Direct Detection of Wiberg's Silene (1,1-Dimethyl-2,2-bis(trimethylsilyl)silene) and Absolute Rate Constants for Its Reactions in Solution

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Photolysis of (pentamethyldisilanyl)(trimethylsilyl)diazomethane (**6a**) and the analogous ketene derivative (**6b**) in hydrocarbon solution in the presence of aliphatic alcohols affords alkoxysilanes from trapping of four isomeric silene reactive intermediates, in yields of ca. 78%, 6%, 9%, and 8%, respectively. Nanosecond laser flash photolysis (193 or 248 nm) of **6a**,**b** allows detection of two transient species, the most prominent of which has been assigned as 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**3**; $\lambda_{max} \sim 265$ nm). The second species exhibits $\lambda_{max} = 310$ nm and much lower reactivity toward alcohols and is consistent with any of *E*-1,2-dimethyl-1,2-bis(trimethylsilyl)silene (*E*-**9**), the corresponding *Z*-isomer (*Z*-**9**), or 1,2,2-trimethyl-2-pentamethyldisilanylsilene (**8g**). The four silenes are the products expected from the various possible 1,2-migrations in the carbene intermediate formed by photoextrusion of nitrogen or carbon monoxide from the precursors. Absolute rate constants for reaction of **3** and **9** (**8g**) with methanol, methanol-*Od*, 2-propanol, cyclohexanol, *tert*-butyl alcohol, *tert*-butylamine, and acetic acid have been determined in hexane solution at 24 °C. In all cases but one, the ratios of the rate constants (relative to *tert*-butyl alcohol) for reaction of silene **3** compare favorably with the relative rate data reported previously for this silene in diethyl ether solution at 100 °C. The rate constant for addition of methanol to **3** in hexane at 25 °C correlates with those of a series of C-substituted 1,1-dimethylsilenes and indicates this silene to be the most highly electrophilic derivative known. The rates exhibit a bell-shaped dependence on temperature over the 0–60 °C range and a maximum at 24 °C, consistent with a stepwise mechanism for reaction with methanol. The transient UV spectra and reactivity observed in THF solution at 24 °C indicate that **3** complexes strongly with the ether solvent, resulting in 10^3- to 10^4-fold reductions in its reactivity toward aliphatic alcohols compared to hexane solution. Smaller (ca. 20-fold) reductions in reactivity are observed for the minor silene product(s) under the same conditions.

Introduction

The kinetics and mechanisms of the reactions of silicon–carbon double bonds have been widely studied over the past thirty years.[1-9] Nucleophilic addition reactions have been particularly thoroughly investigated and have led to the development of an excellent understanding of the factors that govern the kinetic stability of the silicon–carbon double bond in various structural and physical situations.

The development of our current knowledge of substituent effects on silene reactivity began with the seminal work of A. G. Brook and co-workers, which led to the synthesis and isolation of the first kinetically "stable" silene, **1**.[10] As a result of earlier attempts to synthesize silenes with similar substitution patterns[11] and subsequent theoretical work by Apeloig and Karni,[12] it became clear that the Brook silene **1** owes its stability to two factors: steric stabilization owing to the

(1) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.
(2) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.
(3) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 1015–1142.
(4) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.
(5) Muller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; Vol. 2, pp 857–1062.
(6) Sakurai, H. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley and Sons, Ltd: New York, 1998; pp 827–855.
(7) Leigh, W. J. *Pure Appl. Chem.* **1999**, *71*, 453.
(8) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129.
(9) Morkin, T. L.; Owens, T. R.; Leigh, W. J. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 2001; Vol. 3, pp 949–1026.

(10) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.
(11) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M. *J. Am. Chem. Soc.* **1979**, *101*, 83.
(12) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

bulky adamantyl group at carbon, and electronic stabilization due to the placement of the trimethylsilyl groups at silicon and the siloxy and alkyl groups at carbon. Apeloig and Karni's work established that this particular arrangement of the substituents has the effect of reducing the natural $^{\delta+}Si=C^{\delta-}$ polarity of the silenic bond, and they thus concluded that the kinetic stability of silenes should be generally enhanced in derivatives bearing π-donor/σ-acceptor substituents at carbon and/or π-acceptor/σ-donor substituents at silicon. We have recently shown, with the aid of fast kinetic studies on a wide variety of simple C- and Si-substituted silenes, that the absolute rate constants for reaction with methanol (the most commonly used trapping reagent for transient silenes) correlate with inductive and resonance substituent parameters in precisely the manner predicted by theory.[8,13,14]

Given all this, we have always considered the early reports by N. Wiberg and co-workers of the isolation and X-ray crystal structure of silene **2**[15] to be quite remarkable. This silene bears alkyl substituents at silicon and trialkylsilyl groups at carbon, in exactly the opposite electronic arrangement of that of the Brook silenes and hence would be expected to be quite strongly electrophilic. Steric effects associated with the di-*tert*-butylmethylsilyl substituent are clearly an important factor in accounting for the stability of this silene,[15] as the bis(trimethylsilyl) analogue **3** is indeed known to be a transient.[16] Wiberg and co-workers have published a comprehensive set of *relative* rate constants for reaction of silene **3** with various "silenophiles" such as alcohols, amines, carboxylic acids, ketones and aldehydes, and dienes, using the thermolysis of the "silene stores" **4** and **5** to generate the silene in diethyl ether solution at 100 °C (eq 1).[1,17] This body of work established the groundwork for much of what we now know of the mechanisms of the various reactions that silenes undergo.

1

2   **3**

(1)

In view of the central position of the Wiberg silene (**3**) in mechanistic silene chemistry, we have sought to find a means of generating it in solution under conditions where it could be detected directly and its reactivity could be quantified, and have thus identified (pentamethyldisilanyl)(trimethylsilyl)diazomethane **6a** and the analogous ketene derivative **6b** as potentially suitable photochemical precursors. It is well-known that the thermolysis or photolysis of α-silyldiazomethanes leads to the formation of silenes in high yields,[18–20] via 1,2-rearrangement of the carbene intermediate formed upon nitrogen extrusion. A number of years ago, Sekiguchi and Ando reported that photolysis of **6a** in the presence of *tert*-butyl alcohol leads to the formation of alkoxysilane **7_Bu**, attributed to the trapping of silene **3** by the alcohol, and reported the UV spectrum of the silene in a hydrocarbon matrix at 77 K.[21] No other products were detected, suggesting that rearrangement of the putative carbene intermediate via migration of the trimethylsilyl group to the carbenic center (eq 2) occurs with a very high degree of selectivity.

6a   **6b**

(2)

In the present paper, we report a study of the photochemistry of **6a** and **6b** in hexane and THF solution by steady-state and laser flash photolysis techniques. Our results indicate that the photochemistry of **6a** is more complex than previously reported. Nevertheless, these studies allow the reactivity of **3** toward a number of nucleophilic silene traps to be characterized quantitatively at ambient temperatures in solution.

Results and Discussion

Direct Detection of Silenes by Laser Flash Photolysis of 6a and 6b. Laser flash photolysis of a continuously flowing, deoxygenated solution of (pentamethyldisilanyl)(trimethylsilyl)diazomethane (**6a**, 4×10^{-4} M) in dry hexane with the pulses from a Kr/F$_2$ excimer laser (248 nm) led to the formation of readily detectable transient absorptions throughout the 270–330 nm spectral range. The transient decay kinetics varied depending on the observation wavelength, indicating the formation of at least two transient products with overlapping absorption spectra. Transients moni-

(13) Leigh, W. J.; Boukherroub, R.; Kerst, C. *J. Am. Chem. Soc.* **1998**, *120*, 9504.
(14) Leigh, W. J.; Kerst, C.; Boukherroub, R.; Morkin, T. L.; Jenkins, S.; Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1999**, *121*, 4744.
(15) (a) Wiberg, N.; Wagner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005. (b) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 229.
(16) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518.

