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# Substituent Effects on the Reactivity of the Silicon−Carbon Double Bond. Resonance, Inductive, and Steric Effects of Substituents at Silicon on the Reactivity of Simple 1-Methylsilenes

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**Abstract:** The reactivities of a series of substituted 1-methylsilenes RMeSi=$CH_2$ (R = H, methyl, ethyl, *t*-butyl, vinyl, ethynyl, phenyl, trimethylsilyl, and trimethylsilylmethyl) in hydrocarbon solvents have been investigated by far-UV (193-nm) laser flash photolysis techniques, using the corresponding 1-methylsilacyclobutane derivatives as silene precursors. Each of these silacyclobutanes yields ethylene and the corresponding silene, which can be trapped as the alkoxysilane $RSiMe_2OR'$ cleanly upon 193- or 214-nm photolysis in solution in the presence of aliphatic alcohols. UV absorption spectra and absolute rate constants for reaction of the silenes with methanol, ethanol, and *t*-butyl alcohol have been determined in hexane solution at 23 °C. The rate constants vary from a low of $3 \times 10^7$ $M^{-1}$ $s^{-1}$ for reaction of 1-methyl-1-trimethylsilylsilene with *t*-BuOH to a high of $1 \times 10^{10}$ $M^{-1}$ $s^{-1}$ for reaction of 1-ethynyl-1-methylsilene with MeOH. In several cases, rate constants have been determined for addition of the deuterated alcohols, and for addition of methanol over the 0−55 °C range. Invariably, small primary deuterium kinetic isotope effects and negative Arrhenius activation energies are observed. These characteristics are consistent with a mechanism involving reversible formation of a silene−alcohol complex which collapses to alkoxysilane by unimolecular proton transfer from oxygen to carbon. Silene reactivity increases with increasing resonance electron-donating and inductive electron-withdrawing ability of the substituents at silicon and is significantly affected by steric effects within this series of compounds. This is suggested to be due to a combination of effects on both the degree of electrophilicity at silicon (affecting the rate constants for formation and reversion of the complex) and nucleophilicity at carbon (affecting the partitioning of the complex between product and free reactants). Two 1-methyl-1-alkoxysilacyclobutanes were also investigated, but proved to be inert to 193-nm photolysis.

## Introduction

While there has been considerable experimental and theoretical interest over the past thirty years in the properties of the silicon−carbon double bond,[1−4] there have been relatively few quantitative studies of the reactivity of simple silenes in either the gas phase[5−7] or solution.[8−12] Perhaps the best known of the early attempts to quantify silene reactivity is that of Wiberg, who employed simple competition methods to determine relative rate constants for reaction of the transient 1,1-dimethyl-2,2-bis(trimethylsilyl)silene (**1**) with a large number of oxygen, nitrogen, and carbon nucleophiles in ether solution at low temperatures.[13]

$$Me_2Si{=}C(SiMe_3)_2$$

**1**

More recently, several groups have reported absolute rate constants for silene trapping reactions in solution, using laser flash photolysis techniques to generate transient silenes under conditions where they can be detected directly.[8−12,14−21] These studies have been useful in establishing the more quantitative aspects of silene reactivity and have provided detailed informa-

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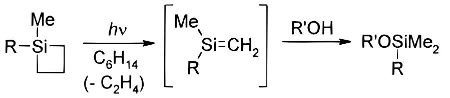
tion on the mechanisms of the reaction of silenes with alcohols[10,18,20,22] and ketones,[9,19,23,24] two of the most widely used reagent types for the trapping of reactive silenes in solution.[1−4]

Relatively few studies, however, have been directed at developing an understanding of the effects of substituents at either silicon or carbon on silene reactivity. Until recently,[22,24] the only systematic investigations of this type have been theoretical.[25−27] The most comprehensive of these is that of Apeloig and Karni, who employed ab initio (6-31G*//3-21G) calculations to examine the geometries, charge distributions, and frontier molecular orbital properties of a number of simple silenes with substituents encompassing a wide range of donor/acceptor strength at silicon and carbon.[25] By considering the structures of the few stable silenes that were known at the time in light of the results of their calculations, they proposed that the polarity of the Si═C bond is the most important factor in controlling its reactivity; $\pi$-electron acceptor and $\sigma$-electron donor substituents at silicon and/or $\pi$-electron donors and $\sigma$-electron acceptors at carbon were suggested to lead to increased kinetic stability because these substituents act to reduce both the degree of positive $\pi$-charge at silicon and the degree of negative $\pi$-charge at carbon. Nagase and co-workers came to similar conclusions on the basis of a theoretical examination of the addition of water and HCl to $H_2Si{=}CH_2$, $Me_2Si{=}CH_2$, $F_2Si{=}CH_2$, and $H_2Si{=}CHOH$, using ab initio calculations at a slightly higher level of theory.[27]

These ideas might be tested quantitatively through the use of laser flash photolysis techniques to generate reactive silenes in solution under conditions where they can be detected directly, and absolute rate constants for their reactions with various silene traps can be measured. Recently, we reported studies of the effects of aryl substituents on the absolute rate constants and Arrhenius parameters for reaction of 1,1-diphenylsilene with alcohols, acetic acid and acetone in solution.[22,24] These reactions are all initiated by nucleophilic attack at silicon, with transfer of a proton to the silenic carbon occurring in a subsequent step.[10,13,16,18,20,27−32] Small positive Hammett $\rho$-values were observed, indicating that substitution with electron-withdrawing groups on the phenyl rings attached to silicon *increases* reactivity toward these reagents. This would appear to contradict theoretical predictions, unless remote substituents at the silicon end of the Si═C bond in these compounds exert mainly an inductive effect on the degree of positive charge character at silicon.[25−27]

With the intent of obtaining experimental data more directly relevant to previous theoretical work in this area, we have undertaken a study of the effects on silene reactivity of several substituents *directly* attached to silicon, using a series of 1-substituted 1-methylsilacyclobutanes (**2a**−**k**; see eq 1) as silene precursors and absolute rate constants for their reactions with aliphatic alcohols as a gauge of their kinetic stabilities. The substituents were chosen to span as wide a range in inductive and resonance electronic properties as possible, within the limitations defined by the ease of synthesis and hydrolytic stability of the required silacyclobutane precursors.



