Aryldisilane Photochemistry. The Role of Silyl Free Radicals in Silene Formation from Photolysis of Methylpentaphenyldisilane

Gregory W. Sluggett and William J. Leigh*
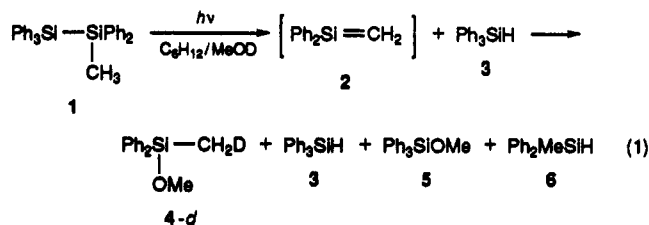
Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1

Direct irradiation of methylpentaphenyldisilane in hydrocarbon solution containing acetone yields triphenylsilane and products derived from acetone trapping of 1,1-diphenylsilene and a 1,3,5-(1-sila)hexatriene reactive intermediate, in chemical yields of 29, 29, and 42%, respectively, relative to consumed disilane. Photolysis of the disilane in the presence of acetone and small amounts of chloroform (0.05 M) results in the formation of the same products in the same chemical yields, along with triphenylsilyl and methyldiphenylsilyl chloride in 18 and 17% yields due to halocarbon trapping of the corresponding silyl radicals. Triplet quenching experiments indicate that silyl radicals are triplet-derived, while the silene and silatriene are derived from the lowest excited singlet state of the disilane. Transient UV absorption spectra of the individual reactive intermediates formed in the photolysis of the disilane have been measured by nanosecond laser flash photolysis, employing selective quenchers to suppress the spectra of the others. Photolysis of the disilane in the presence of high concentrations of chloroform or carbon tetrachloride yields mainly the corresponding silyl chlorides and is thought to proceed by an electron-transfer mechanism under these conditions. The same products are formed upon electron-transfer photosensitization using chloranil as the photosensitizer. The photochemistry of methylpentaphenyldisilane in cyclohexane containing methanol has been reinvestigated.

Introduction

Since the seminal publication by Sommer and co-workers in 1972 on the photolysis of methylpentaphenyldisilane (1) in solution,[1] the photochemistry of aryldisilanes has been the subject of intense investigation.[2–10] Irradiation of 1 in cyclohexane solution containing methanol-*d* at 55 °C was reported to yield products consistent with the formation of 1,1-diphenylsilene (2) in ca. 60% chemical yield (eq 1).[1] The formation of 2 and 3 was

$$Ph_3Si\text{---}SiPh_2 \xrightarrow[C_6H_{12}/MeOD]{h\nu} \left[Ph_2Si\text{==}CH_2 \right] + Ph_3SiH \longrightarrow$$
$$\underset{CH_3}{|}$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2} \qquad\qquad \mathbf{3}$$

$$Ph_2Si\text{---}CH_2D + Ph_3SiH + Ph_3SiOMe + Ph_2MeSiH \qquad (1)$$
$$\underset{OMe}{|} \qquad\quad \mathbf{3} \qquad\qquad \mathbf{5} \qquad\qquad\quad \mathbf{6}$$
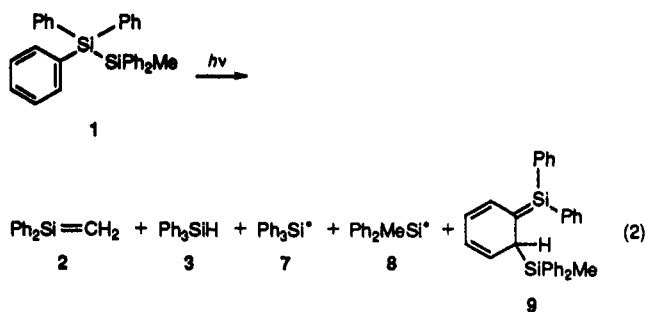$$\mathbf{4\text{-}d}$$

suggested to occur via concerted dehydrosilylation in the lowest excited singlet state of 1, but it was also recognized that these products are derivable from disproportionation

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.
(1) Boudjouk, P.; Roberts, J. R.; Golino, C. M.; Sommer, L. H. *J. Am. Chem. Soc.* 1972, *94*, 7926.
(2) Ishikawa, M. *Pure Appl. Chem.* 1978, *50*, 11.
(3) Sakurai, H. *J. Organomet. Chem.* 1980, *200*, 261.
(4) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* 1981, *19*, 51.
(5) Sakurai, H. In *Silicon Chemistry*; Corey, J. Y., Corey, E. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988; pp 163–172.
(6) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 965–1005.
(7) Shizuka, H.; Hiratsuka, H. *Res. Chem. Intermed.* 1992, *18*, 131.
(8) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* 1993, *115*, 3116.
(9) Braddock-Wilking, J.; Chiang, M. Y.; Gaspar, P. P. *Organometallics* 1993, *12*, 197.
(10) Ishikawa, M.; Kikuchi, M.; Kunai, A.; Takeuchi, T.; Tsukihara, T.; Kido, M. *Organometallics* 1993, *12*, 3474.

of triphenylsilyl and methyldiphenylsilyl radicals (7 and 8, respectively), which would be formed by photolysis of the Si–Si bond in 1.

We recently reported the results of a study of the photochemistry of 1 using nanosecond laser flash photolysis techniques, a study which was originally carried out with the intent of detecting silene 2 directly and investigating the kinetics of its reactions with various silene trapping agents.[11] As it turned out, though, 1 is unsuitable as a precursor of 2 for studies of this type; while there is no doubt that 2 is a major transient product of photolysis of 1 in solution, its absorptions are obscured by much stronger ones, which we assigned to the silyl radicals 7 and 8 and a 1,3,5-(1-sila)hexatriene derivative (9; see eq 2). We

$$Ph_2Si\text{==}CH_2 + Ph_3SiH + Ph_3Si^{\bullet} + Ph_2MeSi^{\bullet} + \qquad (2)$$
$$\mathbf{2} \qquad\qquad \mathbf{3} \qquad\quad \mathbf{7} \qquad\qquad \mathbf{8}$$
$$\mathbf{9}$$

have recently reported the UV absorption spectrum of 2 in fluid solution at room temperature[12] and verified that it occurs in the same spectral region as the relatively strong absorptions due to 7 and 8.

Products derived from 9 were not identified in the original study of Sommer and co-workers;[1] we have

(11) Sluggett, G. W.; Leigh, W. J. *J. Am. Chem. Soc.* 1992, *114*, 1195.
(12) Leigh, W. J.; Bradaric, C. J.; Sluggett, G. W. *J. Am. Chem. Soc.* 1993, *115*, 5332.

assumed that this is because the intermediate is formed in rather low yield,[11] and its trapping by methanol would be expected to yield a mixture of isomeric addition products.[13-18] These products might be difficult to detect by the methods employed in the original study.