(17) Wiberg, N.; Fischer, G.; Schurz, K. *Chem. Ber.* **1987**, *120*, 1605.
(18) Haszeldine, R. N.; Scott, D. L.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1440.
(19) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Turney, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 7844.
(20) Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 1584.
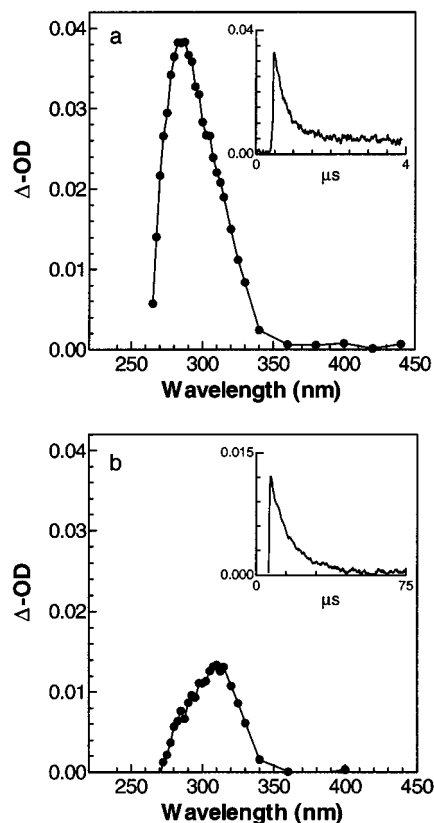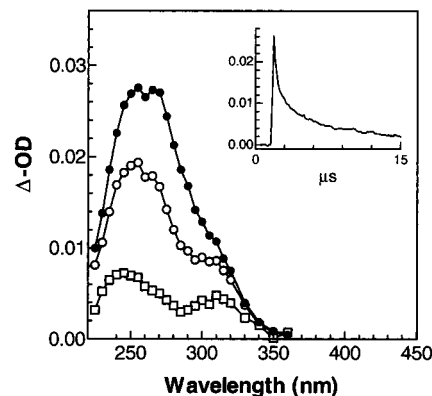(21) Sekiguchi, A.; Ando, W. *Organometallics* **1987**, *6*, 1857.

Figure 1. Transient UV absorption spectra from 248 nm laser flash photolysis of **6a** in deoxygenated hexane solution at 24 °C: (a) recorded 80−100 ns after the laser pulse; (b) after addition of 0.01 M methanol, recorded 1−1.2 μs after the laser pulse. The insets in (a) and (b) show typical decay traces recorded at monitoring wavelengths of 280 and 310 nm, respectively.

tored at 310 nm decayed with mixed first- and second-order kinetics and lifetimes in excess of ~15 μs, while those monitored at 280 nm consisted of a short-lived major component ($\tau \approx 500$ ns) superimposed on a long-lived absorption that decayed with kinetics similar to those of the transient at 310 nm. The lifetime of the latter was invariably long enough that it could be treated as a nondecaying residual absorption in the extraction of first-order decay rate constants for the short-lived component. The lifetime of the short-lived species at 280 nm proved to be quite sensitive to the presence of oxygen ($k_{O2} \approx 7 \times 10^8$ M^{-1} s^{-1}) and moisture in the solvent, whereas that of the 310 nm species was not. Similarly, addition of 0.01 M methanol shortened the lifetime of the 280 nm transient to <30 ns, while causing only modest reductions in the lifetime of the 310 nm species ($\tau \approx 10$ μs) and a change to clean pseudo-first-order decay kinetics.

Figure 1a shows a transient absorption spectrum recorded 80−100 ns after the laser pulse in dry hexane solution, while the inset shows a typical decay trace recorded at 280 nm. Figure 1b shows the spectrum recorded in the presence of 0.01 M methanol, 1−1.2 μs after the laser pulse; it is the same as the spectrum recorded 2−3 μs after the pulse in the experiment of Figure 1a. In both experiments, negative absorptions were observed at monitoring wavelengths less than 265−270 nm due to irreversible bleaching of the precursor. Thus, both spectra (Figure 1a in particular) are

Figure 2. Transient UV absorption spectra from 193 nm laser flash photolysis of ketene **6b** in deoxygenated hexane solution at 24 °C, recorded 0.1−0.3 μs (●), 1.0−2.0 μs (○), and 11.0−13.0 (□) μs after the laser pulse. The inset shows a typical decay trace, recorded at a monitoring wavelength of 280 nm.

skewed so that the apparent absorption maxima are red-shifted from the actual values. With this in mind, the spectrum of Figure 1a agrees well with the one reported by Sekiguchi and Ando from the photolysis of **6a** in a 3-methylpentane glass at 77 K.[21]

Laser flash photolysis of a continuously flowing solution of (pentamethyldisilanyl)(trimethylsilyl)ketene (**6b**, 6 × 10^{-5} M) in deoxygenated hexane with the focused pulses from an Ar/F$_2$ excimer laser (193 nm) yielded transient decays that were weaker and somewhat longer-lived than those obtained from **6a**, but which nevertheless showed similar characteristics over the 260−320 nm monitoring wavelength range. Transient spectra recorded over three time windows after the laser pulse in a typical experiment are shown in Figure 2. Transients recorded at 310−320 nm decayed with mixed first- and second-order kinetics and a lifetime in excess of 30 μs, as were observed at the same wavelength in the experiments with **6a**. Those recorded at 250−300 nm consisted of a short-lived component ($\tau = 2$−4 μs) superimposed on the longer-lived absorption due to the species with $\lambda_{max} \approx 310$. Again, addition of sub-millimolar concentrations of methanol reduced the lifetime of the short-lived species to the point where it could be treated as a clean pseudo-first-order decay superimposed on a nondecaying residual absorption. The lifetime of the short-lived component was also reduced in less completely deoxygenated solutions. With the broader transient spectral range that can be monitored in the experiments with this compound compared to **6a**, the absorption maximum of the short-lived component appears at ~265 nm (see Figure 2). More complex transient behavior was observed at monitoring wavelengths below 250 nm, but this is likely due to trace amounts of oxygen in the solvent[22] and was not investigated further.

Quenching of the short- and long-lived transients from **6a,b** by methanol was studied quantitatively, monitoring the signals at 280 and 310 nm, respectively. Plots of k_{decay} vs methanol concentration were linear in the case of the short-lived species monitored at 280 nm, as shown in Figure 3a. These data were analyzed according to eq 3, where k_0 is the pseudo-first-order rate constant

(22) Kerst, C.; Byloos, M.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 975.

Table 1. Absolute Rate Constants for Reaction of Transient Silenes with Methanol in Deoxygenated Hexane Solution at 23 °C, from 248 and 193 nm Laser Flash Photolysis of 6a and 6b, Respectively[a]

monitoring wavelength (nm)	precursor				
	6a		**6b**		
	280	310	255	280	310
τ (μs)	0.50 ± 0.10	15 ± 2	3 ± 1	3 ± 1	15 ± 2
$k_{MeOH}/10^9$ M^{-1} s^{-1}	13 ± 2	0.049 ± 0.008	12 ± 2	14 ± 2	0.06 ± 0.01
$k_{2MeOH}/10^9$ M^{-2} s^{-1}	b	1.3 ± 0.6	b	b	0.4 ± 0.2