(1)

**2** **3** **4**

**a**. R = Me
**b**. R = Ph
**c**. R = H
**d**. R = Et
**e**. R = *t*-Bu
**f**. R = $CH_2SiMe_3$
**g**. R = $CH{=}CH_2$
**h**. R = $C{\equiv}CH$
**i**. R = $SiMe_3$
**j**. R = OMe
**k**. R = $OSiMe_3$

The first two members of the series, 1,1-dimethylsilene (**3a**)[21] and 1-methyl-1-phenylsilene (**3b**),[24,33] have been studied by us previously by laser flash photolysis techniques, using the corresponding silacyclobutanes (**2a,b**) as precursors. All of the nine additional methylsilacyclobutanes chosen for study in the present work can be expected to (and do) exhibit absorption characteristics similar to **2a**, necessitating the use of far UV steady-state[34] and time-resolved[12,21] photochemical techniques for the study of their photochemistry and the UV absorption spectra and reactivity of the resulting methylsilenes in hydrocarbon solution. As will be shown below, all but the two alkoxy-substituted derivatives (**2j,k**) yield the corresponding silenes cleanly upon 193-nm photolysis in solution. The main limitation of the far-UV flash photolysis technique arises from the necessity for transient quenchers to be transparent at the excitation wavelength, limiting the list to water, aliphatic alcohols, or other nonabsorbing small molecules. Fortunately, the addition of alcohols is mechanistically the best understood of the many characteristic reactions of silicon−carbon double bonds and thus provides an excellent quantitative tool for studies of the reactivities of simple silenes in solution.

## Results

The ultraviolet absorption spectra of **2c**−**k** were recorded in argon-saturated isooctane or hexane solutions. As expected, the spectra of all but **2g,h** show only edge absorption above 190 nm, while those of the vinyl- and ethynyl-substituted compounds (**2g,h**) exhibit absorption maxima of 195 and 200 nm, respectively. Molar extinction coefficients at 193 nm, determined from the slopes of plots of absorbance vs concentration, were found to vary between ∼500 and ∼2500 $M^{-1}$ $cm^{-1}$, depending on the substituent.

Direct irradiation of deoxygenated, 0.01 M solutions of **2c**−**i** in argon-saturated pentane, hexane, or isooctane containing 0.1 M methanol (MeOH) with 185- or 214-nm light led to the formation of ethylene and the corresponding methoxysilane (**4**; eq 1) as the only detectable products (by GC analysis of the crude photolysates) between 5 and 20% conversion of the starting material. The methoxysilanes were identified in the crude photolysates by GC/MS analysis and GC co-injections with authentic samples. In contrast, the alkoxysilacyclobutanes **2j,k** proved to be inert to 214-nm UV light after extensive periods of photolysis under conditions similar to those employed for **2c**−**i**.

Laser flash photolysis experiments were carried out on continuously flowing, deoxygenated solutions of the silacy-

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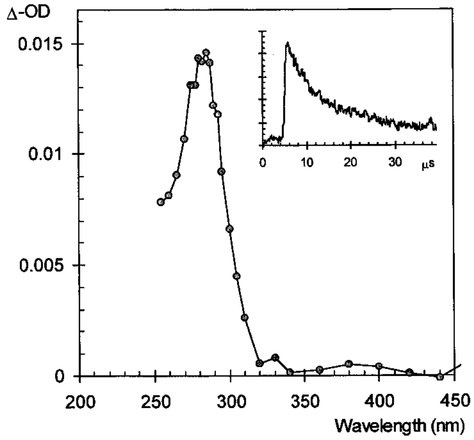

**Figure 1.** Time-resolved UV absorption spectrum of 1-methyl-1-trimethylsilylsilene (**3i**) in deoxygenated hexane solution at 23 °C, from 193-nm laser flash photolysis of silacyclobutane **2i**. The inset shows a decay trace recorded at the wavelength of maximum absorbance (285 nm). UV absorption spectra of silenes **3a**−**h** are available as Supporting Information.

clobutanes ($10^{-3}$−$10^{-4}$ M) in isooctane (**2c**,**g**) or hexane, using the pulses (193 nm; 20−40 mJ; ~20 ns) from an ArF excimer laser. In all cases except those of **2j** and **2k**, readily detectable transient absorptions were observed, which decayed over 1−10 μs with mixed pseudo-first- and -second-order kinetics at normal laser intensities. The decay kinetics could usually be simplified to pseudo-first-order by reducing the laser intensity with neutral density filters. Time-resolved UV absorption spectra were recorded in point-by-point fashion over several time windows after the laser pulse. Figure 1 shows a representative transient spectrum, recorded 0.5−1.0 μs after the pulse from a deoxygenated hexane solution of the trimethylsilyl derivative **2i**, along with a typical decay trace recorded at the wavelength of maximum transient absorption. The transient spectra from photolysis of all nine of the methylsilacyclobutanes **2a**−**i** are very similar in appearance, with only the absorption maximum varying between 255 and 315 nm depending on the substituent. In all cases, addition of aliphatic alcohols to the solutions shortens the transient lifetime and results in a change to clean pseudo-first-order decay kinetics. The common sensitivities of these transients to alcohols and the similarities in their absorption spectra are consistent with their assignments to the corresponding silenes **3**. Flash photolysis of the two alkoxysilacyclobutanes **2j**,**k** led to the formation of very weakly absorbing transient species which could not be reliably identified. These results are consistent with the indication from the steady-state experiments that these two derivatives are essentially photoinert. The UV absorption spectra of these two compounds show only edge absorption above 190 nm, like that of **2a** (for example), and offer no clue as to the reasons for this substituent effect on silacyclobutane photoreactivity.

Absolute rate constants for the quenching of the transients by methanol (MeOH), ethanol (EtOH), and *t*-butyl alcohol (*t*-BuOH) were determined from plots of the pseudo-first-order rate constant for silene decay ($k_{decay}$) versus ROH concentration according to eq 2

$$k_{decay} = k_o + k_{ROH}[ROH] \tag{2}$$

in which $k_o$ is the pseudo-first-order rate constant for decay in the absence of quencher and $k_{ROH}$ is the bimolecular rate constant for quenching by the added alcohol. The silene absorptions decayed with clean pseudo-first-order kinetics in the presence of alcohol throughout the concentrations ranges studied, and the resulting plots of $k_{decay}$ versus [ROH] were linear in every case. Figure 2 shows typical plots of this type for quenching of silene **3g** by MeOH, EtOH, and *t*-BuOH. Quenching by MeOD and *t*-BuOD was also studied in several cases; it was consistently slower than that by the protiated alcohols, but the plots of $k_{decay}$ vs [ROD] were similarly linear over the concentration ranges studied. Table 1 lists the absolute rate constants determined in these experiments along with the absorption maxima from the transient UV absorption spectra of the silenes. The rate constant for reaction of 1,1-dimethylsilene (**3a**) with EtOH in isooctane at 23 °C was also determined and is listed in Table 1 along with the previously reported rate constants for reaction of this silene with MeOH and *t*-BuOH.[21] That for reaction of the least reactive silene (**3i**) with *t*-BuOH was difficult to determine because of screening of the excitation light by the alcohol at the high concentrations required for significant quenching.

