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Mechanistic Studies of the Reactions of Silicon−Carbon Double Bonds. Addition of Alcohols to 1,1-Diphenylsilene

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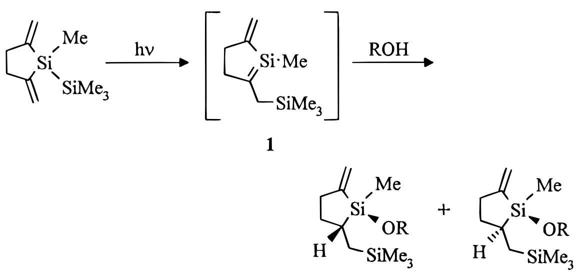
The addition of water, aliphatic alcohols, and acetic acid to 1,1-diphenylsilene (generated by photolysis of 1,1-diphenylsilacyclobutane) has been studied in polar solvents using steady-state and nanosecond laser flash photolysis techniques. Absolute rate constants and (selected) deuterium kinetic isotope effects for the addition of water, methanol, ethanol, 2-propanol, *tert*-butyl alcohol, and acetic acid have been determined at 23 °C in acetonitrile solution. Silene quenching follows a linear dependence on quencher concentration over the range investigated in all cases and proceeds with rate constants which vary over a range $4.1 \times 10^8 - 1.6 \times 10^9$ M^{-1} s^{-1}. The rate constants exhibit small primary deuterium kinetic isotope effects in all cases except acetic acid. Rate constants for addition of methanol, *tert*-butyl alcohol, and acetic acid have also been determined in hexane and THF solution. The transient absorption spectrum of the silene is broadened and red-shifted markedly in the latter solvent compared to that in acetonitrile and hexane, consistent with the formation of a solvent complex. Steady-state competition experiments have been carried out with various pairs of alcohols and water. The product ratios agree with the corresponding relative rate constants for water, methanol, and ethanol. Those for methanol/*tert*-butyl alcohol are significantly different from the rate constant ratio but approach it at very low total alcohol concentrations. The results are consistent with a two-step mechanism involving reversible formation of a silene−alcohol complex, followed by intracomplex proton transfer. The latter is rate-determining in all cases but acetic acid, for which it is proposed that complexation is the rate-determining step for reaction. Proton transfer from the complex to a second molecule of alcohol competes with the intracomplex pathway at higher alcohol concentrations for all cases but *tert*-butyl alcohol and acetic acid.

Introduction

Silenes are involved as reactive intermediates in a wide variety of thermal and photochemical reactions in organosilicon chemistry.[1−9] A number of trapping reactions have been employed to demonstrate their intermediacy, the most common being the addition of alcohols. This reaction is highly regioselective, but the stereoselectivity appears to vary from system to system.[10−12] Kira and co-workers have recently reported results for a cyclic transient silene (**1**), where the stereoselectivity of addition varies with the acidity and nucleophilicity of the alcohol and in most cases varies with alcohol concentration (eq 1).[12] They interpreted their results in terms of a mechanism (a more refined version of one initially proposed by Wiberg[5]) involving initial formation of a silene−alcohol complex which collapses to product by competing intra- and extracomplex proton transfer.



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Further refinement of this mechanism has been possible through the use of nanosecond laser flash photolysis (NLFP) techniques, which allow direct detection of transient silenes and measurement of absolute rate constants for their reaction with various reagents.[13−15] We have recently reported the results of steady-state and laser flash photolysis studies of the

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(1) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11.

(2) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

(3) Barton, T. J. *Pure Appl. Chem.* **1980**, *52*, 615.

(4) Coleman, B.; Jones, M. *Rev. Chem. Intermed.* **1981**, *4*, 297.

(5) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141.

(6) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(7) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(8) Barton, T. J.; Ijadi-Maghsoodi, S.; Magrum, G. R.; Paul, G.; Robinson, L. R.; Yeh, M. H. In *Silicon chemistry*; Corey, E. Y., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U. K., 1988; pp 201−210.

(9) Brook, A. G. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 965−1005.

(10) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913.

(11) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 4338.

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

(13) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89.

(14) Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329.

(15) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* **1992**, *114*, 1195.

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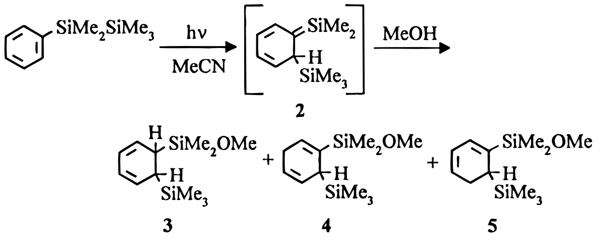
addition of alcohols to a series of conjugated silenes derived from aryldisilanes, of which pentamethylphenyldisilane is the parent compound.[16] Irradiation of the parent in methanolic acetonitrile yields the products of 1,2- (**3**), 1,4- (**4**), and 1,6-addition (**5**) of the alcohol to silene **2** (eq 2). The relative yields of the three products vary with methanol concentration, with **3** predominating at very low (<0.005 M) concentrations and **4** predominating at very high (>1 M) ones. The pseudo-first-order rate constant for decay of **2** in the presence of methanol shows a quadratic dependence on methanol concentration, the first-order component of which exhibits a small primary deuterium kinetic isotope effect. On the basis of these results, the mechanism shown in eq 3 was proposed for the addition of methanol to **2**. The corresponding rate law for decay of the silene (applying the steady-state assumption for the complex) is given in eq 4; this simplifies to eq 5 with the assumption that $k_{-1} \gg (k_2 + k_3[\mathrm{ROH}])$. Kinetic data obtained with diols as quenchers and for methanol in THF solution suggest that the extracomplex proton-transfer process most likely proceeds via a deprotonation−reprotonation sequence, with the alcohol acting as a general base in the initial step.