[a] Errors reported as $\pm 2\sigma$. [b] Not detected.
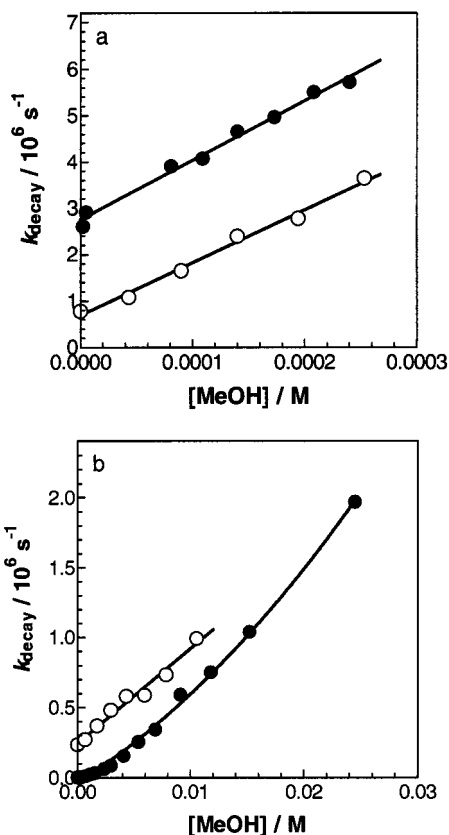
Figure 3. Plots of k_{decay} vs [MeOH] for quenching of silenes from laser flash photolysis of **6a** (●) and **6b** (○) in deoxygenated hexane solution at 24 °C: (a) silene **3**, monitored at 280 nm; (b) silene **9** (**8g**), monitored at 310 nm.

for transient decay in the absence of methanol and k_{MeOH} is the second-order rate constant for reaction of the species with the added alcohol. The corresponding plots for quenching of the 310 nm species appeared to vary in form depending on the precursor (Figure 3b), from linear in the case of **6b** to distinctly nonlinear in the case of **6a**. Because the signals from **6b** tended to weaken at higher methanol concentrations owing to screening of the excitation light by the alcohol, we consider the data from **6a** to be more reliable and hence analyzed both sets of data according to the quadratic expression of eq 4, where k_{2MeOH} is the third-order rate constant for quenching of the silene. Such quadratic dependences of the decay rate on methanol concentration (Figure 3b) are common in silenes exhibiting reactivities of this general magnitude, so the treatment is justifiable.[8,9,23,24] Table 1 lists the second- and third-order rate constants obtained from these experiments;

the agreement between rate constants obtained for both species from the two precursors is excellent. Furthermore, excellent agreement was obtained between rate constants determined for the major component from **6b** at monitoring wavelengths of 255 and 280 nm. Quenching of the 280 nm transient from **6a** with methanol-*Od* (MeOD) proceeded marginally slower than with MeOH, affording a deuterium kinetic isotope effect of $k_H/k_D = 1.1 \pm 0.1$. Quenching of the longer-wavelength transient with the deuterated alcohol was not investigated in hexane solution.

$$k_{decay} = k_0 + k_{MeOH}[MeOH] \quad (3)$$

$$k_{decay} = k_0 + k_{MeOH}[MeOH] + k_{2MeOH}[MeOH]^2 \quad (4)$$

We assign the shorter-lived, more reactive species ($\lambda_{max} \approx 265$ nm; Figure 2) to silene **3**. The value of k_{MeOH} determined for the silene (1.3×10^{10} M^{-1} s^{-1}) is consistent with those reported previously for 1,1-dimethylsilene (**8a**, $k_{MeOH} = 4.9 \times 10^9$ M^{-1} s^{-1})[25] and 1,1-dimethyl-2-trimethylsilylsilene (**8b**, $k_{MeOH} = 8.5 \times 10^9$ M^{-1} s^{-1}),[14] and its prominence in the transient spectrum is consistent with it being the major product of photolysis of **6a** and **6b** (vide infra). The UV absorption maximum observed for **3** in the flash photolysis experiments with **6b** is somewhat lower than that reported in a hydrocarbon matrix at 77 K ($\lambda_{max} = 278$ nm).[21] It is also lower than what would be predicted qualitatively ($\lambda_{max} \approx 285$ nm) from the incremental difference in the absorption maxima of **8a** ($\lambda_{max} = 255$ nm)[25] and **8b** ($\lambda_{max} = 270$ nm).[14]

The UV absorption spectrum and comparatively low reactivity of the long-lived component ($\lambda_{max} = 310$ nm) are consistent with any of three possible silene structures: (*E*)-1,2-dimethyl-1,2-bis(trimethylsilyl)silene (*E*-**9**), the corresponding Z-isomer (*Z*-**9**), or 1,1,2-trimethyl-2-(pentamethyldisilanyl)silene (**8g**). Evidence that these silenes are indeed formed as minor photoproducts from **6a**,**b** will be presented in the next section. The second-order rate constant for reaction of the 310 nm species with methanol ($k_{MeOH} = 4.9 \times 10^7$ M^{-1} s^{-1}) is very close to what would be predicted for **9** and **8g** based on the trends established by other trimethylsilyl-substituted silenes that we have studied.[8] For example, the rate constants for addition of methanol to 1,1-dimethylsilene (**8a**, $k_{MeOH} = 4.9 \times 10^9$ M^{-1} s^{-1})[25] and 1-methyl-1-trimethylsilylsilene (**10**, $k_{MeOH} = 1.8 \times 10^8$ M^{-1} s^{-1})[13] indicate that replacement of a methyl group at silicon with trimethylsilyl results in a ca. 25-fold reduction in reactivity. Applying this factor to the rate constant for reaction of methanol with 1,1,2-trimethyl-2-trimethyl-

(23) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1195.
(24) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.
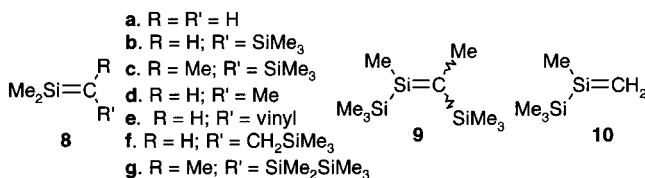
(25) Kerst, C.; Boukherroub, R.; Leigh, W. J. *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 243.

Table 2. Absolute Rate Constants for Reaction of Trimethylsilyl-Substituted Silenes with Methanol in Hexane Solution at 23–25 °C

Me(R)Si=C(R′)(R″)	R	R′	R″	$k_{MeOH}/10^9 \ M^{-1} \ s^{-1}$
8a	Me	H	H	4.9 ± 0.2^a
8b	Me	H	SiMe$_3$	8.5 ± 0.6^b
3	Me	SiMe$_3$	SiMe$_3$	13 ± 2^c
8c	Me	Me	SiMe$_3$	1.8 ± 0.1^b
8d	Me	Me	H	0.15 ± 0.05^b
10	SiMe$_3$	H	H	0.18 ± 0.01^a
9	SiMe$_3$	Me	SiMe$_3$	$0.049 \pm 0.008^{c,d}$

^{a} From ref 13. ^{b} From ref 14. ^{c} This work. Errors are reported as $\pm 2\sigma$. ^{d} Predicted value = $7.5 \times 10^7 \ M^{-1} \ s^{-1}$ (see text); however, the reactivity and UV spectrum of the species also fit with those expected for **8g**.

silylsilene (**8c**, $k_{MeOH} = 1.8 \times 10^9 \ M^{-1} \ s^{-1}$)[14] leads to an expected value for *E*- and *Z*-**9** of $k_{MeOH} \approx 7 \times 10^7 \ M^{-1} \ s^{-1}$, in good agreement with the value observed. The absolute rate constants for methanol addition to **3**, **8a**–**d**, and **10** in hexane solution at 23 °C[13,14] and the value measured for the 310 nm transient are summarized in Table 2. The 310 nm absorption maximum is also consistent with what would be expected for **9**, based on the absorption spectrum of **8c** ($\lambda_{max} = 285$ nm)[14] and the 30 nm red-shift in the absorption maximum of **10** ($\lambda_{max} = 285$ nm) compared to that of **8a**.[13]

a. R = R′ = H
b. R = H; R′ = SiMe$_3$
c. R = Me; R′ = SiMe$_3$
d. R = H; R′ = Me
e. R = H; R′ = vinyl
f. R = H; R′ = CH$_2$SiMe$_3$
g. R = Me; R′ = SiMe$_2$SiMe$_3$

