

# Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond. Mechanistic Studies of the Ene-Addition of Acetone to Reactive Arylsilenes

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Absolute rate constants for the reaction of acetone with phenylsilene, 1-methyl-1-phenylsilene, and a series of ring-substituted 1,1-diphenylsilene derivatives have been determined in polar and nonpolar solvents using nanosecond laser flash photolysis techniques. The reaction (which affords the corresponding silyl enol ether) proceeds significantly faster at 23 °C in hydrocarbon solvents than in acetonitrile in all cases, but the Hammett  $\rho$ -values defined by the data for the substituted 1,1-diphenylsilenes are larger in isooctane ( $\rho \approx +1.5$ ) than in acetonitrile ( $\rho \approx +1.1$ ). Deuterium kinetic isotope effects and Arrhenius parameters have been determined for the reactions of 1-methyl-1-phenyl-, 1,1-diphenyl-, 1,1-bis(4-methylphenyl)-, and 1,1-bis(4-(trifluoromethyl)phenyl)silene in hexane and acetonitrile. All but 1,1-bis(4-(trifluoromethyl)phenyl)silene exhibit negative activation energies for reaction. The trifluoromethyl derivative, the most reactive in the series, exhibits a positive  $E_a$  in acetonitrile and a curved Arrhenius plot in hexane. The results are consistent with a mechanism involving initial, reversible formation of a silene–ketone complex which collapses to product by rate-controlling proton transfer. The trends in the data can be rationalized in terms of variations in the relative rate constants for reversion to reactants and hydrogen transfer as a function of temperature, substituent, and solvent. The differences between acetonitrile and hydrocarbon solvents are rationalized as due to the effects of the strong solvation of the free silene by the nitrile solvent.

## Introduction

Silenes react with aldehydes or ketones to yield [2 + 2]-cycloaddition or ene-addition products, depending primarily on the structure of the carbonyl compound.<sup>1–3</sup> Those with  $\alpha$ -hydrogens undergo ene-addition preferentially, with the carbonyl oxygen bonding to silicon and either the carbonyl  $\alpha$ -hydrogen transferring to the silenic carbon<sup>4–7</sup> or (in special cases) a hydrogen allylic to the silenic Si=C bond transferring to the carbonyl carbon.<sup>8</sup> Saturated carbonyl compounds without enolizable hydrogens undergo [2 + 2]-cycloaddition to yield siloxetanes,<sup>5,9,10</sup> while  $\alpha,\beta$ -unsaturated or phenyl ketones and aldehydes prefer [2 + 4]-cycloaddition, with the silene providing the  $2\pi$  fragment.<sup>11</sup> These reactions are generally quite clean, although a few examples have

been reported where two modes of reaction compete with one another.<sup>5,11–13</sup>

There have been few systematic studies reported of the mechanisms of these reactions. We have reported time-resolved spectroscopic studies of the addition of aliphatic ketones to a series of transient silenes (**1**) derived from the photorearrangement of arylsilanes<sup>12–14</sup> and of a series of aliphatic ketones to 1,1-diphenylsilene (**4c**).<sup>15</sup> The addition of acetone to arylsilane-derived silenes has been known for several years and was thought to yield ene-derived alkoxysilanes (**2**) exclusively.<sup>6,8,16</sup> In fact, siloxetane adducts (**3**) are also formed in these reactions, in relative yields which increase with increasing steric bulk of the substituents at the silenic silicon atom (see eq 1).<sup>12,13,17</sup> The results were rationalized in terms of a stepwise addition mechanism in which the relative yields of the two products (**2** and **3**) are determined by conformational factors in a biradicaloid or zwitterionic intermediate, formed by attack of the carbonyl oxygen at silicon.

