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Substituent Effects on the Reactivity of the Silicon−Carbon Double Bond. Substituted 1,1-Dimethylsilenes from Far-UV Laser Flash Photolysis of α-Silylketenes and (Trimethylsilyl)diazomethane

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Abstract: Photolysis of (trimethylsilyl)-, bis(trimethylsilyl)-, and pentamethyldisilanylketene in hydrocarbon solution in the presence of aliphatic alcohols affords alkoxysilanes from trapping of silene reactive intermediates. The silenes (1,1,2-trimethylsilene, 1,1,2-trimethyl-2-(trimethylsilyl)silene, and 1,1-dimethyl-2-trimethylsilene) can be viewed as the products of [1,2]-methyl or -trimethylsilyl migration in the silyl carbene formed by photodecarbonylation of the ketene, although a competing direct excited-state pathway cannot be ruled out. Far-UV (193 nm) laser flash photolysis of the compounds in hydrocarbon solution affords transients which are formed during the ~20 ns laser pulse and are assignable to the silenes on the basis of their UV absorption spectra and reactivity toward alcohols. 1,1,2-Trimethylsilene has also been generated by laser flash photolysis of (trimethylsilyl)diazomethane and -diazirine in hexane and acetonitrile solution, and its spectrum and rate constants for reaction with MeOH, MeOD, and *t*-BuOH have been determined. Those in hexane agree with those obtained using the corresponding ketene as the precursor. The rate constants for addition of ROH to these and three other 2-substituted 1,1-dimethylsilenes correlate with the resonance substituent parameter $\sigma_R{}^\circ$, affording ρ_R values of +8.0 ± 2.2 and +6.5 ± 2.6 for MeOH and *t*-BuOH, respectively. This allows the conclusion that the reactivity of simple silenes toward nucleophiles is enhanced by resonance electron-acceptor substituents at carbon. To probe for the possible intermediacy of (trimethylsilyl)carbene in the formation of 1,1,2-trimethylsilene from these compounds, flash photolysis experiments with (trimethylsilyl)ketene, -diazomethane, and -diazirine in the presence of pyridine have been carried out. Absorptions assignable to the carbene−pyridine ylide were observed from the ketene and the diazirine, allowing an estimate of between 0.1 and 0.4 ns for the lifetime of singlet (trimethylsilyl)carbene in hydrocarbon solvents at room temperature.

Introduction

There has been considerable experimental and theoretical interest over the past 30 years in the properties of the silicon−carbon double bond.[1−4] Simple silenes of the type RR′Si=CH₂ (where R,R′ = H, alkyl, vinyl, or phenyl) are transients which undergo rapid dimerization and react with nucleophilic reagents such as alcohols, carboxylic acids, amines, ketones, and alkoxysilanes with bimolecular rate constants in the 10⁷−10¹⁰ M⁻¹ s⁻¹ range in solution.[5−8] Numerous stable derivatives are also known, in which the Si=C bond is stabilized by a combination of sterically and electronically stabilizing substituents.[9−14] The famous Brook silenes, for example, bear siloxy and adamantyl substituents at carbon and aryl or trialkylsilyl groups at silicon and exhibit relatively "sluggish" reactivity toward nucleophiles such as alcohols and water.[10] While steric effects clearly contribute substantially to the stability of these silenes, theory suggests that electronic effects also play a significant role: the σ-donor/π-acceptor character of the trialkylsilyl substituents at silicon and the σ-acceptor/π-donor character of the siloxy group at carbon combine to reduce the natural polarity of the Si=C bond, hence reducing its reactivity toward nucleophiles.[15] Until recently,[6,7,16] there have been no experimental studies that test these ideas in a systematic way.

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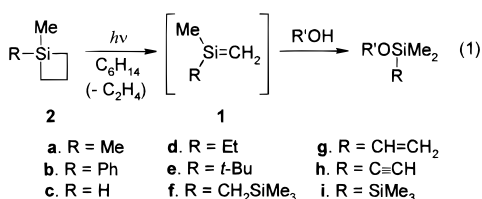(12) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986,** *119,* 1467.
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In a recent paper, we reported the results of a time-resolved spectroscopic study of the reactivity of a homologous series of simple 1-substituted 1-methylsilenes (**1**) toward alcohols in hydrocarbon solution.[7b] The silenes were generated by (193 nm) ArF excimer laser flash photolysis of the corresponding substituted 1-methylsilacyclobutanes (**2**; eq 1). The addition of

a. R = Me   **d**. R = Et   **g**. R = CH=CH$_2$
b. R = Ph   **e**. R = *t*-Bu   **h**. R = C≡CH
**c**. R = H   **f**. R = CH$_2$SiMe$_3$ **i**. R = SiMe$_3$

alcohols is mechanistically the best understood of silene reactions; it proceeds by a mechanism involving reversible complexation of the alcohol at the silenic silicon atom followed by rate-controlling proton transfer from oxygen to carbon.[6,17−22] The bimolecular rate constants for reaction of silenes **1a−i** with methanol in hexane solution correlate (r^2 0.965) with a three-parameter function containing the resonance, inductive, and steric substituent constants σ_R^0, σ_I, and E_s, respectively, yielding the reaction constants $\rho_R = -3.6 \pm 1.2$, $\rho_I = 3.1 \pm 1.0$, and $\rho_s = 0.21 \pm 0.08$. These results indicate that silene reactivity is enhanced by resonance electron donor and/or inductive electron-withdrawing substituents at silicon, in good agreement with theory.[15] Steric effects appear to have only a modest retarding affect on reactivity within this series of compounds.

As a corollary to this work, we wished to undertake a similar study of the effects of substituents *at carbon* on silene reactivity. While silacyclobutane photolysis provides a convenient methodology for the generation of a wide variety of 1-substituted silenes, it is not so convenient for the generation of 2-substituted derivatives. This is because derivatives with substituents at the 2-/4-positions of the silacyclobutane ring are more prone to thermal reaction with nucleophiles[5] and afford more complex mixtures of products upon photolysis in solution;[23] they also generally represent a significantly greater synthetic challenge compared to simple 1,1-disubstituted silacyclobutanes.

One known route to an entire family of 2-substituted 1,1-dimethylsilenes involves the photolysis of α-silyl diazo compounds (e.g., **3a−c**), which yield silenes (**4a−c**; eq 2) by denitrogenation and [1,2]-migration of one of the substituents attached to silicon,[24−37] formally via the intermediacy of the corresponding singlet α-silyl carbenes.

a. R = Me; R' = H
b. R = Me; R' = SiMe$_3$ (2)
c. R = SiMe$_3$; R' = H
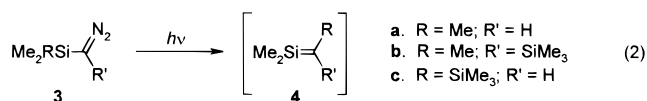
The photochemistry of (trimethylsilyl)diazomethane (**3a**) has been studied in greatest detail and appears to be reasonably complex (see eq 3).[24,27−29,32] Photolysis at 15 K at short
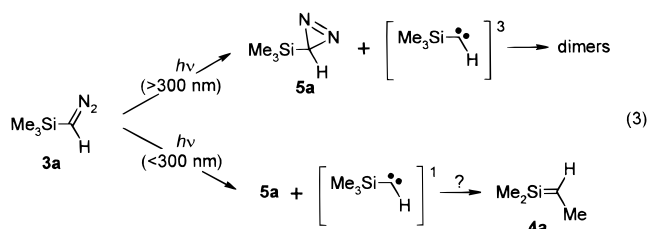
wavelengths (i.e., in the π,π^* absorption band of **3a**) yields the isomeric diazirine **5a** and silene **4a**. On the other hand, irradiation in the lower energy n,π^* absorption band of the diazo compound under the same conditions results in the formation of **5a** and triplet (trimethylsilyl)carbene, which undergoes preferential dimerization upon warming to higher temperatures.[29] The triplet has been shown to be the ground state of the carbene by EPR spectroscopy,[29] and calculations (on :CHSiH$_3$) suggest it to be lower in energy than the singlet by ∼18 kcal/mol.[38] Direct irradiation of diazirine **5a** also results in the formation of **4a**.[28,29] If singlet (trimethylsilyl)carbene is the direct precursor to silene **4a** in the photolyses of **3a** and **5a**, then its lifetime must be very short; it (or the triplet) has been successfully trapped only in the presence of relatively high concentrations of secondary carbene traps such as alkenes, hydridosilanes, or oxygen.[25,37] It is also possible that silene formation results in whole or in part from a direct excited singlet state reaction of these compounds, which is known to be an important pathway to formal carbene-derived products in the photolysis of other diazo compounds and diazirines.[39−42]

