

Aryldisilane Photochemistry. Substituent and Solvent Effects on the Photochemistry of Aryldisilanes and the Reactivity of 1,3,5-(1-Sila)hexatrienes

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The photochemistry of three aryldisilanes $\text{PhRR}'\text{Si}-\text{SiMe}_3$ ($\text{R}, \text{R}' = \text{methyl, phenyl}$) in solution has been studied in detail by steady-state and nanosecond laser flash photolysis techniques. Photolysis in solution results in the formation of transient 1,3,5-(1-sila)hexatriene derivatives by [1,3]-trimethylsilyl migration, simple silenes by dehydrosilylation, and silyl radicals by Si—Si bond homolysis. Silenic products are derived from the lowest excited singlet state and are the major products in nonpolar solvents, while silyl radicals are derived from the lowest excited triplet state and are the major products in polar solvents such as acetonitrile. Reactions of the transient 1,3,5-(1-sila)hexatrienes are nonconcerted in most cases. Reaction with acetone leads to the formation of two products: the corresponding silyl ether from a formal ene reaction of the carbonyl with the Si=C bond, and the 1,2-siloxetane from formal [2 + 2] addition. Similarly, reaction with 2,3-dimethyl-1,3-butadiene leads to the formation of both formal ene and [2 + 2] or [2 + 4] cycloaddition products. Photolysis of the disilanes in the presence of oxygen leads to desilylation, resulting in the formation of phenyltrimethylsilane and silanone oligomers. Nanosecond laser flash photolysis of deoxygenated acetonitrile (MeCN), tetrahydrofuran (THF), or isooctane (OCT) solutions of the disilanes gives rise to readily detectable transient absorptions in the 400–540-nm range which have been assigned to the silatriene intermediates. Time-resolved UV absorption spectra are reported for the three species, along with rate constants for their reaction with acetone, 2,3-dimethyl-1,3-butadiene, oxygen, carbon tetrachloride, and methoxytrimethylsilane in the three solvents. The reactions with acetone and 2,3-dimethylbutadiene are 3–10 times faster in OCT than in MeCN and up to 3 times faster in the latter than in THF, depending on the degree of phenyl substitution at silicon. The dimethyl-substituted silatriene shows discrete evidence for complex formation with THF and is substantially less reactive in that solvent than in MeCN. Rate constants for the reactions of the four reagents with the silatriene from photolysis of pentamethyl(pentadeuteriophenyl)disilane have also been measured, as has that for the reaction of one of the silatrienes with dimethyl sulfoxide. The mechanisms for the reactions of these various reagents with conjugated silenes are discussed in light of these results.

Introduction

It is well-known that direct irradiation of aryldisilanes in solution leads to the formation of transient silenes which are formally derived from disproportionation and recombination of the silyl free radicals formed by homolysis of the Si—Si bond.^{1–9} The bulk of the evidence for the intermediacy of silenes in aryldisilane photolyses has been obtained by chemical trapping studies^{1–9} and has been confirmed recently by transient spectroscopic methods.^{10–13}

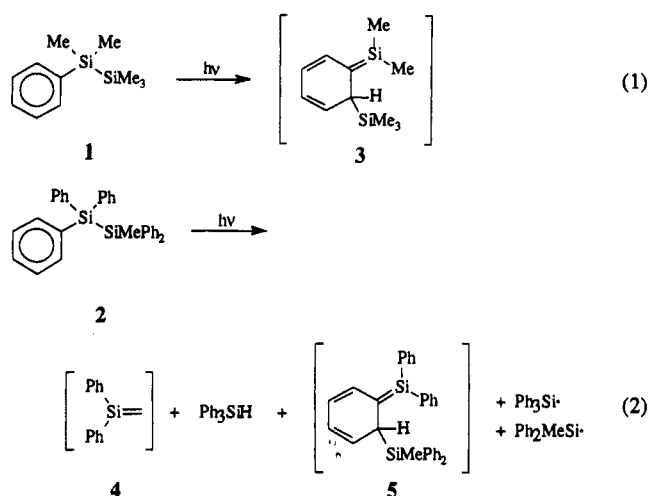
ESR¹⁴ and flash photolysis^{12,13,15} studies have shown that silyl radicals are indeed formed in the reaction, but there are conflicting views as to their role in silene formation. We have shown that the formation of silyl radicals is derived from the disilane triplet state and is enhanced considerably in polar solvents, while silene formation occurs predominantly as a result of reaction of the lowest excited singlet state.¹⁶

Recently, we reported the results of a nanosecond laser flash photolysis study of the photochemistry of pentamethylphenyl- and methylpentaphenylidisilane (1 and 2, respectively),¹² whose photochemistry under steady-state conditions had been reported earlier by other workers.^{1,2,17–24} Photolysis of 1 in hydrocarbon solution in the presence of a silene trap (alcohols,¹⁷ alkenes,^{2,18}

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dienes,^{2,19} alkynes,²⁰ carbonyl compounds,²¹ sulfoxides,^{22,23} etc.²⁴) affords products consistent with the predominant formation of the 1,3,5-(1-sila)hexatriene species **3** (eq 1).

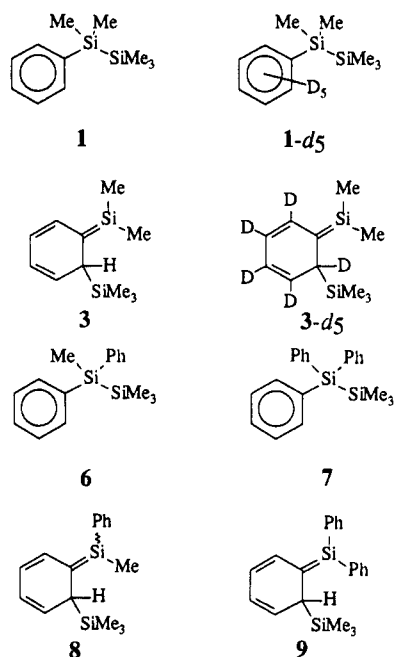


In contrast, steady-state photolysis of **2** under similar conditions leads to products consistent with the formation of 1,1-diphenylsilene (**4**) as the major primary product.¹ Nanosecond laser flash photolysis of **2** in acetonitrile or isooctane solution leads to readily detectable transient absorptions assignable to silatriene **5** and triphenylsilyl and methylphenylsilyl radicals.¹² The strong absorptions of these species in the 330-nm range obscure those due to the simpler silene **4**²⁵ but make it possible to determine absolute rate constants for reaction of the silatriene **5** toward various silene traps.

