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Direct Detection of 1,1-Diphenyl-2-neopentylsilene and the Effects of Solvent Polarity on Its Reactivity with Nucleophiles

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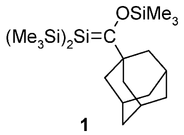
The reactivity of the transient silene 1,1-diphenyl-2-neopentylsilene (**4**) has been studied in various solvents by laser flash photolysis methods, using *trans*-1,1,3,3-tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane as the precursor. Silene **4** exhibits a lifetime of ca. 250 μs and a UV absorption maximum of $\lambda_{max} = 335$ nm ($\epsilon = 10000 \pm 2900$ M^{-1} cm^{-1}) in dry, deoxygenated hexane, where it undergoes head-to-tail dimerization and reacts with oxygen with absolute rate constants of $k_{dim} = (5 \pm 2) \times 10^8$ M^{-1} s^{-1} and $k_{O2} = (6.5 \pm 0.8) \times 10^5$ M^{-1} s^{-1}, respectively. Identical absorption maxima are exhibited by **4** in 1,2-dichloroethane, tetrahydrofuran, and acetonitrile solution, indicating that the silene does not form detectable Lewis acid−base complexes with these solvents, thus making it possible to study the effects of solvent polarity on silene reactivity for the first time. Accordingly, absolute rate constants for reaction of **4** with acetone, methanol, acetic acid, 2,2,2-trifluoroethanol, and *n*-butylamine have been determined as a function of temperature in two or more of the four solvents. The results are compared to previously reported data for 1,1-diphenylsilene (**2a**) and show that the 2-neopentyl substituent in **4** enhances the reactivity of the Si=C bond with oxygen, but reduces its reactivity with nucleophilic reagents and toward [2+2]-dimerization by as much as a factor of 10^3. As with **2a**, the Arrhenius parameters for the reactions of **4** are consistent with stepwise mechanisms, initiated by reversible complexation between the nucleophile and the silene, followed by H-transfer. The absolute rate constants at 25 °C vary by only a factor of 3−10 with solvent in each case, but there is a general trend toward increasingly positive Arrhenius activation energies and pre-exponential factors with increasing solvent polarity. The mechanistic ramifications of these results are discussed.

Introduction

The silicon−carbon double bond constitutes an intrinsically reactive bonding situation, and as a result, most known "silenes" undergo rapid addition reactions with nucleophiles and (in the absence of sterically stabilizing substituents) dimerize via [2+2]- or ene-cycloaddition pathways.[1−5] Theoretical calculations suggest that the high degree of reactivity that is associated with the Si=C bond is due in part to its substantial ($^{\delta+}$Si=C$^{\delta-}$) polarity, which results from the electronegativity difference between silicon and carbon; thus, kinetic stabilization should result in derivatives bearing σ-donor/π-acceptor (e.g., SiR$_3$) substituents at silicon and σ-acceptor/π-donor substituents (e.g., −R, −OR, or NR$_2$) at carbon, due to substituent-induced reductions in the natural Si=C bond polarity.[6,7] Indeed, this is precisely the structural motif contained in the first known stable silene derivative, **1**, synthesized a number of years ago by A. G. Brook and co-workers.[8]



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Direct experimental verification of these ideas has been reported in the form of absolute rate constants for the 1,2-addition reactions of methanol to transient silenes of the type Me(R)Si=CH$_2$[9] and Me$_2$Si=CR(R′)[10] in hydrocarbon solvents. The mechanism of this reaction has been relatively well studied, at least for silenes that lie at the upper end of the electrophilicity scale. With such derivatives, the reaction proceeds by a stepwise mechanism initiated by reversible attack of the neutral

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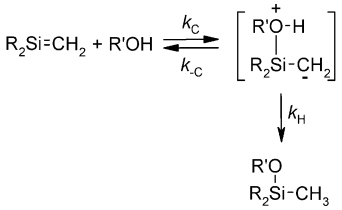
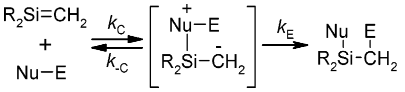
10.1021/om0500117 CCC: $30.25

nucleophile at the silenic silicon to form a zwitterionic addition complex, which then proceeds to product by proton transfer from oxygen to carbon (eq 1).[1,11,12] Both steps in the sequence are reflected in the overall rate constant for reaction, which makes this a useful standard reaction for gauging the effects of substituents on the kinetic stability of the Si═C bond. Indeed, the rate constants obtained for these series of compounds were found to correlate with standard resonance, inductive, and steric substituent parameters in a manner consistent with Si═C bond polarity being the main factor responsible for controlling the reactivity of these silenes toward nucleophilic reagents, as predicted by theory.[6] Within the limited series of compounds studied, those bearing trimethylsilyl substituents at silicon and alkyl substituents at carbon exhibited the largest reductions in reactivity compared to the base compound in the series ($Me_2Si{=}CH_2$).



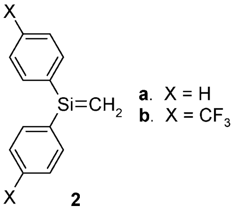
$$R_2Si{=}CH_2 + R'OH \underset{k_{-C}}{\overset{k_C}{\rightleftharpoons}} \left[\begin{array}{c} R'\overset{+}{O}{-}H \\ | \\ R_2Si{-}\underset{-}{C}H_2 \end{array}\right] \xrightarrow{k_H} \begin{array}{c} R'O \\ | \\ R_2Si{-}CH_3 \end{array} \qquad (1)$$

Silenes also undergo 1,2-addition reactions with other nucleophiles such as amines, carboxylic acids, and alkoxysilanes and react with aliphatic ketones and aldehydes to yield [2+2]- or ene-cycloaddition products.[1−5] On the basis of the results of substituent, isotope, and temperature effects on the rate constants for these reactions in the case of 1,1-diphenylsilene (**2a**), it has been concluded that they all proceed via stepwise mechanisms analogous to that of alcohol addition, i.e., by initial, reversible attack of the nucleophilic site in the reagent at silicon to yield an intermediate, which then proceeds to product in a subsequent, electrophile-transfer step (eq 2).[13−17] The latter is rate-determining in all cases except that of carboxylic acid addition, where the proton that is transferred is particularly acidic. All of these reactions exhibit positive Hammett ρ-values, consistent with a mechanism involving initial nucleophilic attack at silicon, and all but acetic acid addition exhibit negative activation energies, consistent with a two-step mechanism in which the first step is reversible and the second is rate-controlling.[13−17]



$$\begin{array}{c} R_2Si{=}CH_2 \\ + \\ Nu{-}E \end{array} \underset{k_{-C}}{\overset{k_C}{\rightleftharpoons}} \left[\begin{array}{c} \overset{+}{N}u{-}E \\ | \quad - \\ R_2Si{-}CH_2 \end{array}\right] \xrightarrow{k_E} \begin{array}{c} Nu \quad E \\ | \quad | \\ R_2Si{-}CH_2 \end{array} \qquad (2)$$

Probing the differences in the nature of the intermediates involved in these reactions is of considerable interest. Some previous experimental work offers information on the structures and bonding in the intermediates involved in the addition of alcohols and amines, to the extent that they can be modeled by the complexes of electrophilic silenes with ethers and tertiary amines.[18−20] Additional information of potentially greater relevance to reactivity might be obtained from a study of solvent effects on the kinetics of the specific reactions, and indeed, a few studies of this type have been reported.[16,17,21−23] However, in most cases the particular silenes that were studied were sufficiently strongly electrophilic to complex strongly with oxygenated solvents such as THF. This has been shown to elicit marked effects on the reactivity of the silene that are essentially unrelated to solvent polarity;[16] in the cases of **2a**, its 4,4′-bis(trifluoromethyl) derivative (**2b**), and the exceedingly strongly electrophilic silene **3**, the effects of solvent complexation on the reaction kinetics could be discerned even with the weakly basic solvent acetonitrile (MeCN).[16,23] In the end, it is clear that in order to study the effects of solvent polarity on silene reactivity in a meaningful way, one must do so with a silene derivative that is intrinsically less electrophilic than those derivatives that have been studied to date, to avoid potential complications from solvent complexation on the reaction kinetics.