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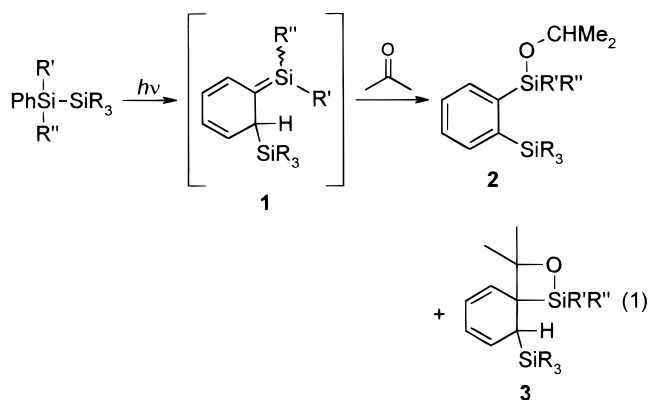
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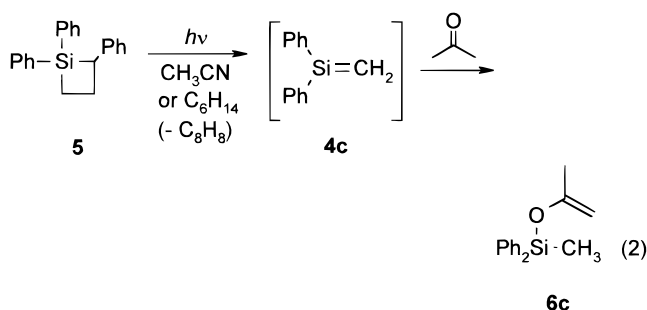
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In contrast, reaction of 1,1-diphenylsilene (**4c**) (generated by photolysis of 1,1,2-triphenylsilacyclobutane **5**<sup>15</sup> or 1,1-diphenylsilacyclobutane **7c**<sup>18,19</sup>) with acetone in solution yields the silyl enol ether (**6c**) exclusively (see eq 2), and analogous products are obtained with a number of other aliphatic ketones as well.<sup>15</sup> The reaction

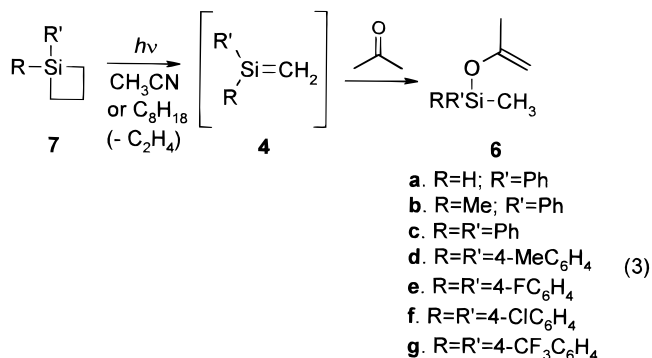


with acetone proceeds with absolute rate constants in the  $10^7$ – $10^8$   $\text{M}^{-1} \text{s}^{-1}$  range, depending on the solvent, and exhibits small deuterium kinetic isotope effects (KIEs) which cannot be conclusively identified as primary or secondary.<sup>15</sup> From the trends in reactivity as a function of ketone structure, it was concluded that Si–O bond formation involves the carbonyl n-orbitals rather than the  $\pi$ -orbital. We speculated that these results might be indicative of a concerted, nonpericyclic mechanism for the addition reaction in this case.

We recently reported solvent, deuterium isotope, and temperature effects on the absolute rate constants for addition of alcohols and acetic acid to the series of ring-substituted 1,1-diphenylsilene derivatives **4c–g**, which were generated by photolysis of the corresponding 1,1-diarylsilacyclobutanes **7c–g**.<sup>20</sup> It is now well-established that the addition of alcohols proceeds by a mechanism involving the initial formation of a zwitterionic silene–alcohol complex, which collapses to product by rate-controlling proton transfer from oxygen to the silenic carbon.<sup>14,21–30</sup> In the case of acetic acid, our results suggest that addition to **4** proceeds by a stepwise

mechanism similar to that of alcohols, but with complex formation being the rate-determining step. Complexation was proposed to involve the carbonyl oxygen, and the subsequent fast proton transfer was proposed to occur via a six-membered transition state. Clearly, this mechanism is potentially relevant to that of the ene-addition of enolizable ketones to silenes.

In this paper, we report a study of the effects of substituents on the rate constants for addition of acetone to arylsilene derivatives. As before, we have employed the photocycloreversion of the appropriate arylsilacyclobutane derivatives (**7**) to generate the corresponding silenes (**4**) in acetonitrile and hydrocarbon solvents (eq 3) and have measured absolute rate constants for their reaction with the ketone using nanosecond laser flash photolysis techniques. Deuterium



kinetic isotope effects and Arrhenius parameters have been determined for several members of the series. The results are consistent with a mechanism involving the intermediacy of a Lewis acid–base complex between the silene and the carbonyl compound, in a manner analogous to the addition of alcohols.

## Results and Discussion

Direct irradiation of the silacyclobutanes ( $\sim 0.015$  M) in hexane or cyclohexane-*d*<sub>12</sub> solution in the presence of 0.05 M acetone results in the formation of the corresponding silyl enol ethers **6a–g** in high chemical yields. The products were not isolated but were identified on the basis of GC/MS and <sup>1</sup>H NMR analysis of the crude photolysis mixtures. No other products are formed in yields in excess of  $\sim 5\%$  relative to that of the enol ether, below  $\sim 40\%$  conversion. Thus, all seven compounds behave similarly with respect to the formation of **6**, the product of ene-addition of acetone to the corresponding arylsilene **4**. Irradiation to higher conversions generally results in the formation of several new, unidentified products due to secondary photolysis of **6**, and unlike the primary formation of the enol ethers by silene trapping, the efficiency of their secondary photochemical reactions varied with substituent.