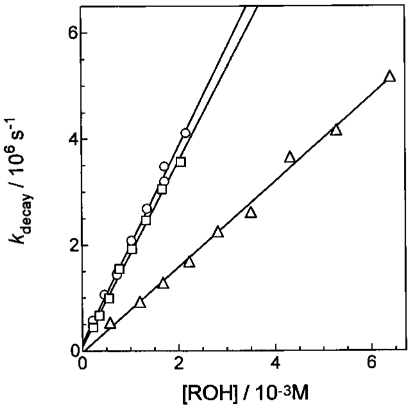

**Figure 2.** Plots of $k_{decay}$ versus [ROH] for the quenching of 2-methyl-1,3-(2-sila)butadiene (**3g**) by MeOH (○), EtOH (□), and *t*-BuOH (Δ) in deoxygenated isooctane solution at 23 °C.

For compound **2c**, a few steady-state competition experiments were attempted in order to check the accuracy of the absolute rate constants for reaction of **3c** with alcohols. For example, argon-saturated isooctane solutions of **2c** (0.01 M) in the presence of equimolar amounts of MeOH and EtOH (total concentration ~ 0.05 M) were irradiated (193 nm) to ca. 20% conversion of silacyclobutane. The photolyses yielded mixtures of methoxy- and ethoxydimethylsilane (**4c**), in the ratio $[EtOSiMe_2H]/[MeOSiMe_2H] = 0.96 \pm 0.02$, in excellent agreement with the ratio of absolute rate constants measured by flash photolysis. Similar experiments using MeOH and *t*-BuOH as the quenchers could not be carried out because the *t*-butoxysilane coelutes with the solvent under our GC conditions.

Arrhenius parameters were estimated for the reaction of methanol with **3c** (R = H), **3f** ($R = CH_2SiMe_3$), **3g** ($R = CH{=}CH_2$), **3h** ($R = C{\equiv}CH$), and **3i** ($R = SiMe_3$) in isooctane or hexane solution, by determining decay rate constants at several temperatures between 2 and 54 °C, for deoxygenated solutions of the silenes containing enough MeOH to reduce the lifetime of the silene to less than 10−15% of its value in the absence of the alcohol at room temperature. Thus, the $k_{MeOH}$ values can be approximated directly from the decay rate constants at each temperature (i.e., $k_{MeOH} \approx k_{decay}/[MeOH]$). It should be noted, however, that these values have not been corrected for decay processes due to other than methanol quenching, so the

**Table 1.** UV Absorption Maxima and Bimolecular Rate Constants for Reaction of Substituted 1-Methylsilenes (**3a**−**i**) with MeOH(D), EtOH, and *t*-BuOH(D) in Deoxygenated Isooctane (**3a,c,g**) or Hexane (**3b,d**−**f,h,i**) Solution at 23 °C[a]

| R'<br>Si=CH$_2$<br>R | | MeOH | | | *t*-BuOH | |
|---|---|---|---|---|---|---|
| R, R′ | UV $\lambda_{max}$ (nm) | $k_q/10^9$ M$^{-1}$ s$^{-1}$ | $k_H/k_D$ | EtOH $k_q/10^9$ M$^{-1}$ s$^{-1}$ | $k_q/10^9$ M$^{-1}$ s$^{-1}$ | $k_H/k_D$ |
| Me, Me (**3a**)[b] | 255 | 4.9 ± 0.2 | 1.5 ± 0.1 | 4.5 ± 0.2 | 1.8 ± 0.1 | 1.6 ± 0.2 |
| Me, $C_6H_5$ (**3b**)[c] | 315 | 3.2 ± 0.2 | | | 1.2 ± 0.1 | |
| Me, H (**3c**) | 265 | 4.41 ± 0.14 | 1.4 ± 0.1 | 4.4 ± 0.2 | 2.57 ± 0.12 | 1.1 ± 0.1 |
| Me,Et (**3d**) | 255 | 4.2 ± 0.5 | | 3.6 ± 0.3 | 1.3 ± 0.1 | |
| Me, *t*-Bu (**3e**) | 260 | 3.7 ± 0.1 | 1.3 ± 0.1 | 2.4 ± 0.2 | 0.33 ± 0.03 | 1.2 ± 0.1 |
| Me, $CH_2SiMe_3$ (**3f**) | 260 | 1.86 ± 0.09 | | 1.80 ± 0.05 | 0.71 ± 0.11 | |
| Me, CH═$CH_2$ (**3g**) | 305 | 1.75 ± 0.10 | 1.6 ± 0.2 | 1.86 ± 0.08 | 0.81 ± 0.04 | 1.8 ± 0.2 |
| Me, C≡CH (**3h**) | 290 | 10.0 ± 0.1 | 1.1 ± 0.1 | 9.8 ± 0.2 | 5.4 ± 0.3 | |
| Me, $SiMe_3$ (**3i**) | 285 | 0.18 ± 0.01 | 1.6 ± 0.2 | 0.19 ± 0.01 | 0.03 ± 0.01 | |

[a] Errors are listed as twice the standard deviation from least-squares analysis of $k_{decay}$−concentration data according to eq 2. [b] Data from ref 21, except for that for EtOH. [c] Data from ref 33.

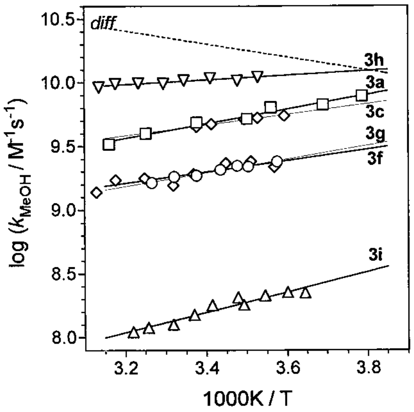

**Figure 3.** Arrhenius plots for the quenching of substituted 1-methylsilenes **3c** (R = H), **3a** (R = Me), **3f** (R = $CH_2SiMe_3$), **3g** (R = CH═$CH_2$), **3h** (R = C≡CH) and **3i** (R = $SiMe_3$) by methanol in deoxygenated hexane or isooctane solution. The dotted line shows the temperature dependence of the rate constant for the diffusion of hexane, calculated using the modified Debye equation ($k_{diff}$ = 8RT/3000$\eta$) and published viscosities.[35]