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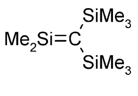

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Additional motivation for a study of this type stems from recent theoretical work on the effects of substitution on the mechanistic details of the addition of water and alcohols to simple silenes,[7] which predicts that the reaction mechanism should change from the stepwise one observed for highly polar silenes (e.g., silene itself) to a concerted mechanism as Si═C bond polarity is reduced by substituents. The mechanistic change is predicted to occur in silenes bearing (two) alkyl substituents at the silenic carbon and persists in silenes bearing even stronger π-donating substituents at this position, such as those in the Brook silene **1** and related analogues.

In the present paper, we report the results of a kinetic study of the reactions of the 2-alkyl-substituted 1,1-diarylsilene derivative **4** with methanol (MeOH), 2,2,2-trifluoroethanol (TFE), acetic acid (AcOH), acetone, and *n*-butylamine (n-$BuNH_2$) in hexane, THF, and MeCN. The reaction with MeOH has also been characterized in 1,2-dichloroethane (DCE), a solvent of similar dielectric constant to THF, and absolute rate constants for the [2+2]-dimerization of **4** and for reaction with oxygen have been determined in hexane solution. The photocycloreversion of 1,3-disilacyclobutane *trans*-**5** (one of

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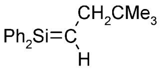
the two stereoisomeric head-to-tail dimers of **4**) has been employed to generate and detect the silene by laser flash photolysis methods, as an earlier study of the photochemistry of this compound[24] suggested that it might yield **4** in high enough quantum yield to serve as a convenient photoprecursor for studies of this type. This supposition has been verified by a quantitative study of the photochemistry of *trans*-**5** and its geometric isomer, *cis*-**5**, at low (<10%) conversions in cyclohexane-d_{12} solution, the results of which are also reported.



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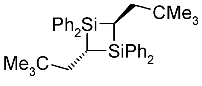
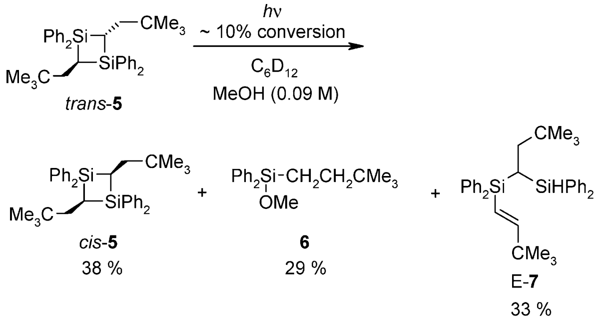


trans-**5**

Results

The previous study of the photolysis of *trans*-**5** involved irradiations carried out to quite high conversions of the substrate, where secondary photolysis of some of the primary products becomes important,[24] and so we began ours with an attempt to quantify the primary product yields. Accordingly, deoxygenated 0.05 M solutions of *trans*-**5** in cyclohexane-d_{12} containing 0.09 M methanol (MeOH) were irradiated with 254 nm light, monitoring the product mixture by ^{1}H NMR spectroscopy over the range of 0−10% conversion of *trans*-**5**. The products of the reaction could be easily identified by comparison of the NMR spectra to the reported spectra of the individual isolated compounds.[24−26] These experiments verified that the isomeric compounds *cis*-**5** and *E*-**7** and the expected MeOH-adduct of silene **4** (**6**) are the only primary products of photolysis of this compound at low (10%) conversions of starting material; product concentration versus time plots were approximately linear over this conversion range (see Supporting Information) and afforded the chemical yields given in eq 3. Continued photolysis led to the additional formation of *Z*-**7** due to secondary *E*,*Z*-photoisomerization of *E*-**7**. Photolysis of the solution to ca. 84% conversion of *trans*-**5** afforded a mixture consisting of *trans*-**5** (16.5%), *cis*-**5** (5.0%), **6** (35.5%), *E*-**7** (26.2%), and *Z*-**7** (16.9%), which is similar to the product distribution originally reported by Jung and co-workers.[24] Similar experiments with *cis*-**5** showed it to be ca. 4 times more photoreactive than the *trans*-isomer, producing *trans*-**5**, **6**, and *E*-**7** in initial yields of 69%, 11%, and 19%, respectively.

The quantum yield for formation of **6** from *trans*-**5** was determined to be $\Phi_6 = 0.16 \pm 0.04$, by merry-go-round photolysis of 0.05 M cyclohexane-d_{12} solutions of *trans*-**5** and 1,1-diphenylsilacyclobutane (**8**) in deoxygenated solution containing 0.25 M methanol; the latter compound affords diphenylmethoxymethylsilane (**9**) with a quantum yield of $\Phi = 0.21 \pm 0.02$ (eq 5) and thus serves as a convenient actinometer.[27] A quantum yield for formation of **6** from *cis*-**5** was not specifically determined, but comparison of the relative slopes of the concentration versus time plots for its formation from the two isomers indicates that it is formed with roughly 1.5 times higher quantum efficiency from *cis*-**5** than from the *trans*-isomer.



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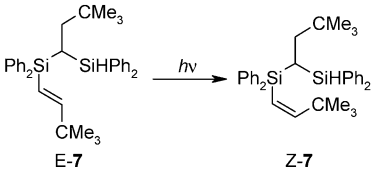

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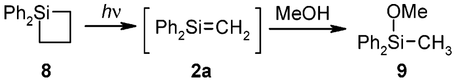
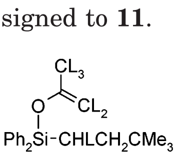
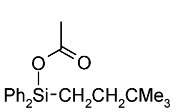


(5)

Additional steady-state photolysis experiments were carried out in order to verify the expected course of the reactions of silene **4** with acetone and acetic acid. Accordingly, solutions containing *trans*-**5** (0.022 M) in deoxygenated cyclohexane-d_{12} containing acetone (0.12 M) or acetic acid (0.13 M) were photolyzed to ca. 30% conversion. Although no attempts were made to isolate them because of the expectation of substantial hydrolytic instability, silyl enol ether **10** and acetoxysilane **11** were tentatively identified in the product mixtures by ^{1}H NMR spectroscopy and GC/MS, along with *cis*-**5** and *E*-/*Z*-**7** in similar yields as in the experiments with MeOH as the silene trap. In the case of **10**, the ^{1}H NMR assignments were confirmed by ^{2}H NMR analysis of a photolyzed solution of *trans*-**5** (0.015 M) and acetone-d_6 (0.02 M) in deoxygenated cyclohexane, which verified that only a single ketone-derived product is formed in the reaction; the compound exhibited resonances at δ 1.18, 1.78, 3.97, and 4.03, consistent with the assigned structure of **10**-d_6. Prolonged photolysis of the *trans*-**5a**/acetone mixture led to the formation of secondary photolysis products, while the mixture containing acetic acid could be photolyzed to over 80% conversion without evidence for the formation of new products in addition to that assigned to **11**.



10 (L = H or D)



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Laser flash photolysis of nitrogen-outgassed solutions of *trans*-**5** in hexane, acetonitrile (MeCN), 1,2-dichloroethane (DCE), and tetrahydrofuran (THF) solutions with the pulses from a KrF excimer laser (248 nm) led to the formation of a single detectable transient species, which decays with predominant first-order kinetics and exhibits $\lambda_{\max}$ = 335 nm in all four solvents. Figure 1

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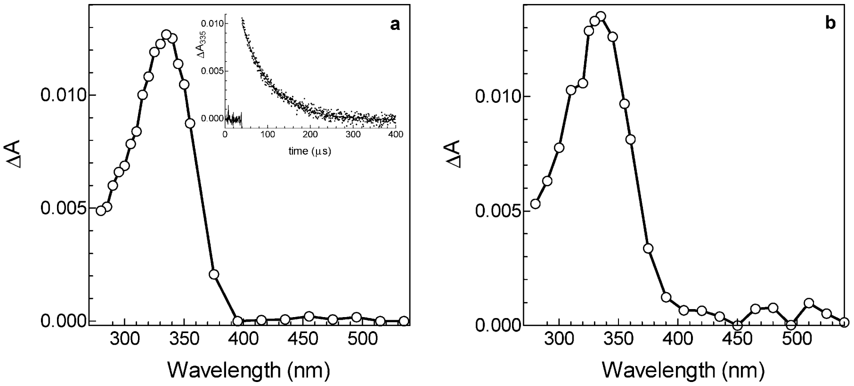
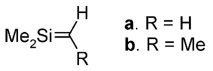