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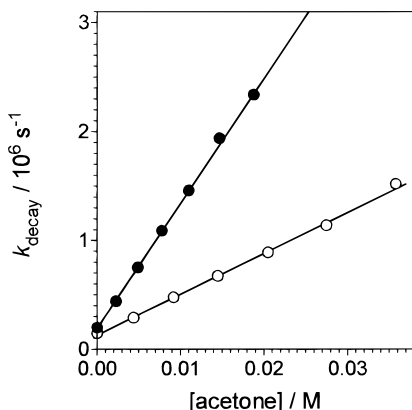
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**Table 1. Bimolecular Rate Constants and Deuterium Kinetic Isotope Effects for Reaction of Arylsilenes (4) with Acetone in Air-Saturated Acetonitrile and Isooctane Solution at 22 ± 1 °C<sup>a</sup>**

4 (RR'Si=CH <sub>2</sub> )	acetonitrile		isooctane	
	<i>k</i> <sub>acetone</sub> (10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> )	<i>k</i> <sub>H</sub> / <i>k</i> <sub>D</sub>	<i>k</i> <sub>acetone</sub> (10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> )	<i>k</i> <sub>H</sub> / <i>k</i> <sub>D</sub>
<b>a</b> (R = H; R' = Ph)	0.66 ± 0.05	1.8 ± 0.3	2.2 ± 0.2 <sup>b</sup>	—
<b>b</b> (R = Me; R' = Ph)	0.48 ± 0.02	1.7 ± 0.2	3.3 ± 0.2 <sup>b</sup>	—
<b>c</b> (R = R' = C <sub>6</sub> H <sub>5</sub> )	1.8 ± 0.1	2.2 ± 0.2	3.8 ± 0.2	2.1 ± 0.2
<b>d</b> (R = R' = 4-MeC <sub>6</sub> H <sub>4</sub> )	1.16 ± 0.03	3.1 ± 0.2	1.7 ± 0.1	1.7 ± 0.2
<b>e</b> (R = R' = 4-FC <sub>6</sub> H <sub>4</sub> )	4.3 ± 0.1	—	12.9 ± 0.9	1.8 ± 0.2
<b>f</b> (R = R' = 4-ClC <sub>6</sub> H <sub>4</sub> )	6.4 ± 0.1	2.1 ± 0.2	20.4 ± 0.20	1.7 ± 0.1
<b>g</b> (R = R' = 4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> )	8.7 ± 0.4	1.3 ± 0.1	35.2 ± 0.40	1.4 ± 0.3
$\rho^c$	+(1.1 ± 0.1)		+(1.5 ± 0.2)	

<sup>a</sup> Errors are listed as twice the standard deviation from least-squares analysis of *k*<sub>decay</sub> – concentration data according to eq 4. <sup>b</sup> In hexane solution. <sup>c</sup> Calculated from the data for **4c–f**. Errors are listed as ±2σ.



**Figure 1.** Plots of *k*<sub>decay</sub> vs [acetone] for quenching of 1,1-bis(4-methylphenyl)silene (**4d**) by acetone (●) and acetone-*d*<sub>6</sub> (○) in acetonitrile solution at 21 °C.

Nanosecond laser flash photolysis of air-saturated solutions of **7a–g** (0.003–0.006 M) in dry acetonitrile, hexane, or isooctane allows for the direct detection of the corresponding arylsilenes **4a–g** as moderately strong transient absorptions centered at  $\lambda_{\max} = 315$  nm for **4a,b**<sup>31</sup> and  $\lambda_{\max} = 325$  nm for **4c–g**.<sup>20</sup> The lifetimes of the silenes are shortened upon addition of acetone to the solutions, consistent with the clean formation of **6** in the steady-state photolysis experiments. Plots of the pseudo-first-order rate constant for silene decay (*k*<sub>decay</sub>) versus acetone concentration according to eq 4 (where *k*<sub>0</sub> is the pseudo-first-order rate constant for silene decay in the absence of the quencher) were linear in every case; the slopes of the plots afford the second-order rate constants for reaction of the silene with acetone (*k*<sub>acetone</sub>).