**Table 2.** Arrhenius Parameters for Reaction of Representative Methylsilenes with MeOH in Hydrocarbon Solution[a]

| Me<br>Si=CH$_2$<br>R | $E_a$ (kcal/mol) | log(A/M$^{-1}$ s$^{-1}$) |
|---|---|---|
| H (**3c**) | −1.9 ± 0.3 | 8.3 ± 0.3 |
| Me (**3a**) | −2.6 ± 0.3 | 7.7 ± 0.3 |
| $CH_2SiMe_3$ (**3f**) | −2.0 ± 0.5 | 7.8 ± 0.6 |
| CH═$CH_2$ (**3g**) | −2.4 ± 0.1 | 7.5 ± 0.3 |
| C≡CH (**3h**) | −0.8 ± 0.1 | 9.3 ± 0.2 |
| $SiMe_3$ (**3i**) | −3.6 ± 0.6 | 5.5 ± 0.5 |

[a] Estimates based on the determination of the silene decay rate constant as a function of temperature between 2−55 °C, using solutions of the corresponding silacyclobutane in hexane or isooctane (**3a,c,g**) containing enough methanol to ensure that >85% of the decay is due to the bimolecular reaction with the alcohol. Errors are reported as twice the standard deviation from least-squares analysis of the data shown in Figure 3.

corresponding Arrhenius plots (Figure 3) will be slightly distorted from their true form. The approximate Arrhenius parameters calculated from these data are listed in Table 2. Table 2 and Figure 3 also contain the previously reported Arrhenius data for reaction of **3a** with methanol in isooctane.[21] The temperature dependence of the diffusional rate constant in hexane, calculated from the modified Debye equation and published viscosities,[35] is also included in Figure 3.

## Discussion

The utility of silacyclobutane derivatives as photochemical or thermal precursors of reactive silenes is well established,[1,4,36,37] but only a few of the silacyclobutane derivatives studied in this work (**2a**,[21,38] **2b**,[24] **2c**,[7] and **2g**[39,40]) have been previously reported to yield products consistent with the intermediacy of the corresponding silenes **3** upon direct photolysis in solution or the gas phase. Indeed, photolysis of all nine compounds in the presence of methanol or *t*-butyl alcohol leads to the alkoxysilane expected from trapping of the corresponding silene by the alcohol. It is particularly important to note that the photolyses are all clean at conversions of <20%, producing only ethylene and the corresponding alkoxysilane within the limits of our GC detection method. There is nothing to indicate that any reactive intermediates other than the silenes **3a**−**i** are produced upon photolysis of any of the corresponding silacyclobutanes in solution, on the basis of these experiments.

Like that of **2a**[21] and **2b**,[24,33] laser flash photolysis of **2c**−**i** gives rise in each case to what appears to be a single transient species, judging from the appearance of the spectra and the fact that the decay kinetics of each transient are the same throughout the observed transient absorption band both in the absence and presence of alcohols. The transient spectra obtained from laser photolysis of all nine of these silacyclobutanes are characterized by a single long wavelength absorption band, which varies only in position as a function of substituent. This, along with the fact that they decay with second-order kinetics at high laser intensities (indicative of dimerization) and exhibit high reactivity toward alcohols, allows the transients to be assigned to the corresponding silenes with a high level of certainty. The transient absorption spectrum observed from flash photolysis of **2c** in isooctane solution agrees well with that reported from gas-phase flash photolysis of this compound, and which was assigned to 1-methylsilene (**3c**).[7] The solution spectrum of **3c** also agrees well with the reported low-temperature matrix spectrum, for which the silene was generated by flash vacuum pyrolysis of a silabicyclo[2.2.2]octadiene precursor.[41] As expected, the UV absorption spectra of the ethyl and *t*-butyl derivatives (**3d,e**) are more or less indistinguishable from that of **3a**. There is a slight red-shift in the absorption maximum of 1-methyl-1-trimethylsilylmethylsilene (**3f**; $\lambda_{max}$ = 260 nm)

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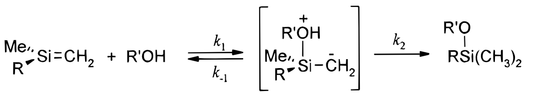
compared to that of **3a** ($\lambda_{max}$ = 255 nm), indicative of a small hyperconjugative effect of the $\beta$-SiMe$_3$ group on the silenic $\pi,\pi^*$ absorption. The effect is smaller than when the -CH$_2$SiMe$_3$ group is attached to the silenic carbon, which results in a ~15-nm red-shift of the long-wavelength shoulder absorption in the UV spectrum of 1,1-dimethyl-2-trimethylsilylmethylsilene compared to that of 1,1,2-trimethylsilene.[42] The absorption maxima of the vinyl (**3g**), ethynyl (**3h**), phenyl (**3b**), and trimethylsilyl (**3i**) derivatives are all red-shifted significantly from the 255–260 nm absorption maxima of the dialkylsilenes, and they follow a similar trend as a function of subsituent as in the spectra of the corresponding alkene analogues.[43]

All of the transient silenes studied here exhibit the expected high degree of reactivity toward aliphatic alcohols, with relative reactivities following the order $k_{MeOH} \approx k_{EtOH} > k_{t-BuOH}$. For **3h**, the most reactive silene yet investigated in solution, the bimolecular rate constant for reaction with methanol is only about a factor of 2 lower than the diffusion rate in hexane at 23 °C. The other silenes are less reactive than this, with the rate constants varying by about a factor of 50 throughout the series. The span in the rate constants is somewhat greater for *t*-BuOH, reflecting its lower reactivity compared to MeOH.

