

Reactive Intermediates from the Photolysis of Methylpentaphenyl- and Pentamethylphenyldisilane

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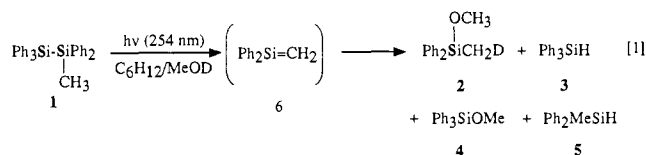
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Abstract: The photochemistry of methylpentaphenyldisilane (**1**) and pentamethylphenyldisilane (**7**) has been investigated using nanosecond laser flash photolysis techniques. Flash photolysis of **1** with 248-nm light in acetonitrile or isooctane solution gives rise to a complex mixture of transient species. A strongly-absorbing transient with $\lambda_{\text{max}} = 490$ nm and $\tau \leq 1.7$ μs (in acetonitrile) has been assigned a 1,3,5-(1-sila)triene structure on the basis of comparisons to the transient spectroscopic behavior of **7**, which is known to rearrange to a silatriene intermediate in high yield upon photolysis, and on the basis of comparisons of the reactivity of these species toward water, a series of alcohols, acetone, acetic acid, ethyl acetate, oxygen, alkenes, and silanes. The extinction coefficient for the long-wavelength absorption band of the silatriene from **1** has been estimated. Silyl-centered radicals have also been identified in the transient mixture on the basis of their UV spectra and quenching with 2-bromopropane. Quenching of the silatrienes from **1** and **7** is linear in concentration for oxygen, acetone, cyclohexene, and 2,3-dimethylbutadiene. While quenching of the two silatrienes by 2,2,2-trifluoroethanol and acetic acid are also linear in concentration, water, methanol, ethanol, and *tert*-butyl alcohol give rise to curved quenching plots. These results are consistent with an addition mechanism which involves initial, reversible formation of a zwitterionic silene-alcohol complex, followed by competing intra- and intermolecular proton transfer. Rate constants for the bi- and termolecular quenching processes have been determined by quadratic least-squares analysis of the quenching plots. A deuterium isotope effect of $k_{\text{H}}/k_{\text{D}} \approx 1.7$ has been measured for the intracomplex proton-transfer process for the reaction of the two silatrienes with water. Similar, nonlinear behavior is observed for the quenching of the silatrienes by methoxytrimethylsilane.

Introduction

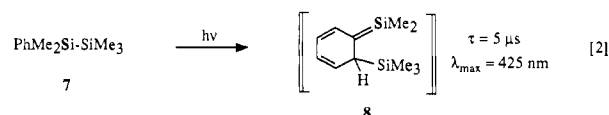
Silenes, compounds that contain the Si=C moiety, have frequently been postulated as reactive intermediates in the photolysis of organosilicon compounds.² These assignments have usually been made on the basis of chemical trapping experiments. Several stable silenes have also been reported, and the factors that account for their stability are well understood.² Conversely, comparatively little is known about the properties of *reactive* (i.e., short-lived) silenes which are far more common in organosilicon chemistry. Some quantitative information has been acquired through the use of matrix isolation techniques at low temperatures.^{2c} However, very few studies have employed transient spectroscopic methods to characterize reactive silenes in fluid solution at room temperature and determine rate constants for their unimolecular decay or self-reaction and reactions with nucleophiles and other reagents.³⁻⁵ Chemical trapping studies can afford only qualitative information of this type.⁶

The steady-state photolysis of methylpentaphenyldisilane (**1**) in methanolic solution has been reported to yield methylmethoxydiphenylsilane (**2**) and triphenylsilane (**3**) in over 60% chemical yield, along with other minor products (**4**, **5**).⁷ From the results of deuterium labeling experiments (see eq 1), it was proposed that **2** is formed by nucleophilic trapping of 1,1-diphenylsilene (**6**), which is formed from **1** either by disproportionation of tri-



phenylsilyl and methylphenylsilyl radicals or via concerted dehydrodesilylation.

In contrast, photolysis of pentamethylphenyldisilane (**7**) yields products consistent with the initial formation of the silatriene intermediate **8**^{8,9} (see eq 2). Products consistent with competitive



formation of simpler silenes, analogous to that from **1**, are evidently also formed but in yields of less than 5%.^{9a} While products **8** (from **7**) and **6** and **3** (from **1**) are formally those of recombination and disproportionation, respectively, of the silyl-centered radicals formed by excited-state homolysis of the disilane Si-Si bond¹⁰ and EPR experiments have demonstrated that silyl free radicals are involved in arylsilane photolysis,¹¹ picosecond experiments suggest that **8** is formed directly from the lowest excited singlet state of **7**.³

The silatriene species **8** has been characterized by nanosecond laser flash photolysis techniques,^{3,4} and rate constants for its reaction with oxygen, 2,3-dimethyl-1,3-butadiene, and ethanol in

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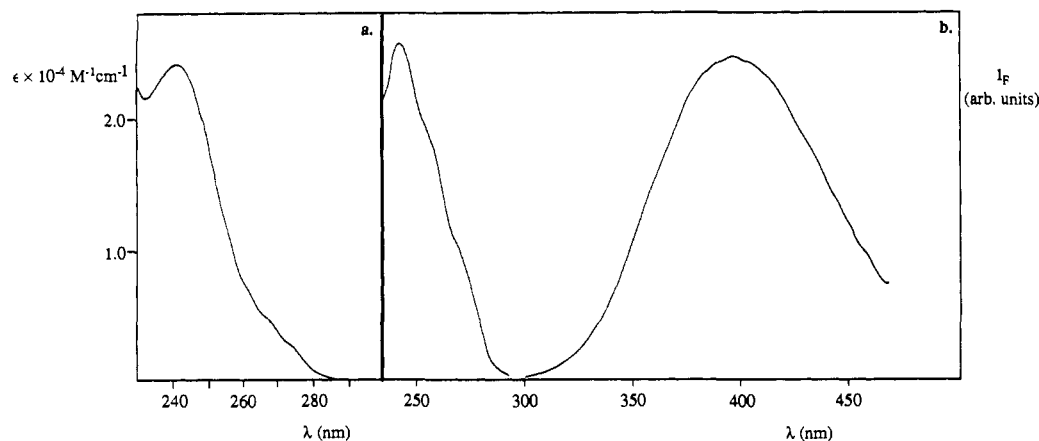


