A Laser Flash Photolysis Study of the Photochemistry of (Phenylethynyl)pentamethyldisilane. Absolute Rate Constants for Trapping of a Reactive 1-Silaallene by Nucleophiles

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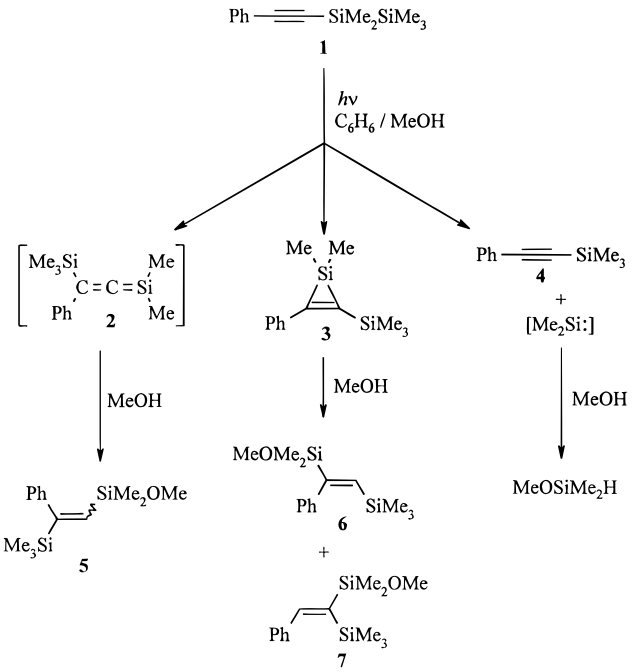
Received March 5, 1997⊗

Laser flash photolysis of nitrogen-saturated hexane solutions of pentamethyl(phenylethynyl)disilane affords a mixture of three transient species and a product which is stable on the millisecond time scale. These are assigned to the triplet state of the disilane ($\tau \sim 5\ \mu$s), 1,1-dimethyl-3-phenyl-3-(trimethylsilyl)-1-silaallene ($\tau \sim 25\ \mu$s), dimethylsilylene ($\tau \sim 100$ ns), and 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1-silacyclopropene ($\tau > 100$ ms), respectively, on the basis of their UV spectra and reactivity toward various reagents. While previous work has shown that the 1-silaallene is formed in less than 25% yield, it can be readily observed in transient absorption experiments in spite of extensive spectral overlap with the alkynyldisilane triplet and the 1-silacyclopropene. Absolute rate constants for reaction of the silaallene with methanol, acetone, acetic acid, and oxygen in hexane solution are reported and compared to data for a related compound.

Introduction

The chemistry of silenes has been of considerable interest over the past 30 years,[1−6] yet analogs in which the $Si{=}C$ bond forms part of a cumulated polyene structure—1-silaallene ($H_2Si{=}C{=}CH_2$) being the simplest homolog—have received only scant attention. The earliest report is that of Ishikawa and his co-workers, who proposed the involvement of a 1-silaallene derivative (**2**) as a reactive intermediate in the benzene-sensitized photolysis of pentamethyl(phenylethynyl)disilane (**1**) in the presence of methanol or acetone (Scheme 1).[7] Products consistent with the intermediacy of **2** were formed in relatively low yield; the major products were shown to be the isomeric 1-silacyclopropene (**3**) and phenyl(trimethylsilyl)ethyne (**4**) from photoextrusion of dimethylsilylene. Later papers from this group on the photochemistry of **1** and related alkynyldisilanes suggested that 1-silaallene formation, though always relatively minor compared to silacyclopropene formation and silylene extrusion, is a general feature of the photochemistry of alkynyldisilanes.[8−11] In the meantime, Gordon and Koob reported the results of ab initio theoretical calculations on the structure and stability of 1-silaallene and the other C_2SiH_4 isomers.[12] Only two stable derivatives are known, one as a "free" silaallene[13] and the other as a complex with ruthenium.[14]

Scheme 1



The photophysical and -chemical properties of arylalkynyldisilanes bear a number of similarities to those

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⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1997.