Figure 1. Transient UV absorption spectrum of 1,1-diphenyl-2-neopentylsilene (**4**) in nitrogen-outgassed hexane (a) and THF (b) solution at 24.5 °C, recorded 5−20 μs after 248 nm laser excitation of *trans*-**5**. The insert in (a) shows a typical decay trace, recorded at the absorption maximum (335 nm).

shows the time-resolved UV-absorption spectra of the species in deoxygenated hexane and THF solution. The form of the decay kinetics and lifetime of the transient varied depending on the rigor with which the solvents were dried prior to the experiment, from clean first-order decays and lifetimes on the order of 70 μs in undried hexane to mixed first- and second-order decays and a lifetime of 285 μs in a more rigorously dried sample of the same solvent. The presence of oxygen had a smaller but nevertheless distinct effect, and an absolute rate constant for reaction of the species with O_2 was determined to be $k_{O2} = (6.5 \pm 0.8) \times 10^5$ M^{-1} s^{-1} from pseudo-first-order lifetimes measured at three different oxygen concentrations in hexane solution (see Supporting Information). The lifetime was also shortened upon addition of alcohols and other nucleophilic reagents, as will be discussed in more detail below. On the basis of these results and the similarity of the spectrum to that of 1,1-diphenylsilene (**2a**; $\lambda_{max} = 325$ nm),[28] the transient is assigned to 1,1-diphenyl-2-neopentylsilene (**4**). The 10 nm bathochromic shift in the absorption maximum of **4** relative to **2a** is similar to that reported previously between 1,1-dimethylsilene (**12a**; $\lambda_{max} = 255$ nm) and 1,1,2-trimethylsilene (**12b**; $\lambda_{max} = 258$, 283 nm) under similar conditions.[10,29] The transient absorption spectrum of **4** in THF was found to be independent of temperature over the 7−55 °C range, indicating that the silene does not complex appreciably with the ether solvent.



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a. R = H
b. R = Me

The extinction coefficient of **4** at its absorption maximum in hexane solution was determined by benzophenone actinometry, using the quantum yield determined above for the formation of **6** as that for formation of silene **4**.[30,31] Duplicate determinations yielded an average value of $\epsilon_{335} = 10000 \pm 2900$ M^{-1} cm^{-1}, which is consistent with measured extinction coefficients of other silenes such as **2a** ($\epsilon_{320\ nm} = 8900 \pm 1800$ M^{-1} cm^{-1}).[32]

As mentioned above, rigorous drying of the solvent and extensive deoxygenation resulted in decays that fit well to mixed first- and second-order decay kinetics, but only in hexane solution. Despite several attempts, in no case could clean, purely second-order decays (reflecting exclusive dimerization of **4**) be obtained. An example of a mixed first- and second-order decay profile for **4** in hexane solution is included as Supporting Information; the data were fit to eq 6, where ΔA_t is the transient absorbance at time = t after the laser pulse, k_1 is the first-order rate coefficient, $[\mathbf{4}]_0$ is the concentration of **4** formed in the laser pulse, and k_{dim} is the absolute rate constant for dimerization. The analysis afforded a second-order rate coefficient of $2k_{dim}[\mathbf{4}]_0 = 4520 \pm 280$ s^{-1}. This yields a value of $k_{dim} = (5 \pm 2) \times 10^8$ M^{-1} s^{-1} in hexane solution at 25.0 °C, using the value of ϵ_{335} determined above and the best-fit value of ΔA_0 obtained from the mixed order kinetic analysis.

$$\Delta A_t = \frac{k_1 \Delta A_0 \exp(-k_1 t)}{k_1 + 2k_{dim}[\mathbf{4}]_0(1 - \exp(k_1 t))} \tag{6}$$

Addition of MeOH, TFE, acetone, AcOH, or n-BuNH$_2$ to the solutions of *trans*-**5** resulted in a shortening of the lifetime of **4** and a change to clean pseudo-first-order decay kinetics. Plots of k_{decay} versus trapping agent (“NuE”) concentration were linear in the cases of acetone, AcOH, and n-BuNH$_2$ and were thus analyzed according to eq 7, where k_0 is the pseudo-first-order rate constant for decay in the absence of added reagent and k_{NuE} is the absolute second-order rate constant for reaction of the silene with NuE. A similar form was observed for quenching by AcOD in hexane solution and yielded a second-order rate constant equal to that for the protiated reagent within experimental error. On the other hand, the corresponding plots for quenching by MeOH in all four solvents and by TFE in hexane exhibited positive curvature, and so were analyzed according to the quadratic expression of eq 8, where k_{2NuE} is the third-order rate coefficient corresponding formally to reaction of the silene with two molecules of the alcohol. Figure 2 shows representative plots for

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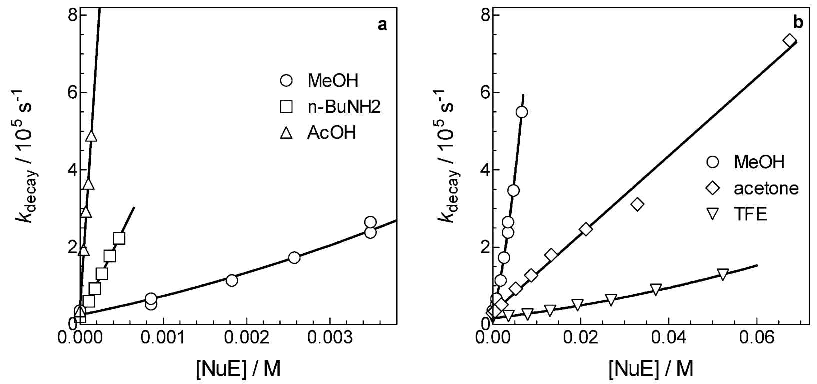

Figure 2. Plots of k_{decay} vs [NuE] for the quenching of silene **4** by MeOH (○), n-BuNH$_2$ (□), AcOH (△), TFE (▽), and acetone (◇) in air-saturated hexane solution at 25 °C.

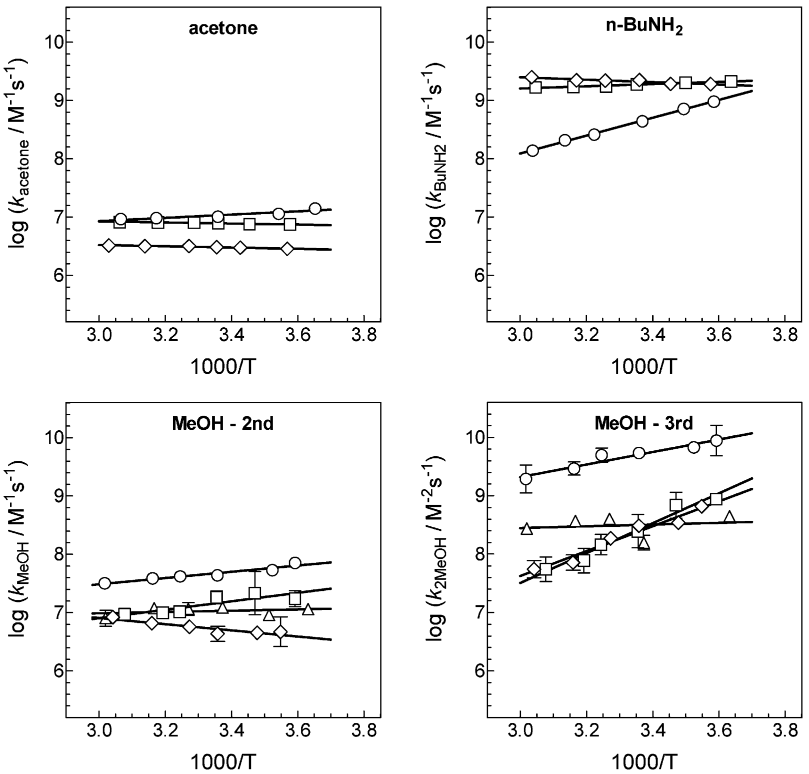

Figure 3. Arrhenius plots of the second- and third-order rate constants for reaction of **4** with acetone, n-BuNH$_2$, and MeOH in hexane (○), THF (□), MeCN (◇), and DCE (△) solution.

quenching of **4** by the five reagents in air-saturated hexane solution at 25 °C, to illustrate the range in reactivity exhibited by **4** toward these various reagents.

$$k_{\mathrm{decay}} = k_0 + k_{\mathrm{NuE}}[\mathrm{NuE}] \tag{7}$$

$$k_{\mathrm{decay}} = k_0 + k_{\mathrm{NuE}}[\mathrm{NuE}] + k_{2\mathrm{NuE}}[\mathrm{NuE}]^2 \tag{8}$$

For most of the silene trapping agents studied, rate constants were determined at several temperatures over the 5−55 °C temperature range in hexane, THF, and MeCN solution. The temperature dependence of the reaction with MeOH was also studied in DCE solution. Arrhenius plots of the second- and third-order rate constants for reaction of **4** with acetone, *n*-BuNH$_2$, and MeOH in the various solvents are shown in Figure 3, while Figure 4 shows the corresponding data for AcOH and TFE. Table 1 summarizes the Arrhenius activation energies and pre-exponential factors determined in these experiments, along with absolute rate constants for reaction at 25 °C interpolated from the Arrhenius data.