Figure 1. (a) Ultraviolet absorption spectrum and (b) fluorescence emission and excitation spectra of **1** in isooctane solution at 22 °C.

cyclohexane solution have been reported.⁴ On the basis of steady-state¹² and time-resolved fluorescence emission results,³ **8** has been proposed to arise from direct [1,3]-silyl migration in a singlet ($p\pi^* \rightarrow d\pi^*$) charge-transfer state of **7**.³ The concerted rearrangement pathway was proposed to account for the fact that the formation of **8** occurs at the same rate as the decay of the charge-transfer fluorescence from **1**. Sakurai and co-workers have recently questioned the ($p\pi^* \rightarrow d\pi^*$) assignment for the emissive charge-transfer state in aryldisilanes. From a study of the fluorescence of a series of aryldisilanes and arylsilylgermanes, they concluded that the emissive charge-transfer state in these compounds more likely has a (σ, π^*)¹ configuration.^{13a,b}

In this paper, we report the results of a study of the photochemistry of **1** using nanosecond laser flash photolysis techniques. Our original goals were to examine the suitability of alkylpolyaryldisilanes as precursors of arylsilenes for study by flash photolysis methods and to provide a better understanding of the mechanism(s) for formation of silenes and silatrienes from photolysis of these compounds and of the differences in the photo-behaviors of **1** and **7**. Steady-state photolysis and static emission spectroscopy experiments have also been carried out to supplement time-resolved experiments. The prominent transient species observed in flash photolysis experiments with **1** has been characterized and assigned, and rate constants for its reaction with a number of silene and silylene trapping agents have been measured. For purposes of comparison, we have carried out similar experiments with disilane **7**.

Results

Compound **1** exhibits weak fluorescence in solution at room temperature, in the form of a diffuse band with $\lambda_{\text{max}} = 395$ nm. Figure 1 shows absorption and emission spectra recorded with a solution of **1** in isooctane solution at 22 °C. Similar results were obtained from solutions of **1** in acetonitrile solution; this contrasts the behavior of **7**, whose emission maximum is blue-shifted by ca. 40 nm in hydrocarbon solvents relative to that in acetonitrile.^{12a} Emission spectra recorded with optically matched solutions of **1** and **7** in acetonitrile revealed that the emission from **1** is about half as intense as that from **7**. Fluorescence emission spectra recorded for solutions of triphenylsilane (**3**) in the same solvent verified that the spectrum observed for solutions of **1** is not due to the formation of **3** from photolysis of **1** by the spectrometer excitation source. Solutions of **1**, photolyzed for extended periods

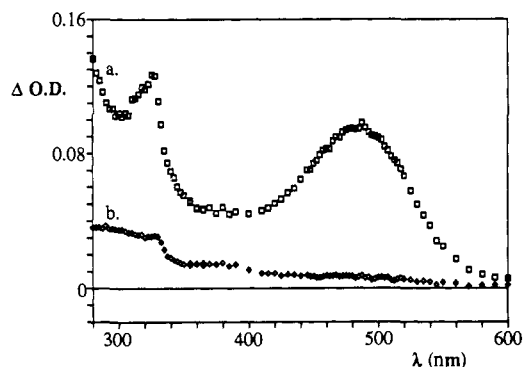


Figure 2. Transient absorption spectra from a 1.7×10^{-4} M solution of **1** in acetonitrile, recorded (a) 70–90 ns and (b) 2.9–3.1 μs after 248-nm laser excitation.

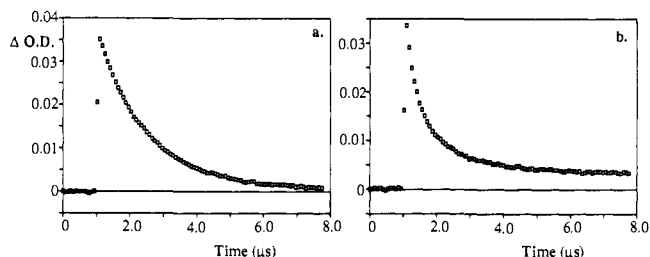


Figure 3. Transient decay traces recorded at (a) 490 nm and (b) 330 nm, from a 1.8×10^{-4} M solution of **1** in acetonitrile.

of time in the emission spectrometer, exhibited fluorescence spectra consisting of superimposed emission from both **1** and **3**. In a methylcyclohexane glass at 77 K, **1** shows benzenoid π, π^* phosphorescence, similar to the behavior typical of **7** and other phenyldisilanes.¹²

Nanosecond laser flash photolysis experiments employed a flow system to contain deoxygenated, ca. 2×10^{-4} M, solutions of **1** in dry acetonitrile or isooctane, the pulses (248 nm, ca. 12 ns, 80–120 mJ) from a Kr/F₂ excimer laser, and a microcomputer-controlled detection system.¹⁴ Transient absorption spectra, recorded in point-by-point fashion 70–90 ns and 2.8–3.2 μs after the laser pulse, are shown in Figure 2 for a 1.7×10^{-4} M solution of **1** in acetonitrile. Representative decay traces, recorded at 490 and 330 nm, are shown in Figure 3. Transient spectra recorded in isooctane solution did not differ significantly from those shown in Figure 2. In acetonitrile solution, the kinetic order and lifetime of the decay of the 490-nm transient depend on the rigor with which the solvent is dried. With acetonitrile that had been refluxed over calcium hydride for >1 week, the transient decayed with mixed first- and second-order kinetics and had a lifetime of 1.7

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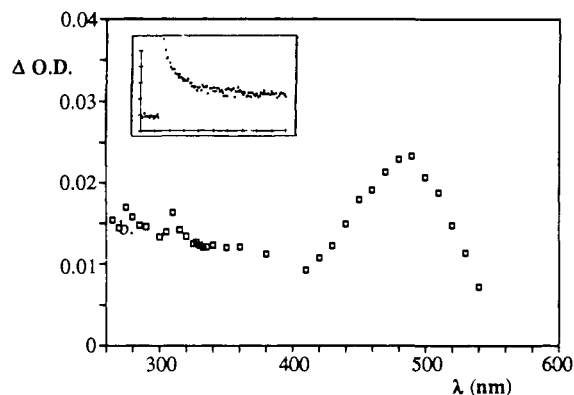


Figure 4. Transient absorption spectrum from a 1.7×10^{-4} M solution of **1** in acetonitrile containing 0.1 M 2-bromopropane, recorded 120–160 ns after 248-nm laser excitation. The insert shows a decay trace recorded at a monitoring wavelength of 330 nm (time scale, 500 ns/division).

