

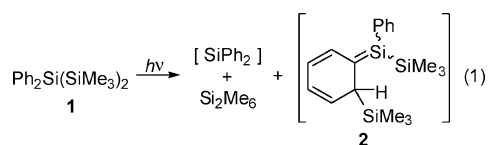
Diphenylsilylene

Andrey G. Moiseev and William J. Leigh*

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

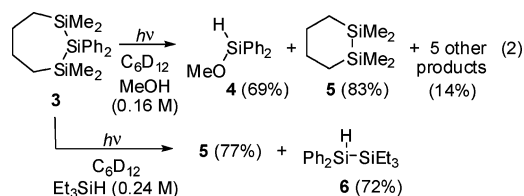
Received July 25, 2006; E-mail: leigh@mcmaster.ca

In spite of great interest over the past 30 years in the chemistry of silylenes,¹ the silicon analogues of singlet carbenes, few quantitative data exist on the reactivity of simple transient derivatives in solution. Dimethylsilylene (SiMe₂) has been studied by Das and Shizuka and co-workers,^{2,3} who measured rate constants for a number of representative reactions in solution by flash photolysis methods, and a similar study of dimethylsilylene (SiMe₂) has been reported by Conlin and co-workers.⁴ Similar studies of methylphenyl- (SiMePh)⁵ and diphenylsilylene (SiPh₂)⁶ had been reported somewhat earlier, but the reported rate constants are so significantly different from those reported later for SiMe₂ and SiMePh with similar substrates that it was soon recognized that misassignments must have been made.^{1a} Indeed, the time-resolved UV/vis spectra assigned to SiMePh and SiPh₂ in these reports (λ_{max} 440–445 nm)^{5,6} differ markedly from those measured in hydrocarbon glasses at 77 K from the same precursors (λ_{max} 490–495 nm).⁷ All of the arylsilylenes that were studied in these early efforts, both in solution and frozen matrixes, were generated by photolysis of acyclic trisilanes, which are known to extrude the central SiRR' group as the major photoreaction. Phenylated systems are known also to afford conjugated silene derivatives, formed by 1,3-silyl migration into the ortho position of one of the phenyl rings.⁸ In the case of trisilane **1**, the compound employed for the generation of SiPh₂, this process (yielding **2**) occurs in solution with similar efficiency to SiPh₂ extrusion (eq 1).⁹ Our own experience with silenes of this type¹⁰ suggested that this might be the source of the complications encountered in early time-resolved studies of **1** and similar derivatives.



Silylene extrusion also occurs in high yield from cyclic trisilanes.¹¹ This led us to wonder whether an appropriately substituted cyclic analogue of **1** might be a significantly cleaner source of SiPh₂ for study by flash photolysis methods, as the isomeric cyclic silene that would be formed by [1,3]-silyl migration might be expected to suffer from sufficient strain that its formation might be suppressed relative to silylene extrusion.

Indeed, steady-state photolysis (254 nm) of a C₆D₁₂ solution of cyclic trisilane **3** (0.05 M) and methanol (MeOH; 0.16 M) led to the formation of diphenylmethoxysilane (**4**, 69%), disilane **5** (83%), and five minor products in 14% combined yield (eq 2), whose ¹H NMR and mass spectra are consistent with adducts of MeOH and an isomer of **3**. The quantum yield for consumption of **3** was determined to be $\Phi_{-3} = 0.54 \pm 0.09$. These results confirm that SiPh₂, which is trapped by MeOH as **4**, is formed in significantly higher yield from **3** than from the acyclic parent (**1**),^{9b} and with high enough efficiency that its direct detection and characterization by flash photolysis methods should be possible.



A competitive trapping experiment was carried out, in which a 0.02 M solution of **3** in C₆D₁₂ containing MeOH (0.09 M) and triethylsilane (Et₃SiH; 0.25 M) was photolyzed to ca. 50% conversion, monitoring by NMR spectroscopy throughout the photolysis. Three products were formed: **4**, **5**, and 1,1,1-triethyl-2,2-diphenyldisilane (**6**), which was identified in a separate experiment in which **3** was photolyzed in C₆D₁₂ containing only Et₃SiH (eq 2). Compounds **4** and **6** were formed in relative yields of $4/6 = 1.59 \pm 0.03$, which yields a rate constant ratio of $k_{\text{MeOH}}/k_{\text{Et}_3\text{SiH}} = 4.4 \pm 0.2$ for the reaction of SiPh₂ with the two substrates.