These mechanistic uncertainties notwithstanding, it seemed reasonable to propose that the analogous photochemically induced process might occur in α-silyl-substituted *ketenes*, whose synthesis, spectroscopy, and ground-state reactivity have been of considerable recent interest to one of our groups.[43] The photochemistry of ketene and various alkyl- and aryl-substituted derivatives has been extensively studied, and they are well-known precursors to the corresponding carbenes.[44] Except for one somewhat special example however,[45] relatively little is known of the photochemistry of α-silyl-substituted derivatives.

In the present paper, we report steady state and laser flash photolysis studies of the photochemistry of three silylketene derivatives in hydrocarbon solution: (trimethylsilyl)ketene (**6a**), bis(trimethylsilyl)ketene (**6b**), and pentamethyldisilanylketene (**6c**). We have also carried out a few laser flash photolysis

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a. R = Me; R' = H
b. R = Me; R' = SiMe$_3$
c. R = SiMe$_3$; R' = H

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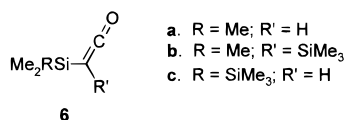
experiments with (trimethylsilyl)diazomethane (**3a**) and its isomer (trimethylsilyl)diazirine **5a**. These experiments were undertaken partly to corroborate the interpretation of our results for **6a**, and partly in an attempt to characterize the unimolecular reactivity of singlet (trimethylsilyl)carbene, the putative intermediate in the formation of silene **4a** from photolysis of these compounds.

Two important considerations in a study of this type are the UV absorption spectra of the substrates and their ground-state reactivity toward alcohols,[43] the reagents of choice for quantifying the effects of substituents on silene reactivity.[7] While all five are adequately stable toward ground-state reaction with aliphatic alcohols, the absorption spectrum of **6b** promised to be problematic. The position of the long-wavelength n,π* absorption bands in these compounds is affected dramatically by the nature of the silyl substituent; in particular, **6b** has a relatively short wavelength absorption centered at 278 nm, and such low extinction coefficients at the excimer laser wavelengths of 248 and 308 nm that prohibitively large quantities of material would be needed to ensure adequate light absorption for flash photolysis experiments. On the other hand, the UV absorption spectra of all three ketenes show considerably more intense (π,π*) absorption bands at short wavelengths, with extinction coefficients that are quite respectable at the ArF excimer wavelength of 193 nm. The photochemistry of ketenes is generally wavelength-dependent, and the quantum yield for photodecarbonylation increases significantly with decreasing excitation wavelength.[44] We have thus employed far-UV (193 nm) laser flash photolysis techniques[46] for the study of **6a**−**c** in hydrocarbon solution and to determine absolute rate constants for reaction of the corresponding silenes (**4a**−**c**) with simple alcohols.

Results and Discussion

Steady-State Photolysis of Silylketenes 6a−c. Direct irradiation of the three silylketenes (**6a**−**c**) as deoxygenated (0.002−0.03 M) solutions in hexane or isooctane containing methanol or *tert*-butyl alcohol (0.15−0.7 M), with the light from a Zn resonance lamp (214 nm), led to the formation of a single product in the case of **6a,b** and two products in an approximate ratio of 9:1 in the case of **6c**. No other products were detected in yields of >5% relative to that of the major product in any case, up to 20−50% conversion of the starting material. These compounds were identified as the alkoxysilanes **7** and **8** (see eqs 4−6) on the basis of spectroscopic data after isolation from the crude reaction mixture (**7b$_{Me}$**) or by GC and/or GC/MS co-injection of the crude photolysis mixtures with authentic samples (**7a$_{Bu}$, 7c$_{Me}$, 8$_{Me}$**). In most cases, very small amounts (<2%) of the esters corresponding to addition of ROH to the starting materials were also formed, but control experiments verified that these were due to dark reaction. Ketene **6a** is significantly more reactive than the others toward ground-state esterification, and thus, MeOH was not used as a trapping agent in this case. Products resulting from dark reaction of the precursor were not detected in the irradiations of **6b** in the presence of either alcohol.

The relative yields of **7c$_{Me}$** and **8$_{Me}$** from photolysis of **6c** in methanolic isooctane solution were estimated from their relative

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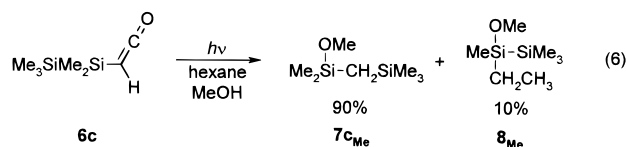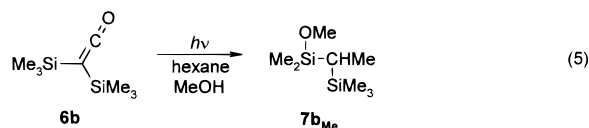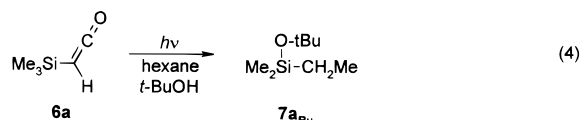
GC/MS peak areas because **8$_{Me}$** coeluted with **6c** on the capillary column employed for our GC/FID analyses. The analogous two products were formed in similar relative yields from photolysis of **6c** in isooctane containing 0.15−0.5 M isopropyl alcohol or *tert*-butyl alcohol, and both could be cleanly resolved from the ketene by GC/FID and GC/MS; the two detection methods gave the same relative yields of the two products within experimental error. The isopropoxy- and *tert*-butoxysilanes were only tentatively identified, however, on the basis of GC/MS evidence. The relative yields of **7c$_{Bu}$** and **8$_{Bu}$** were found to be independent of *t*-BuOH concentration over the range 0.15−0.5 M.

Irradiation of a deoxygenated 0.01 M solution of ketene **6a** in hexane containing 0.26 M *t*-BuOH with 300 nm light also led to the clean formation of alkoxysilane **7a$_{Bu}$**, as the only detectable product up to ~40% conversion of the ketene.

