H), 0.48 (s, 3 H), 0.50 (s, 3 H), 0.51 (s, 3 H), 1.18–1.65 (m, 8 H), 1.73–1.85 (m, 4 H), 4.54–4.64 (m, 4 H), 6.04–6.12 (m, 4 H), 6.86–6.96 (m, 4 H), 7.12–7.55 (m, 40 H); ^{29}Si NMR (CDCl$_3$) δ –38.9, –38.7, –38.6, –38.3, –26.4, –26.24, –26.15, –25.8; MS *m/z* (rel. intensity) 295 (M$^+$ – Me, 1.9), 197 (57), 137 (100); HRMS calcd for $C_{17}H_{19}OSi_2$ (M$^+$ – Me) 295.0975, found: 295.0964.

1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclohexa-3,5-diene (5). Diketene (1.6 mL, 18 mmol) was added to a mixture of **4** (2.85 g, 9.19 mmol) and sodium acetate (20 mg, 0.24 mmol) in dioxane (15 mL), and the mixture was refluxed for 12 h. The resulting mixture was then poured onto water and extracted with ether. The organic layer was washed with a solution of sodium chloride and dried over anhydrous sodium sulfate. The ether was evaporated, and the residue was dissolved in 30 mL of benzene. The benzene solution was passed dropwise through a Pyrex tube (length 320 mm, diameter 14 mm) packed with glass chips heated at 370 °C under a nitrogen flow. The pyrolysates were collected in a receiver cooled at –78 °C. The solvent was removed followed by silica gel column chromatography with hexane to give a mixture of **5a** and **5b** (1.11 g, 3.80 mmol, 41%) in the ratio of 55:45. Pure **5a** and **5b** were separated by preparative gas chromatography. **5a**: ^{1}H NMR (CDCl$_3$) δ 0.38 (s, 6 H), 6.28 (dt, *J* = 15, 3 Hz, 2 H), 7.06 (dt, *J* = 15, 3 Hz, 2 H), 7.35–7.50 (m, 6 H), 7.55–7.66 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ –5.3, 128.1, 129.0, 129.3, 134.3, 136.5, 144.0; ^{29}Si NMR (CDCl$_3$) δ –38.6; MS *m/z* (rel. intensity) 292 (M$^+$, 13), 277 (34), 214 (46), 197 (100), 135 (77), 105 (94); HRMS calcd for $C_{18}H_{20}Si_2$ 292.1104, found 292.1085. **5b**: ^{1}H NMR (CDCl$_3$) δ 0.51 (s, 6 H), 6.19 (dt, *J* = 15, 3 Hz, 2 H), 6.94 (dt, *J* = 15, 3 Hz, 2 H), 7.12–7.29 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ –5.4, 127.6, 128.7, 129.4, 134.4, 135.8, 143.7; ^{29}Si NMR (CDCl$_3$) δ –38.8; MS *m/z* (rel. intensity) 292 (M$^+$, 13), 277 (34), 214 (46), 197 (100), 135 (77), 105 (94); HRMS calcd for $C_{18}H_{20}Si_2$ 292.1104, found 292.1115.

(*E*)-2,3-Bis(trifluoromethyl)-7,8-dimethyl-7,8-diphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (6a). A mixture of (*E*)-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexa-3,5-diene (**5a**) (264 mg, 0.90 mmol), hexafluoro-2-butyne (0.5 mL), and toluene (1.5 mL) was sealed in a Pyrex tube and heated at 90 °C for 36 h. Evaporation of the solvent followed by recrystallization from methanol gave pure **6a** (334 mg, 0.74 mmol, 81%): mp 84–85 °C; ^{1}H NMR (CDCl$_3$) δ 0.59 (s, 3 H), 0.69 (s, 3 H), 3.87 (dd, *J* = 6.2, 1.8 Hz, 1 H), 3.96 (dd, *J* = 6.2, 1.8 Hz, 1 H), 6.11–6.21 (m, 2 H), 7.42–7.50 (m, 6 H), 7.61–7.68 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ –3.8, –2.9, 35.0, 35.8, 121.6 (q, *J* = 275 Hz), 121.9 (q, *J* = 275 Hz), 126.7, 127.3, 128.0, 128.1, 129.6, 129.8, 132.3–134.1 (m, 2C), 134.4 (2C), 134.8 (2C); ^{29}Si NMR (CDCl$_3$) δ –30.5, –29.4; MS *m/z* (rel. intensity) 259 (5.1), 240 (100), 225 (85). Anal. Calcd for $C_{22}H_{20}F_6Si_2$: C, 58.13; H, 4.43. Found: C, 57.96; H, 4.64.