The addition of aliphatic alcohols to transient silenes is thought to proceed by a mechanism initiated by reversible nucleophilic attack at silicon to form a silene–alcohol complex, which collapses to the product by rate-controlling unimolecular proton transfer from oxygen to carbon (see eq 3).[10,12,16,18,20–22,32]



$$\mathrm{Me(R)Si{=}CH_2} + \mathrm{R'OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[\mathrm{Me(R)}\overset{\overset{+}{\mathrm{R'OH}}}{\mathrm{Si}}{-}\overset{-}{\mathrm{C}}\mathrm{H_2}\right] \xrightarrow{k_2} \mathrm{R}\overset{\mathrm{R'O}}{\mathrm{Si}}\mathrm{(CH_3)_2} \qquad (3)$$

The latter can also be catalyzed by a second molecule of alcohol,[11,16,18,20,32] but the linear dependence of $k_{decay}$ on alcohol concentration observed for the silenes studied here indicates that this is unimportant in these cases, at least over the small alcohol concentration ranges employed for our kinetic experiments. In general, reversion of the complex to the free reactants is faster than proton transfer, giving rise to small primary deuterium isotope effects[12,16,18,20–22] and negative Arrhenius activation energies[10,12,21,22] for the overall rate constants for reaction. With the present silenes, the rate constants for reaction with MeOH and *t*-BuOH exhibit deuterium isotope effects in the range 1.1–1.8, which can, in most cases, be clearly identified as a primary kinetic isotope effect. Furthermore, the rate constants for reaction with MeOH all follow similar (negative) temperature dependences, with a trend toward increasingly negative $E_a$ and a smaller preexponential factor with decreasing reactivity throughout the series (see Table 2). Thus, all aspects of their reactivity toward aliphatic alcohols are consistent with the mechanism shown in eq 3. With the application of the steady state approximation for the complex, the experimentally measured second-order rate constant for the reaction can be expressed in terms of the individual rate constants for formation and collapse of the complex, as shown in eq 4.

$$k_{ROH} = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (4)$$

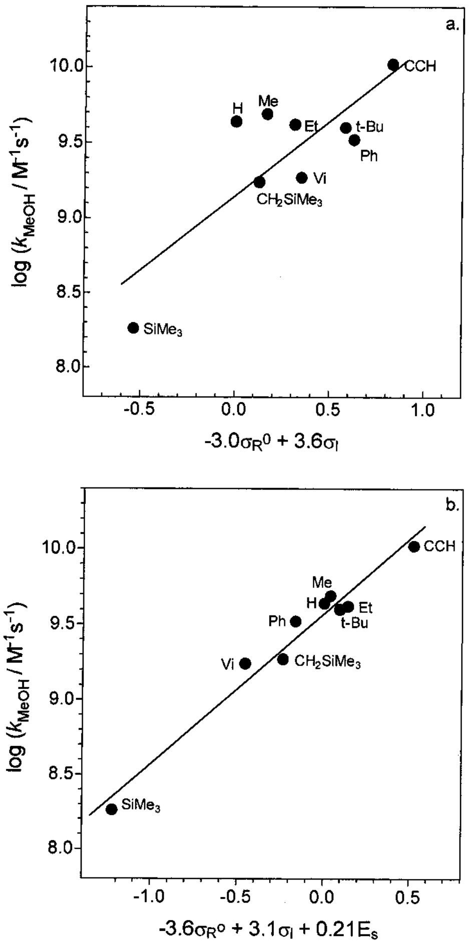


**Figure 4.** Substituent parameter correlations for the quenching of substituted 1-methylsilenes **3a**–**i** by methanol in isooctane or hexane solution at 23 °C: (a) log $k_{MeOH}$ vs ($-3.0\ \sigma_R^0 + 3.6\ \sigma_I$); (b) log $k_{MeOH}$ vs ($-3.6\ \sigma_R^0 + 3.1\sigma_I + 0.21E_s$). The solid line represents the fit of the data to the specified functions ($r^2$ = 0.659 and 0.965 for (a) and (b), respectively).

The rate constants for reaction of **3a**–**i** with MeOH and EtOH vary regularly as a function of the single variable substituent at silicon, increasing in the order SiMe$_3$ ≪ CH=CH$_2$, CH$_2$SiMe$_3$ < Ph < H, Me, Et, *t*-Bu < C≡CH. It became evident rather early in this study that the rate constants for these reactions do not correlate in a straightforward way with either inductive or resonance substituent parameters alone ($\sigma_I$ and $\sigma_R^o$, respectively[44a]), and thus to allow for the possibility of a multiparameter analysis,[45] the series was expanded to include as wide a range in substituent electronic and steric properties as could be accommodated by the conditions necessary for the kinetic measurements. The poor fit of the data to a single substituent parameter is evident, for example, from the similar reactivities of the 1-methyl (**3a**; $\sigma_I$ = 0.10)- and 1-phenyl (**3b**; $\sigma_I$ = −0.10)-substituted derivatives, and from the widely different reactivities of the 1-trimethylsilyl (**3i**; $\sigma_R^o$ = +0.06)- and 1-ethynyl (**3h**; $\sigma_R^o$ = +0.08)-substituted derivatives. Fitting the data to a two-parameter function incorporating both resonance and inductive parameters[45] leads to the relatively poor correlation shown in Figure 4a ($r^2$ = 0.659). A significant improvement is obtained by including the steric substituent

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[42] Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W.; Venneri, P. C.; Conlin, R. T.; Dhurjati, M. S. K.; Ezhova, M. B. *J. Organomet. Chem.* **1998**, *561*, 19.

[43] Robin, M. B. *Higher excited states of polyatomic molecules, Vol. II*; Academic Press: New York, 1975; pp 1–68.

[44] (a) Wayner, D. D. M. In *CRC Handbook of organic photochemistry*; Scaiano, J. C. Ed.; CRC Press: Boca Raton, 1989; pp 395–400. (b) Unger, S. H.; Hansch, C., *Prog. Phys. Org. Chem.* **1976**, *12*, 91. The $E_s$ value employed for the trimethylsilylmethyl substituent ($E_s \approx -3.56$) was approximated from the value for SiMe$_3$, corrected by the difference between the $E_s$ values for CMe$_3$ and CH$_2$CMe$_3$.

[45] Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

parameter $E_s$,[44b] as shown in Figure 4b. The least-squares fit to the nine data points ($r^2 = 0.965$) affords the coefficients, $\rho_R = -3.6 \pm 1.2$, $\rho_I = 3.1 \pm 1.0$, and $\rho_s = 0.21 \pm 0.08$, where the quoted errors represent the 95% confidence limits of the analysis. The results of this fit must obviously be interpreted qualitatively and with a good deal of caution, not just because of the use of three independent variables in the analysis, but also because the intrinsic reactivity of the ethynyl derivative relative to the others might very well be underestimated because it reacts with MeOH with a rate constant within a factor of ca. 2 of the diffusional rate. Nevertheless, the negative $\rho_R$ and positive $\rho_I$ values suggest that the intrinsic reactivity of the Si═C double bond in these compounds is enhanced by $\pi$-electron donor and/or $\sigma$-electron acceptor substituents at silicon, respectively, and the positive $\rho_s$ value indicates that it is reduced slightly (but significantly) by increasing the steric bulk of the one variable substituent in this series of compounds. Clearly, the steric effect would be expected to contribute more significantly if the common substituent in the homologous series of silenes was larger than methyl or if both substituents at silicon were varied.