The alkoxysilanes **7** and **8** are the products of alcohol trapping of the silenes (**4a**−**c**, **9**), which formally result from [1,2]-migration of a silyl substituent in the silylcarbene (**10**) formed by photodecarbonylation (Scheme 1). The possibility that a concerted reaction of the lowest excited singlet states of the ketenes competes with the carbene pathway cannot be ruled out, however. The relative yields of **7c$_{Me}$** and **8$_{Me}$** from photolysis of **6c** in the presence of MeOH (**7c$_{Me}$**:**8$_{Me}$** ~ 9:1) suggest that [1,2]-migration of the trimethylsilyl substituent in the immediate precursor to the silenes proceeds ~9 times faster than [1,2]-methyl migration. As expected, the relative yields of **7c** and **8** are the same when isopropyl alcohol or *tert*-butyl alcohol are employed as silene traps and are independent of alcohol concentration. Sekiguchi and Ando observed formation of the trapping products of only silene **4c** in their study of the photochemistry of diazo compound **3c** in a hydrocarbon glass at 77 K.[33]

Direct Detection of Silenes from Laser Flash Photolysis of 6a−c and 3a/5a. Far-UV (193) laser flash photolysis of a continuously flowing, 0.0015 M solution of (trimethylsilyl)-ketene (**6a**) in deoxygenated hexane, with the pulses (193 nm, 5−7 mJ, ~20 ns) from an ArF excimer laser, led to the formation of weak transient absorptions in the 235−300 nm spectral range. These decayed with mixed pseudo-first- and second-order decay kinetics and at the same rate throughout the entire 235−300 nm monitoring wavelength range. The absorption spectrum of the transient, recorded in point-by-point fashion 0.1−1.0 μs after the laser pulse, is shown in Figure 1a; the insert shows a typical decay trace recorded at a monitoring wavelength of 255 nm.

Similar experiments were carried out on a 0.001 M hexane solution of (trimethylsilyl)diazomethane (**3a**), but using a 248 nm (KrF) excimer laser for excitation. Flash photolysis of this compound gave rise to a considerably more strongly absorbing

Substituent Effects on Reactivity of Si=C

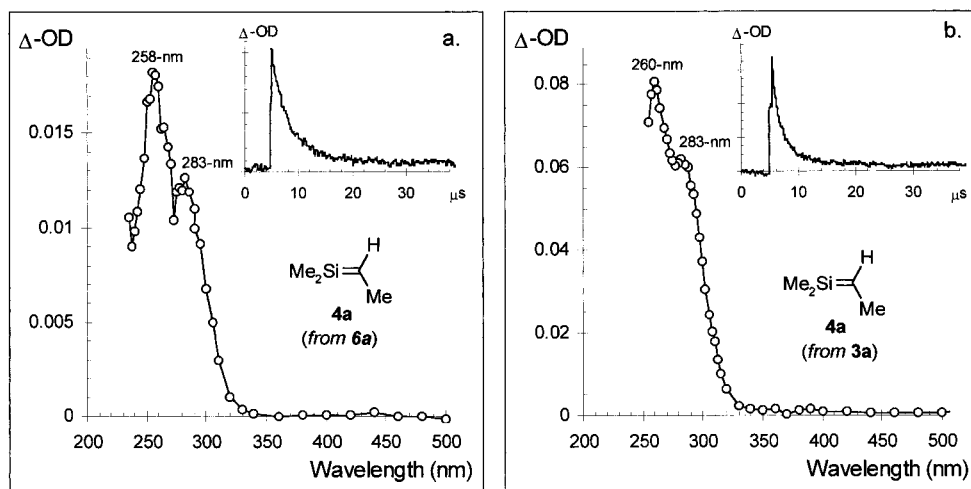*J. Am. Chem. Soc., Vol. 121, No. 20, 1999* 4747

Figure 1. Transient UV absorption spectra, from nanosecond laser flash photolysis of (trimethylsilyl)ketene (**6a**; a) and (trimethylsilyl)diazomethane (**3a**; b) in deoxygenated hexane solution at 23 °C. The spectra were recorded 0.1−1.0 μs after 193 nm (a) or 248 nm (b) excitation. Typical decay traces, recorded at a monitoring wavelength of 255 nm, are shown as Inserts.

Scheme 1
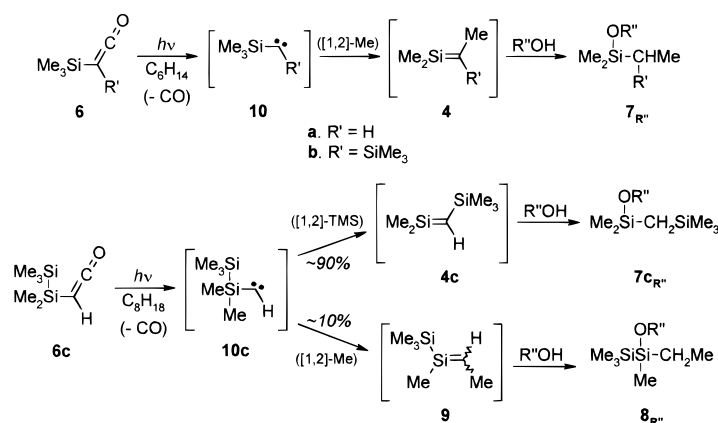
transient, though it exhibited a similar spectrum and decay characteristics (see Figure 1b) to the transient obtained by 193 nm laser photolysis of the silylketene **6a**. The difference in signal strengths obtained in the flash photolysis experiments with **3a** and **6a** is at least partially due to the fact that the 248 nm (KrF) line is 3−6 times more intense than the 193 nm (ArF) line, with the laser employed for these experiments. Saturation of the solution with air or addition of 0.005 M 1,3-octadiene or 0.03 M triethylsilane had no effect on either the signal strength or the lifetime of the transient. As observed for the transient from 193 nm laser photolysis of **6a**, decay of that from **3a** proceeded with mixed pseudo-first- and second-order kinetics ($\tau > 3$ μs), which did not vary as a function of monitoring wavelength between 260 and 300 nm. A much weaker transient with the same absorption spectrum but shorter lifetime ($\tau \sim$ 500 ns) was also observed upon 351 nm laser flash photolysis of a deoxygenated 0.04 M hexane solution of **3a**. The spectra of the transient observed in these experiments are indistinguishable from that observed upon photolysis of **3a** in a hydrocarbon matrix at 77 K, which was assigned to 1,1,2-trimethylsilene (**4a**).[33]

Qualitative GC analysis of product mixtures from steady-state photolysis of hexane solutions of **3a** (0.01 M) and *t*-BuOH (0.24 M) with 214, 254, or 350 nm light indicated the presence of the expected alcohol trapping product **7a$_{Bu}$** in high chemical yields relative to those of other volatile products. This is consistent with the formation of silene **4a** in significant yields

from photolysis of **3a** at all three wavelengths. In addition, static UV analysis of the 350 nm photolyzate confirmed that diazirine **5a** is also formed at this wavelength, although its yield relative to **7a$_{Bu}$** was not determined. Interestingly, photolysis of **3a** in hexane with 419 nm light appeared to yield only the diazirine and less than a 5% total yield of higher molecular weight products which might be ascribable to carbene or silene dimerization.

Addition of MeOH or *t*-BuOH to the solutions of **3a** and **6a** caused a shortening of the transient lifetime and a change to clean pseudo-first-order decay kinetics. Plots of k_{decay} versus alcohol concentration exhibited positive curvature, indicative of a mixed first-order and higher order dependence of k_{decay} on [ROH]. The data from both experiments fit acceptably ($r^2 >$ 0.995) to the quadratic expression in [ROH] of eq 7, where k_0 is the pseudo-first-order rate constant for transient decay in the absence of ROH and k_{ROH} and k_{2ROH} are the second- and third-order rate constants for quenching of the transient(s) by the alcohol. For example, Figure 2 shows plots of k_{decay} vs [MeOH] for the quenching of the transient(s) from **6a** and **3a** by MeOH and the results of the least-squares fits to eq 7. The first-order

$$k_{decay} = k_0 + k_{ROH}[ROH] + k_{2ROH}[ROH]^2 \qquad (7)$$

coefficients from these analyses are the same within experimental error, which further suggests that the transient absorptions from the two precursors are due to the same species: k_{ROH}
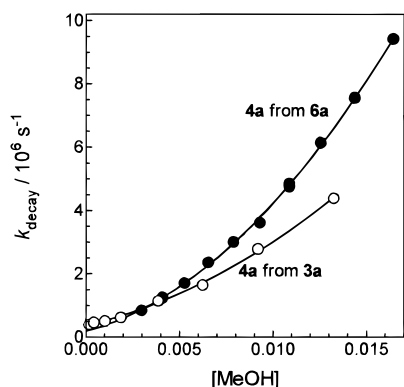
Figure 2. Plots of k_{decay} vs [MeOH] for quenching of silene **4a**, from 193 nm laser flash photolysis of (trimethylsilyl)ketene (**6a**) and 248 nm laser flash photolysis of (trimethylsilyl)diazomethane (**3a**) in deoxygenated methanolic hexane solutions at 23 °C.

