

Substituent Effects on the Reactivity of the Silicon–Carbon Double Bond

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ABSTRACT

Laser flash photolysis of various organosilicon compounds such as aryl-, vinyl-, and alkynylsilanes, silacyclobutanes and silacyclobutenes, and α -silylketenes and -diazomethanes leads to the formation of reactive silenes which can be detected directly in solution, allowing detailed studies of the kinetics and mechanisms of their reactions with nucleophiles. Over 30 transient silenes have now been studied by these methods, providing the opportunity to systematically assess the effects of substituents at silicon and carbon on the reactivity of the Si=C bond.

Introduction

The study of organosilicon reactive intermediates has been a rapidly growing field over the past 20 years. Gas- and condensed-phase studies of such reactive intermediates as silyl radicals,¹ silylenes,^{2,3} disilenes,^{3,4} and silenes have revealed there to be many of the expected commonalities—and many intriguing differences—between the chemistry of these species and that of their counterparts in organic chemistry. In addition to providing answers to basic questions related to chemical bonding, structure, and reactivity involving the Group 14 elements, the study of these reactive intermediates has the potential of providing useful insight and direction for growing fields such as silicon-based polymers,⁵ photolithography,⁶ and silicon surface science.^{7,8}

The chemistry of the silicon–carbon double bond has been an area of active interest since 1967, when Gusel'nikov and Flowers reported the first evidence of the possible existence of such species as a reactive intermediate in the high-temperature pyrolysis of a silacyclobutane derivative.⁹ Hundreds of examples of *silenes* and many of the qualitative aspects of their reactivity are now known, and the area has been regularly reviewed since the mid-

1970s.¹⁰ While a respectable number of “stable” derivatives have been isolated and identified, most silenes—especially relatively simple ones—are transients, formed as reactive intermediates in various thermal and photochemical reactions of organosilicon compounds. Because of this, their direct detection and study requires either matrix isolation or fast time-resolved spectroscopic techniques. While many simple silenes were studied in the 1980s by low-temperature matrix isolation techniques, information on their absolute reactivities in solution or gas phases requires the use of time-resolved methods that have only become readily available in more recent years. This Account describes our efforts to employ these techniques—laser flash photolysis methods in particular—to study the mechanisms of some of the more commonly known reactions of silenes, and to systematically assess the effects of substituents on the kinetic stability of the silicon–carbon double bond.

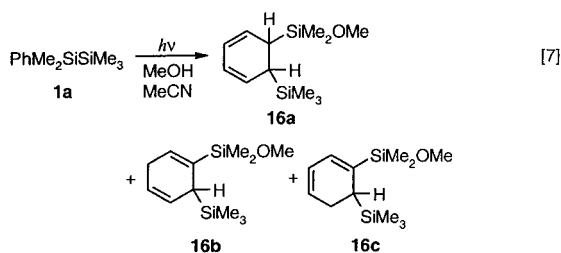
Photochemical Precursors of Transient Silenes

A number of photochemical reactions in organosilicon chemistry afford products consistent with the initial formation of transient silenes,^{11,12} and many of them have proven to be ideal for laser flash photolysis studies of silene reactivity in solution. Our initial efforts employed phenyldisilanes (e.g., **1**) as precursors to the transient (1-sila)hexatriene derivatives **2** (eq 1),¹³ which sprang from the early, product-oriented work of Ishikawa and Kumada on the photochemistry of these compounds under various conditions.¹⁴ Silene formation in these cases is the result of photochemically allowed [1,3]-silyl migration into the ortho position of one of the aromatic rings. This process also occurs in vinylsilanes (**3**; eq 2),^{15–18} which are also useful precursors to transient silenes for time-resolved spectroscopic study.¹⁹ Perhaps the most versatile precursors to simple silenes are silacyclobutanes (**5**), which undergo formal [2 + 2]-photocycloreversion to yield silenes of the type RR'Si=CH₂ (**6**; eq 3).^{20–28} The process occurs with adequate efficiency in derivatives bearing a wide range of aryl and/or alkyl substituents at silicon, using 248-nm laser excitation for aryl-substituted derivatives and 193-nm excitation for non-arylated ones.^{22,29–33} Silacyclobutenes (**7**; eq 4) yield the readily detectable³⁴ 2-vinyl-substituted silenes **8** via photoelectrocyclic ring-opening.^{35–37} Also, α -silyl ketenes (**9_{CO}**) and the analogous diazo compounds (**9_{N2}**) have been used as precursors to the family of carbon-substituted silenes **10** (eq 5).^{38–47} In these cases, silenes are formed by rapid ($k \geq 10^9 \text{ s}^{-1}$) [1,2]-migration (from silicon to carbon)⁴⁷ in the α -silyl carbene formed in the primary photochemical process.