While relative reactivities of stable silenes toward various silene traps have been established,²⁶ few quantitative kinetic data regarding silene reactivity exist in the literature.^{11,12,25,27,28} Thus, little is known of the effects of solvent polarity or substitution at silicon on the kinetics and mechanisms of silene reactions²⁵ or, for that matter, on the photochemistry of aryldisilanes,²⁹ although solvent and substituent effects on the photophysics of these compounds have been extensively studied.^{7,9,29,30} The generality of 1,3,5-(1-sila)hexatriene formation from photolysis of aryldisilanes and the relative ease with which they can be detected by NLFPS techniques (even when they are formed in relatively low yields) suggest that aryldisilanes have considerable potential as precursors in studies of the reactivity of silenes of this type. The kinetic data reported earlier indicate that **5** is significantly less reactive than **3** toward oxygen, acetone, dienes, alcohols, acids, and alkoxysilanes.¹² However, it is unclear whether

this effect is due to the change in substituents at trivalent silicon or the higher steric bulk at C₇ of the 1,3,5-(1-sila)hexatrienyl moiety.

In this paper, we report a study of the photochemistry of the homologous series of aryldisilanes **1**, **6**, and **7** and the reactions of their corresponding silatrienes (**3**, **8**, and **9**) with acetone, 2,3-dimethyl-1,3-butadiene (DMB), methoxytrimethylsilane (MTMS), oxygen, and carbon tetrachloride using steady-state and nanosecond laser flash photolysis techniques. Disilanes **1**, **6**, and **7** have the



common feature that photochemical [1,3]-silyl migration will involve the trimethylsilyl group in each case, so that these compounds should act as convenient precursors to a homologous series of 1,3,5-(1-sila)hexatrienes (**3**, **8**, and **9**) which differ only in the substituents at trivalent silicon. Acetone, DMB, and MTMS are widely used as trapping reagents for transient silenes produced by thermolysis or photolysis of organosilicon compounds; thus we chose these reagents for investigation in the present study. Oxygen is normally relatively unreactive toward silenes^{25,28,31} (cf. ref. 32) but has been found to exhibit substantial reactivity toward aryldisilane-derived silatrienes;^{11,12} product studies have not yet been reported, however. The reaction of **3**, **8**, and **9** with carbon tetrachloride was discovered during the course of our previous study of the photochemistry of **7**.¹⁶

Characterization of the products formed in the photolyses of **1**, **6**, and **7** in the presence of the various silene trapping agents in polar and nonpolar solvents has been carried out. We report the full details of the reaction of silatrienes **3**, **8**, and **9** with acetone, which yields 1,2-siloxetane products¹⁶ in addition to the ene addition products that have been reported by others as the sole product of this reaction.^{21,33,34} UV absorption spectra of the three transient 1,3,5-(1-sila)hexatrienes and absolute rate constants for their reactions with the five reagents listed above have been determined in acetonitrile, tet-

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Table 1. Product Yields from Photolysis of 0.05 M Cyclohexane- d_{12} Solutions of 1, 6, and 7 in the Presence of 0.05 M Acetone (Eq 3) and 0.06 M 2,3-Dimethyl-1,3-butadiene (DMB; Eq 4)^a

disilane	products	acetone			DMB			
		10	11	12	HSiMe ₃	14	others ^b	HSiMe ₃
1	a	41	21	13	19	60	9 (2)	17
6	b	54	28	14	18	72	5 (1)	10
7	c	33	69		<2	34	62 (5)	<2

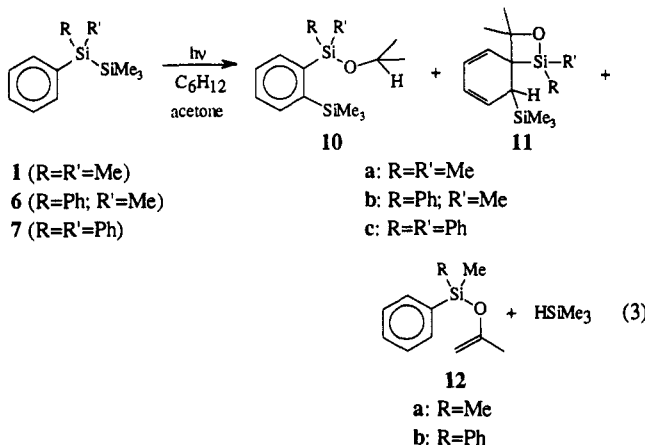
^a Determined by ¹H NMR spectroscopy, after ca. 80% conversion; all values given in percent. Integrated against dichloromethane as internal standard. Errors are considered to be ca. 5%. ^b Unidentified additional products, for which the combined yields and number are listed.

rahydrofuran, and isooctane solution. Also, kinetic deuterium isotope effects on the rate constants for reaction of silatriene 3 with each of these reagents have been determined using the phenyl- d_5 analog of 1 (1- d_5). One of our goals in undertaking this study was to evaluate the role of silyl free radicals in the formation of silenic products from aryldisilane photolysis; to this end, competitive trapping studies, employing chloroform as a silyl radical trap, have also been carried out.

Results

Disilanes 6 and 7 exhibit weak fluorescence emission in acetonitrile or isooctane solution at room temperature, as has been reported previously for 1.^{7,9} The emission maxima for all three disilanes are blue-shifted by ca. 35 nm in hydrocarbon solvents relative to those in acetonitrile. Oxygen has no discernible effect on the intensity of the fluorescence from 1 or 7.

Steady-state photolysis (254 nm) of deoxygenated 0.05 M solutions of 1, 6, and 7 in cyclohexane or cyclohexane- d_{12} containing 0.05 M acetone yields the products shown in eq 3. The products were identified after ca. 80%



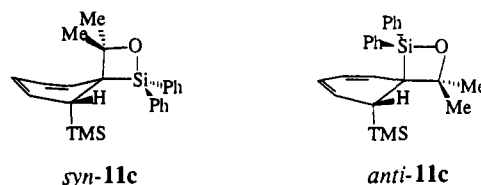
conversion by GC/MS, GC/FTIR, and ¹H and ¹³C NMR spectroscopy using the crude photolysates; the silyl ethers (10) were isolated. Product yields were determined by ¹H NMR spectroscopy and are collected in Table 1. Silyl ether 10a was reported by Ishikawa and co-workers to be the sole product of photolysis of 1 in the presence of acetone.²¹ However, we also find significant yields of the silyl enol ether 12a from photolysis of this compound in the presence of acetone, as well as the 1,2-siloxetane 11a.

Similar results are obtained for photolysis of 6 under similar conditions. While the siloxetanes (11) are observable only in the crude photolysates by NMR spectroscopy, the silyl enol ethers are sufficiently stable to be detectable by GC methods.

The 1,2-siloxetanes 11 are thermally and hydrolytically unstable. They are readily evident in NMR spectra of the crude photolysates (in C₆D₁₂) but decompose slightly upon evaporating the solvent at room temperature under vacuum and redissolving the mixture in deuteriochloroform. They are not detectable in GC analyses of the crude mixtures and decompose upon attempted vacuum distillation or chromatography under either normal or reverse-phase conditions. Siloxetane 11a is particularly unstable and decomposed during an overnight NMR experiment in C₆D₁₂ solution at room temperature. The others survived for several days at room temperature in hydrocarbon solution. We have not yet been able to identify the products of decomposition of 11; a full account of the reactivity of these compounds under various conditions will be published in a separate paper.