$= (1.4 \pm 0.4) \times 10^8$ M^{-1} s^{-1} for the transient from ketene **6a** and $k_{ROH} = (1.6 \pm 0.5) \times 10^8$ M^{-1} s^{-1} for that from diazo compound **3a**. The two quenching plots shown in Figure 2 appear to deviate from one another at methanol concentrations above ∼0.005 M, leading to second-order coefficients (k_{2ROH}) which differ by a factor of ∼2. This difference is probably not significant, given the weakness of the signals observed in the far-UV LFP experiments with **6a**.

Laser flash photolysis of a deoxygenated hexane solution of (trimethylsilyl)diazirine (**5a**) with a nitrogen laser (337 nm, 6 ns, 6 mJ) also led to the formation of a transient, which in this case decayed over a time scale of ∼200 ns. The transient showed only edge absorption over the 275−290 nm range, below which screening of the monitoring beam by the precursor precluded detection of the transient and determination of its absorption maximum. Nevertheless, the lifetime of the transient was quenched by addition of small amounts of methanol, consistent with its assignment to silene **4a**.

Far-UV laser flash photolysis of deoxygenated hexane and isooctane solutions of **6b** and **6c**, respectively, also resulted in the formation of weak transient signals that decayed with pseudo-first-order kinetics and exhibited the UV spectra shown in Figure 3. The spectra are similar to those obtained from photolysis of the corresponding diazo compounds (**3b,c**) in hydrocarbon matrices at 77 K, which were assigned to 1,1,2-trimethyl-2-(trimethylsilyl)silene (**4b**) and 1,1-dimethyl-2-(trimethylsilyl)silene (**4c**).[32,33] As can be seen in Figure 3b, the transient decay profiles from **6c** showed a relatively long-lived residual absorption; the spectrum of this species is very similar to that of the prominent transient which we assign to silene **4c**. The residual absorption could be due to the isomeric silene **9**, which the steady-state results indicate is formed in ∼10% yield relative to **4c** (vide infra). On the basis of our previously reported study of the related silene **1i**[7b] and a comparison of the reactivities of **4a** and 1,1-dimethylsilene (**1a**),[7] silene **9** would be expected to exhibit such low reactivity toward nucleophiles that it could very well appear to be stable over the time scales employed for these experiments. Unfortunately, the transient signals obtained in LFP experiments with **6c** were too weak to investigate this further.

As with silene **4a**, the lifetimes of the transients from the two compounds were shortened upon addition of MeOH, *t*-BuOH, or their deuterated isotopomers to the solutions, consistent with their assignment to the silenes **4b,c**. In these cases, however, the variations in lifetime with alcohol concentration were steeper and plots of k_{decay} vs [ROH] were linear. Figure 4 shows the plots for quenching of **4b,c** by MeOH, along

Table 1. Absolute Rate Constants for Reaction of Silenes **4a−c** with MeOH and *t*-BuOH in Hexane and Acetonitrile Solution at 23 °C

| silene | λ_{max} (nm) | $k_{MeOH}/10^8$ M^{-1} s^{-1} | | $k_{t-BuOH}/10^8$ M^{-1} s^{-1} | |
		hexane	MeCN	hexane	MeCN
4a[a]	258, 283	1.4 ± 0.4	*b*	*b*	*b*
4a[c]	260, 283	1.6 ± 0.6^d	$0.28 \pm 0.03^{d,e}$	0.74 ± 0.25^f	0.03 ± 0.01^f
4b[g]	280	18 ± 1^h	5.3 ± 0.5	7.6 ± 0.7^i	1.1 ± 0.01
4c[g,j]	270	85 ± 6^k	*b*	30 ± 1	*b*

a Using (trimethylsilyl)ketene (**6a**) as precursor. Plots of k_{decay} vs [MeOH] were analyzed using eq 7, which afforded a second-order component of $k_{2MeOH} = (1.2 \pm 0.3) \times 10^{10}$ M^{-2} s^{-1}. *b* Not determined. *c* Using (trimethylsilyl)diazomethane (**3a**) as the precursor. *d* Quadratic in [MeOH] (see eq 7); $k_{2MeOH} = (2.5 \pm 0.3) \times 10^{10}$ M^{-2} s^{-1} in hexane and $(5.4 \pm 0.4) \times 10^8$ M^{-2} s^{-1} in MeCN. *e* Quenching by MeOD was slower: $k_{MeOD} = (1.8 \pm 0.8) \times 10^7$ M^{-1} s^{-1} and $k_{2MeOD} = (3.6 \pm 0.5) \times 10^8$ M^{-2} s^{-1}. *f* Quadratic in [*t*-BuOH] (see eq 7); $k_{2BuOH} = (1.1 \pm 0.2) \times 10^{10}$ M^{-2} s^{-1} in hexane and $(2.5 \pm 0.3) \times 10^7$ M^{-2} s^{-1} in MeCN. *g* k_{decay} varied linearly with [ROH] (see eq 8). *h* $k_H/k_D = 1.8 \pm 0.2$. *i* $k_H/k_D = 1.7 \pm 0.2$. *j* In isooctane solution. *k* $k_H/k_D = 1.3 \pm 0.2$.

Scheme 2
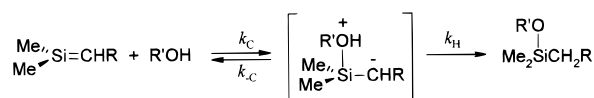
with the least-squares fits of the data to eq 8. The absolute rate constants obtained from these experiments are listed in Table 1.

$$k_{decay} = k_0 + k_{ROH}[ROH] \qquad (8)$$

Quenching of silenes **4a** and **4b** by MeOH, MeOD, and *t*-BuOH was also studied in air-saturated acetonitrile (MeCN) solution, using **3a** and **6b**, respectively, as the precursors. The silenes exhibited the same absorption maxima and decayed over similar time scales, and plots of k_{decay} vs [ROH] (available as Supporting Information) showed similar forms as in hexane solution. The absolute rate constants for reaction of **4a,b** with MeOH(D) and *t*-BuOH in this solvent are listed along with the hexane data in Table 1. Both silenes show the typical reduction in reactivity in acetonitrile compared to hydrocarbon solution, an effect which can be explained by weak Lewis acid−base complexation with the nitrile solvent.[22,47]

Substituent Effects on Silene Reactivity. The addition of alcohols to transient silenes proceeds by a mechanism involving reversible complexation of the alcohol at the silenic silicon atom followed by rate-controlling proton transfer from oxygen to carbon (Scheme 2), such that the overall second-order rate constant for reaction is given by the product of the rate constant for complexation (k_c) and the reactivity ratio describing the partitioning of the complex between free starting materials and the alkoxysilane product (eq 9).[6] In fact, a second mechanistic pathway is known to compete with this one at higher alcohol concentrations; it involves reaction of the complex with a second molecule of alcohol, probably by a deprotonation/protonation sequence which is identifiable as general base-catalyzed proton transfer.[19,20,22] This second pathway is recognizable in kinetic experiments in the form of a second-order dependence of the silene decay rate on alcohol concentration,[19,20] as is observed here for the reaction of **4a** with MeOH and *t*-BuOH in hexane and acetonitrile solution. Behavior of this type tends to be more common in silenes which show relatively low overall reactivity