The fact that irradiation of aryldisilanes in solution yields silyl radicals in addition to silenic species has been known for some time. Sakurai and co-workers first reported ESR evidence for their formation in the direct photolysis of pentamethylphenyldisilane (10) in hydro-

10
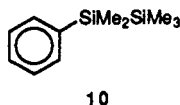
carbon solution[19] and suggested that they might play a crucial role in the formation of silenic products owing to disproportionation and recombination processes. This was later shown to be unlikely by Shizuka and co-workers, who demonstrated that the fluorescence lifetime of 10 in fluid solution at room temperature is identical with the rate of growth of the corresponding silatriene as measured using picosecond transient absorption methods.[20] In addition, we have recently shown that silyl radical formation is a triplet-derived process[21] and verified that the formation of silatrienes derives from an excited singlet state.[21,22]

The involvement of both excited singlet and triplet states in aryldisilane photolyses suggests that the relative yields of silyl radicals and silenic species might be manipulated if the quantum yield for the formation of aryldisilane triplets can be controlled. Indeed, this can be accomplished by triplet sensitization or quenching,[21] by varying the polarity of the solvent (polar solvents enhance intersystem crossing in these compounds[7]),[21,22] or by blocking the formation of silenic species through appropriate substitution.[23]

Since our initial laser flash photolysis study indicated that the photochemistry of 1 is in fact considerably more complex than had originally been reported, we felt it was important to investigate the photochemistry of this molecule under steady-state conditions in detail. In particular, we wished to determine the extent to which silyl free radicals contribute to the formation of 2 in the photolysis of this compound and quantify the partitioning between simple silene, 1,3,5-(1-sila)hexatriene, and silyl radicals which occurs upon photolysis of 2 under different conditions. Compound 1 seemed to be an ideal choice for studying the role of silyl radicals in the formal dehydrosilylation reaction, since this compound appeared to afford the highest chemical yields of simple silene of any aryldisilane that has yet been studied. In this paper, we

(13) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155.

(14) Ishikawa, M.; Oda, M.; Nishimura, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2795.

(15) Ishikawa, M.; Sakamoto, H. *J. Organomet. Chem.* **1991**, *414*, 1.

(16) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *117*, C58.

(17) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37.

(18) Leigh, W. J.; Sluggett, G. W., unpublished results.

(19) Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.

(20) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89.

(21) Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 7531.

(22) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.

(23) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1992**, *11*, 3731.
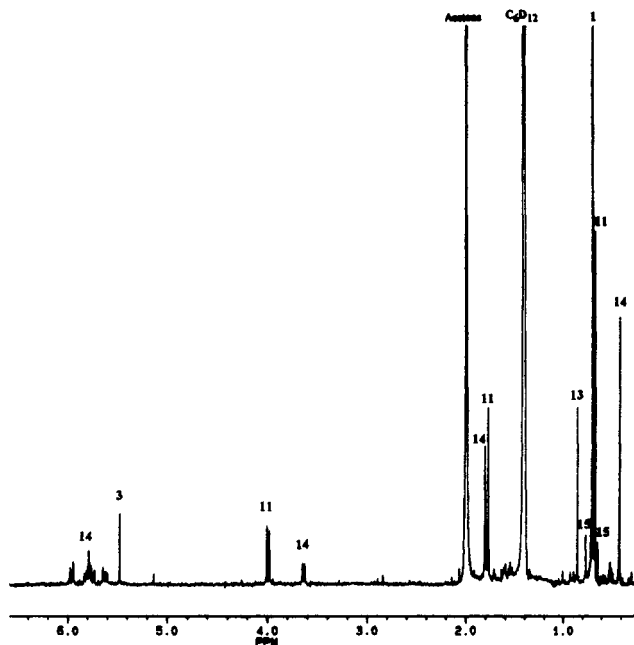
Figure 1. Partial ^{1}H NMR spectrum of the crude mixture from photolysis of a deoxygenated 0.02 M solution of 1 in cyclohexane-d_{12}, in the presence of 0.05 M acetone and 0.05 M chloroform at 23 °C to ca. 30% conversion. Resonances due to the various products are labeled in the spectra.

report the results of a study of the photochemistry of 1 in the presence of acetone and chloroform as silene and silyl radical traps, respectively, using steady-state and nanosecond laser flash photolysis methods. We also report the results of a brief reinvestigation of the photochemistry of this compound in the presence of methanol.

Results

Direct irradiation of deoxygenated cyclohexane or cyclohexane-d_{12} (C_6D_{12}) solutions of 1 (0.02 M) in the presence of acetone (0.05 M) and chloroform (0.05 M) yields the products shown in eq 3. Products 3 and 11–13 were
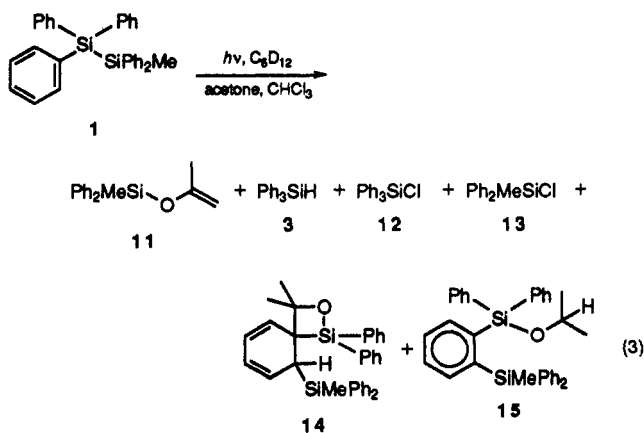
rigorously identified by gas chromatography (GC), by coinjection of the photolysate with authentic samples. Compounds 14 and 15 were tentatively identified from the ^{1}H NMR spectrum of the crude photolysis mixture after ~30% conversion, which is shown in Figure 1. Our assignment of 14 as a 1,2-siloxetane derivative is based on the presence of the prominent absorptions in the δ 5.6–6 range, the doublet at δ 3.61, and other signals in the δ 1.2–2.1 range and at δ 0.41. These features are similar to

Table 1. Product Yields from Photolysis of Methylpentaphenyldisilane (1) in Various Solvents in the Presence of 0.05 M Acetone and Various Additives[a]

solvent	additive	3 (%)	11 (%)	13 (%)[b]	14 (%)
C_6D_{12}	none	29	29		37[c]
C_6D_{12}	$CHCl_3$ (0.05 M)	32	34	17	34[c]
C_6D_{12}	$CHCl_3$ (0.5 M)	30	37	23	e
C_6D_{12}	CCl_4 (1.0 M)	5		88	
C_6D_{12}	$CHCl_3$ (0.2 M) trans-piperylene (0.1 M)	38	38	8	38
CD_3CN	$CHCl_3$ (0.05 M)	7		66[d]	
$CDCl_3$	none	13		79	
$CDCl_3$	chloranil			65	

[a] Determined by ^{1}H NMR spectroscopy, relative to consumed 1, after 30–50% conversion. Errors are ca. 10%. [b] The photolysate also contained 12, in similar yield to 13, as estimated by GC. [c] The photolysate also contained small amounts (ca. 5%) of 15. [d] Yield is the sum of that of 13 and the corresponding silanol. [e] Not determined.

those observed in the NMR spectra of the crude mixtures from photolysis of a number of other aryldisilanes in the presence of acetone.[21,22] Compound 15 was tentatively identified on the basis of the minor resonances appearing on either side of the singlets at δ ~0.7 due to 1 and 11. Examination of the spectrum of the same mixture in $CDCl_3$ (after evaporation of C_6D_{12}) reveals that the higher field signal is part of a doublet, which is overlapped with the singlet due to 11 in the C_6D_{12} spectrum. The mass spectral fragmentation pattern of one of the minor products observable by GC and GC/MS is also consistent with a product of this type.[22] Product yields were determined after ~30% conversion by a combination of NMR and GC analyses and are collected in Table 1. The mass balance was determined to be 90–95% after ~30% conversion of 1. The formation of 1,1,2,2-tetrachloroethane was also evident by NMR spectroscopy and GC/MS analysis.

