5332 *J. Am. Chem. Soc.* **1993,** *115,* 5332–5333

1,1-Diphenylsilene

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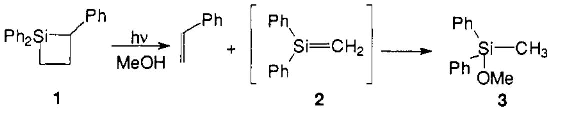
Received March 1, 1993

Silenes have been the subject of considerable interest over the past 20 years.[2] They have frequently been postulated as reactive intermediates in the photolysis and thermolysis of organosilicon compounds, usually on the basis of chemical trapping studies or matrix isolation spectroscopy, and several stable silenes have been synthesized.[2] There have, however, been relatively few reports which describe the spectroscopic properties and reactivity of transient silenes in solution at room temperature.[3-8] We report the preliminary results of a study of the chemistry of 1,1-diphenylsilene (**2**), which has been generated by photolysis of 1,1,2-triphenylsilacyclobutane (**1**) in polar and nonpolar solvents at room temperature and characterized using steady-state and nanosecond laser flash photolysis techniques. We also report rate constants for the reaction of **2** with a series of carbonyl compounds and a diene, and the effect of oxygen on its lifetime in solution. Photolysis of **1** in deoxygenated methanol solution has been reported to yield styrene and **3** in 67% chemical yield (eq 1), consistent with the formation of **2** as an intermediate in this reaction.[9] Other silacyclobutanes are known to behave similarly.[10]

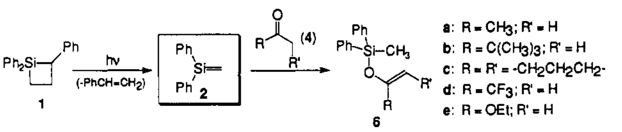


(1)

Nanosecond laser flash photolysis (NLFP)[11] of continuously flowing, deoxygenated 6×10^{-4} M solutions of **1**[12] in isooctane or dried acetonitrile with the pulses (248 nm, ca. 16 ns, 80–120 mJ) from a Kr/F_2 excimer laser gives rise to readily detectable transient absorptions in the 300–330-nm spectral range. These consist of two components in both solvents: an initial, "short-lived" decay which is strictly first order in acetonitrile solution ($\tau = 800$ ns) and largely first order in isooctane ($\tau \leq 13\ \mu s$[14]), and a residual absorption (accounting for *ca.* 30% of the initial transient absorbance at 325 nm) due to a species which is stable on the time scale of these experiments. The lifetime of this long-lived species is less than a few minutes, however, since we are unable to detect it in static UV absorption spectra of solutions of **1** recorded immediately after steady-state photolysis to ca. 50% conversion. Figure 1 shows transient absorption spectra recorded (in isooctane solution) at short and long times after the laser pulse, along with a typical transient decay trace. Spectral subtraction yields the spectrum shown in Figure 1C, which corresponds to that of the short-lived component of the decay trace. Nearly identical behavior was observed with acetonitrile solutions of **1**, though on a shorter time scale.

The lifetime of the short-lived transient species (monitored at 325 nm) is shortened in the presence of known silene traps[2] such as methanol, acetone, or dienes, but is unaffected by saturation of the solution with oxygen. Neither the yield nor the temporal behavior of the species giving rise to the residual absorption is affected by any of these reagents, nor are any new transient species detectable. Plots of the pseudo-first-order rate constants for decay of the short-lived transient (k_{decay}) *versus* concentration of added acetone (**4a**), acetone-d_6 (**4a**-d_6), 3,3-dimethyl-2-butanone (**4b**), cyclopentanone (**4c**), ethyl acetate (**4d**), 1,1,1-trifluoroacetone (**4e**), and 2,3-dimethyl-1,3-butadiene (**5**) were linear in every case, allowing determination of the second-order quenching rate constants listed in Table I. An upper limit for the rate constant for quenching by O_2 is estimated as ca. 5×10^6 M^{-1} s^{-1}.[15]

Steady-state photolysis of deoxygenated, 0.05 M cyclohexane solutions of **1** in the presence of **4a-e** (0.02–0.05 M) leads to the formation of the products (**6a-e**) shown in eq 2.[16] In the cases of **4a-c**, the corresponding silyl enol ether accounted for >80% of consumed **1** after 10–50% conversion. The chemical yields of **6** were lower for **4d,e**, particularly when lower concentrations of **4** were employed. In all cases, the photolysates also contained small amounts of methyldiphenylsilanol and 1,3-dimethyl-1,1,3,3-diphenyldisiloxane, which we tentatively ascribe to competitive trapping of **2** by trace amounts of water. No evidence for the formation of siloxetanes (by formal [2 + 2]-cycloaddition) could be obtained by ^{1}H NMR analysis of photolysates subjected only to evaporation of solvent, styrene, and excess carbonyl compound. Photolysis of **1** alone in cyclohexane solution led to its destruction, along with formation of styrene and small amounts of the silanol and disiloxane as the only products detectable by our analytical method. No other products, which might be attributed to the long-lived species giving rise to the residual absorption in the NLFP experiments, were detected in >5% yield under any conditions. We conclude that the long-lived species is a relatively minor, strongly absorbing product of photolysis of **1**.