(47) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W.; Venneri, P.; Conlin, R. T.; Dhurjati, M. S. K.; Ezhova, M. B. *J. Organomet. Chem.* **1998**, *561*, 19.
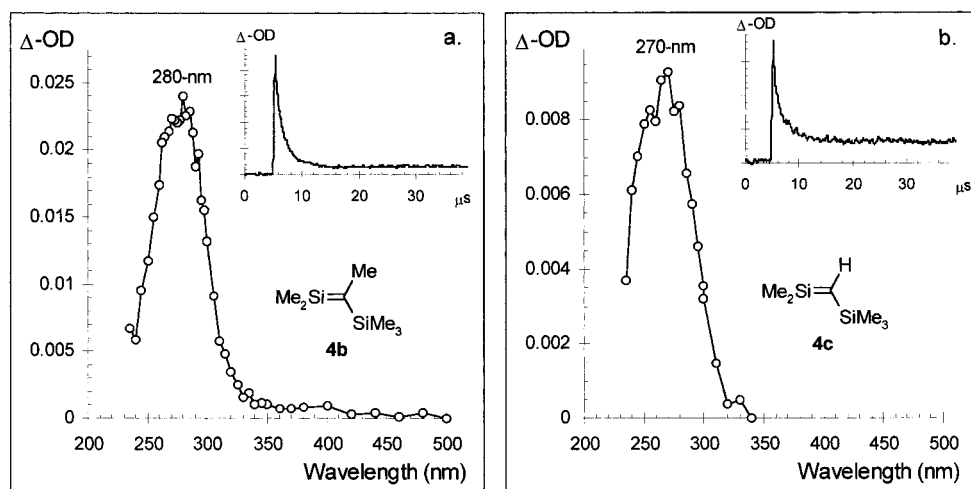
Figure 3. Transient UV absorption spectra, from far-UV (193 nm) laser flash photolysis of bis(trimethylsilyl)ketene (**6b**; a) and pentamethyldisilylketene (**6c**; b) in deoxygenated hexane and isooctane solution, respectively, at 23 °C. The spectra were recorded 0.1−1.0 μs after laser excitation. Typical decay traces, recorded at a monitoring wavelength of 255 nm, are shown as inserts.
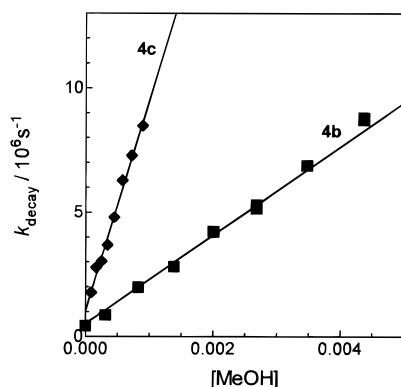

Figure 4. Plots of k_{decay} versus [MeOH], for the quenching of **4b,c** from 193 nm laser flash photolysis of bis(trimethylsilyl)ketene (**6b**) and pentamethyldisilanyl ketene (**6c**) in deoxygenated hexane and isooctane solution, respectively, at 23 °C.

toward silene traps, i.e. in those derivatives for which k_{MeOH} is on the order of 10^8 M^{-1} s^{-1} or less.[19,20,47] Indeed, it is not observable for the more reactive silene derivatives **4b,c** at the alcohol concentrations employed in our kinetic experiments. We thus confine our attention to k_{ROH}, the overall second-order rate constant given by eq 9, which is common to all derivatives in the series.

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

The three transient silenes studied in this work (**4a−c**), combined with 1,1-dimethylsilene (**1a**),[7] 1,1-dimethyl-1,3-(1-sila)butadiene (**4d**),[46] and 1,1-dimethyl-2-(trimethylsilyl)methylsilene (**4e**),[47] form a homologous series of 2-substituted 1,1-
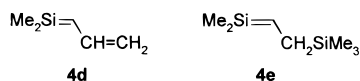
dimethylsilene derivatives whose reactivities with MeOH and *t*-BuOH have all been determined quantitatively in hydrocarbon solution. The rate constants for reaction with the two alcohols correlate reasonably well with the sum of the resonance substituent parameters $\sigma_R°$ of the 2-substituents,[48] as illustrated in Figure 5. The slopes of the plots afford ρ_R values of $+8.0 \pm$
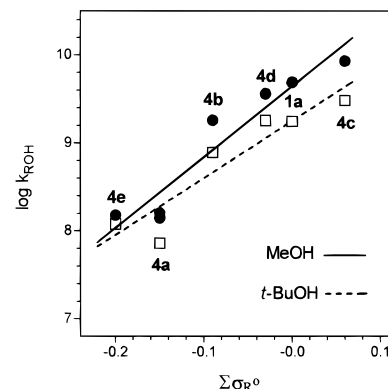
Figure 5. Plot of log k_{ROH} versus the resonance substituent parameter $\sigma_R°$ for the quenching of substituted 1,1-dimethylsilenes **1a** and **4a−e** by MeOH (●) and *t*-BuOH (□) in hexane or isooctane solution at 23 °C. The data for **1a**, **4d**, and **4e** are from refs 7, 46, and 47, respectively.

2.2 for MeOH (r^2 0.909) and $+6.5 \pm 2.6$ for *t*-BuOH (r^2 0.866), where the errors are given as twice the standard deviations from the least-squares analyses of the data. In contrast to what was found with **1a−i**,[8] no significant improvement in the correlations are observed when the linear free energy relationship is expanded to include inductive and/or steric substituent parameters in addition to the resonance parameters.

The large positive ρ_R values are consistent with the conclusions of Apeloig and Karni, made on the basis of ab initio calculations for a series of 2-substituted silene derivatives (H$_2$-Si=CHR),[15] that resonance electron donor substitution at carbon should result in kinetic stabilization of the Si=C bond. According to these calculations, substituents of this type reduce the natural ($^{\delta+}$Si=C$^{\delta-}$) polarity of the bond through effects on both the positive charge density at silicon and the negative charge density at carbon. The present results suggest that the electronic effect of substituents at carbon is dominated by resonance effects, with inductive and steric effects being of relatively low importance. This conclusion must be tempered somewhat by the narrow range in inductive electron-donating/-withdrawing power of these particular substituents and also by the fact that the most reactive derivative in the series (**4c**)

(48) The values employed for these substituents are: Me, −0.15; SiMe$_3$, 0.06; CH=CH$_2$, −0.03; CH$_2$SiMe$_3$, −0.20. See: Wayner, D. D. M. In *CRC Handbook of organic photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; pp 395−400.

exhibits rate constants which are very close to the diffusion rate ($k_{diff} \sim 2.1 \times 10^{10}$ M^{-1} s^{-1} in hexane at 23 °C). While steric effects vary considerably throughout the series of substituents,[49] they appear to have little effect on the reactivity of the Si═C bond in these compounds.