Similar $\rho$ values are obtained from a fit of the EtOH and *t*-BuOH data to the three substituent parameters, $\rho_R = -3.0 \pm 1.7$, $\rho_I = 2.5 \pm 1.6$, and $\rho_s = 0.24 \pm 0.14$ ($r^2 = 0.947$) for EtOH, and $\rho_R = -3.3 \pm 3.7$, $\rho_I = 3.3 \pm 3.1$, and $\rho_s = 0.28 \pm 0.24$ ($r^2 = 0.789$) for *t*-BuOH, where again the errors are listed as the 95% confidence limits (the plots for these two alcohols are available as Supporting Information). The poor fit for the *t*-BuOH data appears to be mostly due to the *t*-butyl silene **3e**, whose reactivity shows a much greater sensitivity to alcohol structure than is observed with the other silenes (see Table 1). We can think of no ready mechanistic explanation for this, short of the possibility that the steric effect of the *t*-butyl group might be under-represented, compared to the other substituents, by the $E_s$ substituent parameter. There is nothing in the product studies, the silene decay kinetics in the presence of alcohols, or the kinetic isotope effects to suggest a difference in the mechanism for the addition of alcohols to this silene compared to that of the others.

The relative importance of steric and electronic effects on the kinetic stabilities of the silenes in the series can be understood more clearly by considering the correlations shown in Figure 4 in more detail. The $\rho_R$ and $\rho_I$ values suggest that resonance and inductive factors oppose one another but are of similar importance in affecting the kinetic stability of the Si═C bond in these compounds. Calculation of the net electronic effect of the R substituent for each member of the series (as $\rho_R\sigma_R{}^o + \rho_I\sigma_I$, where the $\rho$ values are those obtained from the least-squares fit of the data for methanol addition), suggests that the trimethylsilyl substituent (a weak $\pi$-electron acceptor and weak $\sigma$-electron donor) stabilizes the silene relative to R═H, while all of the other substituents destabilize. Because resonance and inductive effects are of similar importance, the net electronic effects of the phenyl (a moderate $\pi$-electron donor and $\sigma$-electron acceptor), *t*-butyl (a strong hyperconjugative $\pi$-electron donor and very weak $\sigma$-electron acceptor), and ethynyl (a moderate $\pi$-electron acceptor and strong $\sigma$-electron acceptor) substituents are roughly equally destabilizing relative to R═H (**3c**). The spread in reactivity for these three compounds thus appears to be due primarily to steric effects, which are minimal in the ethynyl derivative (resulting in nearly diffusion-controlled reactivity; see Figure 3), but roughly cancel the electronic destabilization in the phenyl and *t*-butyl derivatives. Steric and electronic effects are cooperative in the case of the trimethylsilyl derivative **3i**, resulting in a substantial decrease in reactivity compared to the similarly sized *t*-butyl and trimethylsilylmethyl derivatives **3e** and **3f**, respectively. Interestingly, the vinyl substituent in **3g** is approximately electronically neutral, suggesting that its reduced reactivity compared to that of **3c** is almost entirely due to steric effects. Finally, our data suggest that phenyl substitution at silicon produces roughly twice the electronic destabilization that methyl-substitution does. This is compensated for by steric effects, which are 2−3 times greater for phenyl than for methyl substitution;[44b] the result is a modest reduction in reactivity for 1-methyl-1-phenyl- (**3b**) compared to 1,1-dimethylsilene (**3a**). This trend is continued with 1,1-diphenylsilene, which exhibits slightly lower reactivity than **3b** with alcohols under similar conditions.[33] Wiberg and Link have recently reached a similar conclusion from a comparison of the reactivities of the transient silenes $Ph_2Si{=}C(SiMe_3)_2$ and $Me_2Si{=}C(SiMe_3)_2$ toward a wide range of silene trapping agents.[46]

From an analysis of the effects of substituents on the ab initio Si═C bond lengths and charge distributions in silenes of the type $H(R)Si{=}CH_2$, Apeloig and Karni hypothesized that the electronic effects of substituents on the reactivity of silenes should result largely from their ability to reduce or enhance the natural polarity of the Si═C bond.[25] Thus, $\pi$-electron donor and $\sigma$-electron acceptor substituents at silicon were predicted to lead to enhanced reactivity toward *both* electrophiles and nucleophiles because such substituents simultaneously increase both the negative charge density at carbon and the positive charge density at silicon. Exactly the opposite effects were predicted for substituents of the same type at the silenic carbon. With steric effects worked in, this rationale provided a very satisfying explanation for the remarkable stabilities of the few "persistent" silenes that were known at the time. The kinetic results reported here for the addition of alcohols to the series of transient 1-methylsilenes are, for the most part, consistent with these ideas. In this reaction, like many others involving addition of oxygen- and nitrogen-nucleophiles,[12,20,22,24,33] both the nucleophilic and electrophilic stages of the reaction are kinetically significant.

It is difficult to provide a more detailed analysis of the substituent effects on silene reactivity toward alcohols, in terms of the primary rate constant for formation of the complex ($k_1$) and the partitioning ratio for its reversion to free reactants and collapse to alkoxysilane ($k_2/(k_{-1} + k_2)$), the product of which yields the overall rate constant for reaction (see eq 4). For the ethynyl derivative **3h**, the magnitude of $k_{MeOH}$ and the form of its temperature dependence indicate that $k_1$ is approximately equal to the diffusional rate constant in hexane, and that the partitioning ratio is very close to (but slightly less than) 0.5. The latter must be true in order for the Arrhenius activation energy to be negative according to this mechanism; a dominant entropic component to the free energy barrier for intracomplex proton transfer is also required. The trends in the temperature dependences for MeOH addition (toward progressively more negative $E_a$'s and preexponential factors; see Figure 3) and the kinetic isotope effects are consistent with reductions in both $k_1$ and $k_2/(k_{-1}+k_2)$ as overall reactivity decreases throughout the series. The effect on $k_1$ can be ascribed to decreasing electrophilicity at silicon with decreasing $\pi$-electron donor/$\sigma$-electron acceptor power and/or increasing steric bulk of the substituents, while that on the partitioning ratio can be ascribed to increasing entropic demands in the intracomplex proton transfer step with decreasing nucleophilicity at carbon and increasing steric effects

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(46) Wiberg, N.; Link, M. *Chem. Ber.* **1995**, *128*, 1231.

at silicon. We are presently investigating these details of the mechanism of addition of alcohols to silenes and the effects of substituents on the process, using computational methods.