Photolysis of a 0.02 M solution of 1 in C_6D_{12} containing acetone (0.05 M), but without added chloroform, afforded 3, 11, and 14 in chemical yields similar to those observed for the photolysis in the presence of the halocarbon. Small amounts of methyldiphenylsilane (6) were also detected in the photolysate, in a chemical yield of ca. 2%. The material balance was estimated to be ca. 65% after ~30% conversion. The quantum yield for disappearance of 1 in cyclohexane-d_{12} containing 0.05 M acetone was estimated to be ϕ_{dis} = 0.33 ± 0.05 using the photolysis of 1,2-di-tert-butyl-1,1,2,2-tetraphenyldisilane in chloroform as a secondary actinometer.[23] The same value was obtained for the photolysis of 1 in cyclohexane-d_{12} containing both acetone (0.05 M) and chloroform (0.05 M).

As we have also found to be the case for other aryldisilanes,[21,22] photolysis in acetonitrile solution results in substantial increases in the yields of silyl radical derived products compared to the yields in hydrocarbon solution. Thus, photolysis of a deoxygenated 0.005 M solution of 1 in acetonitrile-d_3 containing acetone and chloroform under conditions similar to those used above yields 12 and 13 as the main products, according to ^{1}H NMR, GC, and GC/MS analysis of the crude photolysate after ca. 30% conversion. The NMR spectrum showed evidence for the formation of at least two other unidentifiable products, in yields of <10%. While triphenylsilane (3) was clearly identifiable by NMR and GC analyses, none of the silyl enol ether 11 could be detected in the photolysate after ~30% conversion of 1. Product yields from this experiment are included in Table 1.
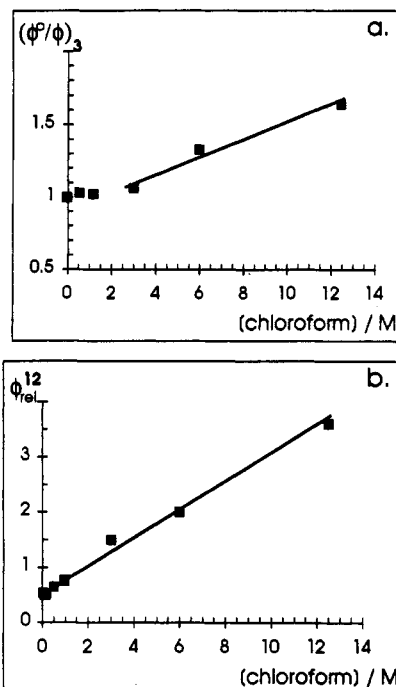

Figure 2. Photolysis of deoxygenated cyclohexane solutions of 1 (0.01 M) containing acetone (0.05 M) and varying concentrations of chloroform: (a) Stern–Volmer plot for product 3; (b) plot of relative quantum yield for formation of 12 vs chloroform concentration.

A triplet quenching experiment was carried out in order to determine whether silyl chlorides 12 and 13 arise from chloroform trapping of triplet-derived silyl radicals, as we have found to be the case in the photolyses of other aryldisilanes related to 1.[21] Thus, a 0.02 M C_6D_{12} solution of 1 containing acetone (0.05 M), chloroform (0.2 M), and trans-piperylene (0.1 M) was irradiated under conditions similar to those employed above. This results in substantial reductions in the yields of chlorosilanes 12 and 13 but has no effect on the yields of 3 and 11, compared to the photolyses in the absence of the diene. Product yields for these experiments are also collected in Table 1.

In order to verify that chloroform acts only as a trap for silyl radicals in the experiments described above and does not alter the course of the primary photochemistry of 1, merry-go-round photolyses of deoxygenated 0.01 M solutions of 1 in cyclohexane containing acetone (0.05 M) and varying amounts of chloroform between 0.02 and 12.5 M (i.e., neat chloroform) were carried out. GC analysis of the photolysates after ca. 10% conversion verified that the quantum yields for formation of 3 and 11–13 are approximately independent of chloroform concentration over the range 0.02–1 M.

At chloroform concentrations above 1 M, however, the apparent yield of 11 drops to zero precipitously while those of 12 and 13 increase monotonically. The quantum yield for formation of triphenylsilane (3) also decreases with increasing chloroform concentration above 0.5 M but continues to be of significant magnitude even in neat chloroform. Figure 2a shows a Stern–Volmer plot detailing the reduction in the yield of 3 (after ca. 10% conversion of 1) with increasing chloroform concentration, along with a plot of the relative quantum yield for formation of silyl chloride 12 versus chloroform concentration (Figure 2b). Least-squares analysis of the Stern–Volmer plot over the 1–12.5 M range yields a $k_q\tau$ value of 0.06 ± 0.02. The
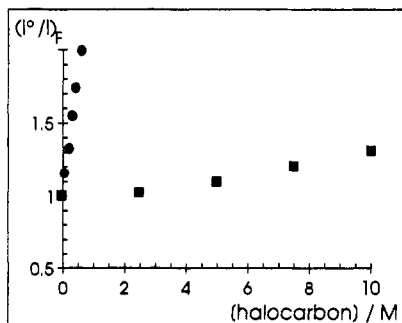
Figure 3. Stern–Volmer plots for quenching of the fluorescence of 1 in deoxygenated cyclohexane solution at 23 °C by chloroform (■) and carbon tetrachloride (●).

quantum yield for disappearance of 1 upon photolysis in CDCl₃ was estimated to be 0.41 ± 0.07 by 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane actinometry (*vide supra*). The triphenylsilane (3) produced in this experiment contained <5% deuterium, from ^{1}H NMR and GC/MS analysis of the crude photolysate after 30% conversion.

The most likely explanation for the results obtained for the photolysis of 1 in the presence of high concentrations of chloroform is that the lowest excited singlet state of 1 is quenched directly by the halocarbon under these conditions. This can be verified by fluorescence quenching experiments, since 1 exhibits weak but readily detectable fluorescence emission in deoxygenated cyclohexane solution at room temperature.[11] Indeed, the intensity of the fluorescence from 1 is unaffected upon addition of small amounts of chloroform (up to ca. 1 M) to the solution but is reduced in intensity with the addition of larger quantities of the halocarbon. The position and shape of the emission band are unaffected by the addition of chloroform in concentrations up to 12.5 M (the neat liquid), however. A Stern–Volmer plot for the quenching of the fluorescence of 1 by chloroform over the 2–12.5 M concentration range (Figure 3) has a slope of $k_q\tau = 0.04 \pm 0.02$ M⁻¹, in satisfactory agreement with the $k_q\tau$ value determined from the product quenching studies described earlier.