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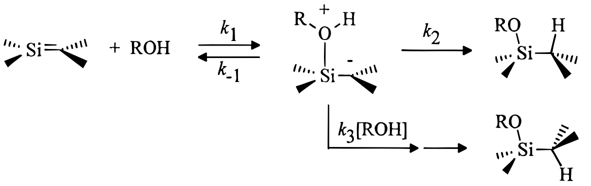


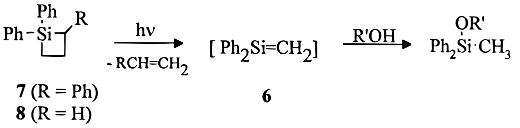
(3)

$$Rate = \frac{k_1}{(k_{-1} + k_2 + k_3[\mathrm{ROH}])}\{k_2 + k_3[\mathrm{ROH}]\}[\mathrm{ROH}][\mathrm{Silene}] \qquad (4)$$

$$Rate \sim \frac{k_1}{k_{-1}}\{k_2 + k_3[\mathrm{ROH}]\}[\mathrm{ROH}][\mathrm{Silene}] \qquad (5)$$

One particularly striking feature of the kinetic data reported for **2** is the ratio of the rate constants for intra- and extracomplex proton transfer (k_2/k_3 from eqs 3−5); in the case of the reaction of **2** with methanol in acetonitrile, a value of $k_2/k_3 \sim 0.05$ M was determined.[16] This can be compared to the value of $k_2/k_3 = 4.6$ M reported by Kira and co-workers for the reaction of silene **1** with methanol in the same solvent.[12] The difference was attributed to a stabilizing effect of the cyclohexadienyl substituent at the silenic carbon in the silene (**2**)−alcohol complex with respect to intracomplex proton transfer.[16] The very low k_2/k_3 value is precisely what makes the two competing proton-transfer pathways *kinetically* observable in the case of silatriene **2**. One can predict that simpler silenes such as that reported by Kira and co-workers (i.e., devoid of anion-stabilizing substituents at the silenic carbon) should show *linear* alcohol-quenching kinetics at relatively low alcohol concentrations, with the effects of the two competing proton-transfer pathways only becoming observable at relatively high alcohol concentrations. These conditions are amenable to investigation by product-study approaches (such as that employed by Kira *et al.*), but in general will be very difficult to study using direct methods.

In this paper, we wish to report the results of a study of the mechanism of alcohol addition to 1,1-diphenylsilene (**6**), a silene which is potentially more representative of this class of organosilicon reactive intermediates than those which have been previously studied by time-resolved methods. Our first report of the direct detection of **6** in solution employed 1,1,2-triphenylsilacyclobutane (**7**) as the precursor (see eq 6).[17] Laser flash photolysis of **7** in isooctane or acetonitrile solution leads to the formation of weak, but readily detectable, transient absorptions which were assigned to **6** on the basis of the spectral maximum ($\lambda_{\max} = 325$ nm) and reactivity toward carbonyl compounds and a diene. Unfortunately, this precursor was found to undergo a dark reaction with methanol, making it unsuitable for NLFP studies of the reactivity of **6** toward alcohols or other protic reagents. In the present work, 1,1-diphenylsilacyclobutane (**8**), another known photochemical precursor of **6**,[18,19] has been employed for the generation of 1,1-diphenylsilene in solution and to allow investigation of its reactivity toward water, aliphatic alcohols, and acetic acid.



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Results

Nanosecond laser flash photolysis of continuously flowing, air-saturated solutions of **8** (0.0075 M) in hexane with the pulses from a KrF excimer laser (248 nm, ~16 ns, 70−100 mJ) leads to weak, but easily detectable, transient absorptions, which decay on the microsecond time scale with mixed first- and second-order kinetics. In acetonitrile (MeCN) or tetrahydrofuran (THF) solution, the transient decays with clean pseudo-first-order kinetics and exhibits lifetimes which are extremely sensitive to the presence of water in the solvent; with rigorous drying, the lifetimes could be reproducibly extended to 3−4 μs. The UV absorption spectra of the transient in the three solvents, recorded in point-by-point fashion just after laser excitation, are shown in Figure 1. Typical decay traces, recorded at monitoring wavelengths of 325 nm (MeCN, hexane) and 350 nm (THF), are shown as inserts in the figure. The spectra in MeCN and hexane are similar to those reported from NLFP of **7** under similar conditions[17] and are thus assigned as due to 1,1-diphenylsilene (**6**). As reported previously, both the lifetime and initial yield

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

[17] Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5332.

[18] Boudjouk, P.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 54.

[19] Jutzi, P.; Langer, P. *J. Organomet. Chem.* **1980**, *202*, 401.