Strictly speaking, treating the k_{decay} versus concentration data for the reactions of **4** with MeOH, TFE, and AcOH in hexane solution in terms of the bulk substrate concentrations is incorrect, since this ignores the fact that these substrates form hydrogen-bonded oligomers in hydrocarbon solvents.[33,34] A plot of the AcOH data against the concentrations of monomeric AcOH, calculated using the equilibrium constant for dimer formation reported by Fujii and co-workers,[33] affords a rate constant of $k_{\mathrm{AcOH}} = 5 \times 10^9$ M^{-1} s^{-1}, roughly 40% higher than that estimated from the bulk concentrations. The differences are also small in the case of MeOH addition; analysis of a plot of the 25 °C k_{decay} values versus

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(33) Fujii, Y.; Yamada, H.; Mizuta, M. *J. Phys. Chem.* **1988**, *92*, 6768.

(34) Landeck, H.; Wolff, H.; Goetz, R. *J. Phys. Chem.* **1977**, *81*, 718.

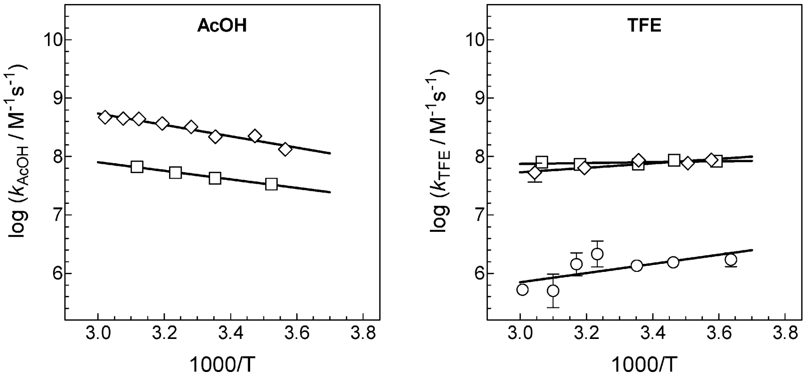

Figure 4. Arrhenius plots of the second-order rate constants for reaction of **4** with acetic acid (AcOH) and 2,2,2-trifluoroethanol (TFE) in hexane (○), THF (□), and MeCN (◇) solution.

Table 1. Arrhenius Parameters and Absolute Rate Constants for Reaction of $Ph_2Si{=}CH(CH_2CMe_3)$ (4) with Various Reagents in Air-Saturated Hexane, DCE, THF, and MeCN Solution[a]

reagent		hexane	DCE	THF	MeCN
acetone	$k_{acetone}{}^{25C}/10^6\ M^{-1}\ s^{-1}$	10.7		7.82	3.05
	E_a (kcal/mol)	−1.3 ± 0.5		0.39 ± 0.24	0.49 ± 0.12
	$\log(A/M^{-1}\ s^{-1})$	6.1 ± 0.2		7.2 ± 0.1	6.8 ± 0.1
n-$BuNH_2$	$k_{amine}{}^{25C}/10^6\ M^{-1}\ s^{-1}$	420		1870	2090
	E_a (kcal/mol)	−7.0 ± 0.3		−0.87 ± 0.18	1.0 ± 0.4
	$\log(A/M^{-1}\ s^{-1})$	3.5 ± 0.2		8.6 ± 0.1	10.0 ± 0.3
MeOH	$k_{MeOH}{}^{25C}/10^6\ M^{-1}\ s^{-1}$	47	10.6	14.5	5.3
	E_a (kcal/mol)	−2.4 ± 0.7	−0.5 ± 1.3	−3.3 ± 2.0	2.4 ± 1.1
	$\log(A/M^{-1}\ s^{-1})$	5.9 ± 0.5	6.7 ± 1.0	4.7 ± 1.4	8.5 ± 0.8
	$k_{2MeOH}{}^{25C}/10^6\ M^{-2}\ s^{-1}$	5020	320	260	240
	E_a (kcal/mol)	−4.8 ± 1.6	−0.7 ± 2.0	−11.7 ± 2.0	−9.7 ± 2.0
	$\log(A/M^{-2}s^{-1})$	6.1 ± 1.0	8.0 ± 2.9	−0.2 ± 1.5	1.2 ± 1.5
TFE	$k_{TFE}{}^{25C}/10^6\ M^{-1}\ s^{-1}$	1.3		80	73
	E_a (kcal/mol)	−3.6 ± 3.4		−0.3 ± 0.7	−1.7 ± 0.9
	$\log(A/M^{-1}\ s^{-1})$	3.5 ± 1.2		7.7 ± 0.4	6.6 ± 0.4
	$k_{2TFE}{}^{25C}/10^6\ M^{-2}\ s^{-1}$	46			
	E_a (kcal/mol)	−6.6 ± 4.2			
	$\log(A/M^{-2}s^{-1})$	2.8 ± 3.0			
AcOH	$k_{AcOH}{}^{25C}/10^6\ M^{-1}\ s^{-1}$	3300 ± 200		44	240
	E_a (kcal/mol)			3.3 ± 0.4	4.4 ± 1.0
	$\log(A/M^{-1}\ s^{-1})$			10.1 ± 0.3	11.7 ± 0.7

[a] Absolute rate constants at 25 °C were interpolated from the Arrhenius data and should be considered accurate to within 20%. The errors listed elsewhere correspond to twice the standard deviation from the linear least-squares analysis of the data.

monomer concentrations, calculated using extrapolated values of the equilibrium constants for formation of hydrogen-bonded dimers and higher oligomers of Landeck et al.,[34] afforded second- and third-order rate coefficients that are ca. 10% smaller and ca. 50% larger, respectively, than the corresponding values obtained from the bulk concentrations. Applying a similar correction over the complete 5−55 °C range would hence result in a negligible change in the Arrhenius parameters for the second-order component and relatively small changes in those for the third-order component, compared to those calculated from the bulk concentration data. To our knowledge, oligomerization of TFE in hydrocarbon solvents has not been characterized, although hydrogen-bonding between fluorinated alcohols and polar solvents such as THF and MeCN has been characterized in some detail.[35] Thus, self-association of this alcohol in hexane can be expected to be significant, and the rate constants and Arrhenius parameters reported for this substrate in Table 1 should hence be considered to be lower and upper limits, respectively, of their true values.

Discussion

The photolysis of *trans*-**5** was first reported several years ago by Jung and co-workers, who demonstrated that silene **4** is formed as a primary product of the photoreaction by the isolation of the products of trapping the silene with MeOH, methoxytrimethylsilane, and triethoxysilane.[24] The present results confirm the original conclusions of Jung et al. and in addition provide an accurate indication of the primary chemical and quantum yields for the reaction. The quantum yield for formation of silene **4** from *trans*-**5** is similar to that for the formation of 1,1-diphenylsilene (**2a**) from silacyclobutane **8**, indicating that the disilacyclobutane should be a more than adequate precursor to **4** for study by laser flash photolysis methods, lending additional confidence to our transient assignment. It is noteworthy that the photocycloreversion of *trans*-**5** is roughly 20 times more efficient than that of the 1,3-disilacyclobutane dimer of **2a** (**13**).[32] This is presumably the result of a stepwise fragmentation mechanism involving the initial formation of the corresponding 1,4-biradical intermediates; the rather sizable difference in the quantum yields for cleavage of the two derivatives is likely to be due to enhanced excited-state cleavage in **5**

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(35) Middleton, W. J.; Lindsey, R. V., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 4948.