A few additional experiments were carried out in an attempt to determine the mechanism of excited singlet state quenching by chloroform. Dichloromethane does not quench the fluorescence from 1 detectably up to 15 M halocarbon, while quenching by carbon tetrachloride follows linear Stern–Volmer behavior. The $k_q\tau$ value was determined to be 1.6 ± 0.2 from the slope of the Stern–Volmer plot (Figure 3). Steady-state photolysis of a 0.02 M solution of 1 in C₆D₁₂ containing carbon tetrachloride (1 M) results in the formation of 3, 12, 13, and hexachloroethane as the only detectable products by ^{1}H NMR and GC analysis after ca. 60% conversion. Finally, irradiation (350 nm) of a deoxygenated chloroform solution containing 1 (0.05 M) and chloranil (~0.001 M) as an electron-transfer photosensitizer affords the chlorosilanes 12 and 13 (in roughly equal yields) as the only silicon-containing products detectable by GC. The ^{1}H NMR spectrum indicated the formation of one minor product in ~10% yield, but it was not identified. The material balance was estimated to be ~75% after 50% conversion of 1.

The quantum yield for fluorescence of 1 in acetonitrile relative to that in cyclohexane was estimated to be ϕ_F(MeCN)/ϕ_F(C₆H₁₂) = 0.74 by comparison of spectra recorded with optically matched solutions of 1 in the two solvents.

Transient UV absorption spectra were recorded by nanosecond laser flash photolysis (NLFP) techniques, in an attempt to obtain isolated spectra of each of the reactive intermediates whose involvement in the photochemistry of 1 is suggested by the steady-state photolysis results described above. These experiments employed a KrF excimer laser (248 nm, 16 ns, 80–120 mJ) and flowed, 1.8 × 10⁻⁴ M solutions of 1 in isooctane solution containing various silyl radical and silene quenchers; spectra were recorded 100–500 ns after the laser pulse in each case and are shown in Figure 4. All four spectra showed evidence for long-lived residual absorption by a product which absorbs at wavelengths <320 nm but whose lifetime is unaffected by addition of oxygen, acetone, methanol, or chloroform to the solution. Figure 4a shows the spectrum recorded under deoxygenated conditions, where 2, 7, 8, and 9 all have lifetimes in excess of 1 μs.[11] The other three spectra were recorded using solutions containing 0.1 M chloroform + 0.01 M methanol (Figure 4b), ~0.015 M oxygen (Figure 4c), and 0.06 M acetone (Figure 4d); they were all corrected by subtraction of the spectrum recorded at times longer than those required for the complete decay of the other transients present in each case. Figure 5 shows representative transient decay traces, recorded at 325 and 490 nm using a partially oxygenated solution of 1 in cyclohexane containing 0.05 M chloroform.

The rate constant for the reaction of 1,1-diphenylsilene (2) with chloroform was estimated to be <10⁴ M⁻¹ s⁻¹, from the lifetime of 2 (generated by laser flash photolysis of 1,1,2-triphenylsilacyclobutane[12]) in isooctane solution containing 1.6 M chloroform. Similarly, the rate constant for reaction of silatriene 9 with chloroform is estimated to be <10⁶ M⁻¹ s⁻¹, from the lifetime of the transient formed by NLFP of a deoxygenated solution of 1 in isooctane containing 1 M chloroform. The rate constant for reaction of *tert*-butyldiphenylsilyl radicals with *trans*-piperylene was determined to be (6.2 ± 0.4) × 10⁷ M⁻¹ s⁻¹, using the previously reported procedure for generation of this radical in isooctane solution.[23]

Finally, the photochemistry of 1 in cyclohexane containing methanol was briefly reinvestigated. Photolysis of a 0.02 M solution of 1 in cyclohexane-d_{12} containing methanol (0.05 M) at 23 °C afforded a complex mixture of at least nine products, according to ^{1}H NMR spectroscopy. The spectrum, recorded after ~50% conversion, is shown in Figure 6. Four of these products could be identified by NMR and GC/MS comparison to authentic samples: 3 (43%), 4 (34%), 5 (3%), and 6 (4%). The other five products were characterized by NMR absorptions in the vinylic, methoxy, and silylmethyl regions of the spectrum and can thus be assigned to the various isomeric addition products (16) of the alcohol to silatriene

16
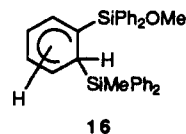
9. The two most important of these were formed in yields of 16 and 12%, based on integration of the methoxy and silylmethyl peaks in the NMR spectrum. The other three minor products were formed in a combined yield of about 10%. Capillary GC and GC/MS analysis of the crude photolysis mixture also shows evidence for the formation of at least four products which elute after
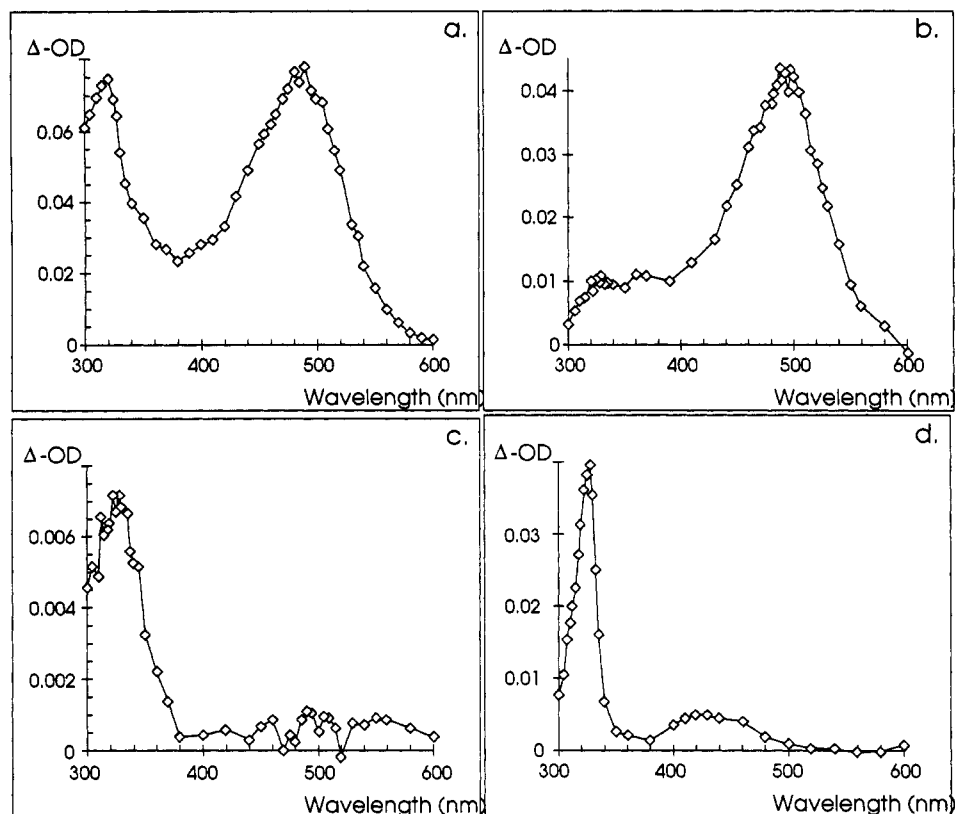
Figure 4. Transient UV absorption spectra, recorded by nanosecond laser flash photolysis of 1.8 × 10⁻⁴ M solutions of 1 in isooctane under the following conditions: (a) deoxygenated solution; (b) deoxygenated solution containing 0.1 M chloroform and 0.01 M methanol; (c) oxygenated solution; (d) deoxygenated solution containing 0.06 M acetone. The spectra were recorded 100–500 ns after 248-nm laser excitation and were corrected for minor, long-lived residual absorption at λ < 320 nm.
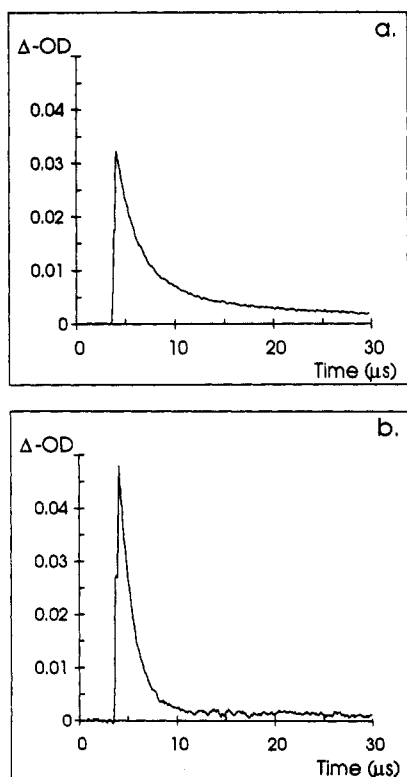

