Triplet-State Photoreactivity of Phenyldisilanes

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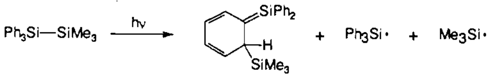
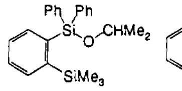
The photochemistry and photophysics of aryldisilanes have been widely studied[1] and continue to be of considerable interest.[2,3] It is well established that direct irradiation of these compounds in solution leads to transient silenes which are formally derived from disproportionation and recombination of the silyl free radicals formed by homolysis of the Si–Si bond[1,2] and that silyl radicals are indeed formed in certain cases.[3–6] It is commonly thought that silene products are singlet-derived, but the role of the triplet state in direct aryldisilane photolyses has never been established. In this paper, we report the results of a study of the photochemistry of 1,1,1-trimethyl-2,2,2-triphenyldisilane (**1**) in solution. Irradiation of **1** yields products ascribable to the 1,3,5-(1-sila)-hexatriene derivative **2**, in addition to triphenyl- and trimethylsilyl radicals (**3** and **4**, respectively; see eq 1). We report evidence of



1 **2** **3** **4** (1)

a remarkable solvent effect on the relative yields of these two types of reactive intermediates and a clear demonstration that silyl radical formation from **1** and other aryldisilanes is triplet-derived. We also report evidence that reaction of silatriene **2** with acetone leads to the formation of a 1,2-siloxetane, in addition to the silyl ether expected on the basis of earlier studies of aryldisilane photochemistry.[1,2,7]

Irradiation (254 nm) of a deoxygenated, 0.05 M solution of **1**[8] in cyclohexane-d_{12} (HEX-d_{12}) containing acetone (0.05 M) as a silene trap,[6,9] under conditions where **1** is the primary absorber, leads to the clean formation of *two* products according to NMR analysis of the crude photolysate. The minor product is readily identifiable as the ene adduct **5** from reaction of **2** with acetone.[7,10]



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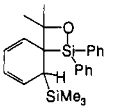

6

R_3SiCl: **7** (R = Ph), **8** (R = Me)

R_3SiD: **9**-*d* (R = Ph), **10**-*d* (R = Me)

Ph_3SiOR: **11** ($R = CHMe_2$), **12** ($R = C(Me)CH_2$)

The major product has been identified as siloxetane **6** on the basis of its ^1H, ^{13}C, and ^{29}Si NMR spectral properties.[10] It survives solvent evaporation and redissolution in deuteriochloroform but is undetectable by gas chromatography and decomposes during attempts to isolate it by liquid chromatography or vacuum distillation. We have found that the formation of products analogous to **6** occurs upon irradiation of other phenyldisilanes in the presence of acetone, although their yields relative to the known ene adducts are generally lower than that observed in the present case.[6b] We are continuing our attempts to isolate this compound and to identify its decomposition products.

Table I. Product Yields (%) from Irradiation of Deoxygenated Solutions of Disilane **1** and Acetone under Various Conditions[a]

solvent	$[CHCl_3]$/M[b]	**5**	**6**	**7**	**8**	**9**-*d*	**10**-*d*
HEX-d_{12}	0	33	69			undet	undet
	0.1	30	62	3	4	undet	undet
MeCN-d_3	0	5	undet			25	48
	0.1[c]	5	undet	70[d]	85[d]	10	13
acetone[b,e]	0[f]	undet	undet			11[g]	nd
	0.1	undet	undet	45[d]	nd	2[g]	nd

[a] Irradiations were carried out in deoxygenated solutions containing 0.05 M **1** and 0.05 M acetone to *ca.* 30% conversion using 254-nm excitation, unless noted otherwise. Product yields were determined by ^1H NMR and GC analyses relative to the disappearance of **1** using internal standards and are considered accurate to ±10%. undet = undetectable; nd = not determined. [b] Irradiations in acetone employed CCl_4 and 0.01 M **1**. [c] 1,1,2,2-Tetrachloroethane (20%) was also produced. [d] Yields calculated as the sum of the chlorosilane and corresponding silanol. [e] 300-nm excitation. [f] The photolysate also contained **11** (17%) and **12** (15%) from trapping of **3** by acetone. [g] Product is **9**-*h*.