The silenes formed in these reactions generally have lifetimes on the order of several microseconds, decay with second-order kinetics in rigorously dry solution, and exhibit UV absorption maxima ranging from 260 to 320 nm, typically 50–80 nm to the red of the corresponding alkene of the same substitution pattern.

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William J. Leigh grew up in Chatham, Ontario. He received the B.Sc. and Ph.D. degrees from the University of Western Ontario, the latter in 1981, and then held postdoctoral positions at the IBM Thomas J. Watson Research Center and the National Research Council of Canada in Ottawa. He joined the Department of Chemistry at McMaster University in 1983, where he is now Professor and Chair. His research is in the areas of organic and organometallic photochemistry, and the chemistry of organosilicon and organogermanium reactive intermediates.



silene was found to react rapidly with water and aliphatic alcohols, and the pseudo-first-order rate constant for decay of **2a** (k_{decay}) was found to vary quadratically with ROH concentration (R = H, Me, Et) according to eq 8, where k_0 is the pseudo-first-order rate constant for silene decay in the absence of ROH, and k_{ROH} and $k_{2\text{ROH}}$ are the second- and third-order rate constants for reaction of the silene with one and two molecules of alcohol, respectively. Figure 1 shows a plot of k_{decay} vs [ROH] for reactive quenching of **2a** by MeOH in acetonitrile solution, fitting of which to eq 8 yields values of $k_{\text{MeOH}} = (2.0 \pm 0.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2\text{MeOH}} = (5.8 \pm 1.0) \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$ for the second- and third-order reaction rate constants, respectively. The ratio of the rate constants for reaction by the second- and third-order pathways ($k_{\text{ROH}}/k_{2\text{ROH}} \approx 0.03$ for **2a**) increases with increasing steric bulk in the alcohol.¹³

$$k_{\text{decay}} = k_0 + k_{\text{ROH}}[\text{ROH}] + k_{2\text{ROH}}[\text{ROH}]^2 \quad (8)$$

This is precisely the behavior predicted by the Kira mechanism, provided that the formation of the silene-ROH complex is reversible and the proton-transfer steps are rate-limiting. The complete mechanism is shown in Scheme 1. Indeed, the first-order term in ROH (k_{ROH}) was found to exhibit a primary deuterium kinetic isotope effect on the order of $k_{\text{H}}/k_{\text{D}} \approx 1.5$ for both H₂O and MeOH addition. Furthermore, k_{decay} was found to obey a linear dependence on [ROH] for addition of 2,2,2-trifluoroethanol and acetic acid,¹³ whose greater acidity and lower nucleophilicity would be expected to result in a change in the rate-determining step from proton transfer (k_{H}) to complexation (k_{C}). In a later, more comprehensive kinetic study of the addition of alcohols to **2a-c**, it was shown that the intercomplex proton-transfer process (represented in Scheme 1 by $k_{\text{H}'}$) most likely proceeds by initial deprotonation of the complex by a second molecule of alcohol or the solvent, followed by fast reprotonation at carbon.⁶³