We have no data on which to base a qualitative prediction of the absolute reactivity and λ_{max} of silene **8g** with the same levels of confidence. Nevertheless, the pentamethyldisilanyl substituent is known to be a reasonably strong hyperconjugative π-donor,[26-28] so we can at least predict that the reactivity of **8g** under these conditions should be significantly lower than that of 1,1,2-trimethylsilylsilene (**8d**; $k_{MeOH} = 1.5 \times 10^8 \ M^{-1} \ s^{-1}$),[14] and from the effects of this substituent on the absorption spectra of alkenes[29,30] and benzene,[31] that the absorption maximum should be red-shifted significantly from that of **8d** ($\lambda_{max} = 260, 283$ nm).[14]

Steady-State Photolysis of 6a and 6b in the Presence of Alcohols. Direct irradiation (254 nm) of **6a** as a deoxygenated solution (0.024 M) in cyclohexane-d_{12} containing methanol (0.15 M) led to the formation of four products in a ratio of ca. 77.8:5.8:8.9:7.6, as determined by ^{1}H NMR analysis of the crude reaction mixture after photolysis to ca. 90% conversion of **6a**. The four products could also be detected by GC/MS, but only three of them could be detected on the two capillary columns that we tried in GC/FID analyses. No other

products could be detected between 5 and >90% conversion of the starting material, and GC/MS analyses indicated that the product distribution remained constant throughout the course of the photolysis. Direct irradiation of a deoxygenated solution (0.003 M) of **6b** in hexane containing methanol (0.2 M) with the light from a Zn resonance lamp (214 nm) led to the same product distribution at conversions <25%, as determined by GC/MS analysis.

a. X = N$_2$ R = Me or t-Bu
b. X = CO

11$_R$ (*R,R* and *S,S*)   **12$_R$** (*R,S* and *S,R*)   **13$_R$**   (5)
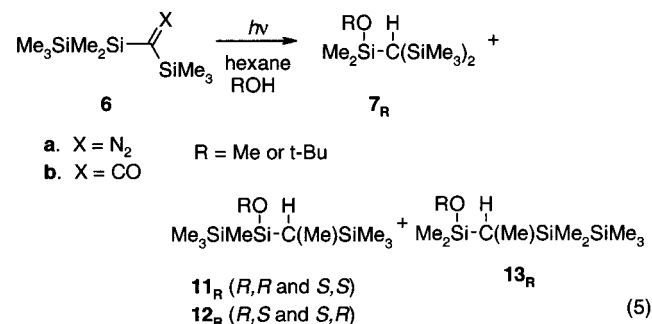
The major product was identified as methoxysilane **7$_{Me}$** (eq 5) on the basis of comparisons of its mass and ^{1}H NMR spectra to published data,[32] after GC isolation of mixtures of the four products from a larger scale photolysis of **6a** in methanolic hexane solution. The minor products were tentatively identified as diastereomers **11$_{Me}$**–**13$_{Me}$** on the basis of the mass and 500 MHz ^{1}H NMR spectra of the product mixture, examples of which are included as Supporting Information. The presence of the minor products was evident in the NMR spectrum as a series of three singlets at δ 3.429, 3.412, and 3.405 ppm and a series of corresponding doublets ($J \approx 9$ Hz) at δ 1.101, 0.977, and 1.048 ppm. The region below 0.5 ppm was exceedingly complicated; nevertheless, the methyl and methine resonances due to **7$_{Me}$** and the requisite one-proton quartet due to one of the minor products could be easily picked out. While the three minor products cannot be considered to be conclusively identified on the basis of these results, the mass and NMR evidence nevertheless indicates that they are all isomers of **7$_{Me}$**, and there are only three reasonable possibilities that would give rise to a three-proton doublet at ca. 1 ppm.

The methanol trapping experiments proved to be the key for identification of the three minor products of photolysis of **6a**. Experiments using *tert*-butyl alcohol as trapping agent, the alcohol employed by Sekiguchi and Ando in their previous investigation of the photochemistry of this compound,[21] afforded results that were much more difficult to interpret without the hindsight provided by the methanol trapping experiments. Three isomeric products were detected by GC methods and identified by GC/MS as **7$_{Bu}$**, **11$_{Bu}$** (or **12$_{Bu}$**), and **13$_{Bu}$**. Their relative yields were similar to those of the corresponding products observed in the methanol experiments; presumably, the remaining expected isomer coelutes with **7$_{Bu}$** under the conditions employed for the analyses. The 500 MHz ^{1}H NMR spectrum of the crude reaction mixture after isolation by semipreparative GC showed prominent resonances matching those reported

(26) Cutress, N. C.; Katritzky, A. R.; Eaborn, C.; Walton, D. R. M.; Topsom, R. D. *J. Organomet. Chem.* **1973**, *43*, 131.

(27) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.
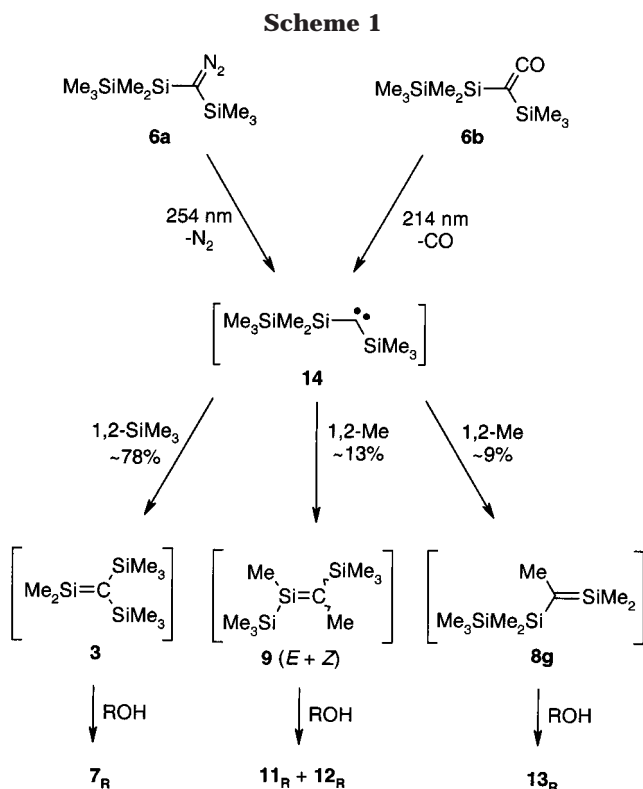
(28) (a) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. (b) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116.

(29) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *117*, C58–C62.

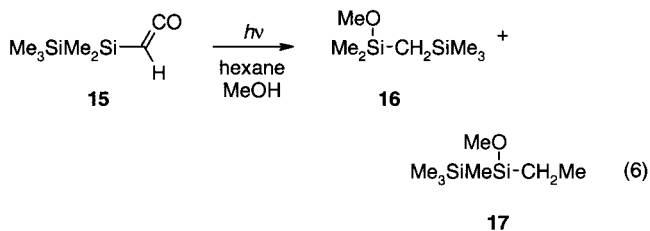(30) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424.

(31) Hague, D. N.; Prince, R. H. *Chem. Ind.* **1964**, *1964*, 1492.