We have thus resorted to a combination of high field NMR experiments to identify the structures of 11a-c, using the crude photolysates after ca. 50% conversion. The chemical shifts of the protons in 11c proved to be very similar in C₆D₁₂ and CDCl₃ solution; thus, NMR experiments were carried out in the former solvent to make the procedures more convenient and to minimize decomposition. Figure 1 shows the ¹H NMR spectrum obtained after photolysis of 7 to ca. 50% conversion, with the resonances assigned to 10c, 11c, and residual 7 labeled. Initial assignments for the spectrum of 11c were made by comparing the spectrum shown in Figure 1 with spectra of authentic samples of 7 and 10c. The assignments for 11c were verified by use of ¹H spin-spin decoupling and NOE experiments. Initial assignments of the ¹³C NMR spectrum of this compound were made in similar fashion and were verified with the ¹H-¹³C shift correlation spectrum of the mixture.

The NOE experiments were initially employed simply to verify that all of the ¹H resonances assigned to 11c do, in fact, belong to the same molecule. As it turned out, though, they also allow assignment of the stereochemistry of the molecule; the structures of the two possible isomers, from molecular mechanics (MMX) calculations, are



Irradiation of the methyl group at δ 1.84 caused enhancement in the allylic proton resonance (δ 2.93), along with enhancements in those due to the other methyl group (δ 1.41), one of the phenyl protons, and the vinyl proton at δ 5.89. The last proton was shown to be vicinal to the allylic proton by ¹H-¹H spin decoupling experiments. In a second experiment, irradiation of the TMS singlet at δ -0.17 caused enhancements in the allylic, vinyl, and aromatic proton resonances. On the basis of these results, we assign the *syn* stereochemistry to siloxetane adduct 11c. The remaining NOE data for this compound are listed in the Experimental Section.

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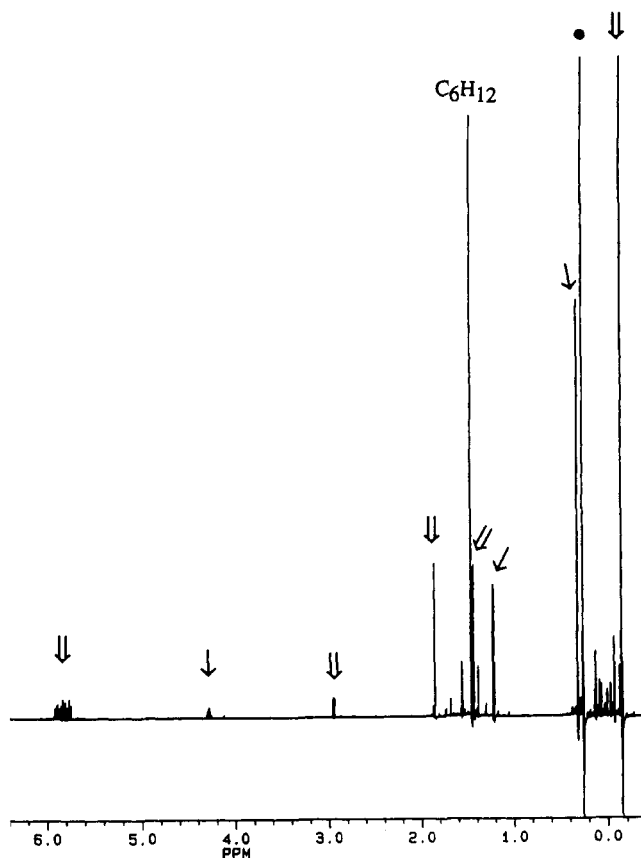


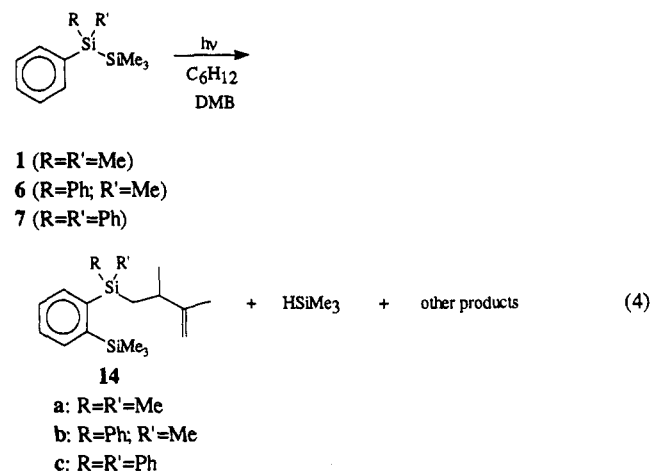
Figure 1. ^1H NMR spectrum (δ -0.4 to 6.4 region) of a crude mixture from photolysis of a deoxygenated, 0.05 M solution of **7** in cyclohexane containing 0.05 M acetone to ca. 50% conversion, after evaporation of solvent and redissolution in CDCl_3 . Resonances due to protons in **7** (\bullet), **10c** (\rightarrow) and **11c** ($\rightarrow\bullet$) are labeled. The spectrum has been enlarged in order to reveal the weak signals in the 2.9–6.0 region.

Additional spectroscopic details consistent with the proposed structure for **11c** were obtained from the ^{13}C and ^{29}Si NMR and infrared spectra of the crude photolysate. The ^{13}C NMR spectrum of **11c** shows quaternary carbon resonances at δ 44.4 and δ 89.4. The latter is assigned to C_3 of the 1,2-siloxetane ring and should be compared to the value of δ 67.1 which is observed for the ketyl carbon in silyl ether **10c**, while the δ 44.4 resonance can be assigned to C_4 of the siloxetane ring. The ^{29}Si spectrum shows resonances at δ 2.2 and 12.4. The latter can be assigned to the siloxetane ring silicon atom and is shielded by ca. 5 ppm compared to the ^{29}Si resonance in 1,1-diphenylsilacyclobutane (**13**). This is reasonable, considering the presence of the oxygen atom and the additional alkyl substitution on the four-membered-ring carbons in **11c** compared to **13**.³⁵ The infrared spectrum of **11c** shows a prominent band at 1057 cm^{-1} , which appears to be characteristic of the siloxetane Si–O stretching vibration.³⁶

The yields of siloxetanes **11a,b** from photolysis of **1** and **6** are much lower than that of **11c** from **7** (see Table 1), but their formation is clearly evident in ^1H NMR spectra of the crude photolysates in C_6D_{12} solution as absorptions in the vinyl and allylic regions of the spectrum. The TMS regions of these spectra were exceedingly complex, making

the spectral analyses more difficult in these cases than in that of **11c**. Nevertheless, the ^1H and ^{13}C NMR spectra of these two compounds were tentatively assigned using a combination of techniques similar to that employed for **11c** and are listed in the Experimental Section. Unfortunately, the yields of these products were too low to allow their ^{29}Si NMR spectra to be obtained.