$\pm 0.2 \mu\text{s}$. Less careful drying of the solvent gives rise to transients with identical absorption spectra but which decay with clean first-order kinetics and lifetimes in the 300–900-ns range. The transient was significantly longer-lived ($\tau > 7 \mu\text{s}$) in isooctane solution and decayed with mixed first- and second-order kinetics. The product of the transient's extinction coefficient and the quantum yield for its formation, $\epsilon_{490}\phi$, was estimated to be ca. $4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in isooctane solution by benzophenone actinometry.

The short-wavelength absorption region (300–330 nm) of the transient absorption spectrum is much more complex in both solvents. The decay traces show mixed kinetics with significant residual absorption (Figure 3b). The latter is long-lived on the microsecond time scale but is not present in the static UV spectrum taken within minutes after photolysis of the solution to 40–50% conversion. The relatively sharp absorption band with $\lambda_{\text{max}} \approx 325$ nm is due to absorption by triphenylsilyl and/or methyl-diphenylsilyl free radicals; transient absorption spectra of these two radicals were recorded independently by laser flash photolysis (337-nm excitation) of solutions of triphenylsilane and methyl-diphenylsilane in 1:4 di-*tert*-butyl peroxide (BOOB)/isooctane. The spectrum and decay characteristics of the triphenylsilyl radical are similar to those reported previously by Ingold and co-workers.^{15a} Addition of 0.1 M 2-bromopropane to acetonitrile solutions of **1** shortened the lifetime(s) of the radicals dramatically, while having no effect on the lifetime or yield of transient absorptions elsewhere in the spectrum. Figure 4 shows the transient absorption spectrum recorded 120–160 ns after the laser pulse under these conditions. Rate constants for quenching of triphenylsilyl and methyl-diphenylsilyl radicals by 2-bromopropane were not determined but can be assumed to be in the 10^7 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ range.¹⁶

The lifetime of the 490-nm transient was shortened only slightly by the addition of 0.05 M 2,3-dimethyl-1,3-butadiene, which suggests that the 490-nm absorption is not that of a triplet-state species (of triplet energy greater than ca. 50 kcal/mol). Similarly, the lifetime was unaffected by the addition of up to 0.3 M triethylsilane, suggesting that the transient is not a silylene. Silylenes are known to be quenched by trialkylsilanes with rates of 10^8 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{17–19}

Similar experiments were carried out with disilane **7**, which has been reported to yield the silatriene **8** in high yield upon

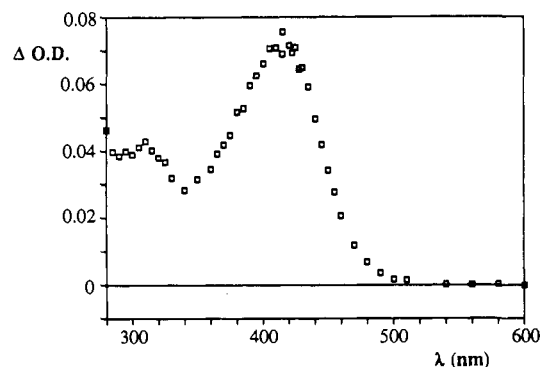


Figure 5. Transient absorption spectrum from a 2.0×10^{-3} M solution of **7** in isooctane, recorded 75–150 ns after 248-nm laser excitation.

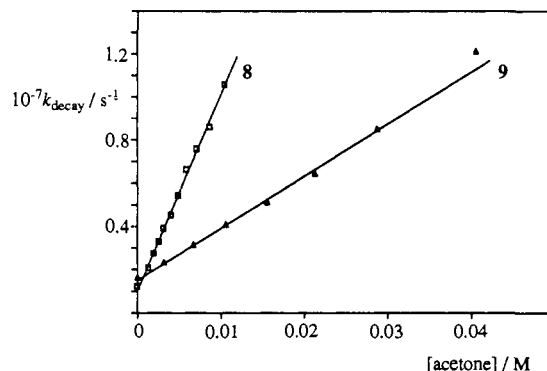
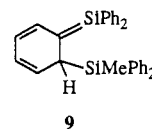
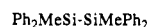


Figure 6. Plots of the pseudo-first-order decay rates of transients **8** (□) and **9** (Δ) vs acetone concentration, from nanosecond laser flash photolysis of deoxygenated 1.7 – 2×10^{-4} M solutions of **7** and **1**, respectively, in acetonitrile at 23 °C.

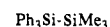
photolysis in cyclohexane solution at room temperature.^{3,4,8,9} Laser flash photolysis of 2×10^{-3} M solutions of **7** in isooctane or acetonitrile yields intense transient absorptions with maxima at <300 and 420 nm. An additional weak absorption with $\lambda_{\text{max}} \approx 310$ nm is evident in the spectrum recorded in isooctane solution (Figure 5); this matches the absorption spectrum previously reported for the dimethylphenylsilyl radical.^{15b} The transient absorption spectrum recorded from **7** in the region >350 nm agrees well with that reported.³ On the basis of the similarities in the absorption spectra and quenching behavior (vide infra) of the long-wavelength transient from photolysis of **1** and that from **7**, we assign the former to the silatriene species **9**.