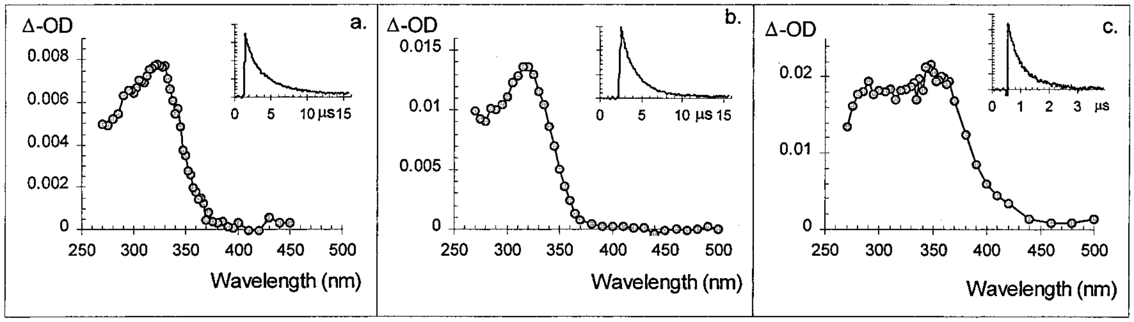


Figure 1. UV absorption spectra of 1,1-diphenylsilene (**6**), from nanosecond laser flash photolysis of air-saturated solutions of **8** (0.0075 M) in (a) hexane, (b) acetonitrile, and (c) tetrahydrofuran. The spectra shown in (a) and (b) were recorded 0.5−1.0 µs after the laser pulse, while that shown in (c) was recorded 0.2−0.5 µs after the pulse. The inserts show decay traces recorded prior to obtaining the spectrum in each case.

of **6** are insensitive to the presence of oxygen, so NLFP experiments were generally carried out in air-saturated solution. This procedure was shown to be satisfactory by determining absolute rate constants for quenching of **6** by methanol (*vide infra*) in nitrogen-, air-, and oxygen-saturated acetonitrile solution; they are the same, within experimental error.

The samples of **8** used in these experiments were purified by column chromatography, which allowed complete removal of the substantial amounts of biphenyl produced as a coproduct in the synthesis of the compound. Samples purified only by repeated vacuum distillation—even to a residual level of ca. 0.2% biphenyl—were unsuitable for NLFP experiments because of interference from biphenyl triplets, which are produced efficiently by competitive excitation of the impurity with the 248-nm laser and which absorb relatively strongly at 325 nm (λ_{max} = 365 nm). Decay traces recorded from such samples typically contained two components, the second of which was particularly prominent (as a slower decay superimposed on the faster one of **6**) in nitrogen-saturated solutions. While the lifetime of the biphenyl component can be selectively reduced to ~100 ns by saturating the solutions with oxygen, the preferable procedure (which is the one we employed) is to use samples containing ≤0.001% of the impurity.

Addition of water, alcohols (methanol, ethanol, 2-propanol, *tert*-butyl alcohol), or acetic acid resulted in shortening of the lifetime of the transient but no reduction in its initial yield or the production of new transient absorptions elsewhere in the spectrum. Similar results were obtained upon addition of the O-deuterated isotopomers of each of the quenchers, with the exception of 2-propanol (because it was not examined). Plots of the rate constant for decay of **6** (k_{decay}) *versus* concentration of added quencher (Q) according to eq 7 (where k_q is the bimolecular rate constant for

$$k_{decay} = k_d^{o} + k_q[Q] \qquad (7)$$

quenching of **6** by Q and k_d^0 is the pseudo-first order decay rate constant in the absence of Q) were linear in every case. Typical quenching plots for methanol and CH_3OD in acetonitrile solution at 23 °C are shown in Figure 2. Bimolecular rate constants for quenching of **6** by the protiated reagents in acetonitrile at 23 °C are listed in Table 1, along with k_H/k_D values calculated from these and the corresponding rate constants for quenching by the deuterated isotopomers. The acetonitrile employed for these experiments contained < 0.0005 M water, as estimated from the lifetime of **6** in the absence of added quencher and the bimolecular rate constant for quenching of **6** by H_2O (7.6 × 10^8 M^{-1} s^{-1}; see Table 1). Since the quencher concentration ranges employed for determination of absolute rate constants were generally significantly higher than this (0.001−0.01 M), systematic errors in the k_H/k_D values owing to exchange of deuterium with spurious water in the solvent can be considered to be negligible or, for the fastest quenchers studied, within the quoted error limits of the values reported.

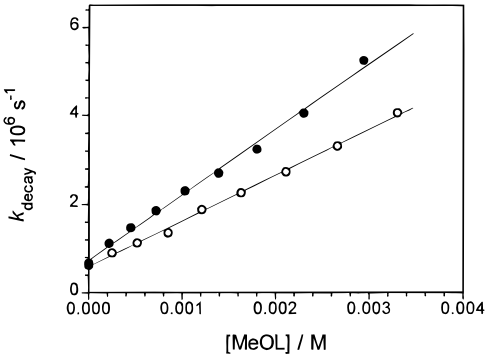


Figure 2. Plots of k_{decay} *vs* methanol concentration, from laser flash photolysis of air-saturated, 0.0075 M solutions of **8** in dry acetonitrile at 23.0 ± 0.2 °C in the presence of methanol (●) and CH_3OD (○).

Table 1. Absolute Rate Constants and Deuterium Kinetic Isotope Effects for Reaction of 1,1-Diphenylsilene (6) with Water, Aliphatic Alcohols, and Acetic Acid (ROH) in Air-Saturated Acetonitrile Solution at 23.5 ± 0.3 °C[a]

ROH	$k_q/10^9$ M^{-1} s^{-1}	k_H/k_D	ROH	$k_q/10^9$ M^{-1} s^{-1}	k_H/k_D
H_2O	0.76 ± 0.09	1.4 ± 0.2	^{i}PrOH	0.72 ± 0.05	*b*
MeOH	1.5 ± 0.1	1.5 ± 0.1	*t*BuOH	0.41 ± 0.02	2.2 ± 0.3
EtOH	1.0 ± 0.1	1.8 ± 0.2	HOAc	1.23 ± 0.07	1.1 ± 0.1

[a] Determined by nanosecond laser (248 nm) flash photolysis. Errors are quoted as twice the standard deviation, from linear least-squares analysis of decay rate−concentration data according to eq 7. [b] Not determined.