Steady-state photolysis (254 nm) of deoxygenated 0.05 M solutions of **1**, **6**, and **7** in cyclohexane or cyclohexane- d_{12} containing 0.06 M 2,3-dimethyl-1,3-butadiene (DMB) to ca. 80% conversion yielded the mixtures of products shown in eq 4. The silatriene ene adducts **14** were



identified by GC/MS, GC/FTIR, and ^1H NMR analyses of the crude photolysis mixtures. Product yields are collected in Table 1. The ^1H NMR spectra of adducts **14a** and **14b** were similar to the previously reported spectra for these compounds.¹⁹ Compound **14b** consists of equal amounts of two diastereomers.¹⁹ In the 300-MHz spectrum of this mixture, we were able to resolve the TMS signals for the two diastereomers, separated by 0.005 ppm. The crude mixtures from photolysis of **1** and **6** in cyclohexane- d_{12} also contained minor amounts of trimethylsilane, characterized in the NMR spectrum by the Si–H multiplet at δ 4.00 ($J = 3.6\text{ Hz}$ ³⁷) and the corresponding methyl doublet at δ 0.08. Minor amounts of other products were also formed in these photolyses, as evidenced by the presence of additional TMS peaks in the ^1H NMR spectra. These products could not be identified because of their low yields and the general complexity of the spectra. There was some evidence for the presence of cyclohexadienyl proton resonances in these spectra, but these were exceedingly minor—we estimate the total yield of products containing the cyclohexadienyl moiety to be <5%.

In contrast, the crude mixture from photolysis of **7** in DMB/cyclohexane is exceedingly complex and contains at least six products, of which the major one is silatriene ene adduct **14c**. From the ^1H NMR spectrum of the crude photolysis mixture, it is clear that at least one of the minor products contains the cyclohexadienyl moiety and is thus likely to be a [2 + 2] or [4 + 2] cycloadduct of DMB with **9**.

Photolysis of **1** as a 0.01 M deoxygenated solution in methoxytrimethylsilane (MTMS) led to the formation of five products which could not be isolated owing to their similar GC retention times. The mass spectra of four of the compounds indicate that they are products of addition

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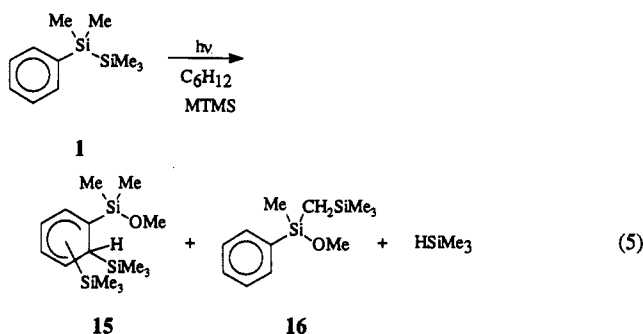
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Table 2. Product Yields from Photolysis of 0.05 M Acetonitrile- d_3 ^a Solutions of 1, 6, and 7 Containing 0.05 M Acetone in the Absence and Presence of Chloroform (See Eq 7)^b

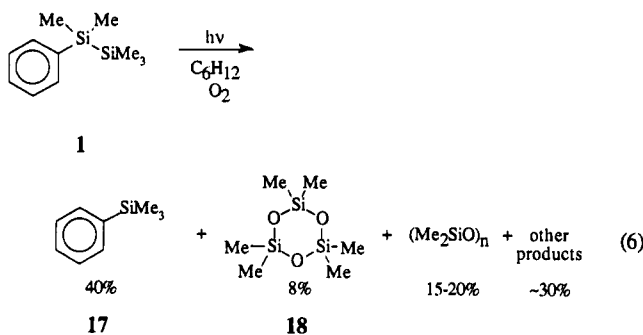
disilane	products	[CHCl ₃]/M	10	11	DSiMe ₃	Me ₃ SiCl ^c	PhRR'SiD	PhRR'SiCl ^c	20 ^d
1	a	0	18	16	9		8		25
		0.05 ^e	5	undet	3	41	1	34	undet
6	b	0	6	undet	4		8		34
		0.05 ^e	5	undet	5	73	6	78	undet
7	c	0	5	undet	48		25		43
		0.1 ^e	5	undet	13	85	10	70	undet

^a The acetonitrile- d_3 employed in these experiments was estimated to contain ≤ 0.005 M water, presumably as D₂O (see Experimental Section). ^b Determined by ¹H NMR spectroscopy, after ca. 30% conversion; all values given in percent except where noted. Errors are considered to be about 5%. undet = undetected. ^c Yields include those of the corresponding siloxanes. ^d Unidentified product with singlet at δ 0.053. Its yield was calculated by assuming that this resonance is due to a single -Si(CH₃)₃ moiety. ^e 1,1,2,2-Tetrachloroethane is also formed as a photolysis product.

of MTMS to the silatriene 3 (15), while the fifth (16) is that of addition of MTMS to 1-methyl-1-phenylsilene, as shown in eq 5. The relative yields of 15 and 16 in the photolysis of 1 were similar to the relative yields of silene- and silatriene-derived products in the acetone-trapping experiments but were not determined quantitatively.



Photolysis of oxygen-saturated cyclohexane (or cyclohexane- d_{12}) solutions of 1 (0.005 M) yields phenyltrimethylsilane (17) and hexamethyl-1,3,5-cyclotrisiloxane (18) as the major products (eq 6). The photolysate also

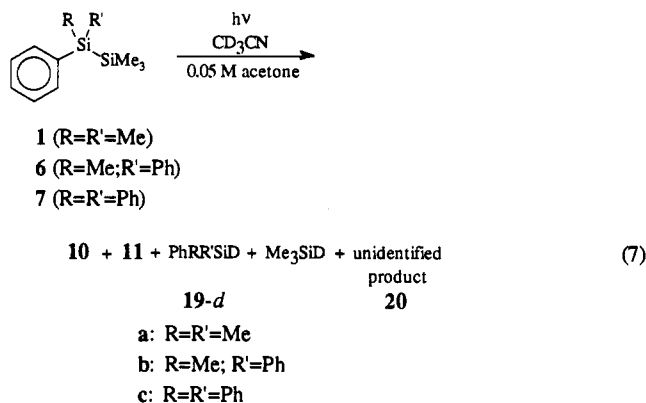


contained at least eight other relatively minor products, of which cyclohexanol, cyclohexanone, dimethylphenylsilanol, and octamethyl-1,3,5,7-cyclotetrasiloxane could be readily identified by GC/MS analysis after ca. 80% conversion. The last compound was present in ca. 5% yield. The photolysis mixture was no less complicated after ca. 10% conversion and contained the same products in approximately the same relative amounts, verifying that 17 and 18 are true primary products of the reaction. Photolysis of 7 under similar conditions yields 17 (69%) and a mixture of at least seven other minor products, in which cyclohexanol, cyclohexanone, and triphenylsilanol could be identified as components.