The high degree of symmetry of the 490-nm absorption band in Figure 2a indicates that the alternate silatriene intermediate, which would be obtained from **1** by formal migration of triphenylsilyl into the methyl-diphenylsilyl group and which contains the methylphenylsilatriene chromophore, is not formed or is formed in much lower yield than **9**. The methylphenylsilatriene chromophore, such as that obtained from photolysis of 1,2-dimethyl-1,1,2,2-tetra-*tert*-phenyldisilane (**10**), gives rise to an absorption



10



11

spectrum with $\lambda_{\text{max}} \approx 465$ nm.²⁰ Furthermore, flash photolysis of acetonitrile solutions of 1,1,1-trimethyl-2,2,2-triphenyldisilane (**11**) gives rise to a transient (also containing the diphenylsilatrienyl chromophore) whose absorption spectrum is very similar to that of **9** ($\lambda_{\text{max}} = 490$ nm).²⁰

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Table I. Rate Constants for Bimolecular Quenching of Silatrienes **8** and **9** by Oxygen, Acetone, Ethyl Acetate, and Alkenes in Acetonitrile Solution at 23 ± 2 °C^a

quencher	$k_Q \times 10^{-8}$ M s	
	8	9
O ₂ ^b	8.5 ± 0.8	3.8 ± 0.3
acetone	9.0 ± 0.3	2.54 ± 0.15
ethyl acetate	0.033 ± 0.003	<i>d</i>
cyclohexene	0.012 ± 0.002	0.009 ± 0.001
2,3-DMB ^c	1.28 ± 0.03	0.23 ± 0.01

^a Errors reported as $\pm 2\sigma$ (95% confidence limits). ^b Calculated assuming a value of 0.01 M for the concentration of oxygen in O₂-saturated acetonitrile. ^c 2,3-DMB, 2,3-dimethyl-1,3-butadiene; isooctane solution. ^d Not determined.

Table II. Bi- and Termolecular Rate Constants for Quenching of Silatrienes **8** and **9** by Water, Alcohols, Acetic Acid, and Methoxytrimethylsilane in Acetonitrile Solution at 23 ± 2 °C^a

quencher	8		9	
	$k_Q \times 10^{-8}$ M s	$k_Q^{(2)} \times 10^{-8}$ M ² s ²	$k_Q \times 10^{-8}$ M s	$k_Q^{(2)} \times 10^{-8}$ M ² s ²
H ₂ O	4.4 ± 1.3	46 ± 60	2.2 ± 0.3	13 ± 5
D ₂ O	2.6 ± 0.8	71 ± 36	1.3 ± 0.2	21 ± 5
MeOH	2.5 ± 0.8	67 ± 36	1.7 ± 0.3	7 ± 7
EtOH	1.5 ± 0.3	32 ± 6	0.67 ± 0.09	9.5 ± 1.6
<i>t</i> -BuOH	0.37 ± 0.08	1 ± 1	0.25 ± 0.04	2.1 ± 0.4
CF ₃ CH ₂ -OH	0.236 ± 0.004	<i>b</i>	0.039 ± 0.002	<i>b</i>
CH ₃ COOH	2.9 ± 0.1	<i>b</i>	0.97 ± 0.03	<i>b</i>
Me ₃ SiOMe	0.14 ± 0.05	1.0 ± 0.3	0.074 ± 0.004	0.094 ± 0.011

^a Rate constants calculated from least-squares fitting of data to eq 5. Errors are reported as $\pm 2\sigma$ (95% confidence limits). ^b Quenching plot linear in concentration.

Addition of oxygen, water, alcohols, acetic acid, ethyl acetate, alkenes, acetone, or methoxytrimethylsilane results in a shortening of the lifetime of the long-wavelength transient absorptions from photolysis of **1** and **7**. Plots of the pseudo-first-order rate constants for decay of the long-wavelength transients from **1** and **7** vs concentration of added quencher are linear in the cases of oxygen, acetone, ethyl acetate, 2,3-dimethylbutadiene, cyclohexene, and acetic acid. Figure 6 shows examples of such plots for quenching of the transients **8** and **9** by acetone in acetonitrile solution. Second-order quenching rate constants, obtained from the slopes of these plots according to eq 3, are collected in Tables I and II.

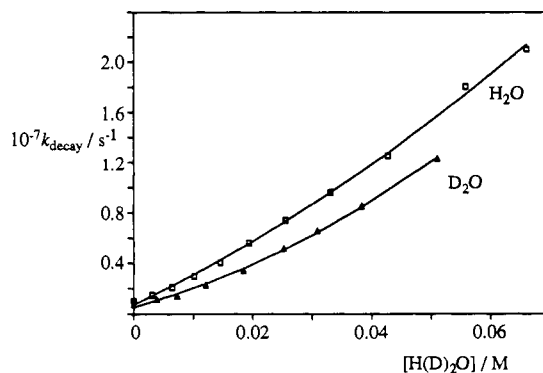
$$k_{\text{decay}} = k_0 + k_Q[\text{Q}] \quad (3)$$

The rate constants for quenching of these transients by oxygen (see Table I) have been calculated using a value of 0.0085 M for the concentration of oxygen in oxygen-saturated acetonitrile.^{21a} In isooctane solution, the transients from **1** and **7** are quenched by oxygen with rates of $(1.52 \pm 0.09) \times 10^8$ and $(6.9 \pm 0.4) \times 10^8$ M⁻¹ s⁻¹, respectively.