Table 2. Absolute Rate Constants and Arrhenius Activation Energies for Reaction of 4 and 1,1-Diphenylsilene (2a) with Acetone, n-BuNH$_2$, MeOH, TFE, and AcOH in MeCN and Hexane Solution

	$k_{NuE}{}^{4}/10^6$ M^{-1} s^{-1} (25 °C) [E_a/kcal mol^{-1}]		$k_{NuE}{}^{2a}/10^6$ M^{-1} s^{-1} (23 °C) [E_a/kcal mol^{-1}]		$k_{NuE}{}^{2a}/k_{NuE}{}^{4}$	
reagent	hexane	MeCN	hexane	MeCN	hexane	MeCN
acetone	10.7 [−1.3 ± 0.5]	3.1 [+0.5 ± 0.1]	330 [−2.6 ± 0.1][a]	140 [−1.3 ± 0.1][a]	31	45
n-BuNH$_2$	420 [−7.0 ± 0.3]	2090 [+1.0 ± 0.4]	6500 [∼0][b]	2810 [+0.5 ± 0.1][b]	15.5	1.34
MeOH	47 [−2.5 ± 0.7]	5.3 [+2.4 ± 1.1]	2900[c] [+2.4 ± 1.1]	1300 [−2.5 ± 0.3][d]	62	245
TFE	1.3 [−3.6 ± 3.4]	73 [−1.7 ± 0.9]		1400[e] [-]		19.2
AcOH	3300	240 [+4.4 ± 1.0]	3100[c]	1500 [+1.9 ± 0.3][d]	0.94	6.2

[a] Absolute rate constant at 25 °C. Ref 15. [b] Arrhenius plot is curved. See ref 17. [c] Ref 27. [d] Ref 14. [e] Ref 41.

relative to **13** due to the radical-stabilizing effects of the 2(4)-alkyl substituents, as well as differences in the conformational preferences of the corresponding 1,4-biradicals. Presumably, the 2(4)-substituents cause a shift in the conformational population of the biradical toward transoid conformers, which results in increased amounts of cleavage to yield the silene.

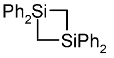

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Table 2 compares the absolute rate constants and Arrhenius activation energies for reaction of the five reagents with **4** in MeCN and hexane solution at ca. 25 °C with the corresponding values for reaction with **2a** determined in previous studies. With only two exceptions (n-BuNH$_2$ in MeCN and AcOH in hexane), the ambient temperature rate constants are significantly smaller and the activation energies more positive for **4** than for its unsubstituted homologue, **2a**. It is thus clear that, in general, the 2-alkyl substituent in **4** significantly reduces the reactivity of the Si=C bond toward nucleophilic reagents, compared to that of the parent compound (**2a**).

It can be further concluded that the effect of 2-neopentyl substitution on the electrophilic reactivity of **2a** is largely electronic in nature, thus lending support to the conclusions of previous experimental[9,10] and theoretical[6,7] studies on the effects of substituents at silicon and carbon on the reactivity of the Si=C double bond. This is based on a comparison of the reactivities of **4** and **2a** with MeOH to the corresponding data for reaction of 1,1-dimethylsilene (**12a**) and its 2-methyl-substituted homologue (**12b**);[10] the trends in the second-order rate constants for MeOH addition in the two solvents, as well as the difference in the form of the plots of k_{decay} versus [MeOH] (i.e., linear for **2a**; curved upward for **4**), mirror the differences in **12a** and **12b** quite closely.[10] For example, **12b** is ca. 30 times less reactive than **12a** in hexane, which can be compared to the ∼40-fold difference observed for **4** and **2a**. The effects of solvent on the second-order rate constants for reaction with MeOH are also quite similar in the two compounds; **12b** is ca. 5 times less reactive in MeCN than in hexane, while **4** exhibits a ca. 9-fold difference in the two solvents. The comparison indicates that the 2-neopentyl substituent in **4** has similar effects to a methyl group on the reactivity of the Si=C bond toward MeOH addition, suggesting that electronic effects play the dominant role in reducing the reactivity of **4** toward nucleophiles compared to the situation with **2a**. Theory suggests that the effect is due mainly to a reduction in the polarity of the Si=C bond by the 2-alkyl substituent[6,7] and predicts a direct (inverse) correlation between Si=C bond polarity and the activation energy for addition of water.[7] Indeed, our results indicate that the activation energy for reaction of **4** with MeOH in MeCN is ca. 5 kcal mol^{-1} higher than that for the corresponding reaction of **2a** under the same conditions.

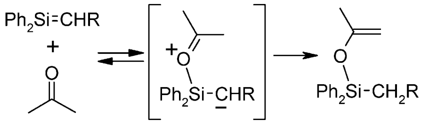
A similar (ca. 20-fold) difference in reactivity is observed for (head-to-tail) [2+2]-dimerization of the two silenes, which in the case of **2a** proceeds with a rate constant within a factor of 2 of the diffusional limit in hexane solution ($k_{dim} = (1.3 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}).[32] Presumably, steric factors play a greater role in contributing to this difference than they do in the case of nucleophilic addition. Of the reactions studied in this work, the only one for which 2-alkyl substitution can be expected to lead to a rate enhancement, based on the trends established by other transient silenes,[5] is that with oxygen. Unfortunately, the effect cannot be fully quantified because only an upper limit of the rate constant for reaction of **2a** with O$_2$ exists; nevertheless, the value reported ($k_{O2} \le 5 \times 10^5$ M^{-1} s^{-1})[5,28] is clearly consistent with the expectation of enhanced reactivity of **4** with O$_2$ ($k_{O2} = (6.5 \pm 0.8) \times 10^5$ M^{-1} s^{-1}) due to the stabilizing effects of the 2-alkyl substituent on the triplet 1,4-biradical intermediate that is thought to be involved in the reaction.[5]

The most striking differences between the reactivities of **4** and **2a** arise in THF solution, where that of **2a** is subject to specific solvation effects owing to nonproductive Lewis acid−base complexation with the ether solvent.[16] This causes substantial rate reductions and positive shifts in the Arrhenius activation energies for reaction of **2a** with these substrates, which can be understood as due essentially to the superposition of the temperature dependence of the silene−solvent complexation equilibrium on that for reaction; the silene−ether complex is substantially less electrophilic than the free silene, and its equilibrium concentration increases relative to that of the free silene with decreasing temperature, hence shifting near-zero or negative activation energies to positive values. The largest effects are observed for reactions involving particularly nonacidic substrates such as acetone[16] and n-BuNH$_2$,[17] because there is no reasonable alternate mechanism by which they might react faster with the complex than with the free silene, such as (for example) by initial protonation at the silenic carbon. The activation energies for reaction of **2a** with these two reagents are in both cases 7−8 kcal mol^{-1} more positive in THF solution than in hydrocarbon solvents,[16,17] a much larger difference than is observed in the activation energies for reaction with the more acidic substrates, MeOH and AcOH.[16] The smaller differences observed in these cases have been interpreted as due to the fact that both the free and complexed forms of the silene are potentially reactive, but in different ways; the free silene reacts as an electrophile, while the complexed form can be expected to possess enhanced nucleophilic character and can hence react by a mechanism involving initial protonation of the Si=C bond rather than by the usual mechanism involving initial nucleophilic attack by the substrate.[16] Silene **4**, on the other hand, does not engage in complexation with THF to any detectable extent over the ca. 0−60 °C temperature range (vide supra). As a result, any variations in reactivity compared to noncoordinating or more weakly coordinating solvents can be expected to be due to bulk solvent polarity effects, at least to a first approximation. Indeed, the rate constants and activation energies for reaction of **4** with acetone and n-BuNH$_2$ in THF solution are intermediate between the values observed in hexane and MeCN solution in both cases, in keeping with the relative polarities of the three solvents as measured by any of the common solvent parameters. While a similar trend in rate constant is observed with MeOH addition, the activation parameters in this solvent appear to be out of line with those in hexane and MeCN, though in a much different way than was observed previously for **2a**.[16] In this case, the general trend of decreasing rate constant and increasing E_a with increasing solvent polarity was confirmed with kinetic measurements in DCE solution, a solvent of dielectric constant similar to THF. Distinct discontinuities are also evident in the trends in the rate constants or activation parameters for AcOH and TFE addition. Possible reasons for these effects will be discussed in detail below.