(*Z*)-2,3-Bis(trifluoromethyl)-7,8-dimethyl-7,8-diphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (6b). This was obtained in 75% yield (294 mg, 0.65 mmol) by a procedure similar to the synthesis of **6a**. The configuration was determined by NOE experiment: mp 73–75 °C; ^{1}H NMR (CDCl$_3$) δ 0.49 (s, 6 H), 3.80–3.86 (m, 2 H), 6.02–6.08 (m, 2 H), 7.19–7.26 (m, 4 H), 7.29–7.38 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ –3.6, 34.9, 121.8 (q, *J* = 275 Hz), 126.9, 127.9, 129.6, 132.7–133.8 (m), 134.0, 135.1; ^{29}Si NMR (CDCl$_3$) δ –28.8; MS *m/z* (rel. intensity) 259 (3.2), 240 (99), 225 (100). Anal. Calcd for $C_{22}H_{20}F_6Si_2$: C, 58.13; H, 4.43. Found: C, 58.16; H, 4.56.

1,2,2-Trimethyl-1-phenyl-1,2-disila-4-cyclohexene. A mixture of 1,2-dichloro-1-phenyltrimethyldisilane (36.2 g, 145 mmol) and 1,4-dibromo-*cis*-2-butene (32.9 g, 153 mmol) in THF (100 mL) was added dropwise to magnesium (8.0 g, 329 mmol) in THF (400 mL) and refluxed for 19 h. Usual workup followed by Kugelrohr distillation gave the product (20.8 g, 89.7 mmol, 62%): bp 75–90 °C/0.05 mmHg; ^{1}H NMR (CDCl$_3$) δ 0.05 (s, 3 H), 0.18 (s, 3 H), 0.37 (s, 3 H), 1.48-1.60 (m, 2 H), 1.60–1.69 (m, 1 H), 1.74–1.84 (m, 1 H), 5.68–5.82 (m, 2 H), 7.30–7.40 (m, 3 H), 7.44–7.54 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ –5.1, –3.4, –3.0, 15.7, 17.2, 125.1, 126.0, 127.7, 128.5, 134.2, 138.3; ^{29}Si NMR (CDCl$_3$) δ –24.6, –20.5; MS *m/z* (rel. intensity) 232 (M$^+$, 10), 217 (25), 178 (34), 163 (100); HRMS calcd for $C_{13}H_{20}Si_2$ 232.1104, found 232.1106.

Photooxygenation of 1,2,2-Trimethyl-1-phenyl-1,2-disila-4-cyclohexene. The Rose–Bengal-sensitized photooxygenation of the title compound was carried out by a procedure similar to that of **3** to give a mixture of 1,2,2-trimethyl-1-phenyl-1,2-disila-3-cyclohexen-5-ol and 1,1,2-trimethyl-2-phenyl-1,2-disila-3-cyclohexen-5-ol (6.33 g, 25.5 mmol, 76%) as a mixture of four stereoisomers: bp 85–100 °C/0.05 mmHg; ^{1}H NMR (CDCl$_3$) δ –0.01 (s, 3 H), 0.03 (s, 3 H), 0.09 (s, 3 H), 0.10 (s, 3 H), 0.15 (s, 3 H), 0.20 (s, 3 H), 0.21 (s, 3 H), 0.22 (s, 3 H), 0.37 (s, 3 H), 0.40 (s, 3 H), 0.42 (s, 6 H), 1.00–1.60 (m, 8 H), 1.76 (brs, 4 H), 4.40–4.56 (m, 4 H), 5.85–6.01 (m, 4 H), 6.62–6.86 (m, 4 H), 7.26 - 7.50 (m, 20 H); ^{29}Si NMR (CDCl$_3$) δ –38.8, –38.3, –37.2, –37.0, –26.3, –26.2, –23.7, –23.6; MS *m/z* (rel. intensity) 233 (M$^+$ – Me, 5), 179 (20), 137 (100), 135 (67); HRMS calcd for $C_{12}H_{17}OSi_2$ (M$^+$ – Me) 233.0818, found: 233.0825.