## Summary and Conclusions

The 193-nm photolysis of substituted alkylsilacyclobutanes provides a convenient means of generating the corresponding silenes in hydrocarbon solution, under conditions where they can be detected directly and where absolute rate constants for their reactions with aliphatic alcohols can be measured. Photocycloreversion proceeds cleanly in alkylsilacyclobutanes bearing substituents such as hydrido, alkyl, vinyl, ethynyl, trimethylsilyl, and phenyl, but alkoxysilacyclobutanes appear to be inert to photolysis with 193−214-nm light. Although it has been explicitly proven only for **3a**[21,47] and **3g**,[20] cycloreversion is thought to involve the lowest excited singlet state, in which the ring Si−C bonds are weakened through population of a $\sigma^*$ molecular orbital.[47a]

The absolute rate constants for the reaction of aliphatic alcohols with the corresponding silenes in hexane solution vary by about 2 orders of magnitude depending on the alcohol, with 1-ethynyl-1-methylsilene (**3h**) reacting the fastest and 1-methyl-1-trimethylsilylsilene (**3i**) the slowest. The former reacts with methanol at very close to the diffusion-controlled rate and is the most reactive silene studied to date. Methanol addition proceeds with a negative Arrhenius activation energy in all cases examined and exhibits a small primary deuterium kinetic isotope effect in all cases but that of the ethynyl-substituted derivative. These characteristics indicate that the silenes react by a common mechanism, involving reversible formation of a silene−alcohol complex which collapses to alkoxysilane by rate-limiting, entropy-controlled proton transfer from oxygen to carbon.

The rate constants for the reaction of nine silenes of the type $R(Me)Si{=}CH_2$ with methanol, ethanol, and *t*-butyl alcohol correlate with a three parameter function incorporating resonance, inductive, and steric substituent parameters. The signs and magnitudes of the coefficients indicate that resonance and inductive effects act in opposing but roughly equal fashion on the kinetic stabilities of transient 1-methylsilenes toward addition of these reagents. Silene reactivity is reduced by $\pi$-electron acceptor and/or $\sigma$-electron donor substituents at silicon, most likely through an effect on the degree of electrophilicity at silicon, which affects the complexation step, and on the degree of nucleophilicity at carbon, which affects the proton-transfer step. Steric effects can act to reinforce, cancel, or even reverse the electronic effects of substituents at silicon on the intrinsic kinetic stability of the Si=C bond. These conclusions are in good agreement with those made several years ago on the basis of ab initio theoretical calculations of the structures, Mulliken charge distributions, and frontier molecular orbital properties of a series of simple 1- and 2-substituted silenes.[25]

For reactions initiated by nucleophilic attack at silicon, steric effects should be less important when the substituents at carbon are varied. A study of this type requires a more extensive list of silene precursors than can be provided by silacyclobutane derivatives and is in progress in our laboratory.

## Experimental Section

NMR spectra were recorded in deuteriochloroform and are referenced to tetramethylsilane. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC200 spectrometer and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer. When absorbance data below 200 nm were desired, the compartment and sample solution were flushed with argon or nitrogen prior to measuring the spectra. Low-resolution mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30 m × 0.25 mm; Chromatographic Specialties, Inc). Infrared spectra were recorded as thin films on a BioRad FTS-40 FTIR spectrometer and are reported in wavenumbers ($cm^{-1}$).

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890II+ gas chromatograph equipped with conventional heated splitless injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and DB1 or DB1701 megabore capillary columns (15m × 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 101 on Chromosorb W, HP 80/100; 6' x 0.25"; Chromatographic Specialties, Inc.).

2,2,4-Trimethylpentane (isooctane; BDH Omnisolv) and hexane (Caledon HPLC grade) exhibited absorbances of <0.2 at 193 nm in a 3-mm cell and were used without further purification. Methanol, ethanol, and *t*-butyl alcohol were of the highest purity available from Aldrich Chemical Co. and were dried over activated 4 Å molecular sieves prior to use. Methanol-O*d*, ethanol-O*d*, and *t*-butyl alcohol-O*d* were used as received from Aldrich.

1,1-Dimethylsilacyclobutane (**2a**) was available from a previous study,[21] while the remaining silacyclobutanes were prepared by methods similar to those published. They exhibited spectroscopic data and boiling points similar to those reported, **2c**, 65 °C (760 mm);[48] **2d**, 72 °C (110 mm);[49] **2f**, 95 °C (97 mm);[50] **2g**, 46 °C (110 mm);[40] **2i**, 68−69 °C (72 mm);[51] **2k**, 38−40 °C (760 mm);[52] **2l**, 61−62 °C (60 mm).[52] 1-Ethynyl-1-methylsilacyclobutane (**2h**, $\lambda_{max}$ 200 nm, $\epsilon_{193\ nm} = 2583 \pm 300$ $M^{-1}$ $cm^{-1}$) codistilled with THF from its reaction mixture and was thus separated by silica gel column chromatography using pentane as eluant and identified by comparison to reported data for this compound.[53] After being distilled the silacyclobutanes were isolated in >99% purity (as estimated by capillary GC analysis) by semipreparative gas chromatography.

**1-Methyl-*t*-butylsilacyclobutane (2e).**[54] To a solution of 1-chloro-1-methylsilacyclobutane (1.5 g, 0.0124 mol) in dry diethyl ether (40 mL) cooled at −78 °C was added a 1.6 M pentane solution of *tert*-butyllithium (8.0 mL, 0.0128 mol) with stirring. A white precipitate formed immediately. The reaction mixture was stirred for 14 h while the dry ice/acetone bath warmed to room temperature. The reaction was carefully quenched with water (20 mL). The aqueous layer was separated and extracted with pentane (3 × 10 mL). The organic fractions were combined, dried over anhydrous magnesium sulfate, filtered, and the solvent was removed on the rotary evaporator

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[54] Auner, N. *J. prakt. Chem./Chem.-Ztg.* **1995**, *337*, 79.

to yield a colorless oil which was distilled under reduced pressure to yield the product as a colorless liquid (bp 72−73 °C, 98 mmHg; 1.1 g, 0.0077 mol, 62%). It was identified as **2e** on the basis of the following spectroscopic data: $^1$H NMR, $\delta = 0.19$ (s, 3H), 0.93 (s, 9H), 0.8−1.2 (m, 4H), 2.01 (tt, 2H); $^{13}$C NMR, $\delta = -4.5$, 11.4, 17.6, 25.8, 32.0; IR (neat, cm$^{-1}$), 2953, 2857, 1468, 1362, 1250, 1119, 1050, 865, 766; UV, $\lambda_{max}$ <190 nm, $\epsilon_{193\ nm} = 2303 \pm 200$ M$^{-1}$ cm$^{-1}$; MS $m/z = 143$ (4), 142 (27), 114 (28), 100 (39), 99 (90), 86 (44), 85 (100), 73 (63), 72 (58), 59 (93), 58 (53).