Figure 5. Representative transient decay traces, recorded using partially deoxygenated isooctane solutions of 1 containing 0.05 M chloroform, at monitoring wavelengths of (a) 325 nm and (b) 490 nm.

1 and show molecular ions and fragmentation patterns consistent with **16**. The adducts elute as a single peak
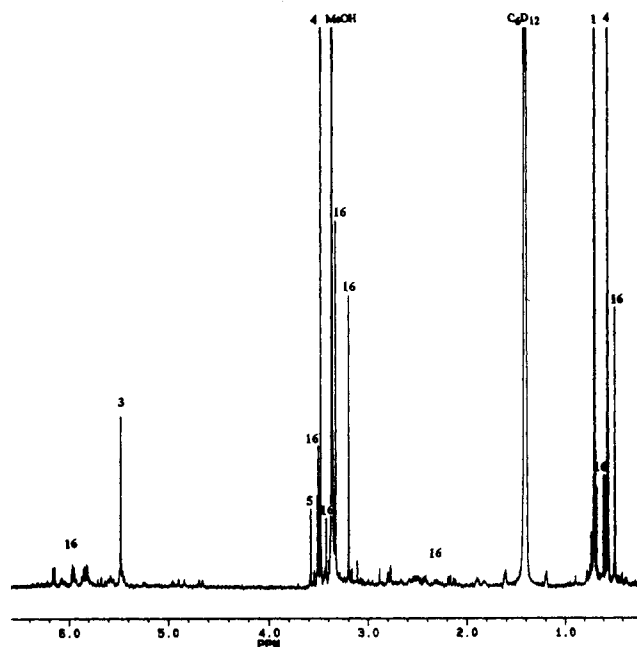

Figure 6. ¹H NMR spectrum of the crude mixture from photolysis of a deoxygenated 0.02 M solution of 1 in cyclohexane-d_{12} in the presence of 0.05 M methanol at 23 °C to ca. 50% conversion. Resonances due to the various products are labeled in the spectra.

under megabore capillary or packed-column GC conditions, as is common for silatriene–alcohol adducts of this type.[13–15] Photolysis of a similar solution at 55–60 °C to ~30% conversion yields the same products in yields similar to those obtained in the room-temperature photolysis. Heating the crude room-temperature photolysis

mixture at 100 °C for 16 h resulted in no apparent change in the product distribution.

Discussion

Photolysis of 1 in hydrocarbon solution in the presence of acetone leads to the formation of three major products—the silyl enol ether 11 from ene addition of the carbonyl compound to 2, triphenylsilane (3), and a compound which has been tentatively identified as the 1,2-siloxetane 14 on the basis of ^{1}H NMR spectroscopy. As has been noted previously for other aryldisilane-derived 1,2-siloxetanes, the last compound is thermally and hydrolytically unstable; we have not yet been successful in isolating any of those derived from the reactions of acetone with a number of aryldisilanes.[21,22] The compound does not survive our GC conditions; therefore, its formation is evident only on the basis of NMR spectroscopy using the crude photolysis mixtures. The isolation and full characterization of a 1,2-siloxetane derived from carbonyl addition to an aryldisilane-derived silatriene are the subjects of continued effort in our laboratory.

It is noteworthy that the silyl ether 15 is formed in extremely low yield in the reaction of silatriene 9 with acetone. Silyl ethers are normally the major products of this reaction[21,22] and are stable enough that they can be readily isolated and characterized. We have previously formalized the mechanism of this reaction in terms of a stepwise process involving the initial formation of a biradical intermediate and explained the variation in the relative yields of siloxetanes and silyl ethers obtained in the reactions of a series of aryldisilane-derived silatrienes as due to sterically induced variations in the relative rates of collapse of the intermediate to the two products (see eq 4).[22] The predominant formation of siloxetane 14 in the present case is consistent with this explanation.
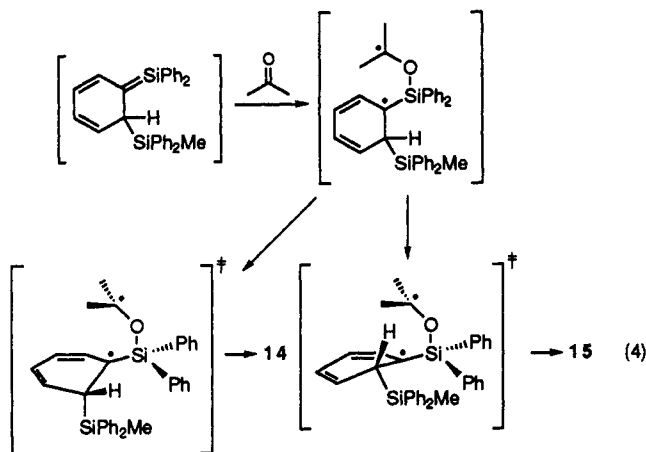
It has been previously shown that silyl radicals and silenes formed in the photolysis of aryldisilanes can be specifically trapped by irradiating solutions of the disilane in the presence of both chloroform and acetone.[21,22] This procedure is successful because chloroform reacts with rate constants in the 10^8 M^{-1} s^{-1} range with silyl radicals but only sluggishly with silenes and silatrienes, while the opposite is true for acetone.[11,21-26] Furthermore, neither

Table 2. Rate Constants (in Units of M^{-1} s^{-1}) for Quenching of 1,1-Diphenylsilene (2), Silatriene 9, and Triphenylsilyl Radicals (7) by Acetone and Chloroform in Isooctane Solution at 23 °C

quencher	Ph$_2$Si=CH$_2$ (2)	9	Ph$_3$Si$^\bullet$ (7)
acetone[a]	$(3.3 \pm 0.2) \times 10^8$	$(5.4 \pm 0.3) \times 10^8$	$<10^5$
chloroform[b]	$<10^4$	$<10^6$	1.1×10^8

[a] Data from ref 11, 12, and 23. [b] Data from this work and ref 26.

trapping agent interacts with the lowest excited singlet state of 1 at the concentrations employed in these experiments; therefore, their roles are confined to simple trapping of the transient intermediates produced upon absorption of light by the disilane. Table 2 lists rate constants for the reactions of silenes 2 and 9 and triphenylsilyl radicals (7) with these two reagents in hydrocarbon solution at room temperature.