1,2,2-Trimethyl-1-phenyl-1,2-disilacyclohexa-3,5-diene. This was obtained in 33% yield (907 mg, 3.94 mmol) by a procedure similar to the synthesis of **5**: bp 75–90 °C/0.05 mmHg (Kugelrohr); ^{1}H NMR (CDCl$_3$) δ 0.03 (s, 3 H), 0.24 (s, 3 H), 0.47 (s, 3 H), 6.07 (d, 1 H, *J* = 14.5 Hz), 6.18 (d, 1 H, *J* = 14.5 Hz), 6.78 (dd, 1 H, *J* = 14.5, 6 Hz), 6.89 (dd, 1 H, *J* = 14.5, 6 Hz), 7.28–7.36 (m, 3 H), 7.44-7.52 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ –5.6, –3.6, –3.5, 127.9, 128.7, 129.5, 131.8, 134.2, 136.9, 142.1, 143.7; ^{29}Si NMR (CDCl$_3$) δ –38.4, –37.0; MS *m/z* (rel. intensity) 230 (M$^+$, 13), 15 (46), 135 (100); HRMS calcd for $C_{13}H_{18}Si_2$ 230.0947, found: 230.0954.

2,3-Bis(trifluoromethyl)-7-phenyl-7,8,8-trimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (8). This was obtained in 76% yield (349 mg, 0.89 mmol) by a procedure similar to the synthesis of **6a**. The configuration was determined by NOE experiment: mp 43–44 °C; ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 6 H), 0.41 (s, 3 H), 3.56 (d, *J* = 6.4 Hz, 1 H), 3.67 (d, *J* = 6.4 Hz, 1 H), 5.91–6.00 (m, 2 H), 7.30–7.38 (m, 3 H), 7.45–7.51 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ –4.9, –3.2 (2C), 35.0, 35.6, 122.0 (q, *J* = 275 Hz, 2C), 126.4, 126.6, 128.1, 129.6, 131.1–132.4 (m), 132.4–133.7 (m), 134.7, 135.0; ^{29}Si NMR (CDCl$_3$) δ –30.3, –24.1; MS *m/z* (rel. intensity) 178 (100), 163 (61). Anal. Calcd for $C_{17}H_{18}F_6Si_2$: C, 52.02; H, 4.62. Found: C, 51.72; H, 4.63.

Matrix Isolation. Matrix isolation was conducted by using an Air Products Inc. Displex refrigerator. Matrix-isolated samples were prepared by gas-phase deposition onto a sapphire window cooled at 10 K. The resulting matrix was irradiated with a 20-W low-pressure mercury arc lamp through the quartz window. The electronic spectra were taken at periodic intervals.

Photolyses of 6a, 6b, and 8 at 77 K in an EPA Matrix. An EPA (ether:isopentane:ethanol = 5:5:2) solution containing the disilene precursor (ca. 2×10^{-3} M) was placed in a quartz cell and degassed by freeze–pump–thaw cycles. The solution was cooled to 77 K, and the resulting matrix was irradiated with a low-pressure mercury arc lamp. The matrix was warmed to room temperature, recooled to 77 K, and then irradiated. This procedure was repeated 8–10 times. Analysis of the photolysate by GC-MS showed the presence of the ethanol addition product of the disilene.

Laser Flash Photolysis. Samples in methylcyclohexane contained in quartz cells with an optical length of 1 cm were degassed by six freeze–pump–thaw cycles. The concentrations of **6a**, 6**b**, and **8** were ca. 3×10^{-3} M. Samples in this study were irradiated with the fourth harmonic Nd: YAG laser (266 nm, pulse width 8 ns) as the exciting light source (Spectron Laser System Inc.). The probe beam was a pulsed 500-W xenon arc lamp. Time-resolved transient spectra were obtained using the Nd: YAG laser in conjunction with an optical multichannel analyzer (Prinston Instruments OSMA System). The decay signals were monitored by a Gould 4082 digital oscilloscope and controlled by an NEC PC 9801 microcomputer. Typically, an entire spectrum was collected at 5-nm increments, and the rate data are the averages from such a set of seven to eight wavelengths for each solution.