$$k_{\text{decay}} = k_0 + k_{\text{acetone}}[\text{acetone}] \quad (4)$$

In selected cases, similar experiments were carried out using acetone-*d*<sub>6</sub> as the quencher. Figure 1 shows representative plots of *k*<sub>decay</sub> vs [acetone] for quenching of silene **4d** by acetone and acetone-*d*<sub>6</sub> in acetonitrile solution at 21 °C. The absolute rate constants for reaction of **4a–g** with acetone in acetonitrile and isooctane solution at 21–23 °C are listed in Table 1, along with *k*<sub>H</sub>/*k*<sub>D</sub> values calculated from these data and the corresponding ones for acetone-*d*<sub>6</sub>.<sup>32</sup> The rate constants for reaction of the silenes with acetone in

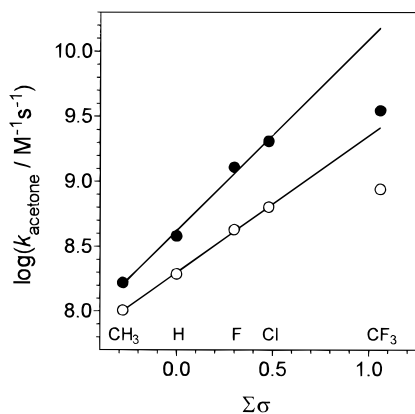
hexane solution did not differ significantly from those measured in isooctane.

The reactivities of the three phenylsilenes **4a–c** differ only slightly in hydrocarbon solution but vary in the order **4a** < **4b** < **4c**. The spread is larger in acetonitrile solution, where **4a** and **4b** are 4–5 times less reactive than they are in hexane or isooctane. While alcohol additions to these three silenes are also slower in acetonitrile than in hydrocarbon solvents, the opposite trend in relative reactivity is observed.<sup>31</sup> The general rate retardation in acetonitrile relative to hydrocarbon solvents most likely results from specific solvation of the silenes by the nitrile, a weak Lewis base. The different relative reactivities of the three compounds toward alcohols and ketones might be explained in terms of steric effects on the preferred geometries of initial complexation of the two nucleophiles at silicon. Ene-addition of the ketone requires transferral of a proton from the carbonyl  $\alpha$ -carbon, which will prefer to be oriented toward the silenic carbon (i.e., in the required geometry) when bulky substituents are attached to silicon. In the addition of alcohols, on the other hand, complexation in the correct geometry for proton transfer will be favored by substituents of low steric bulk at silicon.

For **4c** and the other four silenes, in which steric effects at silicon are constant, the rate constants increase with increasing electron-withdrawing power of the aryl substituents. Although the trend is the same as with alcohols and acetic acid, the variation in the rate constants throughout the series is more pronounced for addition of the ketone and Hammett plots appear to be curved. These are shown in Figure 2 for the data obtained in the two solvents. The rate constants for reaction of four of the compounds (**4c–f**) in both solvents correlate extremely well with Hammett  $\sigma$  values ( $r^2 > 0.99$ ), affording  $\rho$  values of +(1.1 ± 0.1) and +(1.5 ± 0.2) for reaction in acetonitrile and isooctane, respectively. These are significantly higher than those for addition of methanol ( $\rho = +0.31$ ) or acetic acid ( $\rho = +0.17$ ),<sup>20</sup> suggesting that polar factors play a significantly greater role in the reaction of the ketone. In general terms, all three reactions can be viewed as nucleophile–proton additions; thus, the greater sensitivity to substituents of the rate of acetone addition is consistent with the fact that the ketone is less nucleophilic than either the alcohol or the carboxylic acid (as measured by the conjugate acid *pK*<sub>a</sub>'s, which are –0.1, 2.4, and 1.1 for acetone, methanol, and acetic acid, respectively, in acetonitrile<sup>33</sup>) and much less acidic. The

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(32) The previously reported value for the rate constant for quenching of **4c** by acetone in acetonitrile ( $1.1 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> at 21 °C)<sup>15</sup> is incorrect, probably due to an analytical error.

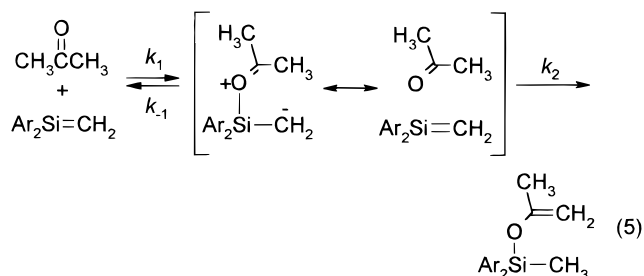


**Figure 2.** Hammett plots for quenching of 1,1-diarylsilenes **4c–g** by acetone in acetonitrile (○) and isoctane (●) solution at  $22 \pm 1$  °C.

rate constants for reaction of the trifluoromethyl derivative **4g** are somewhat slower than would be predicted on the basis of the Hammett correlations for the other four derivatives. The reasons for this behavior will become clearer later.