Authentic samples of the methoxysilanes **4** were either obtained from commercial sources (**4a**), or prepared by treating the appropriate chlorosilane with the appropriate alcohol and triethylamine in anhydrous diethyl or dibutyl ether,[40,55−57] or from dimethoxydimethylsilane and the appropriate Grignard reagent. They exhibited spectroscopic data and/or boiling points similar to those reported, **4b**, 75−80 °C (9 mm);[57] **4c**, 31 °C (760 mm);[59] **4d** (not distilled; identified by ms[47]); **4e**, 58 °C (110 mm); **4g**, 68−70 °C (760 mm);[40] **4h**, 78−80 °C (760 mm);[58] **4i**, 50 °C (85 mm).[60]

Methoxydimethyl(trimethylsilylmethyl)silane (**4f**)[50] was prepared by treating dimethyl(trimethylsilylmethyl)silane (1.0 g, 6.84 mmol) with methanol (0.28 mL, 6.84 mmol) in the presence of a catalytic quantity (ca. 5 mg) of palladium(II) chloride. The mixture was stirred at room temperature for 15 min until the vigorous evolution of hydrogen ceased. The resulting liquid was removed from insoluble palladium salts with a filtering pipet, and excess methanol was removed on the rotary evaporator to yield the product as a colorless liquid (1.0 g, 6.2 mmol, 91%), whose spectroscopic data matched those reported.[61] Dimethyl(trimethylsilylmethyl)silane was prepared from chlorodimethylsilane and trimethylsilylmethylmagnesium chloride in anhydrous ether. The product (bp 88 °C, 760 mm) was identified on the basis of the following spectroscopic data: $^1$H NMR, $\delta = 0.25$ (d, 2H), 0.02 (s, 9H), 0.08 (d, 6H), 3.95 (m, 1H); $^{13}$C NMR, $\delta = -1.5$, 0.8, 1.5; IR (neat) 2956 (s), 2901 (m), 2112 (s), 1425 (w), 1253 (s), 1048 (s), 896 (s), 837 (s); MS $m/z = 146$ (0.1), 145 (3), 133 (8), 132 (16), 131 (100), 73 (43), 59 (13).

Analytical-scale photolyses were carried out using a low-pressure mercury lamp (185 + 254 nm; Osram HNS 10W/UOZ) for **2a,c** or a zinc resonance lamp (214 nm; Philips 93106E) for **2d−k**. The photolyses were carried out in pentane, hexane, or isooctane, depending on the alcohol and silacyclobutane, to allow baseline separation of the alkoxysilane products from the solvent; thus, pentane was used for all irradiations using *t*-butyl alcohol as the silene trap and for irradiation of **2h**, while isooctane was employed as solvent for irradiations with the lighter alcohols. Photolyses of **2d−g** were carried out in hexane solution. Aliquots of the solutions of silacyclobutane (0.01 M) and an alcohol (0.1 M) were placed in Suprasil quartz cuvettes (3 mm × 10 mm), sealed with rubber septa, and saturated with dry argon. Photolysis of the solutions, with monitoring by GC between 5 and 20% conversion, gave rise to the formation of the corresponding alkoxysilane as the only detectable product; their identities were determined by GC/MS analysis of the crude photolyzates; in the cases of the methoxysilanes, these were verified by GC- and GC/MS-co-injection with the authentic samples. The formation of ethylene as a coproduct from photolysis of **2a,c** was evident in experiments carried out in isooctane solution but was not verified in the cases of **2d−h**.

Competition experiments with **2c** were carried out in argon-saturated isooctane solutions containing 0.01 M **2c**, 0.025 M methanol, and 0.025 M ethanol. Solutions were contained in Suprasil cuvettes (10 mm × 10 mm) and stirred vigorously with a small magnetic stirrer during irradiation with an ArF excimer laser (193 nm; ~20 mJ; 5-Hz repetition rate) to a maximum of 20% conversion of the silacyclobutane. Product ratios were determined from the relative peak areas without correction for FID response and are the average of triplicate determinations.

Nanosecond laser flash photolysis experiments employed the pulses from Lumonics 510 or Lambda Physik Compex 120 excimer lasers, filled with Ar/F$_2$/He (193 nm, 12−25 ns, 30−70 mJ), and a microcomputer-controlled detection system.[12,62] The intensity of the beam was reduced to 2−6 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 ($\sim 6 \times 10^{-4}$ to $4 \times 10^{-3}$ M). They were flowed continuously from a calibrated 100 mL reservoir through a 3 × 7 mm Suprasil flow cell, which was contained in a brass sample holder whose temperature was controlled to within 0.1 °C by a VWR 1166 constant-temperature circulating bath. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple which was inserted directly into the flow cell. Solutions of the appropriate silacyclobutane were deoxygenated with a stream of dry nitrogen in the reservoir for 30−60 min prior to flash photolysis experiments. A slightly different procedure was used for **2a,c**, to prevent sample loss due to evaporation. In these two cases, the reservoir was filled with solvent, sealed with a rubber septum bearing a syringe needle vent, and deoxygenated with a stream of dry nitrogen for 1 h. The nitrogen supply was turned off, and the appropriate amount of silacyclobutane was then added by a microliter syringe. The nitrogen supply was either kept off or opened only slightly during flash photolysis experiments to avoid loss of substrate or quencher through evaporation. Quenchers were added directly to the reservoir by a microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate concentration data (6−10 points) which spanned at least a factor of 5 (usually more than 1 order of magnitude) in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

Lifetimes were determined as a function of temperature between ~0 and 55 °C for silenes **3c,f−i**, in deoxygenated hexane solutions containing an appropriate concentration of methanol to reduce the lifetime to 10−15% of its value in the pure, deoxygenated solvent. The solutions were deoxygenated for 1−2 h prior to the addition of alcohol, and then the gas flow was reduced to a trickle in order to avoid evaporation of the quencher during the 3−4-h period required for the experiment. Quenching rate constants ($k_{MeOH}$) were estimated at each temperature as $k_{decay}$/[MeOH], without applying corrections for thermal expansion of the solvent. For **3c**, Arrhenius parameters were also determined from individual absolute quenching rate constants at several temperatures over the same range and were found to be identical to the estimated values within the quoted error limits ($\pm 2\sigma$).

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**Supporting Information Available:** UV absorption spectra and 3-parameter substituent correlation data for quenching of **3a**−**i** with EtOH and *t*-BuOH (12 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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