Photolysis of an oxygen-saturated cyclohexane solution of 1- d_5 under identical conditions led to the formation of 17- d_5 in addition to the other products listed above,

according to GC/MS analysis of the crude reaction mixture after ca. 30% conversion.

Irradiation (254 nm) of deoxygenated solutions of 1, 6, and 7 (0.05 M) in dried acetonitrile containing acetone (0.05 M) results in the formation of the products shown in eq 7. The major product, which we have not yet been



able to identify, is characterized by a singlet at δ 0.053 in the ¹H NMR spectrum of the crude mixture. We have not been able to detect this product by GC or GC/MS, on the basis of which hexamethyldisilane and hexamethyldisiloxane can be excluded as possibilities for its structure. The two silanes (trimethylsilane and 19) were >90% deuterated, as estimated by GC/MS and from the absence of detectable Si-H resonances in the ¹H NMR spectra of the photolysis mixtures. The silyl enol ethers 12 could not be detected as products in these experiments.

Photolysis of similar mixtures in the presence of chloroform (0.05–0.1 M) yields exceedingly complex product mixtures in the cases of 1 and 6. In addition to the products listed above, these mixtures contain small amounts of chlorotrimethylsilane, the corresponding phenylchlorosilane 21, and 1,1,2,2-tetrachloroethane along with several other, unidentifiable products. The photolysis of 7 under these conditions, which has been reported previously,¹⁶ is much cleaner. Product yields were determined by integration of the ¹H NMR spectra of crude photolysis mixtures after ca. 30% conversion and are collected in Table 2, along with the yields of trimethylsilane- d , 10, 11, 19, and 20 obtained from photolysis under similar conditions but in the absence of chloroform.

Photolysis of a deoxygenated cyclohexane- d_{12} solution containing 1 (0.03 M) and CCl₄ (0.03 M) affords small amounts of chlorotrimethylsilane, chlorodimethylphenylsilane (21a), and hexachloroethane, along with a number of other minor products which we have not been able to identify. Photolysis of a solution of 7 under identical conditions yields a similarly complex mixture of products;

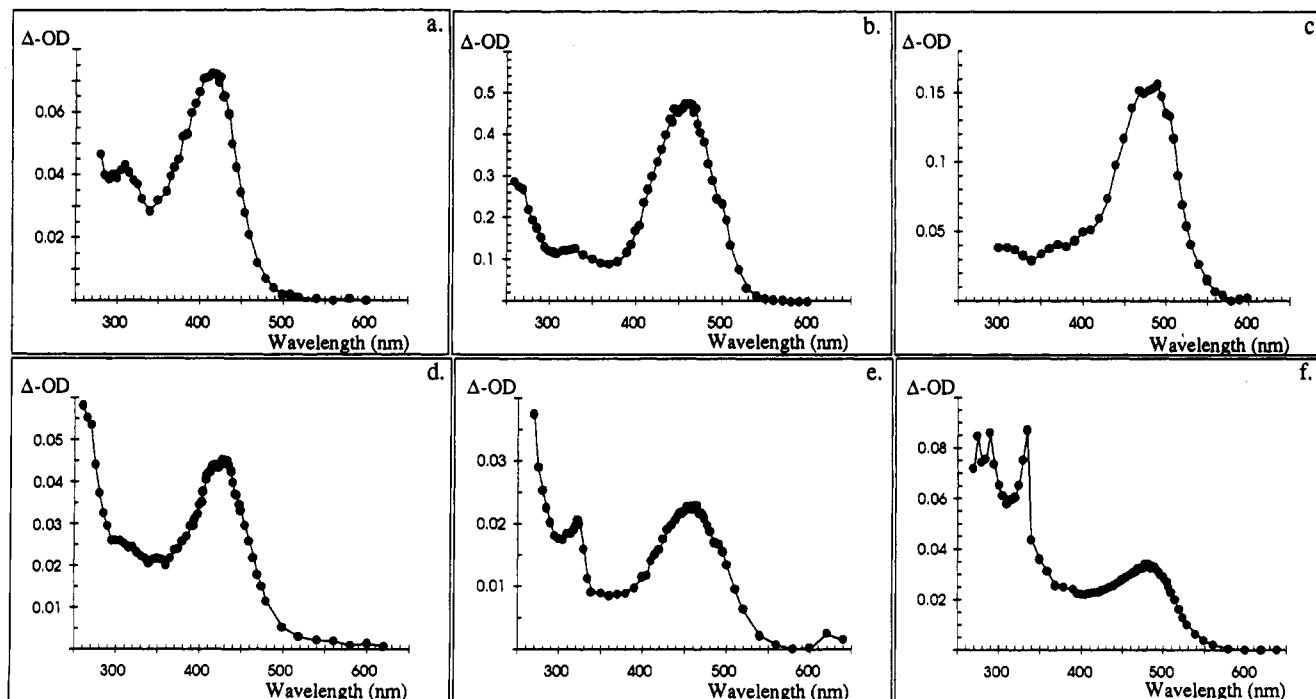
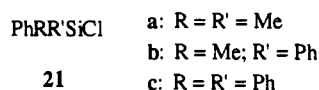


Figure 2. Transient absorption spectra recorded by NLFP, 10–200 ns after 248-nm laser excitation of deoxygenated OCT (a–c) and MeCN (d–f) solutions of 1, 6, and 7.

chlorotriphenylsilane (**21c**) and chlorotrimethylsilane were formed in yields of ca. 5% each, according to ^1H NMR analysis.



Nanosecond laser flash photolysis (NLFP) of continuously flowing, deoxygenated solutions of the disilanes **1**, **6**, and **7** (ca. 10^{-3} M) in dry acetonitrile (MeCN), tetrahydrofuran (THF), or isooctane (OCT) employed the pulses (248 nm, ca. 12 ns, 80–120 mJ) from a KrF excimer laser and a microcomputer-controlled detection system.^{12,13} Transient absorption spectra were recorded in point-by-point fashion by sampling the average transient optical density throughout a preselected time window (starting at a fixed delay time after the laser pulse), as a function of monitoring wavelength. NLFP of solutions of the three disilanes led to strong transient absorptions which decayed with clean first-order kinetics throughout the 270–550-nm range in MeCN and THF, or with mixed first- and second-order decay kinetics in OCT. Figure 2 shows transient absorption spectra recorded within a few hundred nanoseconds after the laser pulse for the OCT (Figure 2a–c) and MeCN (Figure 2d–f) solutions of **1** (Figure 2a,d), **6** (Figure 2b,e), and **7** (Figure 2c,f), respectively. The transient absorption spectrum obtained from NLFP of an *n*-pentane solution of **7** was indistinguishable from that recorded in OCT solution.