The analogous plots for quenching of **8** and **9** in acetonitrile by water, alcohols (except 2,2,2-trifluoroethanol), and methoxytrimethylsilane show distinct curvature. Examples of such plots are shown in Figure 7 for the quenching of **9** by water and D₂O. These data were analyzed according to the quadratic equation shown in eq 4, and the second- and third-order rate constants

$$k_{\text{decay}} = k_0 + k_Q[\text{Q}] + k_Q^{(2)}[\text{Q}]^2 \quad (4)$$

obtained from these analyses are listed in Table II. It should be stressed that the third-order rate constants reported in Table II have rather large associated errors, even though the quencher concentrations employed in these experiments were sufficient to cause the transient decay rate to span a factor of 10–30 and data from 10–12 different quencher concentrations were typically included in the least-squares analyses. The second-order rate constants are considerably more precise. In each case, the value of k_Q obtained from the polynomial least-squares fit to eq 4

**Figure 7.** Plots of the pseudo-first-order decay rates of transient **9** vs H₂O (□) or D₂O (Δ) concentration, from nanosecond laser flash photolysis of deoxygenated 1.7×10^{-4} M solutions of **1** in acetonitrile at 23 °C.

matched that obtained from a linear least-squares fit of the first four or five data points to eq 3 (within the error limits defined by the latter).

The behavior of the transient absorptions below 350 nm toward these reagents was not investigated in detail. Oxygen quenched the short-lived component of the transient absorption at 330 nm as well as the long-lived residual absorptions, while methanol had little effect on either.

Steady-state photolysis (254 nm) of a deoxygenated 0.005 M solution of **1** in cyclohexane containing 0.1 M methanol afforded **2–5** in yields similar to those previously reported by Sommer and co-workers (eq 2).⁷ Careful VPC and GC/MS analysis of the photolysate failed to reveal the presence of additional, higher molecular weight products.

Discussion

The luminescent behavior of **1** shows many of the same characteristics exhibited by **7**.¹² The room temperature fluorescence emission spectrum is broad and featureless and is shifted to considerably longer wavelengths from the lowest energy absorption band. On the basis of these features, it can likely be identified as $(\sigma, \pi^*)^1$ charge-transfer emission, similar to that observed for **7**.^{12,13} The absence of a solvent effect on the emission from **1** can be attributed to the larger number of phenyl groups in this compound compared to **7**, which render the charge-transfer state more symmetrical and reduce its effective dipole moment.²² Compound **1** exhibits π, π^* phosphorescence at 77 K in a hydrocarbon matrix, another general feature that is common to arylsilanes.¹²

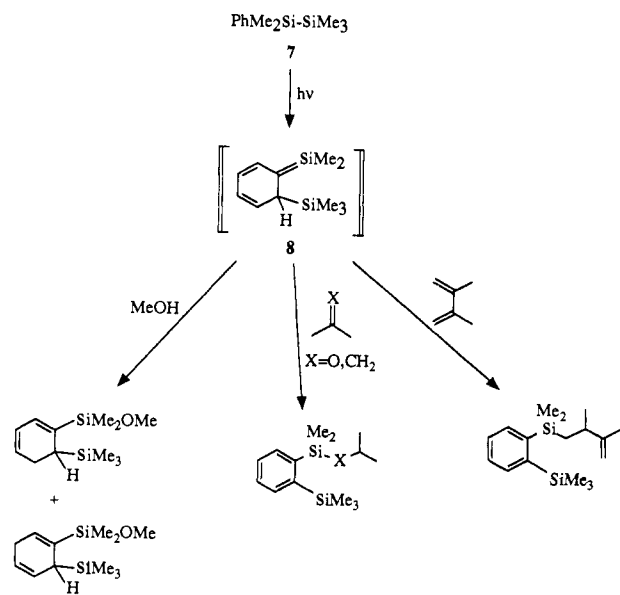
The assignment of the transient species absorbing at 490 nm from flash photolysis of **1** to the silatriene **9** is based on the similarities of its UV absorption spectrum and reactivity to those of the 420-nm transient (**8**) obtained from **7** under similar conditions. The structure of transient **8** has been assigned largely on the basis of product studies; it is consistent with the major products of photolysis of **7** in the presence of alcohols,⁹ alkenes,^{8a,b} dienes,^{8c} and carbonyl compounds.^{8f} The reactions of **8** are summarized in Scheme I.^{8,9} In the absence of trapping agents, photolysis of **7** leads to the formation of higher molecular weight products.⁸ While these have not been characterized, they are presumably the products of dimerization or oligomerization of **8**.⁸

The ca. 70-nm shift in the absorption spectrum of **9** compared to that of **8** is consistent with the increased conjugation in the diphenylsilatriene chromophore (in **9**) compared to the dimethylsilatriene chromophore (in **8**).²⁰ So too is the 2–5-fold reduction in its reactivity toward oxygen, hydroxylic reagents, methoxytrimethylsilane, acetone, and alkenes, considering that the accepted mechanisms for the reactions of these reagents with silenes involve attack at trivalent silicon (or during a fast equilibrium prior to) the rate-determining step.² While all of these

(21) (a) Smith, G. J. *J. Photochem.* **1983**, *22*, 51. (b) Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973.

(22) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971, and references cited therein.

Scheme I

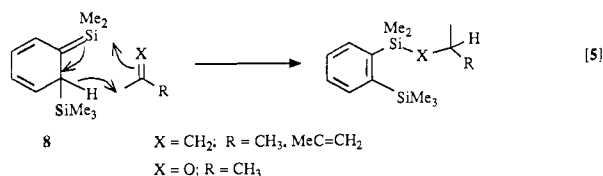


reagents are also known to react with silylenes with similar rates as those reported here for the 490-nm transient from **1**,^{4,17-19} the fact that the transient is unreactive toward triethylsilane effectively rules out the possibility that it should rather be assigned a silylene structure.

Because products attributable to the intermediacy of **9** cannot be detected in significant yield from steady-state photolysis of **1** under any conditions (vide infra), it can be assumed that the quantum yield for the formation of **9** is at least a factor of 10 less than those for formation of 1,1-diphenylsilene (**6**) and triphenylsilene (**3**). This leads to an estimated lower limit of ca. $4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the extinction coefficient at the absorption maximum for **9**.