Rate constants for quenching of **6** by methanol, *tert*-butyl alcohol, and acetic acid were also determined in THF and hexane and are listed in Table 2.

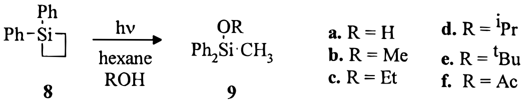
Steady-state irradiation of **8** (0.05 M) in dry hexane containing each of the quenchers listed in Table 1 (0.1 M) at 23 °C results in the formation of the corresponding addition product (**9a**−**f**) in chemical yields of > 90% (see

Table 2. Absolute Rate Constants (in Units of 10^9 M^{-1} s^{-1}) for Reaction of 1,1-Diphenylsilene (6) with Methanol, *tert*-Butyl Alcohol, and Acetic Acid in Air-Saturated Hexane, Acetonitrile, and THF Solution at 23.5 ± 0.3 °C[a]

solvent	MeOH	*t*-BuOH	HOAc
hexane	1.9 ± 0.2	0.40 ± 0.07	3.1 ± 0.3
MeCN	1.5 ± 0.1	0.41 ± 0.02	1.23 ± 0.07
THF	0.31 ± 0.03	0.024 ± 0.002	0.33 ± 0.02

[a] Determined by nanosecond laser (248 nm) flash photolysis. Errors are quoted as twice the standard deviation, from linear least-squares analysis of decay rate−concentration data according to eq 7.

eq 8). The products were identified by coinjection of the crude photolysates with authentic samples or on the basis of spectroscopic data, after isolation by semipreparative gas chromatography (GC). The same products were obtained from photolyses in acetonitrile solution, along with small amounts of **9a** due to the presence of residual water in the solvent. In the absence of a trapping reagent, photolysis of **8** produced a higher molecular weight compound in high (>80%) yield, along with **9a** and several other minor products. The major product formed under these conditions was tentatively identified as 1,1,3,3-tetraphenyl-1,3-disilacyclobutane (**10**) on the basis of its GC retention time and mass spectrum.[19]



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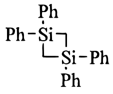

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The quantum yield for photolysis (254 nm; 23 °C) of **8** was determined by potassium ferrioxalate actinometry, using 0.05 M solutions of **8** in hexane solution containing 0.1 M methanol. The value obtained is $\Phi_{-8} = 0.21 \pm 0.03$.

Irradiation (254 nm; 23 °C) of solutions of **8** (0.0027 M) in dried acetonitrile ($[H_2O] \leq 0.01$ M) containing methanol (0.027 M) and various amounts of ethanol (0.02−0.1 M) led to the formation of **9b**,**c** in relative amounts which are directly proportional to the relative concentrations of the two alcohols, in addition to small amounts of **9a**. A plot of product ratio *versus* alcohol concentration ratio according to eq 9 is linear (r^2 =

$$[\mathbf{9b}]/[\mathbf{9}] = C_{ROH}([MeOH]/[ROH]) \qquad (9)$$

0.9980), affording a proportionality constant $C_{EtOH} = 1.54 \pm 0.07$. Similar experiments, using methanol as the standard, were also carried out for water and *tert*-butyl alcohol. The proportionality constants obtained in these experiments are listed in Table 3. The table also contains the corresponding ratios of absolute rate constants, calculated from the data in Table 1. Attempts to carry out similar experiments with acetic acid were abandoned, as it was found that the acyloxysilane **9f** undergoes slow decomposition in acetonitrile (in the dark) under the conditions of the experiment.

Table 3. Proportionality Constants (C_{ROH}) from Steady-State Competition Photolyses of 8 (0.0027 M) in Dry Acetonitrile containing MeOH (0.027 M) and Water, Ethanol or *tert*-Butyl Alcohol at 23 °C, and Rate Constant Ratios (k_{MeOH}/k_{ROH}) from Nanosecond Laser Flash Photolysis Experiments at 23 °C[a]

ROH	C_{ROH}	k_{MeOH}/k_{ROH}	ROH	C_{ROH}	k_{MeOH}/k_{ROH}
H_2O	1.82 ± 0.09	2.0 ± 0.2	*t*-BuOH	12.0 ± 0.7	3.7 ± 0.4
EtOH	1.54 ± 0.07	1.5 ± 0.2			

[a] C_{ROH} values were determined from the slopes of plots of [**9b**]/[**9**] *versus* [MeOH]/[ROH] according to eq 9. Errors are quoted as twice the standard deviation of the least-squares slope. Rate constant ratios were calculated from the data listed in Table 1.