The rate constants for reaction of all five compounds are lowered by  $\alpha$ -deuteration on the ketone to similar extents in the two solvents, leading to kinetic deuterium isotope effects ranging from  $k_H/k_D \sim 1.3$  for the most reactive (**4g**) to  $k_H/k_D \sim 3.1$  for the least reactive (**4d**) silene in the series. It seems most reasonable to conclude that these effects are due to  $\alpha$ -hydrogen transfer occurring in the rate-determining step for reaction, in which case they are the result of small primary effects reinforced by secondary  $\alpha$ -deuterium isotope effects. It is unlikely that they can be ascribed to a pure secondary ( $\beta$ ) isotope effect, as might result from a two-step mechanism initiated by rate-determining nucleophilic attack of the carbonyl oxygen at silicon followed by fast intramolecular proton transfer, since such a process involves no change in hybridization at the carbonyl carbon in the rate-determining step and hence should be affected relatively little by isotopic substitution  $\alpha$  to this center. On a per-deuterium basis, the isotope effect observed for **4d** amounts to  $\sim 1.21$ , which is significantly larger than might reasonably be expected for a secondary isotope effect due to a mechanism of this type.

Coupled with the indication that carbonyl nucleophilicity plays a crucial role in controlling the rate constant for the ene-addition of ketones to **4c**,<sup>15</sup> the substituent and isotope effect data reported here are consistent with a stepwise mechanism analogous to that for addition of alcohols and acetic acid. The mechanism, shown in eq 5, involves initial, reversible association of the carbonyl oxygen and the silenic silicon atom, followed by collapse to product by rate-determining transfer of a carbonyl  $\alpha$ -hydrogen to the silenic carbon. The kinetic scheme resulting from this mechanism is given in eq 6. The positive Hammett  $\rho$  values observed for the reaction of acetone with **4c–g** suggests that it is the initial pre-equilibrium which is primarily responsible for the sensitivity of the rate to aryl substitution, since the



$$k_{\text{decay}} = k_0 + \frac{k_1 k_2}{k_{-1} + k_2} [\text{Me}_2\text{CO}] \quad (6)$$

second step would be expected to exhibit a relatively small  $\rho$  value due to the strong exothermicity involved in product formation and the fact that it involves only charge reorganization in a zwitterionic species. This mechanism would explain the lower reactivity and smaller Hammett  $\rho$  value for reaction in acetonitrile, where complexation of free silene with the solvent should increase in strength with increasing silene electrophilicity and hence work against the substituent effect on complexation with the ketone.

The temperature dependence of the rate constants for reaction of several of the silenes was investigated over the  $-15$  to  $+50$  °C temperature range in acetonitrile and hexane solution. Arrhenius plots for the 1,1-diarylsilenes are shown in Figure 3, while the Arrhenius parameters obtained from linear least-squares analysis of the data are collected in Table 2. For purposes of comparison, the rate constants for diffusion (calculated using the modified Debye equation ( $k_{\text{diff}} = 8RT/3000\eta$ ) and values of  $\eta$  extrapolated from published temperature–viscosity data<sup>34</sup>) are also plotted as a function of temperature in Figure 3. As can be seen from these data, the reaction of the parent compound (**4c**) with acetone exhibits negative activation energies in both solvents, a result which can be most conveniently explained by the involvement of an association complex which proceeds to product at a rate comparable to, but slower than, reversion to the free reactants. In such situations, the negative activation energy results from the free energy of activation for the second step being dominated by the entropic term, with the enthalpy of the transition state lower than that of the free reactants. This is a common feature of fast reactions which proceed by mechanisms of this general type,<sup>35–44</sup> but it does not in itself rule out the possibility that the reaction