The transient absorption spectra in THF solution show distinct differences compared to those in MeCN. In the case of **1**, the absorption maximum of the long-wavelength band (425 nm in MeCN) is shifted to 460 nm. Compound **6** exhibits a ca. 10-nm red shift of its long-wavelength absorption band, while no change is observed in the position of the long-wavelength absorption maximum in the transient absorption spectrum from **7**. There is a 2-fold reduction in intensity of the sharp absorption bands at ca.

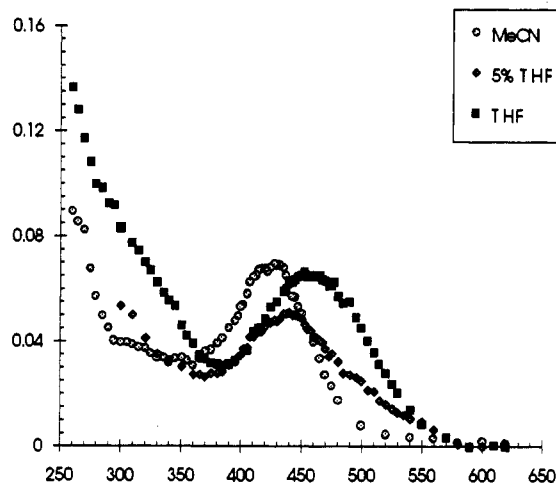


Figure 3. Transient absorption spectra of silatriene **3** in MeCN, 5% THF in MeCN, and THF, recorded by nanosecond laser flash photolysis, under conditions similar to those employed in Figure 2.

330 nm in the spectra from **6** and **7**, however, in THF solution compared to MeCN.

Addition of THF to solutions of **1** in MeCN results in the long-wavelength absorption band being broadened and shifted to longer wavelengths with increasing THF concentration up to ca. 12% THF. For example, Figure 3 shows transient absorption spectra recorded with solutions of **1** in MeCN, THF, and 5% THF in MeCN. The spectra were normalized by determining the maximum transient absorbances of the three optically matched solutions at 425 and 460 nm under conditions of equal laser intensities. Spectra recorded in THF/MeCN mixtures containing >15% THF are indistinguishable from that recorded in pure THF.

The short-wavelength transient absorptions (centered between 315 and 330 nm) from flash photolysis of **1**, **6**, and **7** decay with clean first-order kinetics in MeCN solution, with lifetimes in the 600–700-ns range. The decay traces

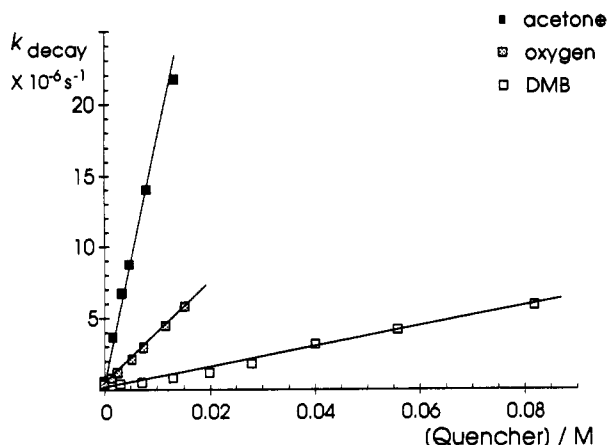


Figure 4. Plots of k_{decay} versus quencher concentration for reaction of silatriene 8 with acetone, DMB, and O_2 in isooctane solution at 21 ± 1 °C.

in this wavelength range showed long-lived residual absorptions, which accounted for ca. 30% of the initial transient absorbances. The short-lived absorptions in this range are assigned to the corresponding arylsilyl radicals, from comparison to the known spectra of these species^{13,38} and from the fact that they are quenched rapidly by carbon tetrachloride or oxygen^{13,39} but not by acetone.⁴⁰

The long-wavelength transient absorptions from flash photolysis of 1, 6, and 7 decay with clean first-order kinetics in dried MeCN ($\tau = 1.1, 1.7,$ and $2.7 \mu\text{s}$, respectively) and THF ($\tau = 1.4, 1.3,$ and $1.6 \mu\text{s}$, respectively). In isooctane solution, the transients are considerably longer lived ($\tau > 5 \mu\text{s}$) and decay with mixed first- and second-order kinetics. Addition of acetone, DMB, oxygen, or CCl_4 to the solutions results in a reduction in lifetime in each case (but no reduction in the initial yield of the transient), and in isooctane solution, the transients decay with clean pseudo-first-order kinetics in the presence of quencher. Plots of k_{decay} versus quencher concentration are linear in every case; Figure 4 shows representative plots of this type for quenching of the long-wavelength transient from NLFP of 6 by acetone, DMB, and O_2 in isooctane solution. In the case of DMB, data were actually collected over a much wider range of concentration (up to 0.21 M) than that shown in Figure 4. Quenching rate constants, determined by least-squares analysis of the data according to eq 8—where k_0 is the pseudo-first-order rate constant for

$$k_{\text{decay}} = k_0 + k_{\text{q}}[\text{Q}] \quad (8)$$

transient decay in the absence of quencher and k_{q} is the second-order rate constant for transient quenching by the quencher Q—are collected in Table 3. The rate constant for quenching of silatriene 3 by chloroform in OCT solution was determined to be $k_{\text{q}} = (1.1 \pm 0.1) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ —a factor of about 4000 slower than that for quenching by acetone under the same conditions.

Rate constants for quenching of 3- d_5 by acetone, DMB, and O_2 in isooctane solution were measured in similar fashion using 1- d_5 as the precursor and were found to be identical to those measured for 3 within experimental error.

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Table 3. Rate Constants (in Units of $10^6 \text{ M}^{-1} \text{ s}^{-1}$) for Reaction of Silatrienes 3, 8, and 9 with Acetone, 2,3-Dimethyl-1,3-butadiene (DMB), Oxygen, and Carbon Tetrachloride in Acetonitrile (MeCN), Tetrahydrofuran (THF), and Isooctane (OCT) Solution at 21 ± 1 °C^a

reagent	solvent			
		3	8	9
acetone	MeCN	7.7 ± 0.2	3.1 ± 0.2	1.5 ± 0.1
	THF	2.46 ± 0.05	1.62 ± 0.02	1.22 ± 0.03
	OCT	45.0 ± 0.6	15.8 ± 0.6	5.42 ± 0.05
DMB	THF	0.09 ± 0.01	0.07 ± 0.01	c
	OCT	1.28 ± 0.03^b	0.68 ± 0.01	0.30 ± 0.01
O_2	MeCN	8.5 ± 0.8^b	4.8 ± 0.6	2.6 ± 0.5
	THF	5.0 ± 0.5	c	c
	OCT	6.9 ± 0.4^b	3.5 ± 0.1	1.9 ± 0.2
CCl_4	MeCN	6.4 ± 0.2	3.8 ± 0.1	c
	OCT	4.4 ± 0.1	1.6 ± 0.1	1.1 ± 0.1

^a Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 8. ^b Data from ref 12. ^c Not determined.