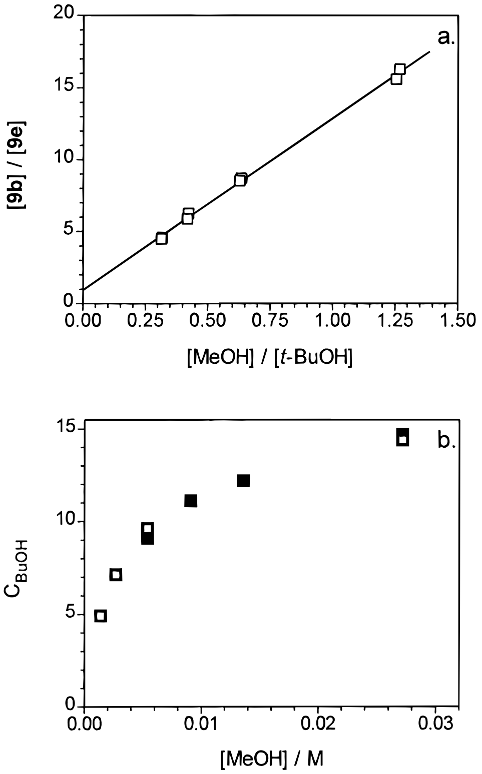


Figure 3. Steady-state product ratios [**9e**]/[**9b**] from photolysis of acetonitrile solutions of **8** in the presence of methanol and *tert*-butyl alcohol: (a) [**9e**]/[**9b**] *vs* [t-BuOH]/[MeOH], for photolyses of 0.0027 M solutions of **8** containing 0.027 M methanol and varying concentrations (0−0.1 M) of *tert*-butyl alcohol; (b) C_{BuOH} (={[**9b**]/[**9e**]}{[t-BuOH]/[MeOH]} *vs* [MeOH], from photolysis of solutions **8**, MeOH, and *t*-BuOH at various methanol concentrations but similar [BuOH]/[MeOH] ratios (■, 2.4; □, 3.2).

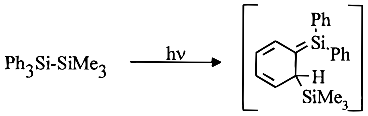
Two sets of experiments were carried out at a constant [MeOH]/[*t*-BuOH] ratio (0.42 or 0.31) but with the total alcohol concentration varying between 0.006 M and 0.093 M. The concentration of **8** was also adjusted so that it was roughly 10% of the methanol concentration, and photolyses were carried out to 15−20% conversion. C_{BuOH} values were calculated from the measured [**9b**]/[**9e**] ratios and the (known) alcohol concentration ratios (see eq 9) and are shown plotted against methanol concentration in Figure 3b.

Discussion

The assignment of the transient observed in this work to 1,1-diphenylsilene (**6**) can be made with a high degree of certainty, as it is based on a number of corroborating pieces of evidence. First, the observation that the transient decays with predominant second-order kinetics in hydrocarbon solvents is consistent with the behavior expected on the basis of steady-state irradiation of **8** under similar conditions; the compound undergoes reasonably efficient photolysis ($\Phi_{-\mathbf{8}} = 0.21 \pm 0.03$), to yield the disilacyclobutane (**10**) corresponding to head-to-tail dimerization of **6** as the major product.[19] The lifetime of the transient is reduced upon addition of water or alcohols to the solution, again consistent with the fact that steady-state photolysis of the compound under similar conditions affords the corresponding alkoxysilane **9** in high chemical yield, to the exclusion of the silene dimer.[18] Second, the same transient absorption spectrum has been reported from laser flash photolysis of other known[19,20] photochemical precursors to **6**: 1,1,3-triphenylsilacyclobutane (**7**)[17] and methylpentaphenyldisilane (**10**).[21] In all three cases, the transient exhibits similar reactivity toward water, alcohols, carbonyl compounds, oxygen, and various other reagents. The trends in reactivity observed (high reactivity toward water, alcohols, and ketones; moderate reactivity toward alkenes and dienes; low reactivity toward oxygen and halocarbons) are consistent with the transient possessing a silicon–carbon double bond.[6,7,9]

The UV absorption spectra of **6** in acetonitrile and hexane are essentially identical, indicating that there is little variation in the spectrum with bulk solvent polarity. This being the case, the substantial broadening and red-shift of the spectrum in THF compared to that in MeCN may be the result of complexation of the silene with the solvent. The appearance of the spectrum is consistent with a superposition of absorption bands due to free and complexed silene, as we proposed previously for silatriene **2** in THF/MeCN mixtures.[22] The latter exhibits well-defined absorption bands in acetonitrile and THF with maxima at 425 nm and 460 nm, respectively;[22] spectra recorded in THF/MeCN mixtures indicate that the spectral changes occur over the 1–12% (THF) composition range. The spectrum of **2** in 5% THF consists of a single broad absorption band centered midway between the two extremes, allowing a rough estimate of $\sim 1.6\ \mathrm{M}^{-1}$ for the equilibrium constant for formation of the **2**–THF complex in acetonitrile solution.[22] If the broad absorption band observed for **6** in THF is due to the presence of more or less equal amounts of complexed and uncomplexed silene, then a value of $K \sim 0.1\ \mathrm{M}^{-1}$ can be estimated for the equilibrium constant for formation of the **6**–THF complex in pure THF. Whether or not the spectrum of **6** in THF can be attributed to the presence of discrete solvent complexes, however, it is clear that the silene is very strongly solvated in THF compared to the situation in MeCN.

It is relevant to note that the diphenyl-substituted silatriene **12** (formed by photolysis of trimethyltriphenyldisilane; see eq 10) shows no spectroscopic evidence for formation of a complex with THF, even in the neat solvent.[22] This being the case, the corresponding equilibrium constant can be given an upper limit of $\sim 0.02\ \mathrm{M}^{-1}$, assuming that this is the lowest value which would allow detection of the complex by UV spectroscopy. The lower equilibrium constant for THF complexation of **12** (or at least, the clearly much weaker solvation of **12** compared to **2**) is presumably due to steric factors, an effect which also results in correspondingly lower rate constants for reaction with alcohols, water, acetic acid, and carbonyl compounds.