(32) Wiberg, N.; Preiner, G.; Wagner, G.; Kopf, H. *Z. Naturforsch. [B]* **1987**, *42B*, 1062.
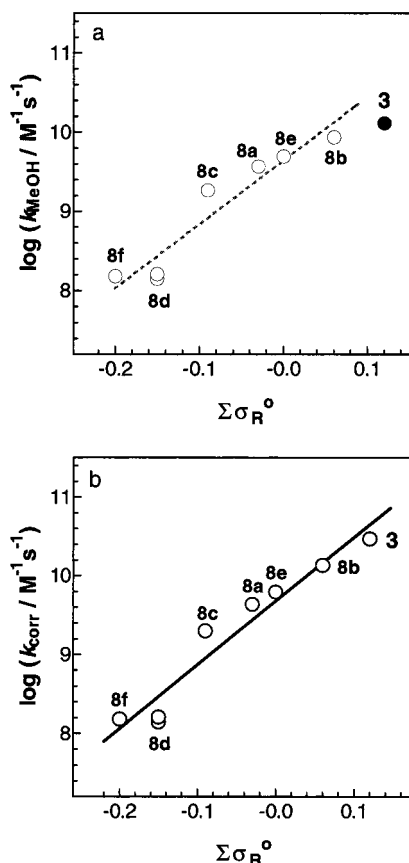
Scheme 1

Figure 4. Rate constants for reaction of methanol with C-substituted 1,1-dimethylsilenes in hexane or isooctane at 23−24 °C vs the resonance substituent parameter $\Sigma\sigma_R°$: (a) log k_{MeOH} vs $\Sigma\sigma_R°$; (b) log k_{corr} vs $\Sigma\sigma_R°$ (see eq 7). The data points for **8a−f** are from ref 14.

earlier for **7$_{Bu}$**.[21] It also showed several small peaks in the 1 and 0 ppm regions that are much more poorly resolved than the corresponding ones in the spectra of the methanol addition products.

Alkoxysilanes **7$_{Me}$** and **7$_{Bu}$** are the products of alcohol trapping of silene **3**, which formally results from [1,2]-migration of the trimethylsilyl group in silylcarbene **14** (see Scheme 1).[14] This is the expected product based on the results of Sekiguchi and Ando from the photolysis of **6a** in the presence of *tert*-butyl alcohol.[21] The three minor products formed in each case (**11$_R$**−**13$_R$**) correspond to those of alcohol trapping of silenes **8g** and **9**, the products of the three nondegenerate [1,2]-methyl migrations in **14**. Their formation is not unexpected. For example, photolysis of pentamethyldisilanylketene (**15**) in methanolic hexane solution leads to the formation of the two methoxysilanes **16** and **17** in a 9:1 ratio (eq 6),[14] corresponding to trapping of the silenes resulting from trimethylsilyl and methyl migration, respectively, in the expected carbene intermediate. The product of trimethylsilyl migration is the major one, as is also observed in the photolyses of **6a,b**.

employing the 193 nm laser, the precursor concentration was lower and therefore reaction with the silene, if it occurs, is insignificant relative to other processes. This hypothesis is further substantiated by the results of steady-state photolysis of **6a** in the absence of nucleophiles. The head-to-tail (1,3-disilacyclobutane) dimer of **3** was observed as the major product, as previously reported,[33,34] as well as several minor nitrogen-containing photoproducts whose mass spectra are consistent with products of reaction of **6a** with **3**.

Comparison of the Absolute Reactivity of Silene 3 to Other 2-Substituted 1,1-Dimethylsilenes. The rate constant for addition of methanol to the Wiberg silene **3** indicates it to be the most potent electrophile of any transient silene that has been studied to date.[8,14] Our previous study of the absolute reactivities of C-substituted 1,1-dimethylsilenes (**8a−f**) showed that the rate constants for methanol addition in hexane solution correlate well with the sum of the resonance substituent parameters $\sigma_R°$ of the two groups on carbon, giving rise to a reaction constant of $\rho_R° = +8.0 \pm 2.2$ ($r^2 = 0.909$).[14] This indicates that the reactivity of silenes as electrophiles is affected mainly through resonance effects of substituents at the silenic carbon and that reactivity is decreased by π-donor substituents as theory predicts.[12] The k_{MeOH} value for **3** falls in more or less the expected position on the original plot (see Figure 4a), but it is

The shorter lifetime obtained for **3** in the flash photolysis experiments with **6a** as precursor (compared to those with **6b**) can likely be attributed to reaction of the silene with the diazomethane precursor, presumably via [2+3]-cycloaddition.[1] In the experiments with **6b**

(33) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 2087.
(34) Eaborn, C.; Smith, J. D.; Hitchcock, P. B.; Sozerli, S. E. *J. Chem. Res. (S)* **1998**, 566.

Table 3. Absolute (k_{NuH}) and Relative Rate Constants (k_{Rel}; Relative to *t*-BuOH) for Reaction of Silenes 3 and 9 (8g) with Nucleophiles (NuH) in Hexane Solution at 24 °C,[a] and Relative Rate Constants for Reaction of 3 in Diethyl Ether Solution at 100 °C[b]

	3		9 (8g)	
NuH	K_{rel} (ether, 100 °C) (k_{rel})[b]	$k_{NuH}/10^9$ M^{-1} s^{-1} (k_{rel})[a]	$k_{NuH}/10^7$ M^{-1} s^{-1} (k_{rel})[a]	$k_{2NuH}/10^7$ M^{-2} s^{-1} (k_{rel})[a]
MeOH	10 500 (3.1)	13 ± 2 (2.2 ± 0.2)	4.9 ± 0.8 (7.8 ± 1.9)	130 ± 60
AcOH	8500 (2.5)	12 ± 4 (2.0 ± 0.4)	620 ± 20 (984 ± 10)	c
i-PrOH	5000 (1.5)	8.3 ± 0.3 (1.4 ± 0.3)	1.0 ± 0.4 (1.6 ± 0.3)	140 ± 20
c-HxOH	380 (0.11)	8.4 ± 0.3 (1.4 ± 0.3)	0.85 ± 0.10 (1.3 ± 0.2)	160 ± 10
t-BuNH₂	5500 (1.6)	8.0 ± 0.4 (1.3 ± 0.3)	0.60 ± 0.08 (0.9 ± 0.2)	4.4 ± 0.8
t-BuOH	3400 (1)	5.9 ± 0.2 (1)	0.63 ± 0.06 (1)	1.1 ± 0.3

[a] This work. Errors are reported as ±2σ. [b] From ref 1. Values of K_{rel} are referenced to 2,3-dimethyl-1,3-butadiene in diethyl ether at 100 °C, while those in parentheses are the recalculated values using *t*-BuOH as the reference compound. [c] Linear dependence of k_{decay} on [NuH].

now particularly clear that the plot levels off as the rate constants approach that of diffusion in hexane ($k_{diff} \approx 2.4 \times 10^{10}$ M^{-1} s^{-1} at 23 °C). The correlation is significantly improved if diffusional effects are accounted for using the expression of eq 7,[35] as is shown in Figure 4b. Linear least-squares analysis of the corrected data (including the point for **3**) affords a slope $\rho_R° = +8.1 \pm 1.6$ ($r^2 = 0.937$).

$$k_{corr} = \frac{k_{diff} \cdot k_{MeOH}}{k_{diff} - k_{MeOH}} \qquad (7)$$

The potent reactivity of the Wiberg silene **3** toward alcohols suggests that it has an exceptionally polarized Si=C bond and is in perfect accord with the trend in reactivity established by related silene derivatives. Ultimately, it can be concluded that the stability of the di-*tert*-butylmethyl analogue **2** is entirely due to steric effects, which substantially outweigh the intrinsic destabilization that is afforded by the electronic effects of the methyl and trialkylsilyl groups in this arrangement.[15,36]

Comparison of the Absolute and Relative Reactivities of Various Nucleophiles with Silene 3. Rate constants were also measured for reaction of **3** in hexane with a number of the nucleophiles that were studied by Wiberg and co-workers using competition techniques,[1,32] including acetic acid (AcOH), 2-propanol (*i*-PrOH), cyclohexanol (CHXOH), *tert*-butylamine (*t*-BuNH₂), and *t*-BuOH. Table 3 lists the absolute rate constants obtained from these experiments, their ratios relative to the rate constant for *t*-BuOH addition, and the published relative rate data for reaction of **3** in diethyl ether solution at 100 °C.[1,32] Rate constants were also measured for the 310 nm species assigned as **8g** and/or **9** and are included as well in the table.