The near-zero or negative activation energies observed for the reactions of **4** with acetone, n-BuNH$_2$, MeOH, and TFE (Table 1) are consistent with two-step reaction mechanisms in which the first is reversible and the second is rate-determining. This general feature is the same as that exhibited by the reactions of amines, acetone, and alcohols with the substantially more reactive 1,1-diarylsilenes **2a** and **2b**. It would thus appear, on the surface at least, that the stabilizing influence of the 2-neopentyl substituent in **4** is insufficient to cause a change in the gross features of the mechanism for reaction of the Si=C bond with nucleophilic reagents. In the case of AcOH addition, we previously proposed a stepwise mechanism analogous to that of eq 2 (with the complexation step being rate-determining rather than the proton-transfer step) on the basis of the fact that the reactions of **2a** and other 1,1-diarylsilenes with AcOD exhibit the same rate constants as with the protiated isotopomer and the assumption that an isotope effect would be measurable if the reaction proceeded by either a concerted mechanism or one involving initial protonation of the Si=C bond.[14,36] Similarly, no isotope effect is evident on the rate constant for reaction of AcOH with **4**, leading to the conclusion that this reagent also reacts with **4** by the same mechanism as that with **2a** and **2b**.

With the absence of specific solvation effects on the reactivity of **4** and the mechanistic equivalencies between **4** and **2a** established, we are now in a position to comment on the effects of solvent polarity on the rate constants and activation parameters for reaction of the Si=C bond with the nucleophilic reagents studied in this work. The first of the common features to be noted (see Table 1) is that the variations in rate constant with solvent are relatively small in each case, amounting to a factor of 10 at most between hexane and MeCN, with the value in THF falling between the two extremes. Nevertheless, the variations are in each case significantly larger than those observed for reaction of **2a** with the same substrates. The second is a general trend toward increasingly positive activation energy with increasing solvent polarity; the reactions with acetone, n-BuNH$_2$, and MeOH all exhibit negative activation energies in hexane solution, which shift to small positive activation energies in the strongly polar solvent, MeCN. Finally, there is a consistent correspondence between decreasing overall rate constant and increasing activation energy for the reactions with acetone, MeOH, and AcOH (the THF values aside in the latter case; vide infra). This generalization does not hold for the reaction with n-BuNH$_2$, for which the rate constants and activation energies *both* increase with increasing solvent polarity. The results observed for reaction with the fluorinated alcohol are also unusual compared to those for the other reagents studied.

The smallest effects of solvent polarity are exhibited by the reaction of **4** with acetone, for which the rate constant decreases by a factor of only ~3 and the activation energy increases by less than 2 kcal mol^{-1} as the solvent is changed from hexane to MeCN. The effect is smaller than that observed with MeOH addition (vide infra), but is nevertheless in the same direction. It is consistent with weakly increasing destabilization of the transition state for product formation with increasing solvent polarity, such as would be expected of (rate-determining) reaction of a polarized complex between the free silene and the ketone (eq 9). The fact that this reaction shows the smallest variation in rate constant and activation energy with solvent suggests that the dipolar character of the requisite intermediate is relatively weak.



(9)

Theoretical studies of the reaction of silenes with carbonyl compounds have been confined to that of the parent silene (H$_2$Si=CH$_2$) with formaldehyde or other nonenolizable aldehydes, of which the product is the

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[36] Owens, T. R.; Harrington, C. R.; Pace, T. C. S.; Leigh, W. J. *Organometallics* **2003**, *22*, 5518.

corresponding 1,2-siloxetane.[37,38] The most recent calculations of Baines and Woo and their co-workers examined the potential energy surfaces for reaction via concerted and stepwise mechanisms involving biradical and zwitterionic intermediates.[38] They concluded that the nonconcerted mechanisms are of similar energies, with that involving a zwitterionic complex being slightly favored over the biradical pathway; both are considerably lower in energy than the concerted mechanism. Solvation effects were also considered and were found to lead to slight stabilization of the zwitterionic mechanism relative to the biradical mechanism as solvent polarity increases and a small (ca. 0.5 kcal/mol) *decrease* in activation energy on changing the solvent from cyclohexane to acetonitrile. Given the uncertainties and the different course of the second step of these reactions, the results are not significantly different from those found here for the related ene-addition of acetone to **4**.

The solvent effect on the second-order rate constants and activation energies for MeOH addition in hexane, DCE, and MeCN are consistent with increasing destabilization of the transition state for the product-forming step with increasing solvent polarity, which again is the expected result for a reaction that involves neutralization of internal charge in a zwitterionic intermediate (see eq 2). The pre-exponential factors exhibit a trend toward increasingly positive values with increasing solvent polarity, consistent with a corresponding loosening of the transition state for proton transfer. Alternatively, the trend can be viewed in terms of preferential stabilization of the relatively polar silene in polar solvents. The results are in good qualitative agreement with the calculations of Bendikov et al. for the reaction of silene ($H_2Si{=}CH_2$) and water in toluene and THF, carried out at the PCM/B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.[7] In the gas-phase reaction, the complex and the transition state for the second step are predicted to lie lower in enthalpy than the free reactants by -5.76 and -1.73 kcal mol^{-1}, respectively. These are predicted to change to more positive values in solution, to -1.2 and $+3.4$ kcal mol^{-1} and to $+4.6$ and $+9.5$ kcal mol^{-1}, respectively, in solvents of dielectric constants equivalent to those of toluene and THF, respectively. The observed solvent effects on the activation energy for reaction of **4** with MeOH are clearly significantly smaller than those predicted at this level of theory for the reaction of water with the more highly polar parent silene, although the calculations were carried out on the gas-phase geometries and hence provide only upper limits to the relative energies of the reactants, complex, and transition state in the presence of the solvent dielectric field. Nevertheless, the trends are the same. It is interesting to note that, on the surface at least, this conclusion conflicts with what might be predicted on the basis of the calculated (B3LYP/6-311++G(d,p)) charge distributions in the free silene, the intermediate complex, and the transition state for H-migration, which were reported earlier by Veszpremi and Kira and their co-workers.[39] These calculations indicate that formation of the silene–H_2O complex is accompanied by a significant increase in charge at Si (positive) and C (negative), and a smaller increase occurs again as the transition state for H-migration is reached. To a first approximation, the resulting implication that the complex and transition state for product formation are both more polar species than the free reactants might lead to the expectation of an increasingly *negative* activation energy with increasing solvent polarity. This is clearly at odds with the present experimental results for the reaction of **4** with MeOH in the various solvents, as well as the solvent effect calculations of Bendikov et al.

While the rate constant for MeOH addition in THF solution follows the trend exhibited by the other solvents, inspection of the Arrhenius parameters indicates there to be something markedly different about the reaction energetics in this solvent; the activation energy and pre-exponential factor are both anomalously *low* considered against their values in the other solvents. A reasonable mechanism to account for the discontinuity is solvent assistance to proton transfer in the rate-determining step of the reaction, leading to enhanced stabilization of the transition state at the expense of a more negative entropic factor because three rather than two molecules are involved in the process.

The kinetic details of the overall third-order component of the reaction are particularly interesting. As with the second-order component, the rate constants are significantly smaller in the more polar solvents compared to that in hexane. However, the Arrhenius parameters appear to divide the four solvents into two groups, one in which the activation energy is strongly negative and the entropic demands severe (THF and MeCN), and one in which the activation energy is less negative and the entropic demands are similar to those for the bimolecular component of the reaction (hexane and DCE). Since the two groups correspond to hydrogen-bond acceptor and nonacceptor solvents, respectively, the simplest conclusion is that the catalytic proton-transfer process is strongly assisted by hydrogen-bond-accepting solvents, but at a relatively large entropic cost. The effect on the activation energy seems consistent with a mechanism in which the second molecule of alcohol acts as a general acid, of enhanced acidity compared to that in non H-bonding solvents, protonating the zwitterionic complex from the opposite side of the Si=C bond to the site of complexation. This is the mechanism first proposed by Kira and co-workers to explain the increased yields of *anti* relative to *syn* addition products from reaction of a cyclic transient silene with alcohols at high concentrations,[11] and we have recently reported corroborating evidence for the mechanism from an analysis of the kinetics of alcohol addition to a series of sterically hindered 1,1-diarylsilenes related to **2a**.[36] However, it seems difficult to rationalize the large difference in entropic factors between H-bond acceptor and nonaccepting solvents in the context of this mechanism.