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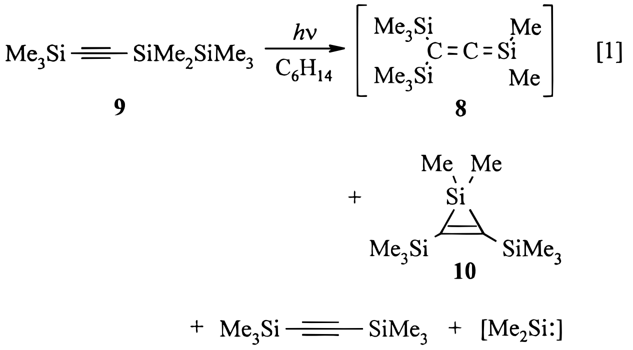
of simpler aryldisilanes.[15−24] There has been great interest in the photochemistry of aryldisilanes, due to their relevance as model compounds for polyarylsilane high polymers, which are of potential importance as photoresists, polymerization initiators, and photoconductors.[25−28] The unique photochemical and photophysical properties of these materials are due in large part to the presence of low-lying intramolecular charge transfer singlet states, which dominate their emissive behavior and photoreactivities. These properties also extend to arylalkynyldisilanes, and fluorescence spectroscopic studies of these compounds have contributed significantly to developing an understanding of the complexities of polyarylsilane photochemistry and photophysics.[9,29−32] The product studies mentioned above indicate that like that of aryldisilanes, the photochemistry of these compounds is dominated by molecular rearrangement and photoextrusion processes. While these are thought to be singlet-derived, there has been little attention paid to the possible role of the triplet state in product formation in solution. Transient spectroscopic studies, which might allow the direct detection and kinetic characterization of the reactive intermediates proposed to be involved in arylalkynyldisilane photochemistry, have not been reported.

Recently, we reported the time-resolved UV absorption spectrum of the reactive 1−silaallene derivative **8** (eq 1) and absolute rate constants for its reaction with alcohols, acetic acid, acetone, a diene, and oxygen in hexane solution at room temperature.[33] The UV spectrum of **8** shows an absorption maximum at 325 nm, a remarkable feature considering that 1,1-dimethylsilene absorbs at 244 nm.[34] Furthermore, although **8** exhibits reactivity toward characteristic silene traps, it does so with remarkable sluggishness compared to other reactive silenes that we have studied by similar methods.[22,35−41]



[1]

We speculated that the unique spectral and chemical properties of **8** might be at least partly due to hyperconjugative interactions between the Si=C bond and the C−Si bonds to the trimethylsilyl substituents at C3, which are perfectly situated for π-type overlap with the Si=C bond. Such interactions, which are directly analogous to the well-known β-silyl effect in carbocation chemistry,[42,43] are known to strongly affect the electronic spectra and reactivity of alkenes.[44,45] There are indications that silenes are affected similarly,[46] although the effect has not yet been studied in a systematic way.

In this paper we report the results of a time-resolved spectroscopic study of the photochemistry of pentamethyl(phenylethynyl)disilane (**1**) in hexane solution, with emphasis on the direct detection of the transient 1-silaallene derivative **2** by UV absorption spectroscopy, and the determination of absolute rate constants for its reaction with representative silene traps such as aliphatic alcohols, carboxylic acids, and acetone. The UV spectrum of **2** and its reactivity are compared to those of the previously studied compound **8**. The results of this comparison provide an indication of some of the structural factors which might be exploited for the synthesis of kinetically stabilized 1-silaallene derivatives.

Results and Discussion

Laser flash photolysis of continuously flowing, deoxygenated 1.3 × 10^{-4} M hexane solutions of **1** ($\epsilon_{248} = 18500 \pm 100$ M^{-1} cm^{-1}) with the 248 nm pulses from a KrF excimer laser produced readily detectable, long-lived absorptions throughout the 250−350 nm spectral range. The appearance of the traces varied markedly depending on the monitoring wavelength (λ_{mon}). Those recorded over the λ_{mon} = 280−350 nm range decayed with complex kinetics over several tens of microseconds to a residual absorption level that was stable over the full 5 ms time scale of our system. Those recorded over the λ_{mon} = 250−275 nm range showed an apparent negative

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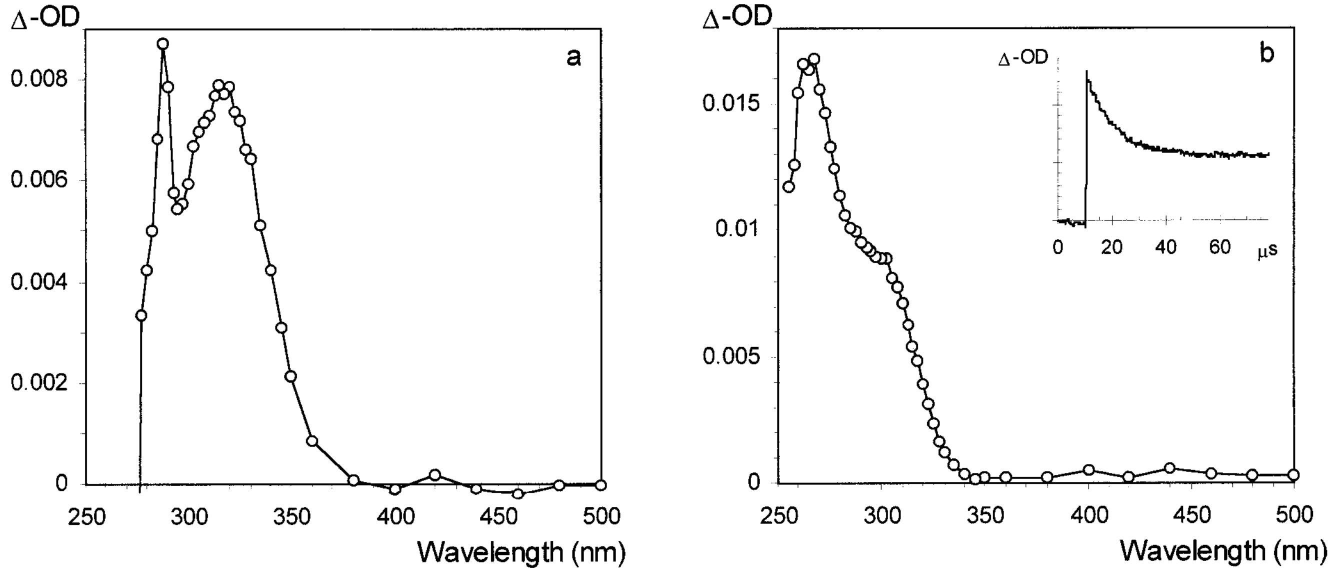