Apart from oxygen, the reagents listed in Tables I and II can be divided into two groups: those in Table I react with silenes via formal pericyclic mechanisms involving their C=X bonds, while those in Table II undergo addition reactions with the Si=C bond.^{2,8} As should be expected, the former reactions proceed with clean second-order kinetics. The latter reactions, however, generally give rise to more complex kinetics indicative of two or more competing mechanistic pathways for reaction. It is noteworthy that the silatrienes **8** and **9** exhibit similar relative reactivities as do stable silenes toward the series of reagents collected in Tables I and II, in spite of the fact that in many cases, the course of reaction differs substantially.^{2b}

Silenes are known to undergo Diels-Alder reactions with conjugated dienes and (2 + 2)- or ene-addition to alkenes and carbonyl compounds bearing α -hydrogens.² In contrast, silatrienes such as **8** have been shown to undergo formal ene reactions in all of these cases, in the manner shown in eq 5.⁸ Presumably, the

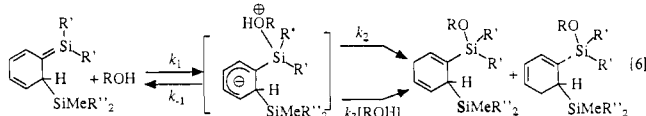


driving force for ene-addition in the reaction of silatrienes with dienes is the gain of aromaticity which accompanies product formation. The photochemistry of **7** in the presence of alkenes and carbonyl compounds has been extensively studied by steady-state methods,^{8,9} but there is little information available with respect to the relative reactivities of these reagents toward **8**.⁴ However, it has been reported that methyl acetate is a substantially less efficient trap for **8** than acetone, on the basis of the results of photolysis of **7** in the presence of a slight molar excess of trapping agent.^{8f} The rate constants reported in Table I for

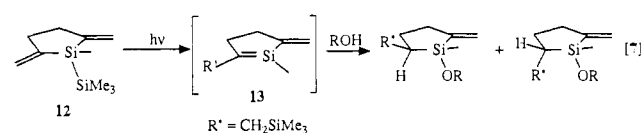
the quenching of **7** by acetone and ethyl acetate are in accord with those results.

Rate constants for the reaction of **8** with oxygen, 2,3-DMB, and ethanol in cyclohexane solution have been reported previously by Gaspar and co-workers.⁴ The previously reported rate constants for 2,3-DMB and ethanol agree fairly well with those reported here. Our value for quenching of **8** by oxygen in nonpolar media is a factor of about 4 lower than that reported previously.⁴ However, since no experimental details were given regarding the procedure employed for the reported determination, it is difficult to assess the reasons for the discrepancy. We note that the rate constants for oxygen quenching reported here were determined using decay rates recorded for at least five different oxygen concentrations.

The curvature in the quenching plots for water, alcohols, and methoxytrimethylsilane is consistent with an addition mechanism that involves rapid, reversible formation of a silatriene-alcohol complex,²³ followed by competing uni- and bimolecular proton transfer, the latter involving a second molecule of alcohol (eq 6).



A similar mechanism has recently been proposed by Sakurai and co-workers to explain the concentration-dependent stereochemistry of addition of a series of alcohols to the cyclic 1,3-(2-sila)diene **13**, proposed to be formed as an intermediate upon photolysis of disilane **12** (eq 7).²⁴



Application of the equilibrium assumption to the alcohol-silatriene complex in eq 7 leads to the quadratic expression shown in eq 9 for the pseudo-first-order rate constant for decay of the

$$k_{\text{decay}} = k_0 + (k_1 k_2 / k_{-1})[\text{ROH}] + (k_1 k_3 / k_{-1})[\text{ROH}]^2 \quad (8)$$

silatriene (k_{decay}), where k_0 is the rate of decay of the species in the absence of trapping agent and the other rate constants correspond to those defined in eq 6. Thus, if this mechanism is correct, then the second- and third-order rate constants shown in Table II can be equated with $k_1 k_2 / k_{-1}$ and $k_1 k_3 / k_{-1}$, respectively. The general trend in the data listed in Table II is that k_Q and $k_Q^{(2)}$ both decrease throughout the series $\text{H}_2\text{O} > \text{MeOH} > \text{EtOH} > t\text{-BuOH}$. According to the mechanism outlined above, these trends are the result of composite variations in the equilibrium constant for formation of the silatriene-alcohol complex and the rate constants for subsequent proton transfer as a function of alcohol.

The second-order component of the reactions of **8** and **9** with water are subject to a kinetic isotope effect. This provides the first clear indication that proton transfer is involved in the rate-determining step for the reaction of silenic double bonds with water.²⁵ From the values of k_Q listed in Table II for H_2O and D_2O we obtain $k_{\text{H}}/k_{\text{D}} = 1.7 \pm 1.0$ for **8** and $k_{\text{H}}/k_{\text{D}} = 1.7 \pm 0.5$ for **9**. Within the framework of the mechanism discussed above, these results verify that formation of the zwitterionic addition complex is fast relative to subsequent proton transfer, at least in the case of water. Given the similarities between the quenching behavior of water and those of the other alcohols, it seems reasonable to suggest that this is probably also true for the latter

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

(25) The addition of methanol to a stable silene has been reported to show no deuterium isotope effect.^{2b}

compounds. Unfortunately, the present data for H₂O and D₂O are not sufficiently detailed to accurately reveal the expected kinetic isotope effect on the intermolecular proton transfer which is described by $k_Q^{(2)}$.

The mechanism shown in eq 6 leads to the prediction that, in reactions with alcohols which are strongly acidic but relatively weakly nucleophilic, formation of the zwitterionic silatriene-alcohol complex described by k_1 may be rate determining, in which case quenching should be linear in alcohol concentration. Such appears to be the case with 2,2,2-trifluoroethanol. Acetic acid, another compound that satisfies this criterion, behaves similarly; it quenches silatriene **8** with $k_Q = (2.9 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and is strictly first order in acetic acid. While acetic acid is known to react with silenes by addition,² product studies have not yet been carried out for the reaction with **8**, so the significance of these results must be considered tentative. We note, however, that quenching of **8** by ethyl acetate occurs ≈ 100 times more slowly than this, indicating that proton transfer is likely to be involved in the reaction of **8** with the carboxylic acid.