As is evident from the data in Table 3, the ratios of the absolute rate constants determined here for **3** generally agree quite well with the relative values determined previously, despite the considerable differences in experimental conditions. The only significant discrepancy is in the relative rate constants for cyclo-

hexanol quenching, where that from the direct measurement is ca. 10 times higher than that reported by Wiberg et al. on the basis of product studies. The accuracy of our data has been checked by steady-state competition experiments, in which a 0.3 M solution of **6a** in hexane containing 1.4 M each of *t*-BuOH and *c*-HxOH was photolyzed with 254 nm light. This gave rise to two major products which were identified as **7_Bu** and **7_CHX** by GC/MS, in the ratio **7_CHX**:**7_Bu** = 1.9 ± 0.3. The **7_CHX**:**7_Bu** product ratio agrees well with the ratio of absolute rate constants measured by flash photolysis. A competitive trapping experiment was also carried out with methanol and *t*-BuOH (1.4 M each) under conditions similar to those described above. The product ratio was found to be **7_Me**:**7_Bu** = 2.9 ± 0.2, which again compares favorably with the absolute rate constant ratio measured by flash photolysis.

The good agreement between the rate constant ratios determined here and the relative rate data reported by Wiberg (in diethyl ether at 100 °C) is quite interesting, considering the differences in solvent and temperature between the two sets of experiments. Ether solvents are known to reduce the reactivity of transient silenes considerably[37,38] and can also alter their relative reactivities toward nucleophilic reagents compared to what they are in noncomplexing solvents.[38] Furthermore, these effects are temperature dependent and, based on the behavior of the two silenes that have been studied in detail (**18a** and **18b**), are larger for more electrophilic
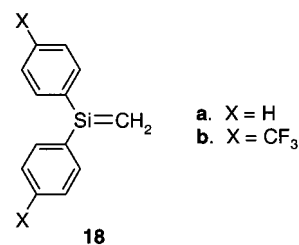
silenes.[38] This seems the most likely reason for the poor agreement between the two sets of data for cyclohexanol quenching of **3**; in fact, it is surprising that this is the

(35) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1995; pp 15−45.
(36) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467.

(37) Auner, N.; Grobe, J.; Muller, T.; Rathmann, H. W. *Organometallics* **2000**, *19*, 3476.
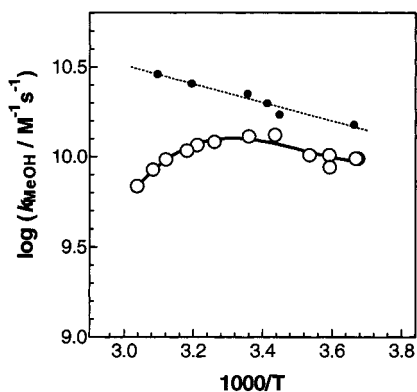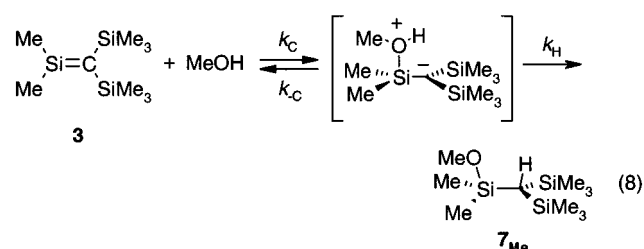(38) Leigh, W. J.; Li, X. *Organometallics*, in press.

Figure 5. Arrhenius plot for reaction of **3** with methanol in deoxygenated hexane solution. The solid points are rate constants for diffusion in hexane at various temperatures, calculated using the standard Debye equation and published temperature–viscosity data (see text).

only nucleophile for which a discrepancy occurs. To investigate the effect of ether solvents and temperature on the reactivity of **3** in more detail, we decided to measure Arrhenius parameters for its reaction with methanol in hexane solution and to investigate its spectroscopic behavior and reactivity in THF solution as a function of temperature.

Temperature Dependence of the Addition of Methanol to 3 in Hexane Solution. Absolute rate constants for the reaction of **3** with MeOH in hexane were determined at several temperatures between 0 and 60 °C using diazo compound **6a** as precursor. The resulting Arrhenius plot is shown in Figure 5. The Arrhenius plot for diffusion in hexane, using diffusional rate constants calculated from the standard Debye equation ($k_{diff} = 8RT/3000\eta$) and published values of η,[39] is also included in the figure. The maximum rate constant for reaction occurs at ∼24 °C and decreases as the temperature is either raised or lowered from this value. Thus, the activation energy for reaction changes from a strongly negative value at the high-temperature limit ($E_a \approx -8$ kcal/mol) to a positive value similar to that of diffusion ($E_a = 2.3 \pm 0.3$ kcal/mol) at low temperatures.

The addition of alcohols to silenes is typically characterized by a negative activation energy,[40,41] resulting from the involvement of a reversibly formed zwitterionic intermediate in the reaction mechanism. The kinetic situation is summarized in eqs 8 and 9, where k_C is the

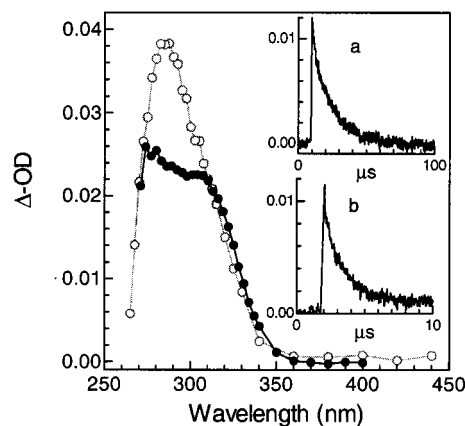$$k_{MeOH} = k_C \cdot \frac{k_H}{k_H + k_{-C}} \qquad (9)$$

(39) *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1995; pp 6−241.
(40) Bradaric, C. J.; Leigh, W. J. *J. Am. Chem. Soc.* **1996**, *118*, 8971.
(41) Bradaric, C. J.; Leigh, W. J. *Can. J. Chem.* **1997**, *75*, 1393.

Figure 6. Transient UV absorption spectrum from 248 nm laser flash photolysis of **6a** in deoxygenated THF solution at 24 °C, recorded 2−3 μs after the laser pulse. The lighter colored spectrum is that in hexane solution from Figure 2, while the insets show typical decay traces at monitoring wavelengths of (a) 290 nm and (b) 320 nm.

bimolecular rate constant for formation of the intermediate, and k_{-C} and k_H are the unimolecular rate constants for its reversion to starting materials and product formation, respectively. The two reaction pathways available to the intermediate have very different entropic requirements; reversion to starting material is entropically favorable and is hence fast at high temperatures ($k_H \ll k_{-C}$), while proton-migration is entropically unfavorable and hence follows the opposite trend with temperature. For a mechanism of this type, the activation energy will be negative over the temperature regime where $k_{-C} > k_H$ and positive over the range where $k_H > k_{-C}$. For less reactive silenes such as the 310 nm species identified above, intermolecular proton transfer involving a second molecule of alcohol also plays a role, which is what leads to the quadratic dependence of k_{decay} vs [ROH].[7,41,42] This process tends to be unimportant for more reactive silenes (such as **3**) over the limited alcohol concentration range that can be studied by laser photolysis methods.