From the product distributions observed in the photolysis of cyclohexane solutions of 1 containing acetone and chloroform at low concentrations, it is clear that silyl radical and silatriene formation both compete significantly with formation of 1,1-diphenylsilene (2) in nonpolar solvents. The three reactive intermediates are formed in yields of about 20, 42, and 35 %, respectively, as estimated from the chemical yields of 12/13, 14 + 15, and 3/11 obtained in the steady-state photolysis experiments. This conclusion is supported qualitatively by the time-resolved UV absorption spectra recorded after laser photolysis of solutions of 1 under various conditions (Figure 4).

The spectrum of the deoxygenated solution (Figure 4a) is the sum of those due to silatriene 9, silene 2, and silyl radicals 7 and 8. It is similar to that reported previously in acetonitrile solution,[11] except that the absorption band in the 300-340-nm region is broader and weaker in the nonpolar solvent owing to the difference in the relative yield of silyl radicals and silene 2 compared to that obtained in acetonitrile solution under these conditions. Transient decay at 325 nm (where 2, 7, and 8 absorb) and at 490 nm (where 9 absorbs) follow mixed first- and second-order kinetics, with estimated lifetimes in excess of 5 μs.

Selective quenching experiments allow the direct detection of each individual transient species produced upon direct excitation of the disilane. For example, addition of 0.06 M acetone to the deoxygenated solution renders silatriene 9 and silene 2 undetectable within the time resolution of our system, resulting in a transient spectrum consisting of absorptions due only to silyl radicals 7 and 8 (Figure 4d). Excellent agreement is observed between the spectrum recorded under these conditions and the published absorption spectra of these radicals.[11,27] Addition of chloroform to partially deoxygenated solutions of 1 quenches silyl radicals 7 and 8 specifically, resulting in a spectrum which consists of combined absorptions due to 1,1-diphenylsilene (2; λ_{max} 325 nm[12]) and silatriene 9 (λ_{max} 490 nm). The spectrum is not shown, but Figure 5 shows transient decay traces recorded (on the same time scale) at the two absorption maxima, from NLFP of a partially oxygenated isooctane solution of 1 containing 0.05 M chloroform. Both transients decay with mixed first- and second-order kinetics under these conditions, but with different lifetimes ($\tau_2 \approx 5 \mu$s; $\tau_9 = 1.5 \mu$s). Rigorous deoxygenation of the solution causes the lifetime of 9 to

(24) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119.

(25) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

(26) Ito, O.; Hoteiya, K.; Watanabe, A.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 962.

(27) Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

increase to >15 μs but has no effect on that of **2**. The decay of the absorptions due to **2** can be selectively enhanced by addition of small amounts of methanol to the chloroform/cyclohexane solution; methanol quenches both **2** and **9**, but the reactivity of the simpler silene is greater.[28] The result is a spectrum (Figure 4c) due only to silatriene **9**. Oxygen is relatively unreactive toward 1,1-diphenylsilene (**2**)[12] but quenches silyl radicals and silatrienes at close to the diffusion-controlled rate. Thus, oxygen saturation of the solution results in selective quenching of the silyl radicals and silatriene **9** and yields a transient spectrum assignable to the simple silene. The spectrum observed (Figure 4c) is relatively weak but matches that previously reported for **2**.[12]

The lack of variation in the yields of silyl enol ether **11** and triphenylsilane (**3**) in the presence of small amounts of chloroform (<1 M) indicates that disproportionation of free silyl radicals does not contribute to the formation of these products to any significant extent. Presumably, the fate of **7** and **8** in the absence of added halocarbon is the formation of higher molecular weight oligomers owing to addition reactions with the disilane. This is consistent with the lower material balance observed for the photolyses in the absence of chloroform compared to those in the presence of the halocarbon. Furthermore, the reaction of arylsilyl radicals with their silane or disilane precursors has been reported previously;[27] this is rapid enough that it usually results in clean pseudo-first-order radical decay kinetics in time-resolved experiments where the radicals are detected directly in the absence of other quenchers.[11,23,27]

As was reported previously for 1,1,1-trimethyl-2,2,2-triphenyldisilane (**17**) and 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (**18**),[21] the formation of silyl radicals in the photolysis of **1** can be assigned to a reaction of the disilane triplet state. The triplet-state assignment is

$$Ph_3Si\text{—}SiMe_3 \qquad Ph_2{}^tBuSi\text{—}Si^tBuPh_2$$
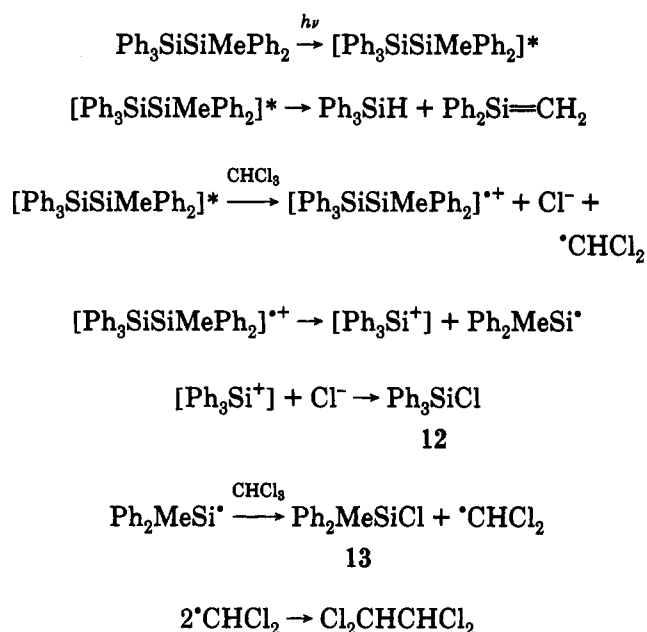$$\textbf{17} \qquad\qquad \textbf{18}$$
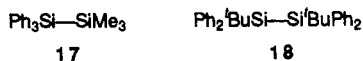
supported by the observation of substantial reductions in the yields of radical-derived products (**12** and **13**) upon photolysis of the disilane in the presence of *trans*-piperylene as a triplet quencher. While the diene reacts with silyl radicals in addition to quenching the triplet state of the disilane, the concentration of chloroform employed in this experiment is high enough to ensure that at least 90% of the radicals are trapped as the corresponding chlorosilanes. The presence of the diene has no effect on the yields of **3**, **11**, and **14**, verifying that these products are not radical-derived. This experiment allows the further conclusion that **2** and **3** arise from reaction of an excited singlet state of **1**, presumably via a concerted dehydrosilylation mechanism.

In the presence of high concentrations of chloroform, the quantum yield for formation of **11** drops precipitously, while those for **12** and **13** increase linearly (Figure 2). We attribute this result to direct electron-transfer quenching of the lowest excited singlet state of the disilane by the halocarbon. The initial products of this process are expected to be the disilane radical cation, chloride ion, and dichloromethyl radical as a result of dissociative electron transfer to the halocarbon from the excited singlet state of **1**. Cleavage of the disilane radical cation to yield

the triphenylsilyl cation and methyldiphenylsilyl radical[29-31] would then yield the observed products through reaction of the cation with chloride ion (to yield **12**) and abstraction of chlorine from the solvent by the radical (to yield **13**). It is interesting to note that this mechanism for the formation of **12** and **13** (Scheme 1) is operationally indistinguishable from one involving triplet-derived Si–Si bond homolysis followed by abstraction of chlorine from the halocarbon by the two radicals. That generation of the radical cation of **1** in chloroform ultimately results in the formation of **12** and **13** is confirmed by the results of the chloranil-sensitized photolysis. In this case, chloranil is the light absorber and is quenched via electron transfer from the disilane. The role of chloroform in this reaction can be most simply envisioned as that of a trap for silyl radicals produced by cleavage of the disilane radical cation, although a more complex role is certainly possible.[32] Presumably, the silyl cation which is also produced in the dissociation of the radical cation is reduced to the radical by the chloranil radical anion.