Owing to the substantial errors associated with the $k_Q^{(2)}$ values measured in the present work, a comparison of the ratios $k_Q/k_Q^{(2)}$ ($=k_2/k_3$) for quenching of **8** and **9** by alcohols to those reported previously for **12**²⁴ is unwarranted. Nevertheless, it is interesting to note that for **8** and **9** they appear to be all considerably less than unity and vary only slightly throughout the series of alcohols. In contrast, the corresponding values for **12** reportedly range from 4.6 for methanol to infinity for *tert*-butyl alcohol.²⁴ The indication, albeit tentative, is that intramolecular proton transfer within the zwitterionic alcohol-sil(atri)ene complex is much slower (compared to intermolecular proton transfer) in the cases of **8** and **9** than it is in **12**. This seems reasonable, since the intramolecular process in **8** must occur by [1,5]- or [1,7]-transfer, as opposed to the [1,3]-transfer proposed for **12**.

Methoxytrimethylsilane is a widely used trapping agent for silenes and is known to react by addition of MeO-SiMe₃ across the Si=C bond.² In principle, the reaction can proceed by a mechanism analogous to that shown in eq 6 for the addition of MeO-H to **8**, which would be consistent with the curvature in the quenching plot for the reaction of methoxytrimethylsilane with **8** and **9**. While the rate constants obtained from quadratic analysis of these data are more than 10 times slower than those for addition of methanol, it is not known whether this reflects a difference in the rate of complex formation for the two quenchers or a difference between the rates of trimethylsilylium transfer and proton transfer. We note that the second-order component for quenching of **8** by MeOSiMe₃, $k_Q = (1.4 \pm 0.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, is similar to that reported by Conlin and co-workers for the reaction of this reagent with a 1,3-(1-sila)butadiene derivative ($k_Q = (3.4 \pm 0.6) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).⁵ Unfortunately, the data reported for the latter compound were not sufficiently detailed to reveal the presence or absence of curvature in the quenching plot.

The intense transient absorptions due to the silatriene **9** and silyl radicals combine to overpower the expectedly weaker absorptions (presumably in the region below 350 nm) due to 1,1-diphenylsilene, even though product studies indicate that the latter is the main product of photolysis of **1** in solution. Clearly, study of the reactivity of simple 1-aryl or 1,1-diarylsilenes by transient spectroscopic methods will require the use of precursors other than alkylphenyldisilanes.

Given the similarities in the emission behavior of **1** and **7**, it is not surprising that both yield silatrienes upon photolysis in solution. Increasing phenyl substitution in the disilane (e.g., as in **1**) results in reduced yields of the silatriene (**9**) and correspondingly higher yields of silene (**6**) and free silyl radicals. This may be due to a combination of increased steric hindrance to concerted [1,3]-migration and a weakening of the Si-Si bond, which favors the formation of bond homolysis products. While we have demonstrated that free silyl radicals are produced upon photolysis of **1** (and, to a lesser extent, **7**), we are unable to determine the extent to which they are responsible for the formation of **6** or **9**. In the case of **1**, the formation of both **9** and silyl radicals occurs within a time scale shorter than the duration

of the excitation pulse (ca. 10 ns).

Summary and Conclusions

Photolysis of methylpentaphenyldisilane (**1**) in solution yields a reactive 1,1-diphenyl-1,3,5-(1-sila)triene species (**9**) in low yield. Because of the strong absorption of this species in the visible spectrum, its formation and subsequent decay are easily monitored by nanosecond flash photolysis techniques. Rate constants for the reaction of **9**, as well as for a 1,1-dimethyl-1,3,5-(1-sila)triene derivative (**8**) (generated by flash photolysis of pentamethylphenyldisilane (**7**)), with oxygen, acetone, acetic acid, ethyl acetate, alkenes, methoxytrimethylsilane, water, and a series of alcohols have been determined.

The rates of decay of **8** and **9** in the presence of water, methanol, ethanol, *tert*-butyl alcohol, and methoxytrimethylsilane show a quadratic dependence on the concentration of the quencher. A primary deuterium kinetic isotope effect of $k_H/k_D \approx 1.7$ has been measured for the reaction of **8** and **9** with water. The results are consistent with an addition mechanism involving reversible formation of a silatriene-ROH complex which collapses to product by competing intracomplex and intermolecular proton transfer involving a second ROH molecule. In the case of water and simple alcohols, the proton-transfer steps are rate determining. An analogous mechanism applies to the addition of methoxytrimethylsilane. Both the bimolecular and termolecular rate constants for quenching by these reagents decrease in the order H₂O > D₂O \approx MeOH > EtOH > *t*-BuOH \gg Me₃SiOMe. The kinetics for reaction of **8** and **9** with 2,2,2-trifluoroethanol and acetic acid are consistent with the idea that when the addend is strongly acidic and weakly nucleophilic, formation of the zwitterionic addition complex is the rate-determining step for reaction.

More detailed, quantitative studies of the reactivity of these and other reactive trivalent silicon compounds toward various nucleophiles is in progress.

Experimental Section

¹H NMR spectra were recorded on Bruker AC200 (200 MHz) or Varian EM390 (90 MHz) NMR spectrometers in deuteriochloroform solution and are reported in parts per million downfield from tetramethylsilane. Ultraviolet absorption spectra were recorded on a Hewlett-Packard HP8451 UV spectrometer or a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 data station. Fluorescence emission spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer, also interfaced to the Model 3600 data station. Mass spectra were recorded on a VGH ZABE mass spectrometer. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph with flame ionization detector and a Hewlett-Packard 3396A integrator, and a HP-1 megabore capillary column (5 m \times 0.53 mm; Hewlett-Packard, Inc.). GC/MS analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 capillary column (25 m \times 0.2 mm; Chromatographic Specialties, Inc.). Melting points were determined on a Reichert hot-stage microscope fitted with a Cole-Parmer Model 8110-10 type K thermocouple and are uncorrected.