Laser flash photolysis of flowing, deoxygenated solutions of **3** (~0.09 mM) in anhydrous hexane gave rise to three distinct transient species with overlapping absorption spectra centered in the 460–520 nm range. Two of these are formed with the laser pulse: a long-lived species ($\tau > 100 \mu\text{s}$) with $\lambda_{\text{max}} = 460 \text{ nm}$ and a shorter-lived one ($\tau \approx 1 \mu\text{s}$) with $\lambda_{\text{max}} \approx 520 \text{ nm}$. A third species, which also exhibits $\lambda_{\text{max}} \approx 460 \text{ nm}$ and $\tau \approx 10 \mu\text{s}$, was observed to grow in over the first 1 μs after excitation. Both the lifetime of the 520 nm transient and the peak intensity of the short-lived 460 nm species showed exquisite sensitivity to adventitious water or intentionally added reagents. For example, the addition of 0.6 mM Et₃SiH reduced the lifetime of the 520 nm transient to $\tau \approx 370 \text{ ns}$ and the peak intensity of the 460 nm signal by ca. 25%, compared to their values in the absence of silane. The lifetime of the long-lived 460 nm species was unaffected under these conditions. Time-resolved UV/vis spectra recorded 64–80 ns and 1.5–1.6 μs after excitation in the presence of 0.6 mM Et₃SiH are shown in Figure 1, along with the isolated spectrum of the 520 nm species, calculated by subtracting the late spectrum from the early one. The figure also shows the spectrum of a photolyzed solution of **3** in a 3-methylpentane (MP) glass at 78 K. The latter spectrum is nearly identical to that obtained from trisilane **1** under the same conditions, exhibiting a long wavelength absorption centered at $\lambda_{\text{max}} = 505 \text{ nm}$, in reasonable agreement with the spectrum originally reported for **1** under similar conditions, and assigned to SiPh₂.⁷

The short-lived species is best monitored at 530 nm, where its absorptions are better separated from those due to the longer-lived transient products. Addition of small amounts of MeOH, Et₃SiH, isoprene, 4,4-dimethyl-1-pentene, or *tert*-butylacetylene¹² led to acceleration of the first-order decay of the species in direct proportion to their concentrations, resulting in linear plots of the decay rate constant (k_{decay}) versus concentration in every case. The slopes of the plots are the absolute second-order rate constants for reaction, and are listed in Table 1. Also listed for comparison are the reported values for reaction of SiMe₂^{2,3} and of the germanium

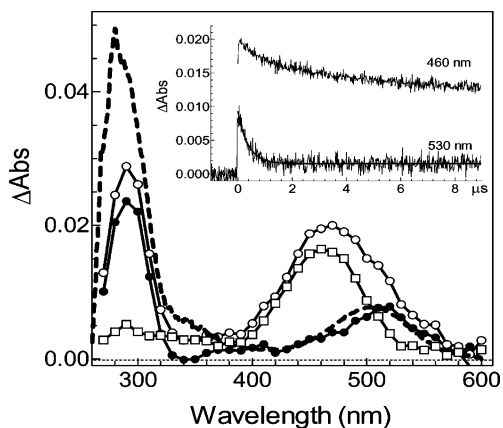


Figure 1. Transient absorption spectra recorded 64–80 ns (○) and 1.5–1.6 μ s (□) after the laser pulse, from laser flash photolysis of a 0.09 mM solution of **3** in deoxygenated, anhydrous hexane containing 0.6 mM Et₃SiH. Also shown is the difference spectrum (●; 80 ns minus 1.6 μ s) and the spectrum obtained after 254 nm photolysis of **3** in a MP glass at 78 K (---). The inset shows transient decays recorded at 460 and 530 nm.