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(10)

The linear dependences of k_{decay} on quencher concentration and the small (but clearly primary) deuterium kinetic isotope effects on the quenching rate constants which are observed for the quenching of **6** by water, methanol, ethanol, and *tert*-butyl alcohol are consistent with the stepwise addition mechanism depicted in eq 3, so long as the rate of proton transfer within the silene–alcohol complex is significantly faster than that of the extracomplex proton–transfer pathway at the low alcohol concentrations employed for the kinetic studies (i.e. $k_2 \gg k_3[\mathrm{ROH}]$ when $[\mathrm{ROH}] < 0.01$ M). They are also consistent with a concerted mechanism, but other observations argue against this possibility. The first is the *lack* of agreement between the absolute rate constant ratios and the corresponding steady-state product ratios for methanol and *tert*-butyl alcohol; in acetonitrile solution, the ratios match only at millimolar total alcohol concentrations, suggesting a more complex dependence of rate on alcohol concentration than a single-step concerted mechanism would allow. The second is the lack of a significant isotope effect for HOAc, even though it quenches **6** in acetonitrile solution with a rate constant similar to those of methanol and ethanol. In this case, the substantially lower nucleophilicity and higher acidity of the quencher might be expected to lead to a change in rate-determining step from proton transfer to complexation. Finally, the spectroscopic behavior of **6** in THF provides indirect support for the involvement of silene–alcohol complexes in the addition of alcohols to this silene.

The magnitude and variation in the rate constants for addition of water and alcohols to **6** in acetonitrile solution (Table 1) are similar to those observed for the reaction of these nucleophiles with diarylcarbenium ions.[23] The trend in the KIE's throughout the series suggests that the variation in rate constant (MeOH > EtOH > H_2O ~ *i*-PrOH > *t*-BuOH) can be attributed to a progressive slowing in the rate of intracomplex proton transfer throughout the series, although the equilibrium constants for complex formation are also contained in the overall rate constants for quenching of **6** ($k_q \sim k_1k_2/(k_{-1} + k_2)$; see eq 3), and these can be expected to vary systematically as ROH nucleophilicity and steric factors vary. This conclusion contradicts that of Kira and coworkers, who suggested that the increase in syn-stereoselectivity in the addition of alcohols to silene **1**, in the order MeOH < *n*-PrOH < *i*-PrOH < *t*-BuOH, is due to a progressive *increase* in the rate of intracomplex proton transfer throughout the series, accompanied by a corresponding decrease in the rate of extracomplex proton transfer involving a second molecule of alcohol.[12] This suggestion was based on the quite reasonable

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(20) Boudjouk, P.; Roberts, J. R.; Golino, C. M.; Sommer, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 7926.

(21) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1994**, *13*, 1005.

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

(23) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710.

proposal that the rate of intracomplex proton transfer should increase with increasing acidity of the hydroxylic proton in the complex, as approximated by the pK_a's of the protonated alcohols. Aqueous ROH_2^+ pK_a values were employed for this analysis, which seems reasonable since the solvents employed were alcohol−acetonitrile mixtures containing rather large amounts of alcohol. In pure acetonitrile containing millimolar amounts of alcohol (the conditions employed in the present study), the ordering of protonated alcohol acidities is opposite to that in aqueous solution.[24] Thus, the same analysis predicts that, under our conditions, the rate of intracomplex proton transfer should be *slower* for the silene/*t*-BuOH complex than for the silene/MeOH one, which is consistent with the trend in the kinetic isotope effects on the absolute rate constants for reaction of **6** with these alcohols. While variations in the individual rate constants of eq 3 with alcohol may be solvent-dependent, it seems clear that the *relative* rate of intracomplex to extracomplex proton transfer is substantially higher for *t*-BuOH than for MeOH *regardless of solvent*; this is borne out by the results for **1** in MeCN−ROH mixtures,[12] kinetic data for the addition of alcohols to other transient silenes in MeCN, THF, and hexane,[15,16] and the results of steady-state competition experiments with **6** in MeCN (*vide infra*). In dipolar aprotic solvents, this must result mainly from variations in the magnitude of the *extra*complex proton transfer pathway throughout the series, however.

The linear dependence of k_{decay} on [ROH] suggests that, over the alcohol concentration ranges employed in the kinetic studies, reaction with **6** proceeds predominantly via the intracomplex proton transfer pathway. This linearity is advantageous in that it allows for ready determination of second-order rate constants for reaction of **6** with these reagents. However, it also masks the presence of the extracomplex proton transfer process, so that extraction of the rate ratio k_2/k_3 for the purposes of quantitative comparisons with data for other systems is precluded. The steady-state competition experiments with methanol and *tert*-butyl alcohol (Figure 3) provide a strong indication that the process *does* occur, at least in the case of methanol, in spite of the fact that we are unable to detect it by direct kinetic measurements; the simple fact that the proportionality constant relating the observed [**9b**]/[**9e**] ratio to the alcohol concentration ratio (C_{BuOH} in eq 9) is *not* concentration-independent (see Figure 3b) indicates that the addition of at least one of the two alcohols is governed by a rate law containing a higher order term in alcohol concentration.