Silene **3** exhibits the most pronounced curvature in Arrhenius behavior that we have yet observed in the reaction of silenes with aliphatic alcohols over the 0−60 °C temperature range. The apex of the plot, which occurs in the present instance at ca. 24 °C, represents the point where $k_{-C} \approx k_H$; the partitioning ratio is therefore equal to 0.5 and thus $k_{MeOH} = 1/2\ k_C$. The value of k_{MeOH} at this temperature is $(1.3 \pm 0.3) \times 10^{10}$ $M^{-1}\ s^{-1}$, exactly half the rate constant for diffusion in hexane within experimental error. We thus conclude that the initial step of the addition of methanol to **3** is fully diffusion-controlled (i.e., $k_C = k_{diff}$) in hexane solution. The negligible deuterium kinetic isotope effect observed for the reaction ($k_H/k_D = 1.1 \pm 0.1$) is consistent with these considerations.

Laser Flash Photolysis of 6a in THF Solution. Laser flash photolysis of deoxygenated solutions of **6a** (4×10^{-4} M) in THF gave rise to transient absorptions that were much longer-lived and slightly red-shifted compared to those observed in hexane solution, as shown by the transient absorption spectra of Figure 6.

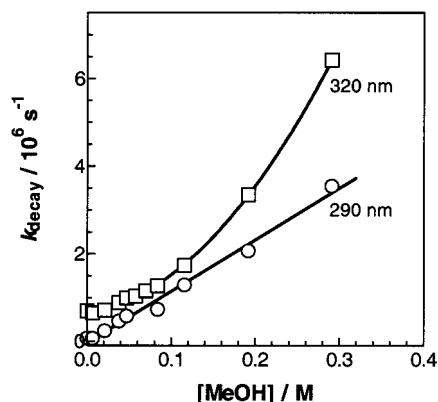(42) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986.

Figure 7. Plots of k_{decay} vs [MeOH] for quenching of silenes detected at 290 nm (○) and 320 nm (□), from 248 nm flash photolysis of **6a** in deoxygenated THF solution at 24 °C.

Table 4. Absolute Rate Constants (k_{NuH}) for Reaction of Methanol, *tert*-Butyl Alcohol, and Acetic Acid with Silenes Detected at 290 and 320 nm in THF at 24 °C[a]

	290 nm	320 nm	
NuH	$k_{NuH}/10^6$ M^{-1} s^{-1}	$k_{NuH}/10^6$ M^{-1} s^{-1}	$k_{2NuH}/10^6$ M^{-2} s^{-1}
MeOH	11.8 ± 0.8	2.6 ± 0.9	59 ± 4
t-BuOH	0.49 ± 0.04	0.30 ± 0.01	0.45 ± 0.01
AcOH	32 ± 4	54 ± 6	*b*

[a] Errors reported as $\pm 2\sigma$. [b] Linear dependence of k_{decay} on [NuH].

Again, the transient decays varied depending on the monitoring wavelength. However, in contrast to the behavior observed in hexane, those monitored at 280–290 nm exhibited *longer* lifetimes ($\tau \approx 30 \mu s$) than those at 310–320 nm ($\tau \approx 5 \mu s$). The variations in k_{decay} with alcohol concentration at the two monitoring wavelengths were similar to those observed in hexane (see Figure 7), in that the short-wavelength species responded linearly to [MeOH] and the long-wavelength species varied quadratically with [MeOH]; however, quenching was much less efficient and required proportionately higher concentrations of added alcohol. Similar behavior was also exhibited in experiments using *t*-BuOH as the quencher. The second- and third-order rate constants obtained in these experiments are listed in Table 4; in contrast to what is observed in hexane solution, the two species now exhibit very similar second-order reactivities toward each of the alcohols, and the only really substantial difference in their behaviors is the third-order reaction kinetics that are observed for one but not for the other. Steady-state photolysis of **6a** in methanolic THF resulted in the formation of a distribution of products similar to that obtained in hexane solution.

Quenching of the two species by methanol-*Od* was also examined and found to be significantly slower than with the protiated alcohol. The data afforded deuterium kinetic isotope effects of $k_H/k_D = 1.9 \pm 0.3$ for reaction of the short-wavelength species with MeOH and $k_H/k_D = 3.1 \pm 0.9$ for the second-order rate constant for reaction of the long-wavelength species.

The assignment of the two transients is unfortunately difficult to make with complete certainty. Our recent study of the UV spectra and reactivity of **18a,b** in THF solution[38] lead to the expectation that both the lifetime and absorption maximum of **3** should be increased significantly in THF relative to hexane, and its reactivity with alcohols should be substantially reduced, owing to complexation of the silene with the ether solvent. For example, silene **18b**, the more electrophilic of **18a,b** in hexane and acetonitrile solution, exhibits a ca. 50 nm red-shift in its absorption maximum, a substantial increase in lifetime, and almost a 20-fold reduction in k_{MeOH} in THF compared to acetonitrile solution. Effects in the same direction are observed for the less electrophilic derivative **18a**, but they are considerably less pronounced, so that the relative reactivities of the two silenes are actually *reversed* in THF solution relative to hexane or acetonitrile. The differences in the electrophilic reactivities of **18a** and **18b** (in noncomplexing solvents) are not nearly as large as those observed here for **3** and **9** (**8g**) in hexane solution, leading to the expectation that the latter (i.e., **9** or **8g**) should exhibit much smaller changes than **3** in absorption maximum, lifetime, and reactivity in THF relative to hexane. We are thus led to conclude that the short-wavelength absorption should most likely be assigned to **3** and the long-wavelength absorption to **9** (**8g**). With the transients assigned in this way, the forms of the concentration dependences of k_{decay} vs [ROH] (linear for **3**, quadratic for **9** (**8g**)) coincide with the behaviors of the two species in hexane solution.

Unfortunately, the use of **6b** as a precursor, to extend the observable transient spectral range and obtain better detail in the region below 280 nm, is not possible because THF absorbs relatively strongly at the laser wavelength (193 nm) required for excitation of this compound.

Regardless of whether **3** has been assigned correctly or not, comparison of the kinetic data of Tables 2 and 4 indicates that its reactivity with methanol at 24 °C is reduced by *at least 3 orders of magnitude* in THF solution relative to that in hexane, and the corresponding difference for *t*-BuOH is even larger. The reactivity of silene **9** (**8g**) is also reduced in the ether solvent, but only by a factor of ca. 20 for both alcohols. The effect on **3** is the largest that we have observed and probably reflects the fact that reaction with both alcohols in hexane is very close to diffusion-limited. The differences also reflect the unique electrophilicity of this silene, which is presumably due to the strong polarization that is associated with the Si=C bond in the molecule.

Experimental Section

^{1}H NMR spectra were recorded in deuteriochloroform or cyclohexane-d_{12} on Bruker AC200 or DRX500 spectrometers and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Low-resolution mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971 mass selective detector and a DB-5 fused silica capillary column (30 m × 0.25 mm; 0.25 μm film; Agilent Technologies).

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890II+ gas chromatograph equipped with a conventional heated splitless injector, flame ionization detector, HP3396A integrator, and DB1 or DB1701 megabore capillary columns (15 m × 0.53 mm; Chromatographic Specialties, Inc.). Semipreparative gas chromatographic separations were carried out using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a stainless

steel column (3% OV-17 on Chromosorb W, HP 80/100; 6 ft × 0.25 in.; Chromatographic Specialties, Inc.).

Hexane (OmniSolv) was refluxed over sodium for several days and distilled under dry nitrogen. Tetrahydrofuran (Caledon Reagent) was refluxed over molten potassium in a nitrogen atmosphere and distilled. Methanol, methanol-*Od*, *tert*-butyl alcohol, cyclohexanol, glacial acetic acid, and 2-propanol were of the highest qualities available from Aldrich Chemical Co. and were used as received. *tert*-Butylamine (Aldrich) was distilled before use from potassium hydroxide.