Table 1. Absolute Rate Constants ($k_Q/10^9 \text{ M}^{-1}\text{s}^{-1}$) for Reaction of SiPh₂, SiMe₂, and GePh₂ with Selected Scavengers in Hydrocarbon Solvents at 25 °C

scavenger (Q)	$k_Q/10^9 \text{ M}^{-1}\text{s}^{-1}$		
	SiPh ₂ ^a	SiMe ₂ ^b	GePh ₂ ^c
MeOH	13.2 ± 0.3	9.1	6.1 ^d
Et ₃ SiH	2.8 ± 0.1	3.6	0.0006
isoprene	11.8 ± 1.0	9.4	5.5 ^d
4,4-dimethyl-1-pentene	8.7 ± 0.4	7.3	4.2 ^d
tert-butylacetylene	9.7 ± 0.4	8.0	5.2

^a From plots of the pseudo-first-order rate constants (k_{decay}) for decay of SiPh₂ in hexane, monitored at 530 nm, versus scavenger concentration; errors are reported as $\pm 2\sigma$. ^b Data from refs 2, 3 (cyclohexane, 22 °C); diene = 2,5-dimethyl-1,3-hexadiene; alkene = 1-hexene; alkyne = trimethylsilylacetylene. ^c Data from refs 13, 14. ^d Reversible, with equilibrium constants in the range 2000–6000 M⁻¹ in hexane at 25 °C (see refs 13, 14).

homologue, GePh₂,^{13,14} with the same or similar substrates. The close correspondence between the rate constants for reaction of the 520 nm species from **3** and of SiMe₂ with corresponding substrates provides strong support for a silylene assignment. Further support is provided by the excellent agreement between the absolute rate constant ratio for reaction of the species with MeOH and Et₃SiH ($k_{\text{MeOH}}/k_{\text{Et}_3\text{SiH}} = 4.7 \pm 0.3$) and the value determined above by competitive steady-state trapping.

Each of these reagents also quenched the formation of the short-lived 460 nm transient completely, suggesting it is a product of reaction of SiPh₂ that is eliminated in the presence of silylene scavengers. A likely candidate is the dimerization product, tetraphenyldisilene (Si₂Ph₄); its spectrum can be compared to that of tetraphenyldigermene (Ge₂Ph₄; $\lambda_{\text{max}} = 440 \text{ nm}$), which is similarly formed from GePh₂ under the same conditions and similarly quenched in the presence of added scavengers.^{13,15} Time-dependent DFT calculations (see Supporting Information) reproduce the red-shifts in the absorption maxima of SiPh₂ and Si₂Ph₄ relative to those of the corresponding germanium analogues¹³ and yield values of λ_{max} (equal to 565 and 486 nm for SiPh₂ and Si₂Ph₄, respectively) that are in acceptable agreement with the experimental spectra.

SiPh₂ and GePh₂ exhibit the same large differences in reactivity toward Si–H insertion as do the parent (MH₂) and dimethyl (MMe₂) metallylene analogues.^{16,17} The kinetic differences are much less pronounced in the reactions with C–C multiple bonds and MeOH, despite substantial differences in the stabilities of the primary

products of these reactions. The latter is evident from the fact that GePh₂ reacts reversibly with MeOH, the alkene, and the diene on the microsecond time scale,^{13,14} while SiPh₂ appears to react irreversibly. The trends are similar to those exhibited by the methylated counterparts, SiMe₂ and GeMe₂, under similar conditions.¹⁶

The insensitivity of the lifetime of the long-lived 460 nm species to added Et₃SiH was mirrored in the experiments with the other scavengers studied. This is the behavior expected¹⁰ of a silene intermediate analogous to that formed in the photolysis of **1**.⁹ As discussed above, minor products consistent with addition of MeOH to such a species were observed in the steady-state experiments, though they have not yet been isolated owing to their very low individual yields. More complete identification of the minor transient products of photolysis of **3** and analogous studies of the transient photoproducts from **1** will be reported in due course, as will the results of further studies of the reactivities of simple transient silylenes in solution.

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Supporting Information Available: Synthesis and characterization of compounds; detailed descriptions of product studies; flash photolysis experiments; TD–DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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