Relative to hydrogen, resonance electron-donating substituents at carbon can be expected to reduce the rate of complexation (k_C), but enhance the reactivity of the complex with respect to both proton transfer (k_H) and reversion to free reactants (k_{-C}). All three of these processes are kinetically significant, as evidenced by the fact that small primary deuterium isotope effects are observed for every compound in the series (e.g., for **1a**, $k_H/k_D = 1.5 \pm 0.1$ in hexane at 23 °C[7a]). These elementary rate constants obviously cannot be extracted from k_{MeOH} with the data we have available, but it is possible to define the magnitudes of k_C and the complex partitioning ratio ($P = k_H/[k_H + k_{-C}]$) within certain limits when the temperature dependence of k_{MeOH} is known. For example, the reaction of MeOH with 1,1-dimethylsilene **1a** exhibits a negative Arrhenius activation energy ($E_a = -2.6 \pm 0.3$ kcal/mol[7a]), indicating that k_H is predominantly entropy-controlled. For a reaction mechanism of this type, a negative E_a is observed over the temperature range where $P < 0.5$.[6] Thus, because k_{MeOH} for this compound is roughly a factor of 4 less than the diffusion rate in hexane at 23 °C,[7a] it can be concluded that $0.5k_{diff} < k_C \le k_{diff}$ and $0.5 > P \ge 0.25$.[6] While we have not determined the temperature dependence of k_{MeOH} for any of the other compounds in the series (except **4d**,[46] whose overall reactivity and E_a do not differ much from those of **1a**), we can get some idea of how P varies throughout the series from the isotope effects on k_{MeOH} (Table 1). These increase in magnitude as overall reactivity decreases, a trend which is due either to an increase in the isotope effect on k_H or a decrease in P with decreasing k_{MeOH} (or both). A similar trend in KIE is observed for the series of Si-substituted silenes **1a−i**, for which the Arrhenius activation energies vary between −0.8 kcal/mol for the most reactive and −3.6 kcal/mol for the least reactive silenes in the series (**1h** and **1i**, respectively).[7b] Since the magnitude of the KIE increases as E_a becomes more negative, it can be concluded that for Si-substituted silenes at least, the increase in the KIE as overall reactivity decreases is due primarily to a reduction (of indeterminable magnitude) in P. We conclude that π-donor substituents at carbon most likely reduce k_{MeOH} through cooperative reductions in both the rate constant for complexation (k_C) *and* the complex partitioning ratio, P. Since π-donors at carbon would be most reasonably expected to *enhance* k_H, then we further conclude that any effect on k_H must be compensated for by an effect on k_{-C} which is in the same direction and is of equal to or greater magnitude to the effect on k_H. Operationally then, the main effect of substituents at carbon appears to be on the complexation step of the reaction (k_C and k_{-C}), which can be most simply understood in terms of substituent-induced variations in the degree of electrophilicity at silicon.

Substituent correlations aside, one definitive conclusion that can be derived from these and our previously published data for 1-substituted 1-methylsilenes[8] concerns the effect of trialkylsilyl substitution at silicon and carbon on silene reactivity. 1,1-Dimethyl-2-(trimethylsilyl)silene (Me$_2$Si═CHSiMe$_3$; **4c**) reacts with methanol almost 2 orders of magnitude faster than 1-methyl-1-(trimethylsilyl)silene (Me(Me$_3$Si)Si═CH$_2$; **1i**) in hexane solution, a difference which is almost certainly truncated by diffusion in the case of **4c**, as mentioned above. Compared to hydrogen, the −SiMe$_3$ substituent provides kinetic stabiliza-

tion of the Si═C bond when it is attached to silicon and destabilization when attached to carbon. It is interesting to note the structural relationship between **4c** and the well-known isolable silene of N. Wiberg (**11a**).[11,12] Steric effects clearly contribute significantly to the kinetic stability of this silene, since the bis(trimethylsilyl) derivative **11b** is not isolable.[17,50] In fact,

Me$_2$Si═C(SiMe$_3$)(SiMe(t-Bu)$_2$)   Me$_2$Si═C(SiMe$_3$)(SiMe$_3$)

11a   **11b**
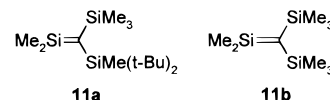
the results reported here suggest that steric effects in **11a** must be enormous and far overshadow the intrinsic kinetic destabilization afforded by the two silyl substituents at carbon and the two methyl groups at silicon. Although it possesses considerable historical significance due to Wiberg's classic determination of relative rate constants for its reaction with a wide variety of reagents,[17] silene **11b** has never been detected directly in fluid solution and the quantitative aspects of its reactivity are still unknown.

Intermediacy of (Trimethylsilyl)carbene (10a) in the Formation of Silene 4a. Inspection of the transient absorptions from flash photolysis of the three precursors to silene **4a** (**3a**, **5a**, and **6a**) at very short time scales showed that the silene is formed within the duration of the laser pulse (6−20 ns) in all cases. The nitrogen laser which was employed for experiments with **5a** has the shortest pulse width of the three (ca. 6 ns). Thus, a lower limit of ca. 2×10^8 s^{-1} can be assigned to the first (or pseudo-first)-order decay rate constant of the immediate precursor(s) to the silene, which can be identified as either the lowest excited singlet states of the precursors and/or singlet (trimethylsilyl)carbene (**10a**; Scheme 1).

Laser flash photolysis of solutions of ketene **6a** and diazirine **5a** in hexane containing 1−10 M pyridine led to the formation of weak absorptions centered at 370−390 nm, whose growths were unresolvable from the laser pulse in every case. They were characterized by a minor initial decay ($\tau \sim 1$ μs) to a residual absorption that comprised >70% of the total initial value and appeared to be stable for at least several hundred microseconds. Laser (308 nm) photolysis of hexane−pyridine mixtures containing ketene **6a** led to the strongest such absorptions, the spectrum of which is shown in Figure 6a. The spectrum is typical of alkylcarbene−pyridine ylides,[41,51−54] and we thus assign it to the pyridine ylide of (singlet) (trimethylsilyl)carbene (**11**; see Scheme 3). The quantum yield of the ylide, as measured by the residual Δ-OD at 370 nm (Δ-OD$_{370}$), increased with increasing pyridine concentration in the manner shown in Figure 6b. Under conditions of constant laser intensity, the functional dependence of Δ-OD$_{370}$ is given by eq 10, where C is a

$$(\Delta\text{-OD})_{370} = Ck_{PYR}\tau_{10a}[\text{PYR}]/(1 + k_{PYR}\tau_{10a}[\text{PYR}]) \quad (10)$$

(constant) function of the incident laser intensity, the quantum yield of the species being quenched by pyridine, the extinction coefficient of the 370 nm absorption, and the static absorptivity of the solution at the laser wavelength and k_{PYR} is the second-order rate constant for quenching of the carbene by pyridine.

(49) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91.

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(53) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.
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Substituent Effects on Reactivity of Si=C

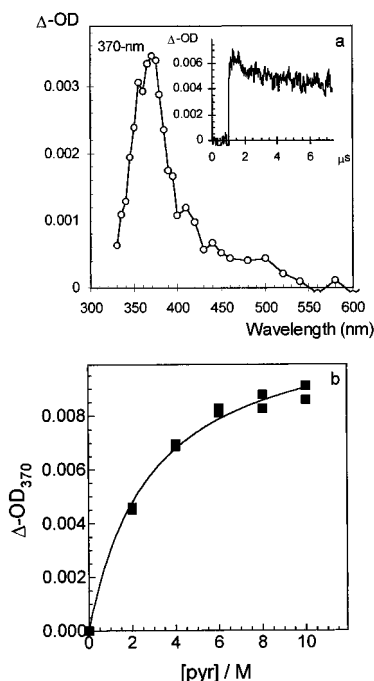*J. Am. Chem. Soc., Vol. 121, No. 20, 1999* 4751

Figure 6. (a) Time-resolved UV absorption spectrum from 308 nm laser flash photolysis of a deoxygenated hexane solution of ketene **6a** in the presence of pyridine (2 M). The Insert shows a typical transient decay profile, recorded at 370 nm. (b) Plot of the residual Δ-OD at 370 nm versus pyridine concentration. The solid line shows the results of nonlinear least-squares fit of the data to eq 10.

Scheme 3
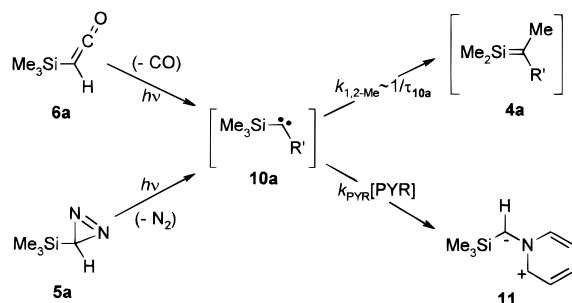
Nonlinear least-squares analysis of the data of Figure 6b according to eq 10 affords $k_{PYR}\tau_{10a} = 0.35 \pm 0.08$ M^{-1} (r^2 0.991), where the error is calculated as twice the standard deviation.