Scheme 1

$$Ph_3SiSiMePh_2 \xrightarrow{h\nu} [Ph_3SiSiMePh_2]^*$$

$$[Ph_3SiSiMePh_2]^* \rightarrow Ph_3SiH + Ph_2Si\text{=}CH_2$$

$$[Ph_3SiSiMePh_2]^* \xrightarrow{CHCl_3} [Ph_3SiSiMePh_2]^{\bullet+} + Cl^- + {}^{\bullet}CHCl_2$$

$$[Ph_3SiSiMePh_2]^{\bullet+} \rightarrow [Ph_3Si^+] + Ph_2MeSi^{\bullet}$$

$$[Ph_3Si^+] + Cl^- \rightarrow Ph_3SiCl$$
$$\textbf{12}$$

$$Ph_2MeSi^{\bullet} \xrightarrow{CHCl_3} Ph_2MeSiCl + {}^{\bullet}CHCl_2$$
$$\textbf{13}$$

$$2{}^{\bullet}CHCl_2 \rightarrow Cl_2CHCHCl_2$$

The persistent formation of triphenylsilane (**3**) even at high chloroform concentrations presumably indicates that quenching of the disilane excited singlet state by the halocarbon is not sufficiently rapid to completely overshadow dehydrosilylation. However, one would also expect to observe the formation of silyl enol ether **11** at high concentrations of chloroform if **3** is formed by dehydrosilylation under these conditions. The absence of **11** in the photolysis mixtures containing high chloroform concentrations is presumably the result of acid-catalyzed or secondary photochemical decomposition. While we have no direct evidence to support this conclusion, it is clear that, at lower halocarbon concentrations, the yields of **3** and **11** are identical within experimental error and thus

---

(28) Leigh, W. J.; Banisch, J. H., unpublished results.

(29) Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327.

(30) Igarashi, M.; Ueda, T.; Wakasa, M.; Sakaguchi, Y. *J. Organomet. Chem.* **1991**, *421*, 9.

(31) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781.

(32) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.

their formation is coupled; furthermore, there is reasonable agreement between the $k_q\tau$ values measured by monitoring the quenching of the formation of 3 and the fluorescence from 1 by chloroform. Assuming that the excited singlet state lifetime of 1 is similar to that reported by Shizuka and co-workers for pentamethylphenyldisilane (10; $\tau \approx 35$ ps), a value of ca. 10^9 M^{-1} s^{-1} can be estimated for the quenching rate constant k_q.

Unfortunately, it is not possible to calculate the expected free energy for electron transfer from the excited singlet state of 1 to chloroform using the Weller equation. While the standard oxidation potential of 1 has been estimated to be ca. 1.7 V *vs* SCE,[33] the standard reduction potential of chloroform cannot be defined because the reduction is dissociative.[34,35] Thus, the Weller equation, which incorporates the standard electrode potentials of the redox pair for the determination of the free energy of excited-state electron transfer, is inapplicable.

The proposed electron-transfer mechanism for the reaction of excited 1 with chloroform is supported by the results of fluorescence quenching experiments with dichloromethane and carbon tetrachloride, which are poorer and better oxidants, respectively, than chloroform.[36] Thus, dichloromethane does not quench the fluorescence of 1 perceptibly even as the neat halocarbon, while carbon tetrachloride ($k_q\tau = 1.6 \pm 0.2$ M^{-1}) is over 20 times more efficient than chloroform. This is also reflected in steady-state photolysis experiments; photolysis of a cyclohexane solution of 1 containing 1 M carbon tetrachloride yields only 3, 12, and 13, with the yield of triphenylsilane (3) reduced substantially relative to that obtained in the photolysis with 1 M chloroform under the same conditions.

These results suggest that the product distributions observed in the steady-state photolysis of acetonitrile solutions of aryldisilanes in the presence of low concentrations of chloroform should be interpreted with care. While we have interpreted them as indicating substantially increased yields of silyl radicals owing to enhanced triplet reactivity, it is possible that direct electron-transfer quenching contributes to chlorosilane formation to some extent under these conditions, even at the low concentrations of chloroform employed in these experiments. Thus, we consider the quantitative aspects of these experiments to be of lower reliability than those carried out in hydrocarbon solution. The higher yields of radicals obtained in acetonitrile are confirmed in nanosecond laser flash photolysis experiments, however (in the absence of *any* trapping agents);[11,21,22] therefore, the general conclusion that photolysis of aryldisilanes in polar solvents affords considerably higher yields of the corresponding silyl radicals than are obtained in hydrocarbon solvents is sound.

Finally, we have briefly reinvestigated the photochemistry of 1 in the presence of methanol, in order to resolve a few apparent discrepancies between the product distributions observed in the present work and those reported previously by Sommer and co-workers.[1] We were particularly intrigued by their observation of significant yields of methoxytriphenylsilane (5) and methyldiphenylsilane (6) in the photolysis of 1 in cyclohexane at 55 °C in the

presence of methanol-*d*, since it is unlikely that these products arise from reaction of the corresponding silyl radicals with the alcohol,[37,38] as they suggested.

Indeed, the ^{1}H NMR spectrum of the crude mixture from photolysis of a cyclohexane solution of 1 containing 0.05 M methanol (at 23 °C) shows compelling evidence for the formation of products of addition of the alcohol to silatriene 9 (Figure 6). The combined yield of these products is about 40%, in good agreement with the combined yields of silatriene-derived products 14 and 15 from the photolysis in the presence of acetone. Interestingly, 5 and 6 are formed in yields of less than 5% each in the photolysis of 1 at room temperature. While we do not fully understand the apparent discrepancy between the present results and those reported previously by Sommer and co-workers,[1] we note that the experimental conditions employed in the original study were not completely specified. It has been shown that photolysis of aryldisilanes in the presence of very high concentrations of alcohols results in direct photosolvolysis and quenching of the formation of silatrienes.[5,8] The conditions employed in our experiments are such that the presence of the alcohol should have no effect on the primary product distribution from photolysis of 1.

Summary and Conclusions

The photochemistry of methylpentaphenyldisilane (1) in cyclohexane solution is considerably more complex than previous reports suggest. Photolysis of cyclohexane solutions of 1 containing small amounts of chloroform and acetone affords products consistent with the formation of the corresponding silyl radicals (7 and 8), 1,1-diphenylsilene (2), and the silatriene (9) in yields of ca. 20, 35, and 42% respectively. The roughly equal yields of 2 and 9 obtained in hydrocarbon solution under these conditions has been confirmed in experiments using methanol as the silene trap.

Radical formation is derived from the disilane triplet state and can thus be suppressed by carrying out the photolysis in the presence of triplet quenchers. Even in the absence of silyl radical trapping agents, silenic products do not result from radical disproportionation and recombination processes to any detectable extent; our results suggest that they are formed by concerted processes in the excited singlet state manifold of the disilane. Individual transient UV absorption spectra of the three types of reactive intermediates formed in the photolysis of 1 can be obtained in flash photolysis experiments using selective quenching techniques.