Such complex kinetic behavior is not observed with simpler silenes of the type Ar₂Si=CH₂ (e.g., **6a,b**), which have been generated in solution by 248-nm photolysis of the corresponding 1,1-diarylsilacyclobutane **5a,b** (eq 9).³⁰ Reaction of these silenes with aliphatic alcohols is significantly faster than is the case with **2**, and the silene decay rate follows a linear dependence on [ROH] over the range of alcohol concentrations that can be studied with our apparatus ([ROH]_{max} ≤ 0.01 M for these silenes). However, evidence that the mechanism of Scheme 1 still operates in these cases has been obtained from steady-state competition studies where the concentration of alcohol used can be much higher. The ratio of alkoxy-

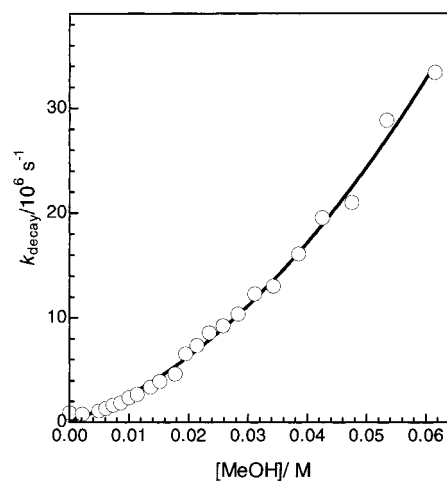
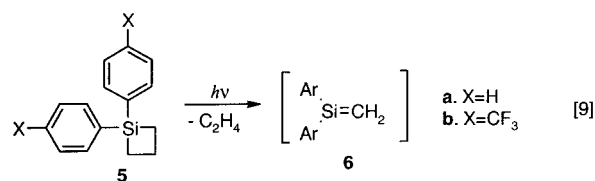


FIGURE 1. Stern–Volmer plot of the pseudo-first-order rate constant for decay of silene **2a** versus MeOH concentration in deoxygenated acetonitrile solution at 23 °C.¹³

lanes obtained from competing reaction of 1,1-diphenylsilene (**6a**) with MeOH and *t*-BuOH was found to vary with bulk alcohol concentration over the 0–0.5 M range.⁶⁴ The results are consistent with the involvement of a second, higher order pathway for reaction, which is more important for MeOH than for *t*-BuOH at any given total ROH concentration.



In these cases, the linear dependence of k_{obs} on [ROH] suggests that $k_{\text{H}} \gg k_{\text{H}'}[\text{ROH}]$ over the range of ROH concentrations that can be studied in our experiments, which simplifies the kinetics considerably. Under these conditions, the overall second-order rate constant for ROH addition (k_{ROH}), using the steady-state approximation for the zwitterionic complex, is given by the product of the rate constant for complexation (k_{C}) and the partitioning ratio for collapse of the complex to starting materials and product ($k_{\text{H}}/(k_{\text{H}} + k_{-\text{C}})$; eq 10). As a result of this and the

$$k_{\text{ROH}} = k_{\text{C}} \frac{k_{\text{H}}}{k_{\text{H}} + k_{-\text{C}}} \quad (10)$$

overall strong exothermicity of the reaction, negative activation energies are observed for addition of MeOH or *t*-BuOH to **6a**; indeed, this behavior appears to be typical of simple silenes of this type.⁶⁵ The negative activation energy results because the rate constant for decomplexation exceeds that of product formation (i.e., $k_{\text{H}} < k_{-\text{C}}$) over the particular range of temperatures studied (–5 to 55 °C), and the latter is strongly entropy-controlled. If all this is correct, then addition of deuterated alcohol (ROD) should lead to a more negative Arrhenius activation energy than ROH addition; indeed, exactly this behavior has been reported for the addition of MeOH to **6a** in acetonitrile (Figure 2).⁶⁶

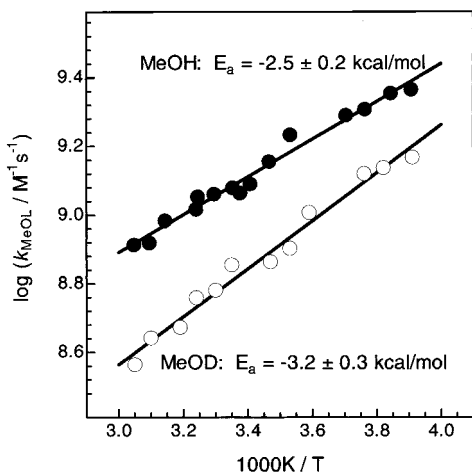


FIGURE 2. Arrhenius plots for the reaction of 1,1-diphenylsilene with MeOH and MeOD in dry acetonitrile solution.⁶⁶