A similar result was obtained for quenching by acetone in MeCN. The rate constant for quenching of 3 by acetone- d_6 in isooctane was determined to be $(4.4 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ —identical to that determined for quenching of 3 by acetone under the same conditions.

Addition of up to 0.6 M MTMS (purified over dry 4-Å molecular sieves to remove traces of methanol) to a MeCN solution of 1 caused no reduction in the lifetime of silatriene 3. This affords an estimate of ca. $10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the upper limit of the rate constant for quenching of silatriene 3 by this reagent. It should be noted that this corrects our earlier report for the reaction of MTMS with 3,¹² the sample of MTMS employed in that study was found to contain trace amounts of methanol.

Finally, rate constants for the reaction of dimethyl sulfoxide (DMSO) with silatriene 3 ($k_{\text{q}} = (3.0 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and with *tert*-butyldiphenylsilyl radicals¹³ ($k_{\text{q}} < 10^5 \text{ M}^{-1} \text{ s}^{-1}$), both in dioxane solution, were also measured using NLFP techniques. Product studies were not carried out, however.

Discussion

(a) Substituent Effects on Disilane Photoreactivity. In general, photolysis of the disilanes 1, 6, and 7 in solution results in competitive [1,3]-trimethylsilyl migration (yielding the silatrienes 3, 8, and 9, respectively), dehydrosilylation (yielding 1-methyl-1-phenylsilene (22) and 1,1-diphenylsilene (4) from 1 and 6, respectively, and trimethylsilane), and Si-Si bond homolysis (yielding the corresponding silyl radicals). The formation of all three



product types is clearly evident from the steady-state photolysis results for these compounds; for example, 10/11 and 12 are the products of acetone trapping of silatriene (3, 8, or 9) and silene (22 or 4), respectively, while deuteriosilanes and chlorosilanes are the products of solvent deuterium and chlorine abstraction by silyl rad-

icals. The formation of silenes **22** and **4** from photolysis of **1** and **6**, respectively, is accompanied by the formation of undeuterated trimethylsilane in deuterated solvents. In NLFP experiments, silyl radical formation is evidenced by the strong absorptions in the 310–335-nm region of the transient absorption spectra,^{13,38,41} while silatriene formation is distinguished by the strong absorptions in the 420–500-nm region.^{10–13} Unfortunately, the silenes **4** and **22** cannot be detected in these experiments owing to their low yields, low extinction coefficients, and the fact that they absorb in the same region as arylsilyl radicals.²⁵

The photochemistry of these compounds in nonpolar solvents such as cyclohexane and isooctane is straightforward, although it is decidedly more complex than previous reports of the photochemistry of **1** suggest.^{2,3,5,17–21,24,33,34} In all cases, the major initial product from photolysis of all three disilanes is the corresponding silatriene. Though not reported previously, the simple silenes (**4** and **22**) are also formed in the photolyses of **1** and **6**, albeit in relatively minor amounts (13% and 14%, respectively). The formation of products derived from **4** and **22** is accompanied by the formation of trimethylsilane. It is interesting that of the two possible routes for silene formation—arylsilene + trimethylsilane vs arylsilane + dimethylsilane—the one leading to the formation of the more highly conjugated silene dominates. The formation of products derived from the corresponding silyl free radicals is detectable only in the presence of chloroform, where the corresponding chlorosilanes are formed in yields of <5%. Since the concentration of chloroform employed in these experiments is sufficiently high to quantitatively trap any silyl free radicals formed in the photolysis ($k_q \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$),^{13,38,41} the fact that the yields of silatriene-derived products are unaffected by the presence of the halocarbon allows the conclusion that silatriene formation occurs directly from the disilane lowest excited singlet state, presumably by concerted [1,3]-silyl migration. Of course, the possibility exists that these products arise from in-cage reaction of singlet-derived radicals which we cannot trap or detect by NLFP owing to their short lifetimes. In an attempt to address this point, the transient UV absorption spectrum due to NLFP of **7** has been measured in *n*-pentane solution, whose lower viscosity should allow more facile cage escape than in isooctane. The transient absorption spectra in the 300–335-nm region (where the triphenylsilyl radical absorbs) are essentially identical in the two solvents; we thus conclude that silatriene formation from photolysis of arylidisilanes is derived from an excited singlet state and results from concerted [1,3]-silyl migration. This agrees with the conclusion of Shizuka and co-workers, who showed that the formation of silatriene **3** occurs on the picosecond time scale, with growth kinetics identical with the decay kinetics of the charge-transfer fluorescence of **1**.¹⁰

The photochemistry of the three disilanes in MeCN solution is relatively complex, on the other hand. In the cases of **6** and **7**, the increased complexity can be ascribed almost completely to a substantial increase in the yield of the corresponding silyl free radicals, whose involvement is indicated in the steady-state experiments by the formation of the corresponding deuteriosilanes and, in the presence of chloroform, chlorosilanes.¹⁶ We have shown that the formation of silyl free radicals is triplet-

derived;¹⁶ presumably, the contribution from the disilane triplet state is higher in MeCN than in hydrocarbon solution because of enhanced intersystem crossing in the more polar medium.^{9,42} The increased radical yields in MeCN compared to those in hydrocarbon solution are also evident in NLFP experiments (Figure 3), which allow the direct detection of all transient intermediates with lifetimes in excess of ca. 20 ns that are formed upon excitation of the disilane.

In the absence of chloroform, photolysis of MeCN solutions of **1**, **6**, and **7** yields small amounts of the acetone-trapping products of the corresponding silatriene (Table 2). The yields of the silatriene-derived adducts in this solvent are highest for **1** (~35%) and fall off markedly for **6** and **7**. Products derived from the simple silenes **22** and **4** are not formed in detectable yields in MeCN, but this is not surprising, considering the much lower relative yields of these products compared to the silatriene-derived ones in hydrocarbon solution. Photolysis of these solutions in the presence of chloroform results in the formation of the corresponding chlorosilanes and partial quenching of the formation of trimethylsilane-*d*, **19-d**, and **20**. In the cases of **6** and **7**, there is little reduction in the yield of **10b,c** compared to the value obtained in the absence of halocarbon, suggesting that the corresponding silatrienes are formed in a primary photochemical process. This is not the case for **1**, where addition of chloroform results in substantial quenching of the formation of the silatriene-derived adducts (**10a** and **11a**). Quenching of the formation of **10a** and **11a** by chloroform is not due to a reaction of the halocarbon with the lowest excited singlet charge-transfer state of the disilane, since there is no effect on the intensity of the fluorescence of **1** over a chloroform concentration range of 0–0.2 M. Since the concentration of acetone in these experiments is high enough to quantitatively trap silatriene **3** (and the rate constant for silatriene quenching by chloroform is $\sim 10^3$ times slower than that for quenching by acetone), we are forced to conclude that, under steady-state conditions, a fraction of the small amounts of silatriene which are formed from **1** in the absence of halocarbon may arise from silyl free radical recombination processes. However, our results are not fully compatible with this conclusion. For example, we have been unable to detect hexamethyldisilane as a coproduct in the photolyses of **1** (and **6** and **7**) in MeCN in the absence of chloroform—hexamethyldisilane would clearly be expected as a product if the silatrienes were formed to any extent by recombination of silyl free radicals.