Irradiation of a HEX-d_{12} solution of **1** (0.05 M) and acetone (0.05 M) in the presence of chloroform (0.1 M) as a silyl radical trap[5,11] yields small amounts of triphenyl- and trimethylchlorosilane (**7** and **8**, respectively) along with **5** and **6**. In contrast, irradiation of an acetonitrile-d_3 (MeCN-d_3) solution of **1**, acetone, and chloroform under similar conditions affords **7** and **8** in 70–85% yield, along with small amounts of **5**, triphenylsilane-*d* and trimethylsilane-*d* (**9**-*d* and **10**-*d*, respectively; both >90% deuterated according to GC/MS or ^1H NMR), and 1,1,2,2-tetrachloroethane. Photolysis of a similar solution in the absence of chloroform leads to the formation of **5**, **9**-*d*, and **10**-*d*, but with poor material balance. Product yields, determined after ~30% conversion by a combination of ^1H NMR and GC analyses of the crude photolysates, are collected in Table I. They are independent of the concentrations of both acetone and chloroform over a range of 0.01–0.1 M. Merry-go-round photolyses indicate that the quantum yields for disappearance of **1** are at most *ca.* 20% higher in hydrocarbon solution than in acetonitrile and are independent of the presence of chloroform.

The relative yields of silatriene- and radical-derived products thus show a remarkable dependence on solvent polarity. Since

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(3) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

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(10) Product **5** was isolated by semipreparative gas chromatography and exhibited ^1H, ^{13}C, and ^{29}Si NMR, infrared, and mass spectra consistent with its proposed structure; its yield was determined by ^1H NMR spectroscopy. Product **6** was identified from the ^1H, ^{13}C, ^{29}Si, and heteronuclear spin correlation NMR spectra of semipreparative scale photolysis mixtures (at *ca.* 50% conversion) after evaporation of the solvent under vacuum. The following lists the ^1H NMR (500 MHz, $CDCl_3$) resonances, along with the signal multiplicity, integral, corresponding ^{13}C resonance, and the protons which show NOEs upon irradiation of that signal: δ –0.17 (s, 9H; C 1.30; NOEs 2.93, 5.7–5.9; phenyl), 1.41 (s, 3H; C 31.8; NOEs 1.84, 5.74; phenyl), 1.84 (s, 3H; C 33.2; NOEs 1.41, 2.93, 5.89; phenyl), 2.93 (d, 1H, $J = 6.3$ Hz; C 29.9), 5.74 (d, 1H, $J = 9.3$ Hz; C 129.0), 5.78 (dd, 1H, $J = 4.9, 9.15$ Hz; C 122.0), 5.84 (dd, 1H, $J = 4.9, 9.3$ Hz; C 125.7), 5.89 (dd, 1H, $J = 6.3, 9.15$ Hz; C 131.0). The ^{13}C NMR spectrum also shows quaternary carbon signals at $\delta = 44.4$ and 89.4, while the ^{29}Si NMR spectrum shows signals at $\delta = 2.2$ and 12.4. Aryl protons and carbons could not be definitively assigned because of overlap with other components of the mixture. ^1H–^1H spin decoupling experiments verified the couplings involving the 2.93-ppm allylic proton and the 5.7–5.9-ppm vinyl protons.

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intersystem crossing in arylsilanes is known to be enhanced in polar media,[12] these results suggest that the two types of products arise from excited states of different multiplicities, with radical formation being triplet-derived. This has been verified on the basis of triplet sensitization and quenching experiments.

Irradiation (300 nm) of deoxygenated acetone solutions of **1** (0.01 M) in the presence or absence of CCl_4,[13] under conditions where the solvent absorbs the light, leads only to the formation of radical-derived products (**7**–**12**; see Table I). Since the triplet energies of phenyldisilanes are known to be on the order of 80 kcal/mol or less,[12] **1** can be expected to quench the triplet state of acetone at close to the diffusion-controlled rate.[14] These results are consistent with silyl radical formation being due to reaction of the disilane triplet state.[15]

Nanosecond laser flash photolysis experiments[5b,6] allow for direct detection of **2** and **3** and verify the solvent effect on their relative yields. Transient absorption spectra of flowed, deoxygenated 5.5×10^{-4} M solutions of **1** in isooctane show only absorptions assignable to silatriene **2** (λ_{max} = 490 nm), while spectra in MeCN show a prominent band with λ_{max} = 328 nm (due to **3**[5,11]) along with much weaker absorptions due to **2**. Saturation of MeCN solutions of **1** with *trans*-piperylene as a triplet quencher leads to a reduction in the silyl radical absorption compared to that of the silatriene, verifying that the disilane triplet state is responsible for silyl radical formation. However, the solubility of the diene in MeCN is too low to completely quench the formation of **3** or to enable an accurate Stern–Volmer analysis of the data. For this reason, quenching studies were carried out in tetrahydrofuran (THF) solution. Figure 1 shows a transient absorption spectrum recorded for a solution of **1** in THF, along with a spectrum of the same solution in the presence of 0.067 M *trans*-piperylene. Stern–Volmer analysis, employing the relative transient absorbances at 328 and 490 nm as an estimate of the radical yield[17] at various diene concentrations between 0 and 0.067 M, afforded a $k_q\tau$ value of 52 ± 23 M^{-1}, where τ is the lifetime of the disilane triplet and k_q is the rate constant for its quenching by the diene. Using a value of 8.5×10^9 M^{-1} s^{-1} for k_q,[18a] we obtain an estimate of 6 ± 3 ns for the lifetime of the triplet state of **1** under these conditions. The addition of 0.1 M chloroform to MeCN solutions of **1** has no effect on either the yield or the temporal behavior of the absorptions due to silatriene **2**. Furthermore, the persistence of these absorptions in the presence of enough diene to quench the disilane triplet (and radical formation) almost quantitatively[17] indicates that **2** is derived largely (if not totally) from an excited singlet state of **1**.[6,15,19]