Figure 1. UV absorption spectra, recorded by nanosecond laser flash photolysis of air-saturated, 1.3×10^{-4} M solutions of (phenylethynyl)pentamethyldisilane (**1**): (a) UV spectrum of silacyclopropene **3**, recorded 43–66 μs after 248-nm laser excitation of a hexane solution of **1** containing either 1.0 M methanol or 0.002 M 1,3-octadiene; (b) UV spectrum of silaallene **2**, obtained by subtracting the residual spectrum a from that recorded 1.2–3.5 μs after laser excitation of a hexane solution of **1** containing 0.002 M 1,3-octadiene. The Inset in b shows a decay trace recorded at 310 nm.

absorption due to bleaching of the precursor; the initial bleaching of the signal recovered over several tens of microseconds with pseudo first-order kinetics to a "stable" negative absorption value, indicating that the destruction of the precursor is only partially reversible.

Saturation of the solution with air or addition of 1,3-octadiene led to an increase in the pseudo-first-order rate constant for the partial recovery of the bleaching signal at 255 nm but had no effect on the negative (255–275-nm) or positive (280–350 nm) residual absorption levels. Addition of 0.002 M 1,3-octadiene to this solution increased the rate of bleach recovery to such an extent that it became unresolvable from the laser pulse. Under these conditions, the transient absorption in the 280–350 nm range decayed with clean pseudo-first-order kinetics and a lifetime of ~10-μs, but again, the stable residual absorption levels were unaffected. These experiments indicate that the transient portion of the bleaching signal is due to the formation of a species (with no absorption in this region) which decays to regenerate mainly its precursor, alkynyldisilane **1**. This transient is identified below as the triplet state of the alkynyldisilane.

Time-resolved UV absorption spectra were recorded for a deoxygenated solution of **1** in hexane containing 0.002 M 1,3-octadiene (to reduce the lifetime of the triplet to <10 ns), in point-by-point fashion 1.2–3.5 and 43–66 μs after the laser pulse. Figure 1a shows the spectrum recorded 43–66 μs after the laser pulse, corresponding to that of the "stable" product (the spectral range below 290 nm is distorted due to precursor bleaching). We assign this species to the known 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)1-silacycloprop-2-ene (**3**);[7,9] while the UV spectrum of **3** has not been reported, the long-wavelength spectral maximum observed here ($\lambda_{max} \sim 320$ nm) is similar to that reported for a closely related analog which also bears phenyl- and trimethylsilyl-substituents on the C=C bond.[29] Figure 1b shows the spectrum of the transient species absorbing in the 280–350 nm range, obtained by subtraction of the spectrum in Figure 1a from that recorded right after the laser pulse (not shown). The insert in Figure 1b shows a typical transient decay trace, recorded at 310 nm. The lifetime of this species is shortened upon addition of alcohols, acetone, acetic acid, or oxygen to the solution (*vide infra*). On the basis of this behavior, the transient species giving rise to the absorption spectrum of Figure 1b is assigned to 1,1-dimethyl-3-phenyl-3-(trimethylsilyl)-1-silaallene (**2**).