Acetonitrile (Caledon HPLC) was refluxed over calcium hydride for several days and distilled under nitrogen. Methanol (Fischer HPLC) was refluxed over magnesium, distilled under nitrogen, and stored over molecular sieves (3 Å). *tert*-Butyl alcohol (Fisher) was refluxed over calcium oxide and distilled. Tetrahydrofuran used in the preparation of **1**, and **7** was refluxed over sodium benzophenone and distilled under nitrogen. Cyclohexene (Aldrich Gold Label) and 2-bromopropane (Matheson Coleman and Bell) were distilled before use. Ethyl acetate (BDH) was distilled from phosphorus pentoxide. Cyclohexane (Aldrich spectro-grade), 2,2,4-trimethylpentane (Baker HPLC), water (Caledon HPLC), acetone (Baker reagent), deuterium oxide (MSD Isotopes), glacial acetic acid (Fisher), and absolute ethanol were all used as received from the suppliers. Trimethylmethoxysilane, triethylsilane, triphenylsilane, methylidiphenylsilane, 2,3-dimethyl-1,3-butadiene (Gold Label), and 2,2,2-trifluoroethanol (NMR grade) were all used as received from Aldrich Chemical Co.

Methylpentaphenyldisilane²⁶ (**1**), pentamethylphenyldisilane (**7**),²⁶ methoxytriphenylsilane,²⁷ and methoxymethyldiphenylsilane²⁷ were pre-

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pared according to modifications of the published procedures and exhibited melting or boiling points and spectral data that agreed satisfactorily with those reported in each case. The chlorosilanes employed in these syntheses were used as received from Petrarch Systems or Aldrich.

Nanosecond laser flash photolysis experiments were carried out using the pulses from a Lumonics TE-861M excimer laser filled with F₂/Kr/He (248 nm, ca. 12 ns, 80–120 mJ) or N₂/He (337 nm, 6 ns, ca. 3 mJ) and a microcomputer-controlled detection system that has been described elsewhere.¹⁴ All laser samples were continuously deoxygenated with bubbling nitrogen. Solutions of **1** and **7** were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was 0.8 (1.7–2 × 10⁻⁴ M for **1**; ca. 0.002 M for **7**). The disilane solutions were flowed continuously through a 3 × 7 mm quartz flow cell, supplied by a calibrated 100-mL-capacity reservoir. Quenchers were added to the reservoir by microliter syringe as aliquots of standard solutions in dry acetonitrile. Oxygen quenching studies were carried out using a Matheson 600 gas proportioner to regulate the composition of oxygen/nitrogen

mixtures, which were then bubbled continuously through the solution contained in the reservoir. A value of 3.18 × 10⁻³ M for the concentration of oxygen in air-saturated isooctane^{21b} was used to calculate the oxygen concentration for the various mixtures in this solvent.

Samples for laser flash photolysis of solutions of methylphenylsilane and triphenylsilane in 1:4 di-*tert*-butyl peroxide/isooctane were contained in 7 × 7 mm quartz cells. The concentrations of the two silanes were 0.125 and 0.068 M for Ph₂MeSiH and Ph₃SiH, respectively.

Steady-state photolyses of deoxygenated 0.005 M solutions of **1** in cyclohexane containing 0.1 M methanol were carried out using a Rayonet photochemical reactor equipped with 254-nm lamps and the unfocused pulses of the KrF excimer laser (248 nm) as excitation sources. Photoproducts were identified by GC/MS and by coinjection of the photolysates with authentic samples.

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Reversible Adsorption on a Single Langmuir–Blodgett Monolayer

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Abstract: The reversibility of the adsorption of NO₂/N₂O₄ (NO_x) on a single Langmuir–Blodgett monolayer of phthalocyanine (Pc) complexes is demonstrated using surface-enhanced Raman scattering on Au island films. The effect of the adsorbate on the relative Raman intensity of characteristic vibrational fundamentals of the Pc molecule permits the monitoring of the kinetics and the nature of the small molecule–macrocycle interaction. The localization and strength of the interaction can be correlated with patterns observed in the change of the electronic and resonant Raman spectra in the series of Pc molecules. The approach presented in this work allows one to study, at a molecular level, the properties that control the adsorption of small molecules on Pc monolayers. The results are relevant to the general understanding of an adsorption process that has been demonstrated to have applications in the development of phthalocyanine-based gas sensors, and the use of Pc as a catalyst.

Introduction

It is known that the surface of crystals and thin solid films of phthalocyanine (Pc) and other organic macrocycles adsorb small gaseous molecules which strongly alter the electrical properties of the material.^{1,2} The changes in the semiconducting and photoconducting properties of Pc materials due to adsorption are so dramatic that they may be the basis for the development of these materials as chemical sensors for gases.^{3,4} For instance, Honeybourne and Ewen¹ have studied the effect of NO₂/N₂O₄ on CuPc and reported an increase of 6 orders of magnitude in conductance upon gas adsorption. Recently, Zhu and Petty⁵ have reported a potential optical sensor for nitrogen dioxide based on copper tetra-*tert*-butylphthalocyanine (CuTTPc) using surface plasmon resonance on Ag. However, in the adsorption process the nature of the interaction between gas and phthalocyanine is not well known, and there is a need for experimental techniques that would permit the characterization of the Pc adduct. It should be pointed out that the problem of metalated Pc–small molecule interaction is also central to the electrocatalytic activity of Pc complexes⁶ or the use of Pc complexes as catalysts.⁷ Surface-enhanced (resonant) Raman scattering (SERS or SERRS⁸) and electronic absorption spectroscopy are powerful analytical techniques that contribute to characterize and monitor the nature of

the interaction between an electron acceptor molecule and Pc derivatives laid down in the form of a single Langmuir–Blodgett (LB) monolayer. In the present report the reversible adsorption of NO_x on a single LB monolayer of H₂TTPc (metal-free tetra-*tert*-butylphthalocyanine), CuTTPc, and YbPc₂ (ytterbium bisphthalocyanine) monitored by SERRS is presented. The observations are rationalized in terms of effect of the NO_x–Pc interaction on the molecular properties of the Pc monolayer: the large delocalized π system (and changes in the electronic spectrum), the presence of pyrrole and azomethine groups in the macrocycle (and changes in the vibrational spectrum), and the electronic structure of the central metal atom.

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