(2)

In acetonitrile solution containing methanol, **1** undergoes dark reaction to yield the acyclic silyl methyl ether **7** shown in eq 3. We were initially surprised by this result,[9] but it is reasonable considering the substantial reactivity of this compound toward nucleophiles under basic conditions.[13] Steady-state photolysis of the solution immediately after addition of MeOH resulted in the formation of **3** in addition to **7**, however. Photolysis of **1** alone in acetonitrile led to the formation of silanol and disiloxane, as

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(12) Compound **1** was synthesized according to the published method[13] and was purified by column chromatography (silica gel) followed by recrystallization from ligroin. Its melting point (63–64 °C) and spectroscopic properties are similar to those reported.

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(14) The fit to simple first-order kinetics of the initial decay obtained with isooctane solutions improves with attenuation of the laser beam with neutral density filters. The lifetime quoted was obtained at low laser intensities.

(15) Estimated as 10% of the observed pseudo-first-order rate constant for decay of the transient in O_2-saturated isooctane, since it was the same (within error) as that recorded in N_2-saturated solution, and using a value of 0.015 M for the concentration of oxygen at saturation in this solvent: Murov, S. *Handbook of Photochemistry*; Dekker: New York, 1973.

(16) Compounds **6a-c** were isolated by semipreparative gas chromatography from semipreparative photolyses of cyclohexane solutions containing 0.02 M **1** and 0.05 M trapping reagent, and identified by ^{1}H NMR and mass spectrometry. Compounds **6d,e** were identified by ^{1}H NMR and GC/MS analyses of photolysis mixtures at ca. 70% conversion.

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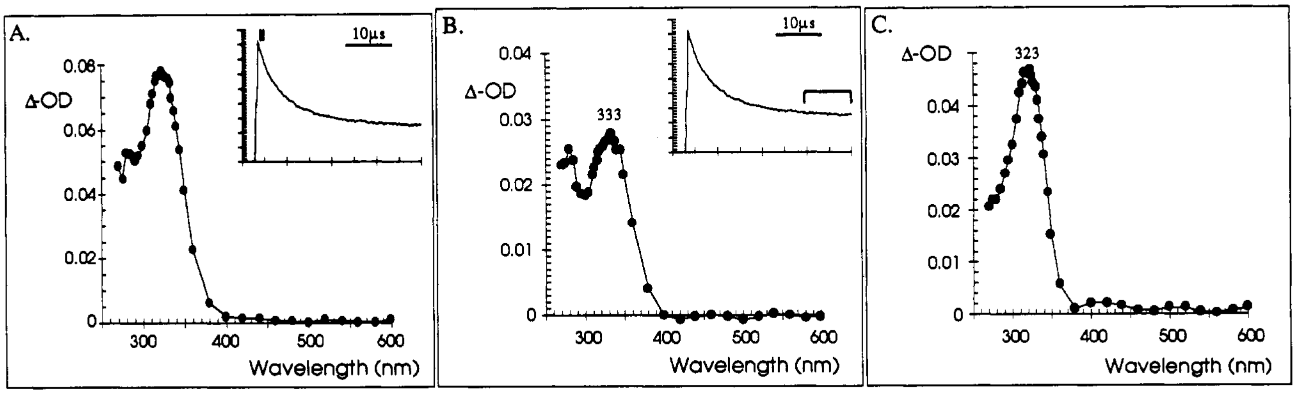


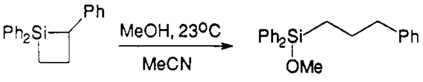
Figure 1. Transient absorption spectra from a deoxygenated, 6.2 × 10^{-4} M solution of **1** in isooctane at 21 °C: (A) spectrum recorded 1–2.5 μs after 248-nm laser excitation; (B) spectrum of long-lived component, recorded 30–40 μs after excitation; (C) corrected spectrum of 1,1-diphenylsilene (**2**), obtained by subtraction of spectrum B from spectrum A. The inserts in A and B show transient decay traces recorded at a monitoring wavelength of 325 nm (40 μs full scale) and indicate the time windows over which the two spectra were recorded.