Photolyses of 6a and 6b in Alcohols. A solution of the disilene precursor **6a** (ca. 0.1 M) in hexane/alcohol was irradiated with a high-pressure mercury arc lamp through a cut-off filter ($\lambda > 280$ nm). Separation of the reaction mixture by a 6-mm × 1.5-m column packed with 5% SE-30 on Celite 545 gave alkoxyhydrodisilanes **10** and **11**. Photolyses of **6b** in alcohols were also carried out in a similar manner. The ratio of the diastereomers was determined by the integration of the Si(H)Me methyl protons (Tables III and IV). The diastereomers could not be separated by GC. The yields of alkoxyhydrodisilanes were 24–62%. **10a**: ^{1}H NMR ($CDCl_3$) δ 0.45 (d, J = 4.7 Hz, 3H), 0.51 (s, 3 H), 1.11 (d, J = 6.0 Hz, 3 H), 1.13 (d, J = 6.0 Hz, 3H), 4.00 (qq, J = 6.0, 6.0 Hz, 1 H), 4.37 (q, J = 4.7 Hz, 1 H), 7.27–7.34 (m, 6 H), 7.44–7.53 (m, 4 H); ^{29}Si NMR ($CDCl_3$) δ –41.1, 1.8; MS *m/z* (rel. intensity) 300 (M^+, 0.1), 299 (0.1), 285 (0.4), 257 (40), 179 (44), 137 (100); HRMS calcd for $C_{17}H_{24}OSi_2$ 300.1365, found 300.1355. **11a**: ^{1}H NMR ($CDCl_3$) δ 0.40 (d, J = 4.7 Hz, 3 H), 0.49 (s, 3 H), 1.11 (d, J = 5.9 Hz, 6 H), 4.01 (qq, J = 5.9, 5.9 Hz, 1 H), 4.39 (q, J = 4.7Hz, 1 H), 7.28–7.35 (m, 6 H), 7.45–7.52 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ –7.6, –0.9, 25.7, 25.8, 66.7, 127.8, 127.9, 128.8, 129.4, 133.7, 134.98, 135.02, 138.3; ^{29}Si NMR ($CDCl_3$) δ –41.1, 1.8; MS *m/z* (rel. intensity) 300 (M^+, 0.1), 299 (0.1), 285 (0.4), 257 (40), 179 (44), 137 (100); HRMS calcd for $C_{17}H_{24}OSi_2$ 300.1365, found 300.1376. **10b**: ^{1}H NMR ($CDCl_3$) δ 0.40 (d, J = 4.7 Hz, 3 H), 0.54 (s, 3 H), 1.20 (s, 9 H), 4.28 (q, J = 4.7 Hz, 1 H), 7.25–7.33 (m, 6 H), 7.41–7.46 (m, 2 H), 7.49–7.53 (m, 2 H); ^{29}Si NMR ($CDCl_3$) δ –39.1, –6.3; MS *m/z* (rel. intensity) 299 (M^+ – Me, 0.4), 257 (29), 137 (100); HRMS (for M^+ – Me) calcd for $C_{17}H_{23}OSi_2$ 299.1287, found 299.1265. **11b**: ^{1}H NMR ($CDCl_3$) δ 0.35 (d, J = 4.6 Hz, 3 H), 0.52 (s, 3 H), 1.23 (s, 9 H), 4.32 (q, J = 4.6 Hz, 1 H), 7.26–7.35 (m, 6 H), 7.43–7.51 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ –7.6, 1.3, 32.1, 73.4, 127.66, 127.71, 128.7, 129.0, 133.7, 135.1, 135.5, 139.7; ^{29}Si NMR ($CDCl_3$) δ –38.9, –6.4; MS *m/z* (rel. intensity) 299 (M^+ – Me, 0.4), 257 (30), 137 (100); HRMS calcd for $C_{18}H_{26}OSi_2$ 314.1522, found 314.1550. **10c**: ^{1}H NMR ($CDCl_3$) δ 0.44 (d, J = 4.7 Hz, 3 H), 0.48 (s, 3 H), 1.15 (t, J = 7.0 Hz, 3 H), 3.68 (q, J = 7.0 Hz, 2 H), 4.37 (q, J = 4.7 Hz, 1 H), 7.27–7.34 (m, 6 H), 7.44–7.50 (m, 4 H); MS *m/z* (rel. intensity) 286 (M^+, 1.7), 285 (1.8), 257 (68), 179 (62), 137 (57), 121 (100); HRMS calcd for $C_{16}H_{22}OSi_2$ 286.1209, found 286.1210. **11c**: ^{1}H NMR ($CDCl_3$) δ 0.41 (d, J = 4.7 Hz, 3H), 0.48 (s, 3 H), 1.14 (t, J = 7.0 Hz, 3 H), 3.67 (q, J = 7.0 Hz, 2 H), 4.39 (q, J = 4.7 Hz, 1 H), 7.28–7.35 (m, 6 H), 7.45–7.51 (m, 4 H); MS *m/z* (rel. intensity) 286 (M^+, 1.7), 285 (1.8), 257 (68), 179 (62), 137 (57), 121 (100); HRMS calcd for $C_{16}H_{22}OSi_2$ 286.1209, found 286.1203.