The triplet–triplet absorption spectrum of **1** could be obtained by laser flash photolysis of nitrogen-saturated solutions of **1** in hexane containing 1.0 M methanol, which reduces the lifetime of silaallene **2** to <10 ns. Under these conditions, a transient absorption is observed with a maximum at 310 nm, which decays with clean pseudo-first-order kinetics ($\tau \sim 5$ μs) to a similar residual level as observed in the experiments described above. Figure 2 shows the transient difference spectrum, obtained by subtracting the long-time spectrum from one recorded 0.08–0.4 μs after the laser pulse; the insert shows a transient decay trace recorded at 310 nm. At the 255 nm monitoring wavelength, the partial recovery of the bleach signal occurred with the same rate constant as the transient decay shown in Figure 2. As expected, addition of 1,3-octadiene to the solution resulted in an increase in the pseudo-first-order rate constant for decay of the transient at 310 nm. A plot of k_{decay} *versus* 1,3-octadiene according to eqn 2 was linear, affording a bimolecular rate constant of $k_q = (6.6 \pm 0.8) \times 10^9$ M^{-1} s^{-1} for quenching of the species by the diene. On the basis of this rate constant, the sensitivity of the lifetime of the transient to oxygen, and the fact that the transient decays to regenerate its precursor, we assign the rate constant to the triplet state of alkynyldisilane **1**. Since quenching the triplet with air or diene has no effect on the intensities of the absorptions due to silaallene **2** or silacyclopropene **3**, it can be concluded that these products are singlet-derived and are formed competitively with the alkynyldisilane triplet state. Flash photolysis of hexane solutions of **1** containing both

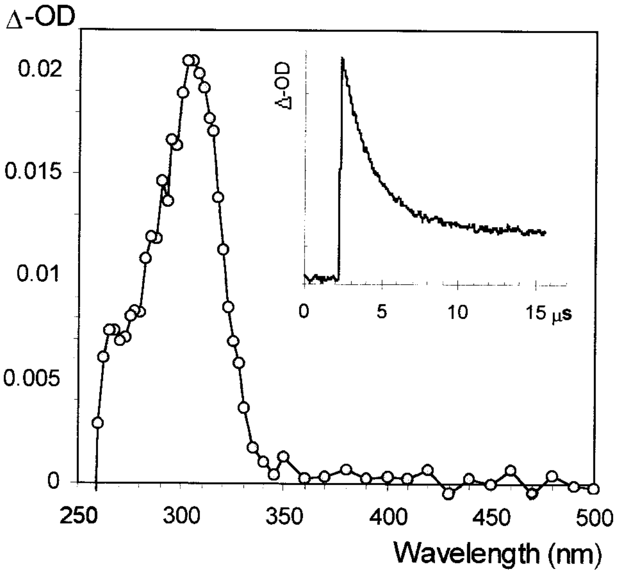

Figure 2. Triplet−triplet absorption spectrum of (phenylethynyl)pentamethyldisilane (**1**), recorded by nanosecond laser flash photolysis of a nitrogen-saturated 1.3 × 10^{-4} M solution of **1** in hexane containing 1.0 M methanol. The spectrum was obtained by subtracting the residual spectrum (Figure 1a) from that recorded 0.08−0.4 μs after the laser pulse. The Inset shows a decay trace recorded at 310 nm.

1.0 M methanol and 0.002 M 1,3-octadiene shows only the stable residual absorptions due to silacyclopropene **3** or irreversible precursor bleaching; no other transient species with lifetimes longer than that of the laser pulse could be detected under these conditions.

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

Laser flash photolysis of deoxygenated hexane solutions of **1**, with monitoring over a much shorter time scale (*ca.* 1 μs full scale), allowed for the ready detection of dimethylsilylene, characterized by its characteristic UV absorption spectrum (λ_{max} = 450 nm) and the extreme sensitivity of its lifetime ($\tau \sim 100$ ns) to the presence of oxygen, alcohols, or water.[33,47] This result verifies the indication from steady state trapping studies that it, along with phenyl(trimethylsilyl)ethyne (**4**), is a major product from photolysis of **1**.[7,9] Its presence has no effect on the spectra of the longer-lived species or on the rate constants for quenching of **2** (*vide infra*).

The products of photolysis of **1** have been suggested to arise from reaction of a charge transfer (CT) excited singlet state,[9,30,31] which has been assigned a $^1(\sigma,\pi^*)$ configuration by Horn and co-workers.[31] The singlet CT state, whose formation can be understood as resulting from charge transfer from the Si−Si σ-MO to the lower singly occupied MO of the benzenoid $^1(\pi,\pi^*)$ state,[31] is strongly fluorescent in rigid media at 77 K (ϕ_f = 0.26), where photochemical reaction is suppressed.[9] In fluid media, on the other hand, the fluorescence is quenched completely and product formation proceeds with quantum yields in excess of 0.5. The main driving force for *formation* of the CT state in **1** has been linked to the difference in ionization potentials between the disilanyl and aryl substituents,[31] while the main factor affecting its decay via radiative vs reactive pathways is the relative conformation of the two substituents. The triplet state of **1** has been detected previously only at low temperatures in rigid media, by phosphorescence emission (ϕ_p = 0.24)[9,31] and EPR[31] spectroscopy. Both the phosphorescence and EPR spectra, as well as the triplet-triplet absorption spectrum reported here in fluid media, are typical of substituted benzene derivatives having lowest $^3(\pi,\pi^*)$ states.[31,48,49] The fact that the triplet state of **1** is detectable in both fluid and rigid media suggests that the rate constant for its formation is not as strongly dependent on the conformational mobility of the molecule as are those for fluorescence or reaction from the singlet CT state. Triplet formation has also been proposed to occur from the CT singlet state,[9] but a $^1(\pi,\pi^*)$ state origin cannot be ruled out.