Similar experiments with diazirine **5a** (308 or 337 nm excitation) gave rise to similar but much weaker absorptions in the 350−400 nm range, even in the presence of 8 M pyridine. The spectrum, an example of which is available as Supporting Information, exhibited a maximum at ∼390 nm. The apparent shift in the absorption maximum relative to that observed with **6a** is simply attributable to bleaching of the diazirine, which is observable in the spectrum as a negative absorption at wavelengths below 360 nm. A plot of $(\Delta$-OD$)_{370}$ vs [PYR] (see the Supporting Information) exhibited a form similar to that shown in Figure 6b from **6a**. Least-squares analysis of the data according to eq 10 afforded $k_{PYR}\tau_{10a} = 0.33 \pm 0.10$ M^{-1} (r^2 0.939), in excellent agreement with the value obtained from experiments with ketene **6a**.

No absorptions suggestive of pyridine ylide formation were observed from 351 nm flash photolysis of **3a** in hexane containing 3−8 M pyridine. It is interesting to note that, while no trappable carbene is formed upon photolysis at this wave-

length, silene **4a** *is* clearly formed. This suggests that with long-wavelength excitation (at least) silene formation from **3a** occurs largely by a direct excited-state reaction. Unfortunately, the absorption spectrum of this compound does not permit pyridine trapping experiments to be carried out at shorter wavelengths.[29] A significantly more quantitative experimental approach would be required to establish the relative contributions of the carbene and direct excited-state pathways for silene formation from **3a** and **5a** at various excitation wavelengths, which is beyond the scope of the present work. This mechanistic duality is quite common in the photochemistry of alkyldiazo compounds and diazirines, however.[39−42] Nevertheless, our results for **5a** and **6a** suggest very strongly that, in these two cases, silene formation occurs via the intermediacy of singlet (trimethylsilyl)-carbene (**10a**), at least to some extent.

Assuming a value of k_{PYR} in the range typically assumed for other alkyl- and dialkylcarbenes ($k_{PYR} = (1-5) \times 10^9$ M^{-1} s^{-1}),[41,51−54] the results of the pyridine probe experiments with these two compounds lead to an estimate of 0.07−0.4 ns for the lifetime of carbene **10a** in deoxygenated hexane solution at 23 °C in the absence of added pyridine and, hence, to an estimate of $k \sim (8 \pm 6) \times 10^9$ s^{-1} for the first-order rate constant for its decay. This rate constant is the sum of the pseudo-first-order rate constants for all processes contributing to the decay of the carbene: intersystem crossing to the triplet state and [1,2]-methyl migration to form silene **4a** (bimolecular reaction with the carbene precursor can be neglected at the low precursor concentrations employed for experiments with **6a**). However, we note that triplet carbene-derived products could not be detected in significant yields (i.e., >ca. 5% relative to that of **7a$_{Bu}$**) in the photolysis of **6a** in the presence of *t*-BuOH, suggesting that intersystem crossing is much slower than silene formation. We can thus approximate the rate constant for [1,2]-methyl migration in (trimethylsilyl)carbene as $k_{1,2-Me} \sim (8 \pm 6) \times 10^9$ s^{-1}.

Summary and Conclusions

Photolysis of (trimethylsilyl)-, bis(trimethylsilyl), and pentamethyldisilanylketene (**6a−c**, respectively) in hydrocarbon solution results in the formation of transient silenes, formally via [1,2]-methyl or -trimethylsilyl migration in the α-silylcarbene formed by photodecarbonylation of the excited ketene. The silenes have been trapped as the corresponding alkoxysilanes by methanol and/or *tert*-butyl alcohol and detected directly using far-UV (193 nm) laser flash photolysis techniques. Absolute rate constants for reaction of the silenes with methanol and *tert*-butyl alcohol have been determined and compared to those for reaction of three other homologous 2-substituted 1,1-dimethylsilenes under similar conditions. Correlation of the rate constants with the resonance substituent parameter $\sigma_R°$ leads to reaction constants on the order of $\rho_R \sim +8$ for both alcohols, indicating that the reactivity of the Si=C bond in simple silenes is enhanced by resonance electron-acceptor substituents at carbon.

As with silylketene **6a**, laser flash photolysis of (trimethylsilyl)diazomethane (**3a**) and (trimethylsilyl)diazirine (**5a**) also leads to transient absorptions assignable to 1,1,2-trimethylsilene (**4a**). Experiments with **3a** in acetonitrile solution allow study of the effects of solvent polarity and isotopic substitution on the reactivity of this silene with alcohols, and the results are similar to those reported previously for other transient silenes.[20,22,47,55]

(55) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.

Laser flash photolysis of **5a** and **6a** in hexane−pyridine mixtures results in the formation of "stable" absorptions centered at 370 nm, which are assigned to the pyridine ylide of singlet (trimethylsilyl)carbene (**11**). From the variation in the yield of the ylide as a function of pyridine concentration, a value of 0.07−0.4 ns is estimated for the lifetime of the carbene in deoxygenated hexane solution at room temperature, assuming a value of $k = (1-5) \times 10^9$ M^{-1} s^{-1} for the rate constant for pyridine trapping of the carbene. This affords an estimate of $k_{1,2-Me} \sim (8 \pm 6) \times 10^9$ s^{-1} for the rate constant for formation of 1,1,2-trimethylsilene by [1,2]-methyl migration in the carbene intermediate, a value comparable to those for [1,2]-*hydrogen* migration in simple alkyl- and dialkylcarbenes.[56] In the case of the nitrogenous precursors at least, silene formation probably also occurs by a competing, direct excited-state pathway. The product distribution obtained from photolysis of pentamethyl-disilanylketene (**6c**) in the presence of alcohols suggests that [1,2]-trimethylsilyl migration in disilanylcarbenes is almost 10 times faster than [1,2]-methyl migration.

Further studies of the photochemistry of α-silylcarbene precursors and the reactivity of the corresponding carbenes and silenes are in progress.

Experimental Section

Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer interfaced to a Pentium microcomputer. Gas chromatographic (GC) analyses were carried out using a Hewlett-Packard 5890II+ gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and DB1 or DB1701 megabore capillary columns (15m × 0.53 mm; Chromatographic Specialties, Inc.). Mass spectra and GC/MS analyses were recorded on a Hewlett-Packard 5890II gas chromatograph equipped with an HP-5971A mass selective detector and a DB5 fused silica capillary column (30m × 0.25 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 3.8% UCW982 on 80/100 Supelcoport (24 ft × 0.25 in.; Supelco, Inc.) stainless steel column.

2,2,4-Trimethylpentane (isooctane) and hexane (BDH Omnisolv) both exhibited an absorbance of <0.2 at 193 nm in a 3 mm cell and were used without further purification. Methanol, methanol-*O-d*, and *tert*-butyl alcohol were of the highest purity available and were used as received from Aldrich Chemical Co. Pyridine (BDH Reagent) was distilled from anhydrous barium oxide. Ethyldimethylchlorosilane was used as received from Aldrich Chemical Co. (Trimethylsilyl)diazomethane (**3a**) was obtained from Aldrich as a 2 M solution in hexane and was purified by semipreparative gas chromatography. (Trimethylsilyl)diazirine (**5a**) was prepared by photolysis of an argon-saturated 0.2 M solution of **3a** in pentane, in a Rayonet reactor fitted with 10 RPR-419X lamps (419 nm). The progress of the photolysis was followed by UV spectroscopy and GC and continued to >97% conversion of the diazo compound. The resulting solution was concentrated by careful distillation and then re-diluted with hexane or hexane/pyridine mixtures to an appropriate concentration for laser flash photolysis experiments (0.04−0.1 M).