Configurations of 10 and 11. The configurations of alkoxyhydrodisilanes **10** and **11** were determined as follows. First, pure (*meso*)-1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane (**13**) was separated by fractional crystallization from pentane: ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 6 H), 7.38–7.47 (m, 6 H), 7.59–7.63 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 0.08, 128.3, 130.5, 133.6, 133.7; ^{29}Si NMR ($CDCl_3$) δ 6.31. The structure of *meso*-**13** was determined by X-ray diffraction. Crystal data: $C_{14}H_{16}Cl_2Si_2$, orthorhombic, $a = 17.519(8)$ Å, $b = 11.206(7)$ Å, $c = 8.241(3)$ Å, $V = 1618.0(14)$ Å^3, space group *Pbca*, $Z = 4$. The final R factor was 0.0886 (R_w=0.0887) for 1046 reflections with $F_o > 3\sigma(F_o)$. Reduction of *meso*-**13** (1.64 g, 5.27 mmol) with $LiAlH_4$ (0.41 g, 10.8 mmol) in ether (20 mL) gave (*meso*)-1,2-dimethyl-1,2-diphenyldisilane (**12**) (0.93 g, 3.84 mmol, 73%): ^{1}H NMR ($CDCl_3$) δ 0.43 (d, J = 4.5 Hz, 6 H), 4.35–4.44 (m, 2 H), 7.28–7.34 (m, 6 H), 7.43–7.47 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ –7.7, 127.9, 129.0, 134.7, 134.8; ^{29}Si NMR ($CDCl_3$) δ –36.65. Reduction of **11a** from the photolysis of **6b** with *i*-Bu_2AlH in hexane gave the exclusive formation of *meso*-**12**. Reduction of **10a** from the photolysis of **6a** with *i*-Bu_2AlH in hexane gave only *d,l*-**12**: ^{1}H NMR ($CDCl_3$) δ 0.43 (d, J = 4.5 Hz, 6 H), 4.35–4.44 (m, 2 H), 7.28–7.34 (m, 6 H), 7.43–7.47 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ –7.4, 127.9, 129.0, 134.7, 134.8; ^{29}Si NMR ($CDCl_3$) δ –36.23.