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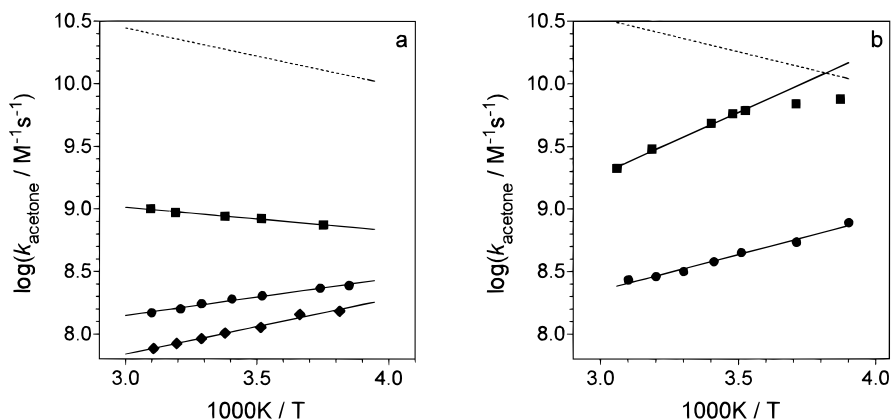
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**Figure 3.** Arrhenius plots for quenching of 1,1-diarylsilenes **4c** ( $R = R' = \text{C}_6\text{H}_5$ ; ●), **4d** ( $R = R' = 4\text{-MeC}_6\text{H}_4$ ; ◆), and **4g** ( $R = R' = 4\text{-CF}_3\text{C}_6\text{H}_4$ ; ■) by acetone in (a) acetonitrile and (b) hexane. The dotted lines are plots of the diffusion rate constants vs temperature, calculated using the Debye equation and published viscosities.<sup>34</sup>

**Table 2.** Arrhenius Activation Parameters for Addition of Acetone to Selected Arylsilenes in Acetonitrile and Hexane Solution<sup>a</sup>

<b>4</b> ( $\text{RR}'\text{Si}=\text{CH}_2$ )	solvent	$k_q^{25\text{ }^\circ\text{C}}$ ( $10^8 \text{M}^{-1} \text{s}^{-1}$ ) <sup>b</sup>	$E_a$ (kcal mol <sup>-1</sup> )	$\log(A/\text{M}^{-1} \text{s}^{-1})$
<b>b</b> ( $R = \text{Me}$ ; $R' = \text{Ph}$ )	MeCN	$0.5 \pm 0.3$	$-0.8 \pm 0.3$	$7.1 \pm 0.2$
	hexane	$3.1 \pm 1.0$	$-1.9 \pm 0.2$	$7.1 \pm 0.1$
<b>d</b> ( $R = R' = 4\text{-MeC}_6\text{H}_4$ )	MeCN	$0.9 \pm 0.3$	$-2.0 \pm 0.1$	$6.5 \pm 0.1$
	hexane	$3.3 \pm 0.9$	$-2.6 \pm 0.1$	$6.6 \pm 0.1$
<b>c</b> ( $R = R' = \text{C}_6\text{H}_5$ )	MeCN	$1.4 \pm 0.5$	$-1.3 \pm 0.1$	$7.2 \pm 0.1$
	hexane	$3.3 \pm 0.9$	$-2.6 \pm 0.1$	$6.6 \pm 0.1$
<b>g</b> ( $R = R' = 4\text{-CF}_3\text{C}_6\text{H}_4$ )	MeCN	$9.4 \pm 1.2$	$0.85 \pm 0.05$	$9.6 \pm 0.1$
	hexane	$41 \pm 9$	$-4.5 \pm 0.2^c$	$6.3 \pm 0.1^c$

<sup>a</sup> Errors are listed as twice the standard deviation from the linear least-squares analyses. The rate constants employed for calculation of the activation parameters were corrected for thermal expansion of the solvent. <sup>b</sup> Interpolated from Arrhenius data. <sup>c</sup> High-temperature limiting values.

proceeds by a concerted mechanism.<sup>36,39,41,45–47</sup> The Arrhenius plots for addition of acetone to **4c**, **4d**, and **4g** depend on the substituent in a manner which is strikingly similar to alcohol additions,<sup>20</sup> however, for which excellent evidence for the involvement of complexes exists.<sup>14,21–30</sup> Thus, we favor the analogous mechanism for ketone additions, even though there is presently no direct evidence for the involvement of complexes in the reaction. Within the confines of this mechanism, the trend in the temperature dependences can be rationalized in terms of the variations of the individual rate constants for formation of ( $k_1$ ), reversion of ( $k_{-1}$ ), and hydrogen transfer within ( $k_2$ ) the association complex as a function of substituent.

For a mechanism of this general type, reversion of the intermediate to reactants is expected to be characterized by a positive entropy of activation, while its collapse to product should be characterized by a negative one. If the enthalpic components of the free energies of activation for the two processes are small in relation to the corresponding entropic components, then the rate constants will respond in opposite ways to changes in temperature, with  $k_{-1}$  increasing and  $k_2$  decreasing as the temperature increases. The opposing temperature dependences of the two reaction channels available to the intermediate results in a bell-shaped Arrhenius dependence for the overall reaction rate constant over a very wide range in temperature. The high-tempera-