The UV absorption spectrum of silaallene **2** ($\lambda_{max} \leq$ 268 nm; shoulder at ~305 nm) can be qualitatively understood as the superposition of a benzenoid ^1L_b absorption (268 nm) with the π,π* absorption of the silenic double bond (305 nm). The latter is significantly blue-shifted relative to the position of the longest wavelength absorption band in the spectrum of **8** (λ_{max} = 275, 325 nm[33]). This trend can most likely be attributed to hyperconjugative interactions between the Si=C bond and the C−$SiMe_3$ bond,[44−46] which would clearly be expected to be more pronounced in the bis(trimethylsilyl)substituted derivative. These interactions would also be expected to affect the positive π-charge density at the silenic silicon atom, resulting in a difference in the reactivities of the two compounds toward nucleophiles.

Our assignment of the 305 nm transient absorption to silaallene **2** rests upon the response of its lifetime to the addition of classical silene-trapping reagents such as aliphatic alcohols, acetone, acetic acid, and oxygen. As would be expected for a silene, the lifetime of the transient is shortened upon addition of any of these reagents to hexane/octadiene solutions of **1**. On the other hand, addition of silene traps has no effect on the initial yield of the species or on the yield or stability of the residual absorption over a 5 ms time scale, indicating that the transient is produced competitively with the long-lived product (silacyclopropene **3**) from a precursor which is not quenched efficiently by submolar concentrations of dienes or silene traps—most likely the lowest excited CT singlet state of the disilane (**1**). For acetone, a plot of the transient decay rate constant (k_{decay}) versus quencher (Q) concentration (eq 2) was linear, affording a value of $k_q = (5.8 \pm 0.6) \times 10^7$ M^{-1} s^{-1}. The rate constant for quenching by O_2 was estimated to be $k_q = (1.5 \pm 0.7) \times 10^7$ M^{-1} s^{-1} from the lifetimes of the transient in air- ($\tau \sim 10$-μs) and nitrogen-saturated ($\tau \sim 25$-μs) solution.

Plots of k_{decay} *vs* bulk quencher concentration for methanol, *tert*-butyl alcohol, and acetic acid were curved. The plots for the alcohols exhibit distinct positive curvature; for example, Figure 3a shows a plot of k_{decay} *vs* [ROH] for quenching of **2** by MeOH in hexane/octadiene solution at 23 °C. In contrast, the plot for AcOH exhibits negative curvature (Figure 3b), similar to that observed for quenching of silaallene **8** by this reagent and ascribed to the effects of the carboxylic acid

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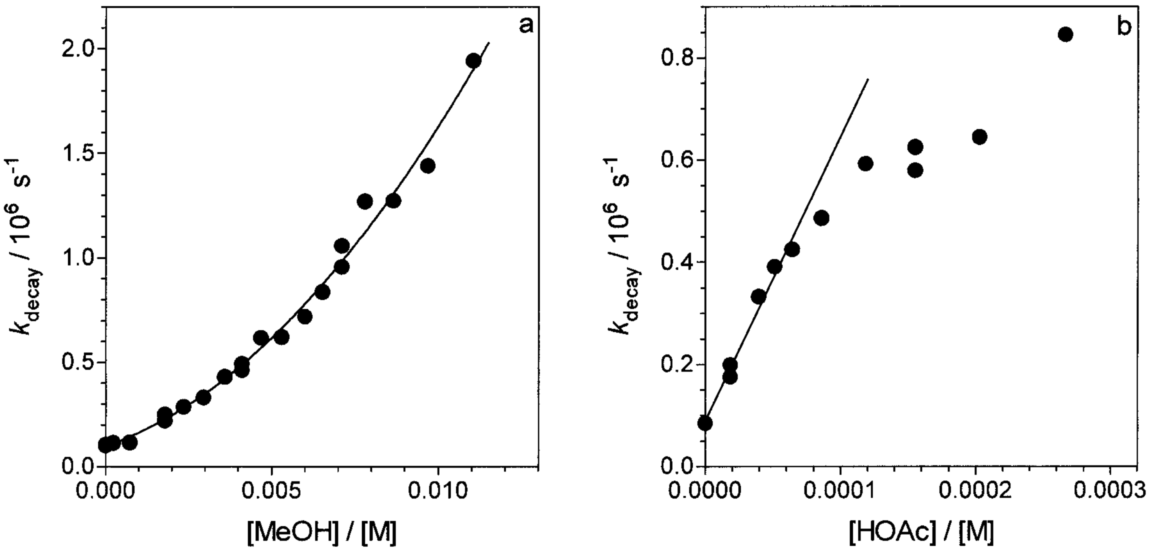