An alternative explanation is that the mechanism is different in silenes of reduced Si=C bond polarity, perhaps proceeding via a cyclic transition state in which the second molecule of alcohol assists H-transfer in the complex by acting as a proton shuttle. The mechanism is kinetically equivalent (as is also that involving *anti*-

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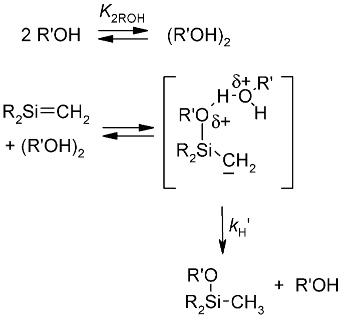
[37] Khabashesku, V. N.; Kudin, K. N.; Margrave, J. L. *Russ. Chem. Bull.* **2001**, *50*, 20.

[38] Mosey, N. J.; Baines, K. M.; Woo, T. K. *J. Am. Chem. Soc.* **2002**, *124*, 13306.

[39] Veszpremi, T.; Takahashi, M.; Hajgato, B.; Kira, M. *J. Am. Chem. Soc.* **2001**, *123*, 6629.

protonation of the complex by a second molecule of alcohol) to one in which the free silene reacts directly with the hydrogen-bonded dimer of the alcohol (eq 10), again via the prior formation of a zwitterionic complex. In fact, the mechanism of eq 10 seems to be most compatible with the marked difference in entropic factors in H-bond accepting and nonaccepting solvents; MeOH is known to form H-bonded dimers and higher oligomers at relatively low bulk concentrations in hexane solution,[34] but is solvated largely as the monomer in hydrogen-bond accepting solvents.[40] This would presumably add an additional entropic requirement to the reaction in H-bond-accepting solvents, relative to the situation in nonaccepting solvents where the alcohol is already significantly self-associated. If this is correct, then an approximate value for the rate constant for reaction of **4** with methanol dimers ($(\mathrm{(MeOH)_2})$) can be obtained by analyzing the k_{decay} data of Figure 2 against the monomeric MeOH concentration and dividing the resulting third-order rate coefficient by the equilibrium constant K_{2ROH}. As mentioned earlier, this analysis affords a second-order rate coefficient that is only ca. 10% lower than that obtained from the bulk concentrations and a third-order coefficient that is ca. 50% higher (at 25 °C). In any event, the procedure affords a value of $k \approx 2 \times 10^8$ M^{-1} s^{-1} for the (hypothetical) rate constant for reaction of the free silene with methanol dimers in hexane solution, roughly 5 times greater than the rate constant for reaction with the monomeric form of the alcohol.



(10)

The results for AcOH addition can be best understood by considering this reaction in the same context as acetone addition; indeed, both are formally ene-additions, with the main difference being the acidity of the proton that is transferred to the silenic carbon in the second step of the reaction. While this step is rate-determining in the case of acetone addition, it is fast relative to the initial complexation step in the case of the acid, and hence the reaction exhibits a negligible deuterium kinetic isotope effect,[13,14] even with more highly hindered 1,1-diarylsilenes for which the rate constant is several orders of magnitude slower than in the parent (**2a**).[36] Thus, the activation energy and pre-exponential factor for reaction with AcOH reflect solely that for formation of the intermediate complex,[13] and hence the kinetics can be expected to respond somewhat differently to solvent than those for alcohol or acetone addition. The pre-exponential factors are as expected for a simple, relatively fast bimolecular process. The similarity in the rate constants for reaction of **4** and **2a** with AcOH in hexane solution implies similar barriers for complexation in the nonpolar solvent, which is reasonable considering that the rates are within a factor of ca. 5 of the diffusional limit. The expected effects of reduced electrophilicity in **4** relative to **2a** become evident only in polar solvents, where the activation energy for reaction of **4** is ca. 2.5 kcal mol^{-1} higher than that for **2a**, resulting in a ca. 6-fold difference in rate constant between the two derivatives. This suggests that the stability of the complex decreases relative to that of the free reactants with increasing solvent polarity, analogous to the trend suggested for the silene−water reaction on the basis of theoretical calculations (vide supra).[7]

The solvent effect on the addition of 2,2,2-trifluoroethanol (TFE) to **4** is different from those observed for either MeOH or AcOH addition; in this case, the results indicate significant rate *accelerations* in the polar solvents compared to that in hexane solution and a change from mixed second- and third-order reaction kinetics in hexane to pure second-order kinetics in THF and MeCN. The kinetics of this reaction have not been extensively characterized in the case of **2a**, but a rate constant of $k_{\mathrm{TFE}} = 1.4 \times 10^9$ M^{-1} s^{-1} has been measured previously in MeCN solution at 25 °C.[41] The mixed order behavior observed in hexane solution is consistent with the mechanism proposed for MeOH addition, in which the first step is complexation by the neutral nucleophile, followed by competing uni- and bimolecular proton transfer. As expected, the rate constants for both processes are considerably smaller in the case of TFE addition, presumably owing mainly to the much weaker nucleophilicity of this alcohol compared to MeOH. Given the solvent effect on the kinetics of the latter reaction, those for TFE seem best accommodated by a substantial change in mechanism in polar solvents, perhaps to one in which the alcohol reacts mainly as its hydrogen-bonded complex with the solvent; TFE and other fluorinated alcohols are known to be exceptionally strong hydrogen-bond donors in ethers and other polar solvents.[35] The H-bonded complex of TFE with the solvent can be expected to be more nucleophilic than the free alcohol, which accelerates the first step of the reaction. The second step is then presumably also accelerated because the solvent is directly involved in the H-transfer process. The pre-exponential factors are consistent with a somewhat looser transition state for proton transfer in the H-bond acceptor solvents, as might be expected on the basis of this mechanism.

Finally, the Arrhenius parameters for n-BuNH$_2$ addition exhibit a trend similar to that exhibited by the (second-order) MeOH data, with both the activation energy and pre-exponential factor increasing with increasing solvent polarity. The trend is quite dramatic, however, with the activation energy increasing from −7 kcal mol^{-1} in hexane, the largest (negative) E_a yet observed for a silene reaction in solution, to +1 kcal mol^{-1} in MeCN, and the *A*-factor increasing by close to 6 orders of magnitude. This reaction can proceed only via the mechanism of eq 2; the substantially greater nucleophilicity and Lewis basicity of the amine compared to the oxygen-centered nucleophiles lead to the

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(40) Kirmse, W.; Guth, M.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 10838.

(41) Banisch, J. H. A mechanistic study of alcohol addition to 1,1-diphenylsilene. M. Sc. Thesis, McMaster University, 1995.

expectation of a significantly more favorable pre-equilibrium and correspondingly tighter binding in the complex. The activation parameters indicate that in the nonpolar solvent the barrier to proton transfer within the complex is largely entropic in origin. The solvent effect is again consistent with a relatively nonpolar transition state for the latter process, which loosens and increases in enthalpy as solvent polarity increases; the magnitude of the effect suggests that there is considerably greater neutralization of (zwitterionic) charge in the transition state relative to that involved in alcohol addition. Interestingly, the trend in reactivity of **4** with n-BuNH$_2$ as a function of solvent is much different than with **2a**, for which the rate constant in hexane is ca. 3 times faster than that in MeCN and $E_a \approx 0$ kcal mol^{-1} in both solvents.[17] This indicates that in nonpolar solvents the intracomplex proton-transfer step is intrinsically much faster in the parent compound (**2a**) than in **4**, resulting in overall reaction kinetics that are more strongly dominated by the complexation step of the reaction. Indeed, the rate constants for reaction of **2a** with *tert*-butyl- and diethylamine, which are more hindered than n-BuNH$_2$ and hence likely to be less tightly bound in the corresponding silene–amine complexes, exhibit solvent effects that are more similar to that observed with **4** and n-BuNH$_2$.[17] Taken together, the results for **2a** and **4** suggest that the rate constants and Arrhenius parameters for amine addition are far less sensitive to substituents on either the silene or the amine in polar solvents than they are in nonpolar media. This too is consistent with a much tighter transition state for intracomplex proton transfer in nonpolar solvents compared to polar ones.