We have also determined absolute rate constants and their Arrhenius parameters for the reactions of **6a** and the ring-substituted derivative **6b** with a number of other nucleophiles, including aliphatic ketones,⁶⁷ acetic acid,⁶⁶ aliphatic amines,⁶⁸ and alkoxysilanes.⁶⁹ All appear to react via two-step mechanisms analogous to that for alcohol addition, with nucleophilic attack occurring in the first step. However, since alcohol addition is the most widely used, most convenient, and mechanistically the best understood of silene trapping reactions, it is the most logical choice of a diagnostic reaction with which to quantify the effects of substituent on silene reactivity.

Substituent Effects on Silene Reactivity

The first systematic study of substituent effects on the electronic structure of the Si=C bond was reported in the mid-1980s by Apeloig and Karni, who carried out ab initio calculations on a series of simple 1- and 2-substituted silenes of the types $\text{RHSi}=\text{CH}_2$ and $\text{H}_2\text{Si}=\text{CHR}$, respectively.⁷⁰ They suggested that bond polarity factors are primarily responsible for the high intrinsic reactivity of silenes, and that the remarkable stability of isolable silenes such as those of Brook and co-workers ($(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{R})\text{OSiMe}_3$) is due mainly to electronic effects which act to reduce the natural polarity of the $\delta^+\text{Si}=\text{C}^{\delta-}$ bond. This proposal was made on the basis of observed variations in calculated Mulliken charge densities, which are reduced by π -acceptor/ σ -donor substituents at silicon and π -donor/ σ -acceptor substituents at carbon. These considerations lead one to predict that Wiberg's silenes (**11** and **12**), having σ -donor substituents at carbon, should in fact be quite potent electrophiles, making the fact that **12** is isolable all the more remarkable. It should be remembered, however, that isolability implies only that the silene is stable toward dimerization. Indeed, both Brook's and Wiberg's silenes were isolated under inert atmosphere conditions, and both evidently disappear rapidly upon exposure to air or moisture.^{58,71} This suggests that they both retain some degree of reactivity toward nucleophiles, the extent of which can only be determined experimentally.

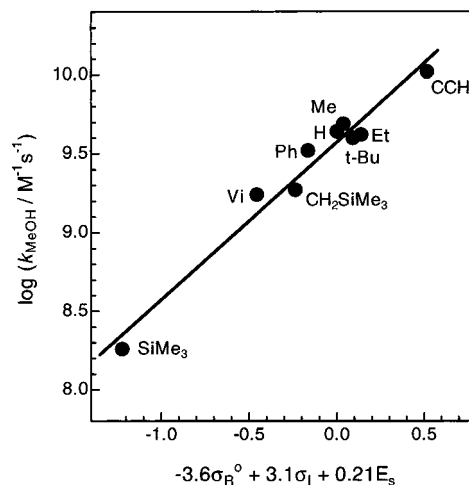
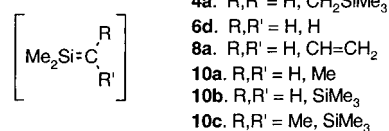
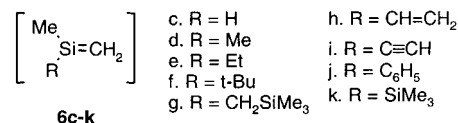


FIGURE 3. Three-parameter substituent correlation of the rates of reaction of Si-substituted 1-methylsilenes (**6c–k**) with methanol in dry hexane solution at 23 °C.³³