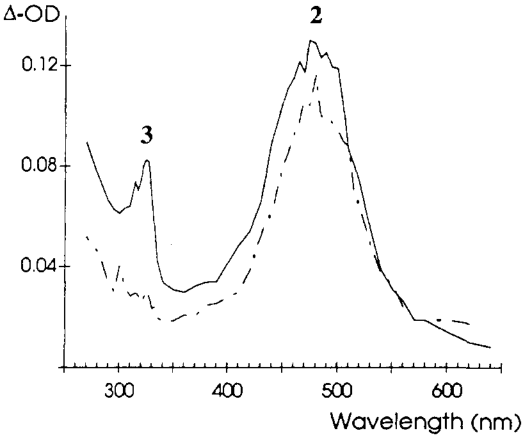

Figure 1. Transient absorption spectra recorded by nanosecond laser flash photolysis, 0–40 ns after 248-nm laser excitation of deoxygenated 5.5×10^{-4} M THF solutions of **1** in the absence (—) and presence (- • -) of *trans*-piperylene (0.067 M). The absorption bands due to silatriene **2** and triphenylsilyl radical (**3**) are labeled. The spectrum recorded in the presence of diene has been multiplied by 3.5 for clarity.

A few experiments were also carried out with 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**13**), whose photolysis in cyclohexane solution has been shown to yield *tert*-butyldiphenylsilyl radicals (**14**) as the sole product by trapping with chloroform (eq 2; ϕ_{15} = 0.64).[5b] The relative quantum yield for radical formation in

$$\underset{\mathbf{13}}{Ph_2{}^tBuSi\text{-}Si^tBuPh_2} \xrightarrow[HEX]{h\nu} \underset{\mathbf{14}}{2\ Ph_2{}^tBuSi\cdot} \xrightarrow{CHCl_3} \underset{\mathbf{15}}{2\ Ph_2{}^tBuSiCl} \qquad (2)$$

THF compared to HEX solution was determined to be ϕ_{THF}/ϕ_{HEX} = 1.4 ± 0.1 from the relative yields of chlorosilane **15** from photolysis of 0.01 M solutions containing 0.1 M chloroform, indicating that the solvent effect on the quantum yield for radical formation from **13** is similar to that observed for **1**. Analysis of the chlorosilane yields from merry-go-round photolysis (>270 nm) of 0.01 M solutions of **13** in cyclohexane in the presence of 0.1 M chloroform and varying amounts of *trans*-piperylene (0–0.1 M) led to a $k_q\tau$ value of 9.5 ± 1.9 M^{-1}, from which a value of τ = 1.4 ± 0.3 ns is estimated for the triplet lifetime of **13**.[18b] No curvature is observed in the Stern–Volmer plot, indicating that radical formation in the photolysis of this compound is *entirely* triplet-derived.

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(15) It is possible that silyl radicals arise from electron transfer sensitization,[16a] because the oxidation potential of **1** is <1.8 volts vs Ag/AgCl in MeCN.[16b] However, **7** and **8** are also produced (along with small amounts of silene(**2**)-derived products) upon benzene-sensitized photolysis of **1**, in which a benzene solution of **1** (0.001 M) is irradiated at 254 nm in the presence of methanol and chloroform (as the silene and silyl radical traps, respectively). We attribute the formation of both radical- and silene-derived products to competitive triplet and singlet quenching; irradiation of a 0.05 M solution of **1** under similar conditions produces only silene(**2**)-derived products.

(16) (a) Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327. (b) Workentin, M. S., unpublished results.

(17) This procedure corrects for screening of the disilane by the diene (the molar extinction coefficient of *trans*-piperylene is *ca.* 100 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ at 248 nm) and variations in laser intensity throughout the course of the experiment. It is a valid procedure since the formation of **2** is not quenched by added diene over the concentration range employed; the reduction in the 490-nm transient absorbance in the presence of diene is accounted for approximately by the increase in static optical density (at 248 nm) of the sample. The lifetimes of **2** (*ca.* 1 μs) and **3** (*ca.* 2.5 μs) are shortened only slightly by the addition of 0.05 M diene.

(18) (a) The rate constant for quenching of 4-methoxyacetophenone triplets by *trans*-piperylene in THF solution at 23 °C. (b) Using a value of $k_q \sim 7 \times 10^9$ M^{-1} s^{-1}.[14]

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