ture extreme corresponds to the limit  $k_{-1} \gg k_2$ , where formation of the intermediate is fully reversible; it is in this limit that the maximum negative value of the Arrhenius activation energy is obtained. The low-temperature extreme corresponds to the limit  $k_{-1} \ll k_2$ , where formation of the intermediate is fully rate determining. In this limit, the observed activation energy is that for formation of the intermediate from the free reactants and it will have a (positive) value equal to or greater than the activation energy for diffusion. The change from negative to positive  $E_a$  occurs as  $k_{-1}$  decreases in magnitude relative to  $k_2$ , with the apex in the plot corresponding to the temperature where  $k_{-1} \approx k_2$ . Experimentally, the portion of this ideal plot that one actually observes will depend on the relative magnitudes of the three individual rate constants over the limited temperature range investigated. For a series of compounds reacting by identical mechanisms, the position of this “window” will change with each compound as the relative magnitudes of  $k_1$ ,  $k_{-1}$ , and  $k_2$  change.

The variation in the temperature dependences for reaction of **4c**, **4d**, and **4g** with acetone in acetonitrile can be explained in simplest terms by considering only the variation in the reactivity ratio characterizing the association complex,  $[k_2/(k_{-1} + k_2)]$ , as a function of substituent.<sup>20</sup> Both the parent compound (**4c**) and the 4-methyl derivative (**4d**) exhibit negative activation energies, indicating that in both cases, the complex reverts to reactants faster than it proceeds to products over the temperature range investigated (i.e.,  $[k_2/(k_{-1} + k_2)] < 0.5$ ). From the fact that the  $E_a$  for reaction of **4d** is more negative than that for **4c**, it can be concluded

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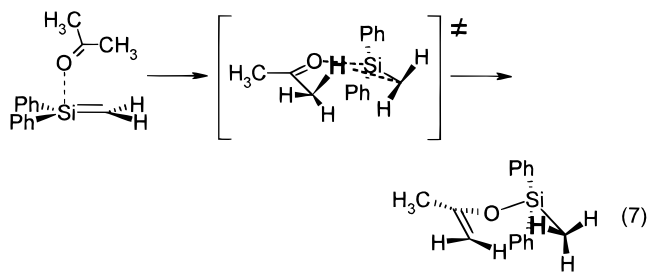
that  $k_{-1}$  is larger (and/or  $k_2$  is smaller) for the 4-methyl derivative than for the parent compound. The 4-trifluoromethyl derivative **4g** exhibits a small positive  $E_a$ , indicating that in this case reversion of the complex to reactants is slower than product formation over this temperature range (i.e.,  $[k_2/(k_{-1} + k_2)] > 0.5$ ). The Arrhenius data thus indicate that  $k_{-1}$  decreases in the order **4d** > **4c** > **4g** relative to  $k_2$ , which is consistent with the positive Hammett  $\rho$  value given by the overall reaction rate constants. It is also consistent with the decrease in the KIE throughout the series of compounds, since the observed isotope effect will be a maximum in the limit  $k_{-1} \gg k_2$  and decrease as  $k_2$  increases relative to  $k_{-1}$ .

The Arrhenius behavior of **4c** and **4g** in hexane suggests that the variation in the reactivity ratio of the complex as a function of substituent follows the same trend in this solvent as in acetonitrile. One important difference is indicated by the curved Arrhenius plot for silene **4g**, which appears to be converging with that for diffusion at lower temperatures (see Figure 3b). This behavior suggests that the formation of the association complex occurs at the diffusion-controlled rate in this case. The fact that the plot is so distinctly curved over the temperature range investigated indicates that the variation in the reactivity ratio  $[k_2/(k_{-1} + k_2)]$  with temperature is much steeper in this solvent than in acetonitrile, perhaps due to the effects of complexation of the latter solvent with the silene.

As pointed out earlier, the rate constants for reaction of **4g** in the two solvents deviate from the excellent correlation with Hammett substituent constants defined by the other four compounds in the series. In hexane, this is probably because the overall rate constant for reaction of this compound is so close to that of diffusion at ambient temperatures. In acetonitrile, on the other hand, the deviation is more likely to be due to the fact that the temperature at which the comparison is made is within that of positive temperature dependence (positive  $E_a$ ) for **4g** and within that of a negative temperature dependence for the other compounds. It would thus be predicted that the correlation would improve if it were obtained at much higher temperatures, within the negative temperature dependence ranges of all five compounds in the series.

Most reasonably, complexation of the carbonyl oxygen at silicon would yield a species in which the silicon lies in the  $n$ -orbital plane, with the  $\pi$ -systems of the Si=C and C=O bonds arranged perpendicular to one another. Presumably, facile transfer of the enolic hydrogen to the silenic carbon within the complex requires some degree of overlap between the C-H bond and the  $\pi$ -orbital on the carbonyl carbon. This overlap cannot be perfect owing to geometric constraints, but if the enolic C-H and C=O bonds assume an angle of  $\sim 45^\circ$ , the hydrogen can be transferred to the silenic carbon via a distorted chair transition state like that depicted in eq 7.