The results shown in Figure 3b are qualitatively consistent with expectations based on previously reported results for the addition of methanol and *tert*-butyl alcohol to **1**, **2**, and **12**,[12,15,16] *i.e.*, that the extracomplex proton-transfer pathway is much slower (relative to the intracomplex pathway) for *tert*-butyl alcohol than methanol. If this is the case for **6** as well, then one would expect C_{BuOH} to be independent of alcohol concentration when the bulk alcohol concentration is relatively high (*i.e.*, formation of methoxysilane **9b** occurs predominantly by the extracomplex proton transfer pathway) and when it is relatively low (i.e., in the range employed for the flash photolysis experiments (<0.005 M), where the extracomplex pathway is relatively unimportant). Figure 3b shows indications of adhering to the predicted behavior only in the range of high alcohol concentrations; however, the C_{BuOH} value measured at the lowest alcohol concentrations employed ([MeOH] = 0.0014 M; [*t*-BuOH] = 0.0046 M) is $C_{\mathrm{BuOH}} = 4.9 \pm 0.2$, in reasonable agreement with the absolute rate constant ratio determined by laser photolysis techniques at a similar temperature ($k_{\mathrm{MeOH}}/k_{t\text{-}\mathrm{BuOH}} = 3.7 \pm 0.5$). The failure of the plot to level off in the low alcohol concentration range may be the result of the presence of water in the solvent, which can contribute to the formation of **9b** by assisting in the extracomplex proton transfer (in addition to leading to the formation of **9a**, which is observed as a coproduct in all of the irradiations carried out in acetonitrile solution). The concentration of adventitious water in the steady-state photolysis experiments is particularly difficult to reduce below ~0.01 M without employing considerably more rigorous experimental techniques than those used in this work.

For water and ethanol, excellent agreement is observed between C_{ROH} and the absolute rate constant ratios determined by flash photolysis, presumably because contributions to product formation by the extracomplex proton-transfer pathway are similar for water, methanol, and ethanol.

The variation in the absolute rate constants for reaction of methanol, *tert*-butyl alcohol, and acetic acid in hexane, MeCN, and THF follows the hydrogen-bonding abilities of the solvents rather than their bulk polarities and can be attributed to increasingly strong solvation of the silene with increasing solvent Lewis basicity. For THF, this effect overshadows the ability of the solvent to act as a general base for deprotonation of the silene−alcohol complex, which would be expected to *increase* the second-order rate constant for reaction of methanol relative to its value in acetonitrile. Such increases are observed only when solvation of the silene by THF is relatively weak (as with silene **12**, for example[22]).

The reaction of *t*-BuOH with **6** shows a much larger rate reduction in THF than that of MeOH, presumably due to the difference in importance of the extracomplex proton-transfer mechanism for the two alcohols. Solvent-assisted deprotonation of the silene-methanol complex accelerates its decay to some extent in THF relative to MeCN but not enough to overcome the retarding influence of strong silene solvation by the ether. This is less important for *t*-BuOH, and consequently the rate reduction in THF is much larger. Acetic acid might be expected to show a similar rate reduction in THF to that exhibited by *tert*-butyl alcohol. It does not, perhaps because the nucleophilicity of the carboxylic acid is increased in THF due to strong hydrogen-bonding to the solvent.

Fluorinated alcohols are poorer nucleophiles and stronger acids than water and the aliphatic alcohols reported here and would be expected to exhibit analogous behavior to acetic acid in their reactions with **6**. However, preliminary experiments indicate that these compounds exhibit unexpectedly high reactivity toward this silene and afford products in addition to the

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(24) Izutsu, K. *Acid-base dissociation constants in dipolar aprotic solvents. IUPAC Chemical Data Series No. 35*; Blackwell Scientific Publications: Oxford, U.K., 1990; pp 17−35.

expected alkoxysilanes in polar solvents.[25] These intriguing results are the subject of continued investigation.

Summary and Conclusions

1,1-Diphenylsilene reacts with water, alcohols, and acetic acid with rate constants which are only 1 order of magnitude slower than the diffusion-controlled limit and which show little sensitivity to nucleophilicity or acidity. The observation of small but clearly primary deuterium kinetic isotope effects, a substantial broadening and red-shift of the UV absorption spectrum of the silene in THF solution, and a complex dependence of the relative reactivity of methanol and *tert*-butyl alcohol on alcohol concentration are consistent with a mechanism involving initial, reversible formation of a silene–alcohol complex, followed by rate-determining proton transfer to yield the corresponding alkoxysilane. While undetectable by kinetic methods, the concentration dependence of the product ratios in steady-state competition experiments provides evidence that proton transfer occurs by competing intracomplex and extracomplex mechanisms. The weaker nucleophile HOAc exhibits similar overall reactivity to methanol but does not exhibit a significant deuterium isotope effect. This is proposed to be due to a change in the rate-determining step from proton transfer to complexation.

Further work is in progress to more completely delineate the mechanism of this widely-used trapping reaction for transient silenes and to define the effects of substituents—on both the silene and the nucleophile—on the kinetics and mechanism of the reaction.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 NMR spectrometer in deuterated chloroform solution, while ^{29}Si NMR spectra were recorded on a Bruker AC300 spectrometer using the DEPT pulse sequence; all are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low-resolution mass spectra and GC/MS analyses were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 fused silica capillary column (12 m × 0.2 mm; Chromatographic Specialties, Inc). High-resolution desorption electron impact (DEI) mass spectra and exact masses were recorded on a VGH ZABE mass spectrometer. Exact masses employed a mass of 12.000000 for carbon. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer.

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, conventional heated splitless injector, and a DB-1 fused silica capillary column (15 m × 0.20-mm; Chromatographic Specialties, Inc.). Semipreparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a 6 ft × 0.25 in. stainless steel OV-101 packed column (Chromatographic Specialties).