The silylketenes **6a**−**c** were prepared as described previously[43,57] and were purified by semipreparative GC, affording samples of >99% purity as estimated by capillary GC. Ethyldimethyl-*tert*-butoxysilane (**7a_Bu**) was prepared by reaction of ethyldimethylchlorosilane with *tert*-butyl alcohol and triethylamine in ether, purified by preparative GC, and identified on the basis of spectroscopic data: ^{1}H NMR δ 0.064 (s, 6H), 0.507 (q, 2H), 0.905 (t, 3H), 1.220 (s, 9H); ^{13}C NMR δ 0.35, 6.97, 10.39, 32.03, 71.88; MS *m/z*(I) = 160 (0.05), 145 (15), 131 (19), 89 (20), 87 (22), 75 (100), 61 (22), 59 (21), 45 (13). Dimethyl-

((trimethylsilyl)methyl)methoxysilane (**7c_Me**) was available from a previous study.[8]

1-Ethyl-1-methoxy-1,2,2,2-tetramethyldisilane (**8_Me**) was prepared from 1-ethyl-1-phenyl-1,2,2,2-tetramethyldisilane by the method of Auner and co-workers.[58] 1-Ethyl-1-phenyl-1,2,2,2-tetramethyldisilane was prepared by reaction of (ethylmethylphenylsilyl)lithium and trimethylchlorosilane in anhydrous tetrahydrofuran, using the general procedure of Gilman and co-workers.[59] The compound was isolated as a colorless liquid (bp 50−54 °C, 10.2 mmHg) and identified on the basis of the following spectroscopic data: ^{1}H NMR δ 0.07 (s, 9H), 0.31 (s, 3H), 0.89 (m, 2H), 1.00 (m, 3H), 7.32 (m, 3,H), 7.43 (m, 2H); ^{13}C NMR δ −6.74, −1.78, 5.41, 8.18, 127.68, 128.26, 134.06, 138.56; IR (neat) 3068.0 (w), 2952.6 (s), 2893.4 (m), 1427.3 (m), 1245.8 (s), 1104.5 (s), 1010.3 (m), 859.3 (s), 834.2 (s), 782.8 (s) 720.4 (m); MS *m/z*(I) = 222 (18), 193 (15), 179 (11), 149 (34), 135 (44), 121 (100), 105 (25), 73 (22); HRMS calcd for C$_{12}$H$_{22}$Si$_2$ 222.1260, found 222.1261. The disilane (7.1 g, 0.032 mol) was dissolved in pentane (30 mL) in a flame-dried 100-mL two-neck round-bottom flask equipped with a reflux condenser, nitrogen inlet, rubber septum, and magnetic stirrer. The solution was cooled with an ice bath, and trifluoromethanesulfonic acid (2.83 mL, 0.032 mol) was added via syringe. The mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature, after which it was stirred for another 30 min. The mixture was then recooled to 0 °C, and a solution of sodium methoxide in methanol (prepared from sodium (1.3 g) and 10 mL of anhydrous methanol) was added slowly, resulting in the formation of a white precipitate. The mixture was stirred for an additional 1 h and then filtered. After evaporation of solvent, the product was distilled under vacuum to yield a colorless oil (2.2 g, 0.0125 mol, 39%; bp 58 °C, 70 mmHg) which was identified as **8_Me** on the basis of the following spectroscopic data: ^{1}H NMR δ 0.093 (s, 9H), 0.147 (s, 3H), 0.678 (q, 2H), 0.961 (t, 3H), 3.411 (s, 3H); ^{13}C NMR δ −3.613, −1.546, 6.832, 7.863, 51.415; IR (neat) 2953.9 (s), 2879.1 (s), 2827.3 (s) 1460.5 (m), 1246.5 (s), 1186.6 (w), 1087.1 (s), 1008.7 (m), 864.9 (m), 834.5 (m), 776.8 (m), 734.5 (m); MS *m/z*(I) = 176 (1.2), 161 (19), 147 (11), 133 (100), 117 (16), 103 (14), 75 (30), 73 (27), 59 (34).

Preparative-scale photolysis of **6b** in the presence of MeOH was carried out on a deoxygenated 15 mL sample of the ketene (0.032 M) and the alcohol (0.8 M) in hexane. The solution was placed in two 1 cm × 15 cm quartz tubes, which were then sealed with rubber septa, deoxygenated with a stream of argon, and placed in a merry-go-round surrounding a 16 W zinc resonance lamp (214 nm; Philips 93106E). Irradiation of the solutions for 18 h resulted in the formation of a very clean mixture of **6b** and a single product in a ∼1:2 ratio by capillary GC. The solvent was removed on the rotary evaporator, and the components were then separated by semipreparative GC. The product, which was isolated in 99.3% purity (by capillary GC) after this procedure, was identified as 1-(methoxydimethylsilyl)-1-(trimethylsilyl)-ethane (**7b_Me**) on the basis of the following spectroscopic data: ^{1}H NMR δ −0.130 (q, 2H), 0.084 (d, 6H), 0.090 (s, 9H), 1.018 (d, 3H), 3.224 (s, 3H); ^{13}C NMR δ −2.096, −1.950, −0.896, 8.026, 8.897, 49.963; ^{29}Si NMR δ 2.49, 18.82; MS *m/z* = 176 (20), 175 (100), 147 (7), 131 (5), 117 (6), 89 (46), 73 (20), 59 (35), 45 (11).

Analytical-scale photolyses were carried out using the 16 W zinc lamp or in a Rayonet reactor containing five RPR-3000 lamps. Aliquots of hexane or isooctane solutions containing **6** (0.01 M) and methanol or *tert*-butyl alcohol (0.5 M) were placed in Suprasil quartz cuvettes (3-mm × 10-mm), sealed with rubber septums, and saturated with dry argon. One tube was left in the dark to monitor ground-state esterification over a time period of 5−10 h; this was found to be significant only for **6a** in the presence of methanol. The others were irradiated in a merry-go-round for periods of up to 1 h, with periodic monitoring of the photolyzates by capillary GC. Products were identified by capillary GC co-injection with authentic samples of the corresponding alkoxysilanes.

Nanosecond laser flash photolysis experiments employed a microcomputer-controlled detection system[6,60] and the pulses from a Lu-

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monics 510 excimer laser filled with Ar/F$_2$/He (193 nm; ca. 15 ns; 20 mJ) or Kr/F$_2$/He (248 nm; ca. 20 ns; 55 mJ) mixtures, a Lumonics 760M excimer laser filled with Xe/HCl/He (308 nm; ca. 15 ns; 45 mJ) or N$_2$/He (337 nm; 6 ns; 5 mJ) mixtures, or a Lambda Physik Compex 120 excimer laser filled with Xe/F$_2$/Ne (351 nm, 25 ns; 15 mJ). For 193 nm experiments, the laser beam was focused on the front face of the sample compartment using a single 193 nm dichroic mirror and a Suprasil lens, and the intensity of the beam was reduced to <2 mJ at the cell using a series of stainless steel wire meshes as neutral density filters. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was ca. 0.7 and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Dry nitrogen was bubbled continuously through the reservoir throughout the experiments. Solution temperatures were controlled to within 0.1 °C with a VWR 1166 constant-temperature circulating bath plumbed to a brass sample holder and measured with a Teflon-coated copper/constantan thermocouple which was inserted directly into the flow cell. Quenchers were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (six or more points) which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

Supporting Information Available: Figures giving plots of k_{decay} vs [ROH], UV absorption spectrum of **5a**, and plot of (Δ-OD)$_{370}$ vs [PYR] (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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