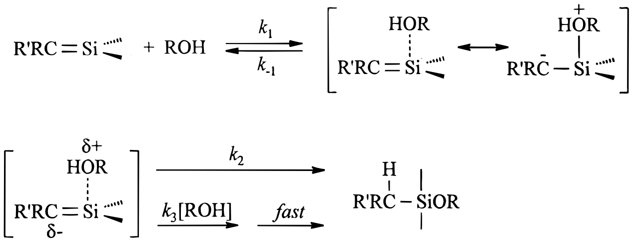
Figure 3. Plots of k_{decay} *vs* bulk ROH concentration, for quenching of silaallene **2** by (a) MeOH and (b) HOAc in an air-saturated hexane solution containing 0.002 M 1,3-octadiene at 23 °C.

monomer–dimer equilibrium in the hydrocarbon solvent.[33] As was found for **8**,[33] a plot of k_{decay} *vs* monomeric AcOH concentration (calculated from the bulk AcOH concentrations and the reported equilibrium constants for dimerization of AcOH in hexane at ~25 °C, $K_2 = 3200 \pm 500$ M^{-1} [50]) is acceptably linear. Linear least-squares analysis ($r^2 = 0.971$) affords a rate constant $k_q = (5.1 \pm 0.5) \times 10^9$ M^{-1} s^{-1} for the reaction of AcOH monomers with silaallene **2**. This is in satisfactory agreement with the value estimated from linear least-squares analysis of the first six points in Figure 3b ($k_q \sim (5.6 \pm 0.6) \times 10^9$ M^{-1} s^{-1}), which correspond to the concentration range where AcOH exists largely in monomeric form.

Methanol and *tert*-butyl alcohol are much less extensively oligomerized in hexane at the concentrations employed here (<0.012 M for MeOH; <0.06 M for *t*-BuOH),[51,52] so similar corrections for the alcohols are unnecessary. The positive curvature exhibited by the quenching plots for these two reagents is indicative of a reaction mechanism characterized by a dependence on alcohol concentration of higher order than 1. Similar kinetic behavior has been reported previously for the quenching of aryl- and vinyldisilane-derived silenes by alcohols in solution, where k_{decay}–concentration data were found to fit acceptably to the quadratic expression in [ROH] shown in eq 3.[35,37,46,53] Nonlinear least-squares treatment of the data for quenching of **2** by MeOH and *t*-BuOH leads in both cases to excellent fits to eq 3; that for quenching by MeOH is shown in Figure 3a and affords a value of $k_{MeOH} = (5.3 \pm 2.0) \times 10^7$ M^{-1} s^{-1} for the component of the reaction which involves a first order dependence on alcohol concentration.

$$k_{decay} = k_o + k_{ROH}[ROH] + k_{2ROH}[ROH]^2 \qquad (3)$$

Scheme 2



For other reactive silenes that have been studied, this behavior has been ascribed to a mechanism involving reversible nucleophilic attack at silicon to form an alcohol–silene complex, which collapses to product by rate-limiting proton transfer by competing uni- and bimolecular mechanisms (Scheme 2). The intracomplex proton transfer results in a first-order dependence of k_{decay} on [ROH], while the extracomplex pathway involves a second molecule of alcohol and accounts for the dependence on [ROH]^2.[35] In general, this second pathway also results in a change in the stereo- or regiochemistry of addition of alcohols to silenes at higher alcohol concentrations.[37,38,53,54] There is a great deal of evidence consistent with this mechanism, derived from both product[37,38,41,53] and kinetic studies[33,35,37,38,40,41,46] of a variety of transient silenes in polar and nonpolar solvents. Kinetic studies of the addition of alcohols and acetic acid to substituted 1,1-diphenylsilene derivatives have led to the conclusion that the addition of acetic acid also proceeds by a mechanism initiated by nucleophilic attack at the silenic silicon atom, but in this case proton transfer to carbon is the faster step.[41] The present data are not sufficiently detailed to permit a reliable mechanistic assignment for the addition of alcohols and acetic acid to silaallene **2**. Our results are consistent with the mechanisms outlined above for simpler silenes, but there are other possibilities which cannot be ruled out.

In contrast to the situation with **2**, significant quenching of silaallene **8** by MeOH and *t*-BuOH is observed only at much higher alcohol concentrations (0.1–1.0 M), and the silaallene decay rate constant follows an approximately linear dependence on bulk alcohol concen-