Acetonitrile (BDH or Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days, distilled under dry nitrogen, and then cycled three times through a 1 in. × 6 in. column of neutral alumina (Fisher) which had been activated by heating under vacuum (ca. 0.05 Torr) at 320 °C for 10 h (with periodic shaking). Methanol (Baker Reagent) and absolute ethanol were predried with calcium hydride, distilled from magnesium under nitrogen, and stored over 3 Å molecular sieves. *tert*-Butyl alcohol (Fisher Reagent) and 2-propanol (Caledon Reagent) were predried with calcium oxide, distilled from calcium hydride under nitrogen, and stored over 4 Å molecular sieves. Hexane (Caledon Reagent) was stirred for several days over concentrated sulfuric acid, washed several times with water and once with saturated aqueous sodium bicarbonate, dried over anhydrous sodium sulfate, and distilled from sodium. Tetrahydrofuran (BDH Omnisolv) was refluxed for several days over sodium under nitrogen and distilled. Deuterated materials were used as received from MSD Isotopes or Isotec, Inc. 1,1-Dichlorosilacyclobutane was used as received from Huls America or synthesized from 1-chloropropyl-3-trichlorosilane (Petrarch) by the method of Laane.[26]

1,1-Diphenylsilacyclobutane (**8**) was prepared by a modification of the method of Auner and Grobe.[27] Bromobenzene (8.9 g, 0.057 mol) and 1,1-dichlorosilacyclobutane (4.0 g, 0.028 mol) were dissolved in dry diethyl ether (20 mL) and placed in a 100 mL addition funnel. The solution was added dropwise over 2 h to a 250 mL round bottom flask fitted with a reflux condenser, nitrogen inlet, and magnetic stirrer and containing magnesium turnings (1.7 g, 0.07 mol) in diethyl ether (10 mL). After the addition was complete the resulting mixture was refluxed gently for 2 h. The reaction mixture was cooled and gravity-filtered into a 500 mL separatory funnel, washing the salts several times with diethyl ether. The filtrate was then extracted with saturated aqueous ammonium chloride (3 × 25 mL) and water (3 × 25 mL), dried over anhydrous magnesium sulfate, and then distilled on the rotary evaporator to yield a light yellow viscous liquid. The liquid was dissolved in a small amount of hexane and chromatographed on a 40 × 2.5 cm silica gel 60 column, eluting with hexanes. The purity of fractions containing **8** (the first component to elute from the column) was determined by GC; those containing >0.001% biphenyl were combined and rechromatographed. 1,1-Diphenylsilacyclobutane was obtained as a colorless oil (3.3 g, 0.0145 mol, 51%; bp 80–90 °C (0.05 mmHg); lit. bp 110–115 °C (0.001 mm Hg)[27]). The compound exhibited spectroscopic and analytical properties similar to the reported data.[27] The UV absorption spectrum showed a long wavelength absorption band with $\lambda_{\max} = 260$ nm ($\epsilon = 790$ M^{-1} cm^{-1}) in hexane solution. The ^{29}Si NMR spectrum showed a single peak at δ 6.78.

Methoxymethyldiphenylsilane (**9b**) and ethoxymethyldiphenylsilane (**9c**) were identified by GC and GC/MS coinjections of crude photolysis mixtures with authentic samples, synthesized from chloromethyldiphenylsilane (Aldrich) and the appropriate alcohol in pyridine.[28] Compounds **9a,d–f** were identified spectroscopically after semipreparative GC isolation from crude photolysis mixtures. Generally, a 0.02 M solution of **8** in hexane containing the appropriate alcohol, water, or acetic acid (0.1 M) was irradiated (254 nm) through quartz in a Rayonet reactor to *ca.* 65% conversion. After evaporation of the solvent and excess alcohol by distillation, the crude photolysate was redissolved in a small amount of pentane and then fractionated by semipreparative GC. Samples of greater than 99.9% purity (as estimated by analytical GC) were obtained in each case. Spectroscopic data obtained for the three compounds were similar to reported data.[29,30]

Competitive photolysis experiments were carried out using a Rayonet reactor containing eight RPR2537 lamps. Quartz tubes (0.5 × 8 cm) containing dried acetonitrile solutions (*ca.* 1 mL) of **8** (0.0027 M), methanol (0.027 M), and another alcohol (in varying concentrations) were sealed with rubber septums

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[25] Bradaric, C. J.; Kerst, C.; Leigh, W. J. Unpublished results.

[26] Laane, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144.

[27] Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *188*, 25.

[28] Brook, A. G.; Dillon, P. J. *Can. J. Chem.* **1969**, *47*, 4347.

[29] Lycka, A.; Snobl, D.; Hanklir, K.; Holecek, J.; Nadvornik, M. *Coll. Czech. Chem. Commun.* **1982**, *47*, 603.

[30] Liepins, E.; Zicmane, I.; Lukevics, E. *J. Organomet. Chem.* **1986**, *306*, 167.

and irradiated for 5 min (*ca.* 15% conversion of **8**). The solutions were analyzed in triplicate by GC. Relative product yields were calculated from the relative product peak areas, after correction for relative GC response factors (determined for each compound using working curves constructed from analysis of standard solutions). Plots of alkoxysilane product ratios *versus* alcohol concentration ratios were linear in every case. The data shown in Figure 3b were obtained from irradiations of a series of solutions containing various concentrations of methanol and *tert*-butyl alcohol in ratios of 0.31 or 0.42. The concentration of **8** was adjusted so as to be < one-fifth of that of the methanol present, and irradiations were taken to conversions of <15%. The particularly dilute solutions in this series employed alumina-dried acetonitrile and were concentrated by vacuum distillation prior to analysis by GC.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; *ca.* 16 ns; 70−120 mJ) from a Lumonics 510 excimer laser, filled with F_2/Kr/He mixtures, and a microcomputer-controlled detection system.[31] The system incorporates a brass sample holder whose temperature is controlled to within 0.1 °C by a VWR 1166 constant-temperature circulating bath. Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was *ca.* 0.7 (0.0071 M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were 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 (6−10 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 analysis in each case.

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[31] Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A: Chem.* ***1991***, *57*, 97.