(Pentamethyldisilanyl)(trimethylsilyl)diazomethane (**6a**) was synthesized using a modification of the procedure of Seyferth and co-workers.[43] It exhibited the following spectral and analytical data: ^{1}H NMR (CDCl$_3$) δ 0.106 (s, 9H), 0.152 (s, 9H), 0.179 (s, 6H); IR (neat) 2955.3 (w), 2943.2 (w), 2040.5 (s), 1251.2 (m), 1221.5 (m), 922.8 (w), 836.7 (m), 790.9 (m); MS (EI) *m/z* 244 (2), 216 (20), 201 (100), 185 (10), 171 (5), 141 (3), 130 (17), 113 (10), 73 (80), 59 (30), 45 (25). The data are in satisfactory agreement with those reported previously for this compound.[21]

(Pentamethyldisilanyl)(trimethylsilyl)ketene (**6b**) was synthesized by the general procedure of Sakurai and Efimova and their co-workers.[44,45] A solution of ethoxy(pentamethyldisilanyl)ethyne (**19**)[46] (0.298 g, 1.49 mmol) and iodotrimethylsilane (212 μL, 1.49 mmol) in deuteriochloroform was heated in a sealed ampule at 55 °C for 20 h. The ^{1}H NMR spectrum showed complete disappearance of **19** and conversion to **6b**, which was isolated and purified by preparative gas chromatography (3 m × 1 cm OV-17 column, 100 °C) as a colorless oil (40 mg, 0.164 mmol, 11%): ^{1}H NMR (CDCl$_3$) δ 0.12 (s, 9), 0.20 (s, 9), 0.22 (s, 6); ^{13}C NMR (CDCl$_3$) δ −2.2, −1.5, −0.9, 1.6, 166.6; ^{17}O NMR (CDCl$_3$) δ 207.0; ^{29}Si NMR (CDCl$_3$) δ −18.2, −17.8, 0.33; IR (CDCl$_3$) 2074 cm^{-1}; UV λ_{max} (hexane) 285 nm (ϵ 110); EIMS *m/z* 244 (M$^+$, 17), 229 (31), 216 (21) 171 (100), 73 (17); HRMS (EI), *m/z* calcd. for C$_{10}$H$_{24}$OSi$_3$ 244.1135, found 244.1125.

Nanosecond laser flash photolysis experiments employed a Lambda Physik Compex 100 excimer laser in conjunction with the home-built detection system we have described previously,[47] or a Luzchem LS-100 laser flash photolysis system. The laser was filled with F$_2$/Kr/Ne or F$_2$/Ar/Ne mixtures to provide pulses at 248 nm (15−20 ns, 70−120 mJ) or 193 nm (12−25 ns; 30−70 mJ), respectively. Solutions of **6a** or **6b** were prepared at concentrations such that the absorbance at the excitation wavelength was ca. 0.7 and were flowed continuously through 3 × 7 mm or 7 × 7 mm Suprasil flow cells connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by least-squares analysis of decay rate−concentration data (6−15 points) that spanned at least a factor of 5 in the transient decay rate. Errors are quoted as twice the standard deviation (±2σ) obtained from the least-squares analysis in each case.

Analytical scale photolyses were carried out using a Rayonet reactor fitted with one or two RPR2537A low-pressure mercury lamps (254 nm) for **6a** or a zinc resonance lamp (214 nm; Philips 93106E) for **6b**. Aliquots of hexane solutions of **6a** (0.001 M) or **6b** (0.003 M) containing methanol or *tert*-butanol

(0.02 M) were contained in quartz tubes (3 mm × 10 mm) and were saturated with dry argon after sealing the tubes with rubber septa. Photolysis of the solutions, with monitoring by GC/MS (DB1701 column) between 5 and 20% conversion, allowed the detection of one major product (**7$_R$**) and two minor ones, the relative yields of which were nearly identical from the two compounds. The two minor products detected are **12$_R$** and **13$_R$**; it was later learned that a third (**11$_R$**) coelutes with **7$_R$** under these GC conditions. Continued photolysis of **6b** resulted in the formation of a variety of low molecular weight secondary photolysis products. The longer-wavelength excitation source used for **6a** allowed it to be taken to quite high conversions with no evidence for the formation of these products.

Preparative scale photolysis of **6a** (250 mg) was carried out in hexane solution (25 mL) containing 0.2 M methanol and carried to 90−95% conversion of **6a** as determined by GC. The crude photolysis mixture was stripped of solvent, and the resulting products were collected as mixtures by semipreparative GC, taking two different cuts to produce mixtures of different compositions. Comparison of the ^{1}H NMR spectra of the two mixtures in CDCl$_3$ allowed partial assignment of the NMR spectra of the three minor products. Yields were determined by ^{1}H NMR spectroscopy from a smaller scale photolysis carried out in C$_6$D$_{12}$ solution in a quartz NMR tube, carried to ca. 95% conversion of **6a**, which showed the four products to be formed in a ratio of 77.8:5.8:8.9:7.6. Similarly, GC/MS analysis of the mixture showed four peaks in the ratio 79.6:7.9:4.5:8.7 (in order of increasing retention time on the DB5 column). The product formed in 8.7% yield (8.9% by NMR) was assigned to **13$_{Me}$** on the basis of its substantially stronger M-73 peak compared to those in the mass spectra of the other three products. The data are listed below (see Supplementary Information for the spectra of the two product mixtures); the ^{1}H NMR spectrum determined for **7$_{Me}$** agrees well with that reported previously for this compound.[32] The 500 MHz ^{1}H NMR and GC/MS data obtained from this and a similar experiment with *t*-BuOH as trapping agent are included as Supporting Information.

7$_{Me}$ (79.6%): ^{1}H NMR (CDCl$_3$) δ −0.5165 (s, 1H), 0.1021 (s, 18H), 0.1687 (s, 6H), 3.3709 (3H); MS *m/z* 248 (0.5), 233 (100), 203 (7), 175 (2), 147 (3), 145 (4), 129 (20), 115 (5), 89 (5), 73 (13), 59 (12).

11$_{Me}$ (5.8%): ^{1}H NMR (CDCl$_3$) δ 0.9775 (d, 3H), 3.4122 (s, 3H); MS *m/z* 248 (4), 233 (100), 203 (7), 175 (48), 147 (11), 145 (14), 129 (23), 117 (11), 89 (30), 73 (46), 59 (30).

12$_{Me}$ (7.6%): ^{1}H NMR (CDCl$_3$) δ 1.105 (d, 3H), 3.429 (s, 3H); MS *m/z* 248 (8), 233 (90), 203 (10), 175 (100), 147 (28), 145 (26), 129 (26), 117 (26), 89 (60), 73 (81), 59 (54).

13$_{Me}$ (8.9%): ^{1}H NMR (CDCl$_3$) δ 0.2061 (q, 1H), 1.0431 (d, 3H), 3.405 (s, 3H); MS *m/z* 248 (3), 233 (11), 203 (3), 175 (100), 147 (3), 145 (5), 131 (5), 129 (5), 117 (7), 89 (24), 73 (24), 59 (17).

Supporting Information Available: 500 MHz ^{1}H NMR and GC/MS data for product mixtures from photolysis of **6a** in hexane or cyclohexane-*d*$_{12}$ in the presence of methanol and *tert*-butanol. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010777G

(43) Seyferth, D.; Flood, T. C. *J. Organomet. Chem.* **1971**, *29*, C25−C28.
(44) Sakurai, H.; Shirahata, A.; Sasaki, K.; Hosomi, A. *Synthesis* **1979**, 740.
(45) Efimova, I. V.; Kazankova, M. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1985**, *55*, 1647.
(46) Sung, K.; Tidwell, T. T. *Organometallics* **1997**, *16*, 78.
(47) Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A: Chem.* **1991**, *57*, 97.