Summary and Conclusions

Alkyl substitution at the silenic carbon of 1,1-diarylsilenes results in a marked reduction in the reactivity of the Si=C bond toward nucleophiles, but a small increase in reactivity toward radicaloid species such as (triplet) oxygen. The reduced electrophilicity of the Si=C bond results in a markedly lower propensity for nonproductive Lewis acid–base complexation with polar solvents such as THF and MeCN. This allows one to study the effects of solvent polarity on silene reactivity in a much more precise and meaningful way than has been possible with the unsubstituted (at the 2-position) 1,1-diarylsilenes that have been studied previously, for which these effects are masked by specific solvation phenomena. The results afford considerable new insight into the mechanistic details of various nucleophilic addition reactions to transient silenes, such as those with alcohols, amines, carboxylic acids, and enolizable ketones, since the broad mechanistic features of these reactions are not changed as a result of the presence of the 2-alkyl substituent. These reactions each proceed via a mechanism involving the initial (reversible) formation of a zwitterionic complex, which proceeds to product by H-transfer in a subsequent step.

The effects of solvent polarity on the reactions of relatively nonacidic substrates such as acetone, MeOH, and n-BuNH$_2$ all point to a transition state for collapse of the complex to product that is looser and significantly destabilized in polar solvents relative to nonpolar ones. As a result, the variation in rate constant with solvent polarity is relatively small in each case, varying only by a factor of 3–10 between hexane and MeCN solution. With acidic substrates such as acetic acid, for which the complexation step is rate-determining, the results indicate a slight enhancement in the rate constant in MeCN relative to that in THF. This appears to originate mainly in the entropic component of the reaction, which is more favorable (i.e., less negative) in the more polar solvent. Relatively acidic, non-nucleophilic alcohols such as 2,2,2-trifluoroethanol (TFE) appear to react by a mechanism similar to that with MeOH in hydrocarbon solvents, but at much reduced rates owing to prohibitive entropic factors in the rate-determining step. In this case significant rate enhancements are observed in THF and MeCN, which is rationalized in terms of a mechanism involving reaction of the alcohol as its hydrogen-bonded complex with the solvent.

The reaction of silenes with alcohols is known to proceed via competing mechanisms in which either one or two molecules of alcohol are involved in the rate-determining (proton transfer) step for the reaction. The role of the second alcohol molecule is thought to be as a general acid, protonating the silenic carbon of the zwitterionic complex from the opposite side to which the first alcohol moiety is complexed. In **4**, the kinetics of this process are enormously affected by solvent polarity, an effect that can be linked to the hydrogen-bond-accepting properties of the solvents. Both the activation energy and pre-exponential factor are strongly reduced in H-bonding solvents compared to non-H-bonding solvents, which seems more consistent with a mechanism involving either stepwise reaction of the free silene with the hydrogen-bonded dimer of the alcohol or a general base-catalyzed mechanism (in which the second molecule of the alcohol acts as a proton shuttle, and protonation of the Si=C bond should occur in *syn* fashion), rather than the established mechanism involving *anti*-protonation of the complex by a second molecule of (monomeric) alcohol. It is too early to speculate on whether the onset of this new mechanism is due solely to the reduced polarity of the Si=C bond in **4**, in which case it should prove to be general, or whether steric effects associated with the substituent on the silenic carbon also play a role in promoting reaction along this pathway.

In any event, this constitutes the first hint of a change in the mechanisms of nucleophilic additions to silene derivatives, which can be expected to occur as the polarity of the Si=C bond is reduced by substituents and it becomes more “alkene-like”. Continued work to elucidate the effects of Si=C bond polarity and steric factors on the mechanisms of silene reactions is in progress in our laboratory.

Experimental Section

^{1}H NMR spectra were recorded in deuteriochloroform or cyclohexane-d_{12} on Bruker AC200 or DRX500 spectrometers and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971 mass selective detector and a DB-5 fused silica capillary column (30 m × 0.25 mm; 0.25 μm film; Agilent Technologies). Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890II+ gas chromatograph equipped with a conventional heated splitless injector, flame ionization detector, HP3396A integrator, and DB1 or DB1701 megabore capillary columns (15 m × 0.53 mm; Chromatographic Specialties, Inc.).

Hexane (OmniSolv Reagent) and acetonitrile (Caledon HPLC) were used as received from the suppliers. Tetrahydrofuran (Caledon Reagent) was dried by passage through activated neutral alumina (250 mesh; Sigma-Aldrich) under nitrogen, using a Solvtek solvent purification system. Acetone, methanol, 2,2,2-trifluoroethanol, glacial acetic acid, and acetic acid-O*d* were the highest quality available from Sigma-Aldrich and were used as received. *n*-Butylamine (Sigma-Aldrich) was distilled from solid potassium hydroxide. *trans*-1,1,3,3-Tetraphenyl-2,4-dineopentyl-1,3-disilacyclobutane (*trans*-**5**; mp 208−209 °C) was prepared and purified according to the method of Jones and co-workers and exhibited ^{1}H NMR and mass spectral data similar to the published data.[25]

Solutions of *trans*-**5** (0.039 g, 7.5×10^{-6} mol) in cyclohexane-d_{12} (2 mL) containing methanol (0.09 M) were placed in quartz NMR tubes, sealed with rubber septa, deoxygenated with a stream of dry argon, and photolyzed in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with three RPR-2537 lamps for 2 h, with periodic monitoring of the course of the photolyses by ^{1}H NMR spectroscopy. The products (*cis*-**5**, **6**, *trans*-**7**, and *cis*-**7**) were identified by comparison of their ^{1}H NMR and mass spectra to the published data.[24]

The quantum yield for formation of **6** from *trans*-**5** was determined by merry-go-round photolysis of 0.05 M solutions of *trans*-**5** and 1,1-diphenylsilacyclobutane (**8**) in deoxygenated cyclohexane-d_{12} solution containing 0.25 M methanol; the latter compound affords diphenylmethoxymethylsilane (**9**) with a quantum yield of $\Phi = 0.21 \pm 0.02$ (eq 5).[27] Product formation in the two solutions was monitored by ^{1}H NMR spectroscopy as a function of photolysis time at low (<10%) conversions of the starting materials, and the relative quantum yields for the formation of **6** and **9** were calculated from the slopes of product concentration versus time plots. The quantum yield for formation of **6** under these conditions was thus determined to be $\Phi_{\mathbf{6}} = 0.16 \pm 0.04$.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser filled with F_2/Kr/Ne mixtures (248 nm, ca. 25 ns; 80−125 mJ) and a Luzchem Research mLFP-111 laser flash photolysis system. Air-saturated solutions of *trans*-**5** ($(9.5{-}9.9) \times 10^{-5}$ M) were flowed through a thermostated 7 × 7 Suprasil flow cell connected to a calibrated 100 mL reservoir and exhibited optical densities of ~0.7 at the excitation laser wavelength. Solution temperatures were measured with a Teflon-coated copper−constantan thermocouple inserted directly into the flow cell. Reagents were added to the reservoir as neat liquids with a 10 or 50 μL syringe. Rate constants were calculated by least-squares analysis of decay rate-concentration data (6−15 points) that spanned at least a factor of 5 in the transient decay rate. Errors are quoted as twice the standard deviation ($\pm 2\sigma$) obtained from the least-squares analysis in each case. Transient absorption spectra were recorded in point-by-point fashion over four selected time windows after the laser pulse.

The extinction coefficient of **4** at its absorption maximum in hexane solution was determined by the intensity variation method using benzophenone as the actinometer.[30,31] The method involves comparing the initial ΔA value at 335 nm ($\Delta A_{335,0}$) due to **4** to that recorded at 525 nm for a solution of benzophenone, whose irradiation yields the triplet state ($\lambda_{max} = 525$ nm, $\epsilon_{525-nm} = 7640 \pm 1050$ M^{-1} cm^{-1}) with unit quantum yield.[42] The substrate and actinometer solutions were optically matched at the laser wavelength (248 nm) to ensure equal light absorption, and the laser intensity was varied using neutral density filters. As expected, plots of $\Delta A_{\lambda,0}$ versus laser intensity at the two monitoring wavelengths were linear for both compounds at low to moderate laser intensities (see Supporting Information).[30] The extinction coefficient for **4** at its absorption maximum was then calculated from the relative slopes of the plots and the quantum yield for formation of **6** determined above. Duplicate determinations yielded an average value of $\epsilon_{335} = 10000 \pm 2900$ M^{-1} cm^{-1}.

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Supporting Information Available: Product concentration versus time plots for the photolysis of *trans*- and *cis*-**5** in the presence of methanol, experimental data employed for the determination of absolute rate constants for dimerization and reaction of **4** with oxygen, and absolute rate constants for the reactions of **4** with the nucleophilic reagents studied in this work in MeCN, DCE, THF, and hexane solutions at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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