We are currently investigating the mechanisms of both ene- and [2 + 2]-addition of carbonyl compounds to silenes using computational methods, where the intermediacy of a complex common to both reaction pathways is predicted at both the semiempirical (AM1 and PM3) and ab initio (6-31g\*) levels of theory. The results of these studies will be reported soon.



## Summary and Conclusions

The effects of ring substituents on the rate constants, deuterium kinetic isotope effects, and Arrhenius parameters for ene-addition of acetone to 1,1-diphenylsilene are most easily explained in terms of a mechanism involving fast, reversible formation of a zwitterionic silene-ketone complex, followed by rate-limiting proton transfer between the  $\alpha$ -carbonyl and silenic carbons. The variation in Arrhenius behavior and isotope effect as a function of substituent indicate that electron-withdrawing substituents at silicon increase both the rate at which the complex is formed and the rate of its collapse to the silyl enol ether relative to reversion to starting materials. In extreme cases, this results in a change in the identity of the slower step from proton transfer to complex formation over the temperature range studied ( $-15$  to  $+50^\circ\text{C}$ ), allowing observation of part of the bell-shaped Arrhenius plot which is predicted for a mechanism of this type.

It seems reasonable to suggest that the formal [2 + 2]-addition of nonenolizable carbonyl compounds to reactive silenes might also proceed through the intermediacy of silene-carbonyl complexes, in which case similar kinetic characteristics to those of ene-addition might be expected. This is currently under investigation in our laboratory.

## Experimental Section

NMR spectra were recorded in deuteriochloroform and are referenced to tetramethylsilane.  $^1\text{H}$  NMR spectra were recorded on Bruker AC200 or DRX500 spectrometers and were referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low-resolution mass spectra were determined by GC/MS, using a Hewlett-Packard 5890II gas chromatograph equipped with a HP-5971A mass-selective detector and DB-5 fused silica capillary column (30 m  $\times$  0.25 mm; Chromatographic Specialties, Inc.).

Analytical gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a conventional heated splitless injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a DB1701 megabore capillary column (15 m  $\times$  0.53 mm; Chromatographic Specialties, Inc.). Semipreparative gas chromatographic separations were carried out using a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a metal column (3% OV 101 on Chromosorb W, HP 80/100; 6 ft  $\times$  0.25 in.; Chromatographic Specialties, Inc.).

Acetonitrile (BDH or Caledon Reagent) was refluxed over calcium hydride (Fisher) for several days, distilled under dry nitrogen, and then cycled 3 times through a 1 in.  $\times$  6 in. column of neutral alumina (Aldrich) which had been activated by heating under vacuum (ca. 0.05 Torr) at  $320^\circ\text{C}$  for 10 h with periodic shaking. Hexane and isooctane were Caledon HPLC grade and used as received from the supplier. Acetone (Caledon Reagent) was refluxed over barium oxide and dis-

tilled. Acetone- $d_6$  was used as received from Isotec, Inc. The arylsilylcyclobutanes (**7a–g**) were prepared according to the published methods<sup>20,48,49</sup> and purified to >99% purity (as estimated by GC) by repeated column chromatography on silica gel using hexanes as eluant.

Steady-state photolysis experiments were carried out using a Rayonet reactor containing five RPR2537 lamps. Quartz NMR tubes containing cyclohexane- $d_{12}$  solutions (ca. 0.7 mL) of **7a–g** (~0.015 M) and 0.05 M acetone were sealed with rubber septa and irradiated for 10–30 min, with periodic monitoring of the course of the photolyses by GC and  $^1\text{H}$  NMR spectroscopy. Both methods indicated there to be only a single major product formed in each case, up to ~40% conversion of **7**. These were identified as the silyl enol ethers **6** by GC/MS and the  $^1\text{H}$  NMR spectra of the crude photolysis mixtures, which in each case showed a diagnostic pair of resonances at  $\delta \sim 4.0$  ppm due to the vinyl protons, in addition to a methyl singlet (doublet in the case of **6a**) at  $\delta \sim 0.5$  ppm. For **6a–c**, the assignments were verified by GC co-injection of authentic samples prepared using the published methods.<sup>50,51</sup>

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Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 16 ns; 70–120 mJ) from a Lumonics 510 excimer laser, filled with  $\text{F}_2/\text{Kr}/\text{He}$  mixtures and a microcomputer-controlled detection system.<sup>52</sup> 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 (0.004 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 a factor of 5 (usually more than 1 order of magnitude) in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

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