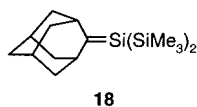
Our experimental studies of the effects of substituents at silicon and carbon on silene electrophilicity have focused on two series of simple silenes—of the types $\text{Me}(\text{R})\text{Si}=\text{CH}_2$ (**6c–k**) and $\text{Me}_2\text{Si}=\text{C}(\text{R})(\text{R}')$ (**6d**, **4a**, **8a**, **10**)—and have employed the absolute rate constants for addition of MeOH in hydrocarbon solution as a representative gauge of silene reactivity toward nucleophilic addition. The silenes **6c–k** were generated and detected



by 193- or 248-nm laser flash photolysis of the corresponding 1-methylsilacyclobutanes (**5c–k**; eq 3), while the series of C-substituted 1,1-dimethylsilenes $\text{Me}_2\text{Si}=\text{C}(\text{R})(\text{R}')$ were generated in a similar fashion from silacyclobutene (**7a**; eq 4), vinyldisilane (**3a**; eq 2), or α -silylketene or -diazomethane precursors (**9**; eq 5). All of them exhibit characteristically high reactivity toward methanol, with absolute rate constants varying over the range 2×10^8 – $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, depending on substituent.

The rate constants for reaction of the Si-substituted silenes correlate acceptably with a three-parameter function incorporating standard resonance and inductive and steric substituent parameters (σ_{R}^0 , σ_{I} , and E_{s} , respectively), as is shown in Figure 3.³³ This correlation indicates that the electrophilic reactivity of silicon–carbon double bonds is enhanced by π -donor/ σ -acceptor substituents at silicon, and retarded by steric effects at this position. According to the calculations of Apeloig and Karni, substituents of these types act to increase Si=C bond polarity, an effect which would be expected to enhance reactivity toward both nucleophilic attack at silicon and electrophilic attack

appears to support both of these predictions. Silene **18** is



so unreactive toward MeOH that reaction can be detected only (at least with our laser photolysis system) in essentially neat methanol solution, where the lifetime is on the order of ca. 30 ms at room temperature, and decreases with increasing temperature. In contrast to its sluggish reactivity as an electrophile, it remains reactive toward (head-to-head⁷⁴) dimerization, the absolute rate constant for which is on the order of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ in hexane solution at 25 °C. This should be compared to that for head-to-tail dimerization of 1,1-diphenylsilene (**6a**) under the same conditions, $k_{\text{dim}} = (1.1 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁷⁶

Conclusions

Alcohol addition and [2 + 2]-dimerization are the two best-known and most highly exothermic reactions of silene and simple substituted derivatives in the gas phase and in solution. With “naturally polarized” silenes such as $\text{Ph}_2\text{Si}=\text{CH}_2$ (**6a**), these two reactions proceed regiospecifically and with absolute rate constants that are within an order of magnitude of the diffusional rate constant in hexane solution.

The rate of alcohol addition varies markedly with substitution at the Si=C bond in simple silenes. Comparison of absolute rate data with the results of high-level *ab initio* calculations of the structures and electronic properties of substituted silenes verifies earlier suggestions that bond polarity is the main factor affecting the electrophilic reactivity of the Si=C bond; substituents at either silicon or carbon which act to reduce the natural polarity of the bond through resonance and/or inductive effects kinetically stabilize silenes toward addition of nucleophiles. While the regiochemistry of the reaction is substituent-independent, the mechanism of the reaction appears to change as Si=C bond polarity is reduced significantly.

Bond polarity factors also control the regiochemistry of [2 + 2]-dimerization⁷⁷ but appear to have a smaller effect on the absolute rate constant for the reaction. For example, the (head-to-head) dimerization of the 1,1-bis(trimethylsilyl)silene **18** proceeds about 10^5 times slower than the corresponding (head-to-tail) process in 1,1-diphenylsilene (**6a**) under the same conditions.⁷⁵ Given that these two silenes differ by about 9 orders of magnitude in their reactivity toward methanol under similar conditions, the smaller effect of substituents on the rate of silene dimerization is fascinating indeed. Current work in our laboratory is directed at investigating the implications of these results in greater detail.

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