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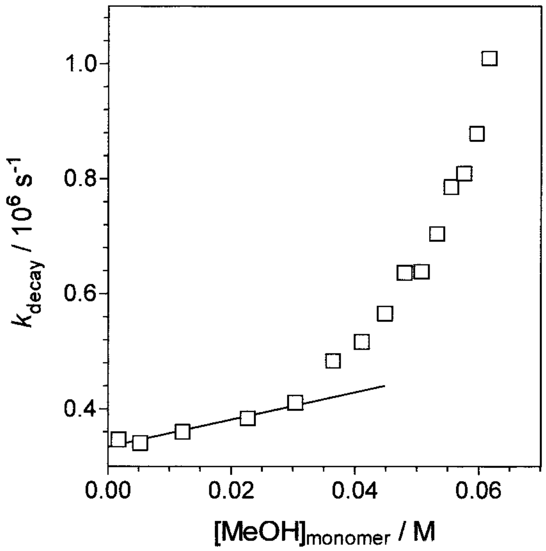

Figure 4. Plot of k_{decay} *vs* monomeric MeOH concentration, for quenching of silaallene **8** in deoxygenated hexane solution at 23 °C (data from ref 33).

tration over the 0–0.6 M range.[33] Methanol is extensively oligomerized in hexane at concentrations above ~0.03 M,[52,55] which makes the mechanistic significance of the linear quenching plot reported for **8** particularly difficult to unravel. We previously interpreted it as being at least partially due to a mixed first- and second-order dependence on monomeric alcohol concentration ($[MeOH]_{monomer}$), in terms of the general mechanism of Scheme 2, but noted that the measured k_{decay} values did not fit acceptably to eq 3 using $[MeOH]_{monomer}$ values calculated from the bulk concentrations and published equilibrium constants for methanol oligomerization in hexane.[52] A plot of the data of ref 33 against $[MeOH]_{monomer}$ is shown in Figure 4; repeated experiments indicate that the data are reproducible and suggest that the poor quality of the fit to eq 3 is significant, even when possible systematic errors in the calculation of $[MeOH]_{monomer}$ values (due to the uncertainties in the published oligomerization equilibrium constants) are taken into account. We are led to conclude that the mechanism for alcohol addition to **8** (and possibly to **2** as well) may be more complex—or possibly even different—than that for simple silenes. The fact that k_{decay} does not level off significantly at very high bulk methanol concentrations probably indicates that *all* oligomeric forms of the alcohol are kinetically significant in the reaction with silaallene **8**. This could be consistent with a mechanism involving alcohol-catalyzed proton transfer in a reversibly-formed complex, but other mechanisms are also possible. One possibility is that reaction initiates with protonation at C2; this is consistent with the facts that methanol oligomers are more acidic than the monomer[51] and that the difference in the reactivity of **8** toward acetic acid and methanol is substantially greater than has been observed for any of the simple silenes whose reaction kinetics have been studied in solution. However, it is difficult to rationalize the fact that both **2** and **8** exhibit similar reactivities toward methanol and the weaker nucleophile acetone on the basis of such a mechanism.

While we do not have the data to justify further comment on these mechanistic possibilities, it is at least possible to compare the second-order rate constants for reaction of the two silaallenes with monomeric methanol. For **8**, an upper limit of $k_{MeOH} = (2.4 \pm 0.6) \times 10^6$ M^{-1} s^{-1} can be estimated from the first five points in the plot of Figure 4, where the alcohol is predominantly monomeric. Thus, the bis(trimethylsilyl)silaallene **8** is a factor of at least 20 less reactive than **2** toward addition of monomeric methanol. A considerably larger difference in reactivity is observed for addition of the bulkier alcohol, *t*-BuOH.

The absolute rate constants for reaction of **2** with all of the reagents studied in this work are listed in Table 1, along with those reported previously (or re-evaluated here) for silaallene **8**.[33] The data show that both silaallenes exhibit the "normal" ordering of silene reactivity toward alcohols, carboxylic acids, and ketones. Furthermore, with the exception of oxygen, silaallene **2** exhibits 20–1000 times greater reactivity toward these reagents than the related compound **8**.

Mechanistic uncertainties aside, the substantially greater reactivity of **2** than **8** toward alcohols, acetone, and acetic acid provides a clear indication that bistrimethylsilyl substitution at C3 of the silaallene moiety leads to significant kinetic stabilization of the Si=C bond toward bimolecular reaction with nucleophilic silene trapping agents. Undoubtedly, this is at least partially due to steric effects; molecular modeling studies indicate that trimethylsilyl substitution at C3 provides considerable steric protection at C2, the site of protonation subsequent to (or possibly preceding) nucleophilic attack at silicon. Presumably, there will also be a somewhat smaller effect on the ease with which the nucleophile can complex at the silenic silicon. Replacing one of the trimethylsilyl substituents with phenyl provides less sterically hindered sites for both nucleophilic attack at silicon and protonation at carbon. Hyperconjugation effects may also contribute to the differences in reactivity of the two compounds, to the extent that π-type overlap between the C3–Si σ-bonds and the Si=C π-bond is more effective for two C–Si bonds than for one. These interactions have significant effects on the frontier molecular orbitals of **2** and **8**, as is shown by the differences in the UV absorption spectra of the two compounds. They would also be expected to result in a reduction in the electrophilicity of the silenic silicon atom due to resonance electron donation, in a manner analogous to the β-silyl effect on carbenium ion reactivity.