Table I. Rate Constants for Quenching of 1,1-Diphenylsilene (**2**) by Carbonyl Compounds (**4a–e**) and 2,3-Dimethyl-1,3-butadiene (**5**) in Deoxygenated Isooctane and Acetonitrile Solution at 21 °C[a]

	$k_q \times 10^{-8}$ M·s	
reagent	isooctane	acetonitrile
cyclopentanone (**4c**)	11.7 ± 0.8	5.1 ± 0.2
$CH_3COC(CH_3)_3$ (**4b**)	4.0 ± 0.2	2.3 ± 0.1
CH_3COCH_3 (**4a**)	3.3 ± 0.2	1.07 ± 0.05
CD_3COCD_3 (**4a**-d_6)	1.7 ± 0.1	0.80 ± 0.06
CH_3COCF_3 (**4e**)	0.16 ± 0.01	*c*
CH_3COOEt (**4d**)	0.088 ± 0.002	0.073 ± 0.004
2,3-DMB (**5**)[b]	0.037 ± 0.002	*c*

[a] Measured by nanosecond laser flash photolysis techniques, using deoxygenated 6 × 10^{-4} M solutions of **1** in isooctane or dried acetonitrile. Errors in rate constants are reported as twice the standard deviation from least squares analyses of the expression $k_{decay} = k_0 + k_q[Q]$. [b] 2,3-Dimethyl-1,3-butadiene. [c] Not determined.

well as several other products which have not yet been rigorously identified. At least one of these is the product of addition of the solvent to **2**, according to GC/MS analysis of the crude photolysate.



(3)

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These data are consistent with the assignment of the short-lived transient observed by NLFP to 1,1-diphenylsilene (**2**). The position of its UV absorption maximum in isooctane solution (323 nm) is shifted by ca. 75 nm compared to that of the carbon analog 1,1-diphenylethylene,[17a] which is similar to the difference between the UV absorption maxima of silene ($H_2C{=}SiH_2$; 258 nm[18]) and ethylene (165 nm[17b]). Furthermore, silenes are known to be quenched by alcohols, carbonyl compounds, and dienes with bimolecular rate constants in the 10^6–10^9 M^{-1} s^{-1} range,[3-7] as is observed in the present case for the transient from photolysis of **1**. Similar transient spectroscopic behavior (minus the residual absorption) is observed upon NLFP of isooctane or acetonitrile solutions of 1,1-diphenylsilacyclobutane (**8**),[19] another known photochemical precursor of **2**.[10]

Photolysis of silene **2** in isooctane solution with a nitrogen laser (337 nm) within 300 ns of its formation by 248-nm laser photolysis of **1** results in no detectable decrease in transient signal.[20] This experiment suggests that the silene is photostable under these conditions, perhaps as a result of facile excited-state decay by torsional relaxation about the Si=C bond.

The reaction of simple silenes with carbonyl compounds is well-known to yield silyl enol ethers when the latter contains enolizable hydrogens, and formal [2 + 2]- or [4 + 2]-cycloaddition products when it does not.[2] These reactions are thought to involve the carbonyl n-orbital and proceed by a nonpericyclic mechanism, but it is not known whether the reaction is concerted or stepwise. The relative rates of reaction of **2** with **4a-e** correlate roughly with the calculated (AM1)[21] energies of the carbonyl nonbonding MOs, but not with those of the π-MOs, verifying both the involvement of the carbonyl n-orbital and the nonpericyclic nature of the formal ene-addition. The present data strongly suggest that Si–O bonding is involved in the rate-determining step of the reaction and indicate that the reaction is slowed in polar solvents, presumably due to stabilization of the carbonyl n-orbital (and perhaps also the polar Si=C bond) at the expense of a relatively nonpolar transition state or intermediate. While the magnitude of the KIE observed for the reaction with acetone (**4a**) is consistent with either a primary or secondary effect,[23] the fact that *both* the rate constant *and* the KIE for the reaction of **2** with acetone are smaller in MeCN (k_H/k_D = 1.34 ± 0.17) than in isooctane (k_H/k_D = 1.9 ± 0.2) provides good evidence for a concerted mechanism in which Si–O bonding and H-transfer proceed asynchronously. A two-step mechanism involving initial Si–O bond formation followed by H–transfer should exhibit an increase in the KIE with a decrease in the overall rate constant, irrespective of which step is rate-determining. With a concerted mechanism, a lower isotope effect in MeCN is explainable if the transition state for reaction in polar solvents is characterized by less complete H-transfer and more complete Si–O bonding than in the transition state for reaction in nonpolar solvents. Further studies of the mechanisms of this and other classic silene-trapping reactions are in progress.

Acknowledgment. We wish to thank the McMaster University Regional Centre for Mass Spectrometry for its services and the Natural Sciences and Engineering Research Council of Canada for financial support.

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(20) The two-laser system incorporates our conventional NLFP system[11] and a Lumonics TE-861M excimer laser filled with nitrogen/helium mixtures (337 nm, ca. 6 ns, 5–6 mJ). The second laser is timed with respect to the 248-nm laser pulse using a Stanford Research Systems DG535 digital delay/pulse generator. A deoxygenated isooctane solution of α,α,α-triphenylacetophenone[20b] was used as a standard to optimize the spatial overlap of the two laser beams and calibrate the relative timing of the two trigger pulses. (b) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta* **1990**, *46A*, 551.

(21) AM1 (Version 2.1) reproduces the relative ordering of the n- and π-ionization potentials[22] in each compound and within the series of compounds **4a-e**.

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