The yields of silyl radical derived products from direct aryldisilane photolyses are enhanced considerably in polar solvents (probably due to enhanced intersystem crossing) or in the presence of electron acceptors such as chloroform (at high concentrations) or carbon tetrachloride. The same products are observed in sensitized irradiations using chloranil as the electron-transfer photosensitizer.

Experimental Section

^{1}H NMR spectra were recorded on Bruker AC200, AC300, and AM500 spectrometers. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, an HP-1 megabore capillary column (5 m × 0.53 mm; Hewlett-Packard, Inc.) with

(33) Workentin, M. S., unpublished results.
(34) Andrieux, C. P.; Le Gorande, A.; Saveant, J.-M. *J. Am. Chem. Soc.* 1992, *114*, 6892.
(35) Saveant, J.-M. *Adv. Phys. Org. Chem.* 1990, *26*, 1.
(36) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; pp 201–244.

(37) Jackson, R. A. *Adv. Free-Radical Chem.* 1969, *3*, 231.
(38) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 741–808.

a conventional (heated) injector, and Hewlett-Packard 3396A integrator. 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 (12 m × 0.2 mm; Chromatographic Specialties, Inc.). UV absorption spectra were recorded on a Hewlett-Packard 8451 UV spectrometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter, which was interfaced to an IBM PS/2 Model 30 microcomputer and controlled with Perkin-Elmer software. Melting points were determined using a Mettler FP82 hot stage (controlled by a Mettler FP80 central processor) mounted on an Olympus BH-2 microscope and are uncorrected.

Cyclohexane (BDH Omnisolv), 2,2,4-trimethylpentane (isooctane; Baker HPLC), triphenylsilyl chloride (Aldrich), methyldiphenylsilyl chloride (Aldrich), methyldiphenylsilane (Aldrich), triphenylsilane (Aldrich), and *trans*-piperylene (Aldrich) were all used as received from the suppliers. Methoxytriphenylsilane (5) and methoxymethyldiphenylsilane (4) were prepared from the corresponding chlorosilanes.[39,40] Acetonitrile (BDH Omnisolv) was distilled under nitrogen after refluxing over calcium hydride for several days. Acetone (Baker Reagent), chloroform (BDH Omnisolv), and carbon tetrachloride (Matheson, Coleman and Bell Spectrograde) were distilled from potassium carbonate and stored over activated molecular sieves (4 Å). Acetonitrile-d_3 and cyclohexane-d_{12} were used as received from Isotec, Inc. Chloranil (Aldrich) was recrystallized twice from ethanol.

Methylpentaphenyldisilane was prepared by the method of Gilman and Lichtenwalter[41] and was recrystallized three times from ethanol (mp 146–148 °C; lit.[41] mp 148–149 °C).

Steady-state photolysis experiments were carried out in a Rayonet photochemical reactor equipped with a merry-go-round and 6–12 RPR-254 (254 nm), RPR-300 (300 nm), or RPR-350 (350 nm) lamps. Experiments in which the disilane was irradiated directly employed the 254-nm lamps, except for those carried out in the presence of *trans*-piperylene or carbon tetrachloride, which employed the 300-nm lamps. The chloranil-sensitized photolysis employed 350-nm lamps and a Pyrex filter. Photolysis solutions were contained in 5 × 75 mm quartz tubes or 5-mm quartz NMR tubes, which were sealed with rubber septa and deoxygenated prior to photolysis with a stream of dry nitrogen.

Photoproducts 3 and 11–13 were identified by GC coinjection with authentic samples.[12] Siloxetane 14 was tentatively identified by ¹H NMR spectroscopy using the crude photolysate, after evaporation of solvent and excess acetone and redissolution in deuteriochloroform: ¹H NMR (CDCl₃) δ 0.41 (s, 3H), 1.79 (s, 3H), 2.08 (s, 3H), 3.61 (d, J = 6.1 Hz, 1H), 5.6–6.0 (m, 4H). Silyl ether 15 was tentatively identified on the basis of the presence of the following signals in the ¹H NMR spectrum: ¹H NMR (CDCl₃) δ 0.61 (d, J = 6.1 Hz, 6H), 0.79 (s, 3H), 3.92 (sept, J = 6.1 Hz, 1H). GC/MS analysis revealed a minor product eluting after 1. This peak is assigned to 15 on the basis of similarities

of its mass spectral fragmentation pattern to those of the analogous acetone adducts with other aryldisilane-derived silatrienes:[22,42] *m/e* (*I*) 514 (1), 499 (2), 457 (4), 437 (6), 395 (23), 379 (3), 317 (100), 257 (18), 199 (28), 105 (7), 77 (4).

Photolysis of a deoxygenated 0.02 M solution of 1 in C₆D₁₂ containing methanol (0.05 M) at 23 °C was monitored by ¹H NMR spectroscopy. The spectrum of the crude photolysis mixture after *ca.* 50% conversion is shown in Figure 6. GC/MS analysis of the mixture verified the formation of 3, 4, 5, and 6 and showed four other isomeric products which elute after 1 on the capillary column. The strongest of these peaks exhibited the following mass spectrum and is tentatively assigned as due to 16: *m/e* (*I*) 488 (10), 473 (38), 395 (6), 317 (13), 259 (40), 213 (100), 197 (94), 183 (74), 155 (10), 105 (40), 59 (14). The resonances in the ¹H NMR spectrum assignable to the various isomers of 16 are labeled in Figure 6.

Chemical yields were determined by integration of the ¹H NMR (300 MHz) spectra of the crude photolysates from small-scale (*ca.* 10 mg of disilane) runs in deuterated solvents and are listed in Table 1. For these experiments, a known amount of dichloromethane or methyl *tert*-butyl ether was included as an internal integration standard. Chemical yields were calculated relative to the amount of disilane photolyzed in all cases.

Absolute quantum yields were determined using the photolysis of 1,2-di-*tert*-butyl-1,1,2,2-tetraphenyldisilane (0.02 M) in deoxygenated CDCl₃ solution as an actinometer (ϕ_{dis} = 0.35).[23] Deoxygenated 0.02 M solutions of 1 in C₆D₁₂ containing 0.05 M acetone and 0 and 0.05 M CHCl₃ were irradiated along with the actinometer for 5 min, in a merry-go-round apparatus using six 254-nm lamps. Disappearance of starting material for the three samples was measured by integration of the ¹H NMR spectra, using methyl *tert*-butyl ether as an internal integration standard.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, *ca.* 16 ns, 80–120 mJ) from a Lumonics 510 excimer laser filled with F₂/Kr/He mixtures, and a microcomputer-controlled detection system.[11,23,43] Disilane solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was *ca.* 0.7 (1.8 × 10⁻⁴ M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100-mL reservoir. The solutions were saturated with nitrogen, oxygen, or nitrogen/oxygen mixtures by continuous bubbling of the appropriate gas through the reservoir. Quenchers were added to the reservoir as aliquots of the neat liquids.

(39) Brook, A. G.; Gilman, H. *J. Am. Chem. Soc.* **1955**, *77*, 2322.
(40) Brook, A. G.; Dillon, P. J. *Can. J. Chem.* **1969**, *47*, 4347.
(41) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 608.

(42) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *133*, 19.
(43) Leigh, W. J.; Workentin, M. S.; Andrew, D. *J. Photochem. Photobiol. A* **1991**, *57*, 97.