Unfortunately, the complexities of the product mixtures obtained from both steady state and laser flash photolysis of **1** and **9**, coupled with the fact that the silaallenes **2** and **8** are formed only as minor products in hexane solution, make it difficult to study the reactivity of these compounds in as much mechanistic detail as has been possible for other reactive silene derivatives. Further studies of this type will require the use of considerably more efficient photochemical precursors of transient silaallenes than those which have been reported to date.

Summary and Conclusions

Direct photolysis of pentamethyl(phenylethynyl)disilane (**1**) in hexane solution results in the competitive

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Table 1. Bimolecular Rate Constants for Reaction of Silaallenes 2 and 8 with Oxygen, Methanol, *tert*-Butyl Alcohol, Acetic Acid, and Acetone in Hexane Solution at 23 °C[a]

	$k_q/10^7$ M^{-1} s^{-1}	
reagent	Ph(Me$_3$Si)C=C=SiMe$_2$ (**2**)	(Me$_3$Si)$_2$C=C=SiMe$_2$ (**8**)[b]
MeOH	$k_{MeOH} = (5.3 \pm 2.0) \times 10^7$ M^{-1} s^{-1} $k_{2MeOH} = (9.9 \pm 1.8) \times 10^9$ M^{-2} s^{-1}	$k_{MeOH} = (2.4 \pm 0.6) \times 10^6$ M^{-1} s^{-1}[d]
t-BuOH	$k_{BuOH} = (1.6 \pm 0.5) \times 10^7$ M^{-1} s^{-1} $k_{2BuOH} = (2.2 \pm 0.9) \times 10^8$ M^{-2} s^{-1}	$k_{BuOH} \leq (2 \pm 1) \times 10^4$ M^{-1} s^{-1}
AcOH[c]	511 ± 50	9.8 ± 0.6
acetone	5.8 ± 0.6	0.18 ± 0.01
O$_2$	1.5 ± 0.7	11 ± 2

[a] Errors are listed as twice the standard deviation from least squares analysis of k_{decay} − concentration data according to eq 3 or curve-fitting according to eq 4. [b] Data from ref 33, unless otherwise noted. [c] Quenching by monomeric AcOH (see text). [d] Estimated by linear least-squares analysis of the first five points in a plot of k_{decay} vs [MeOH]$_{monomer}$ (Figure 4).

formation of the disilane triplet state, 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)(1-sila)cycloproprene (**3**), 1,1-dimethyl-3-phenyl-3-(trimethylsilyl)-1-silaallene (**2**), and dimethylsilylene, which have all been detected and characterized by laser flash photolysis techniques. Silaallene **2** exhibits a pseudo-first-order lifetime of about 25 μs in nitrogen-saturated hexane solution at ambient temperature and reacts with alcohols, acetic acid, and acetone with rate constants in the 10^7−10^9 M^{-1} s^{-1} range. The rate law for the reaction with alcohols contains both first- and second-order terms in alcohol concentration, indicating a complex mechanism for reaction which may be analogous to that for simpler silenes that have been studied in greater detail. Substitution of the C3-phenyl group in **2** with a second trimethylsilyl group (**8**) results in a 20- to 1000-fold decrease in reactivity toward the same reagents. This is suggested to be due to a combination of steric effects and hyperconjugative stabilization of the Si=C bond by the trimethylsilyl substituents at C3 of the silaallene moiety. The electronic effects of bis-trimethylsilyl substitution at C3 on the silaallenic Si=C bond are clearly evident in the UV absorption spectra of the two compounds.

Experimental Section

Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer interfaced to a Pentium microcomputer. Gas chromatographic (GC) analyses were carried out using a Hewlett-Packard 5890II+ gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a DB1701 megabore capillary column (15 m × 0.53 mm; Chromatographic Specialties, Inc). Radial chromatography was carried out using a Chromatotron (Harrison Research, Inc.) and 2 or 4 mm silica gel 60 thick layer plates.

Hexane (BDH Omnisolv) was used as received from the supplier. Quenchers were of the highest purity available and were used as received from Aldrich Chemical Co. Pentamethyl(phenylethynyl)disilane (**3**) was prepared by the method of Ishikawa and co-workers[9] and was obtained in >99% purity (by GC) by radial or column chromatography. Its spectroscopic properties and mass spectrum were similar to those reported.[9]

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 16 ns; 70−120 mJ) from a Lumonics 510 excimer laser filled with F$_2$/Kr/He mixtures and a microcomputer-controlled detection system.[56] 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 (1.3×10^{-4} M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. When required, nitrogen was bubbled continuously through the reservoir throughout the experiments. 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 or more points) which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and the Max-Planck-Gesellschaft zur Förderung der Wissenschaften for an Otto Hahn Fellowship to C.K.

OM9701837

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