Photolyses of 8 in Alcohols. A solution of the disilene precursor **8** (ca. 0.1 M) in hexane/alcohol was irradiated with a high-pressure mercury arc lamp through a cut-off filter ($\lambda > 280$ nm). Separation of the reaction mixture by a 6-mm × 1.5-m column packed with 5% SE-30 on Celite 545 gave alkoxyhydrodisilanes **14** and **15** (10–27%). The product ratio was as follows: **14a/15a** = 92/8 (MeOH), **14b/15b** = 95/5 (EtOH), **14c/15c** = 97/3 (*i*-PrOH), **14d/15d** = >99/1 (*t*-BuOH). **14a**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3 H), 0.25 (s, 3 H), 0.43 (d, J = 4.8 Hz, 3 H), 3.38 (s, 3 H), 4.26 (q, J = 4.8 Hz, 1 H), 7.30–7.35 (m, 3 H), 7.48–7.55 (m, 2 H); MS *m/z* (rel. intensity) 210 (M^+, 1.0), 75 (100). **15a**: ^{1}H NMR ($CDCl_3$) δ 0.17 (d, J = 4.7 Hz, 3 H), 0.18 (d, J = 4.7 Hz, 3 H), 0.49 (s, 3 H), 3.47 (s, 3 H), 3.82 (sept, J = 4.7 Hz, 1 H), 7.34–7.40 (m, 3 H), 7.48–7.55 (m, 2 H); MS *m/z* (rel. intensity) 210 (M^+, 1.0), 75 (100); HRMS (a mixture of **14a** and **15a**) calcd for $C_{10}H_{18}OSi_2$ 210.0896, found 210.0878. **14b**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3 H), 0.25 (s, 3 H), 0.43 (d, J = 4.7 Hz, 3 H), 1.13 (t, J = 7.0 Hz, 3 H), 3.61 (q, J = 7.0 Hz, 2 H), 4.25 (q, J = 4.7 Hz, 1 H), 7.28–7.33 (m, 3 H), 7.46–7.53 (m, 2 H); MS *m/z* (rel. intensity) 224 (M^+, 1.0), 223 (1.5), 195 (91), 103 (81), 75 (100). **15b**: ^{1}H NMR ($CDCl_3$) δ 0.16 (d, J = 5.0 Hz, 3H), 0.17 (d, J = 5.0 Hz, 3 H), 0.48 (s, 3 H), 1.19 (t, J = 7.0 Hz, 3H), 3.70 (q, J = 7.0 Hz, 2 H), 3.81 (sept, J = 5.0 Hz, 1 H), 7.32-7.38 (m, 3 H), 7.48–7.55 (m, 2 H); MS *m/z* (rel. intensity) 224 (M^+, 1.0), 223 (1.5), 195 (91), 103 (81), 75 (100); HRMS (a mixture of **14b** and **15b**) calcd for $C_{11}H_{20}OSi_2$ 224.1053, found 224.1032. **14c**: ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3 H), 0.25 (s, 3 H), 0.42 (d, J = 4.7 Hz, 3 H), 1.09 (d, J = 6.0 Hz, 3 H), 1.10 (d, J = 6.0 Hz, 3 H), 3.91 (qq, J = 6.0, 6.0 Hz, 1 H), 4.23 (q, J = 4.7 Hz, 1 H), 7.28–7.34 (m, 3 H), 7.47–7.53 (m, 2 H); MS *m/z* (rel. intensity) 238 (M^+, 0.2), 237 (0.2), 223 (1.4), 195 (55), 75 (100). Product **15c** was based on the GC-MS; HRMS (a mixture of **14c** and **15c**) calcd for $C_{11}H_{19}OSi_2$ (M^+ – Me) 223.0975, found: 223.0971. **14d**: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3 H), 0.25 (s, 3 H), 0.40 (d, J = 4.7 Hz, 3 H), 1.20 (s, 9 H), 4.19 (q, J = 4.7 Hz, 1 H), 7.28–7.32 (m, 3 H), 7.47–7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ –7.7, 2.7, 2.8, 31.2, 32.1, 72.7, 127.8, 128.6, 134.9, 136.0; ^{29}Si NMR ($CDCl_3$) δ –38.4, 3.0; MS *m/z* (rel. intensity) 237 (M^+ – Me, 0.8), 195 (30), 75 (100). Product **15d** was based on the GC-MS; HRMS (a mixture of **14d** and **15d**) calcd for $C_{12}H_{21}OSi_2$ (M^+ – Me) 237.1131, found 237.1128.

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Supplementary Material Available: Details of X-ray experiments, ORTEP drawing, atomic parameters, anisotropic temperature factors, and lists of distances and angles for (*meso*)-1,2-dichloro-1,2-dimethyl-1,2-diphenyldisilane (**13**) (8 pages); lists of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.