The formation of the corresponding deuterated silanes in the photolyses of **1**, **6**, and **7** in MeCN-*d*₃ in the presence of 0.05 M chloroform suggests that the solvent plays some direct role in the photochemistry of these compounds. Certainly, deuterated silanes cannot be formed by deuterium atom abstraction from MeCN-*d*₃ ($k < 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; estimated from the lifetime of the triphenylsilyl radical in MeCN) in the presence of 0.05 M chloroform ($k \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).^{13,38,41} Furthermore, the formation of these products due to reaction of the disilane excited singlet or triplet states with traces of D₂O²⁹ can also be ruled out, since the concentration of water in the acetonitrile employed in these experiments ($\leq 0.005 \text{ M}$) is too low for excited-state quenching to occur to any significant extent.

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The only discernible result of the presence of water in these experiments is partial hydrolysis of the chlorosilanes formed in the photolyses in the presence of chloroform. The silanols which are formed in this reaction are present in concentrations which are also too low to interact significantly with the disilane excited states directly, however, so their presence in the photolysates probably cannot account for the formation of deuterated silanes either.⁴³

We have been unable to identify the major product (20) of photolysis of 1, 6, and 7 in acetonitrile-*d*₃ solution, as it escapes GC detection under the conditions that we have employed. GC spiking experiments indicate that hexamethyldisilane and hexamethyldisiloxane can be ruled out as possible structures for this product, however. Since the formation of 20 is quenched in the presence of chloroform in each case, we conclude that the product is silyl free radical derived.

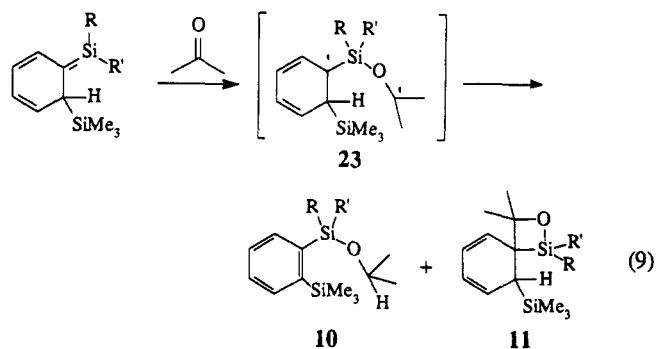
(b) **Substituent and Solvent Effects on the UV Absorption Spectra and Reactivity of 1,3,5-(1-sila)-hexatrienes.** As might be expected, the position of the absorption maximum in the silatriene transient UV spectrum shifts to longer wavelengths with increasing phenyl substitution at the trivalent silicon atom. In both isooctane and acetonitrile solution, λ_{\max} varies among 425 nm for 3, 460 nm for 8, and 490 nm for 9. The absorption spectrum of the diphenyl-substituted silatriene 9 is indistinguishable from that reported previously for silatriene 5, which bears identical substitution at the trivalent silicon atom.¹²

The absorption maximum of silatriene 3 is shifted to ca. 460 nm in THF solution. This can be attributed to complexation with the solvent,⁴⁴ on the basis of the observation that spectra recorded in THF/MeCN mixtures at low THF concentrations are broadened with respect to those recorded in either of the two pure solvents. Figure 3 demonstrates this effect. We interpret the spectrum recorded in 5% THF/MeCN as being the composite of spectra due to roughly equal proportions of complexed and uncomplexed silatriene. If it can be assumed that the extinction coefficient of the silatriene/THF complex is similar to that of the uncomplexed silatriene, the spectrum allows a rough estimate of ca. 1.6 M⁻¹ for the equilibrium constant for formation of the complex in acetonitrile solution.

The transient absorption spectrum of silatriene 8 (from NLFP of disilane 6) is shifted only slightly in THF solution (λ_{\max} = 470 nm) compared to that in MeCN, indicating that phenyl substitution at silicon either reduces the equilibrium constant for complex formation or leads to a "looser" complex. Further phenyl substitution (as in silatriene 9) appears to have a correspondingly larger effect, since the absorption spectra in MeCN and THF solution are almost identical. These effects are reflected in the absolute rate constants for reaction of the three silatrienes with acetone and oxygen in the two solvents. The reduction in the rate constant for both reactions in THF compared to those in MeCN is accounted for by the equilibrium constant for formation of the silatriene/THF complex, within the error limits of our estimate for that number. The rate constants are more similar for the reaction of acetone with 8 in the two solvents and almost identical for those with 9, consistent with our conclusion

(based on the smaller spectral shifts observed for these species) that the equilibrium constant for solvent complexation decreases with increasing phenyl substitution in the silatriene. The formation of THF complexes with silenes is well established, and Wiberg and co-workers have concluded that, in THF solution, silene trapping reactions involve the free silene and not the complex.⁴⁴

The reactions of 3 and several other aryldisilane-derived silatrienes with acetone and DMB have been reported previously by a number of workers.^{2,19,21} In our hands, however, these reactions are considerably more complex than others have reported. The types of products observed in the two reactions suggest that they both proceed in stepwise fashion and involve biradical (or zwitterionic) intermediates.^{2,14} The acetone reaction can be formulated as involving initial attack at trivalent silicon by the carbonyl oxygen to yield intermediate 23 (eq 9), which



undergoes coupling and H-migration to yield siloxetane and silyl ether, respectively. Additional evidence for the stepwise nature of the reaction is provided by the absence of a deuterium kinetic isotope effect (KIE) on the absolute rate constant for reaction in either isooctane or acetonitrile, when the aryl hydrogens in 1 are replaced with deuteriums. We favor a biradical intermediate in this reaction because the reaction is slower in MeCN than in isooctane; one would expect the rate constants to be more similar (or even reversed in relative magnitude) in polar and nonpolar solvents if the reaction involved rate-determining formation of a relatively polar intermediate. Furthermore, the absence of a detectable KIE for the reaction of 3 with acetone-*d*₈ (k_H/k_D = 1.0 ± 0.1 in isooctane) is more consistent with a biradical intermediate than a zwitterionic one in which positive charge resides at the ketyl carbon, since rate-determining formation of such an intermediate might be expected to show a sizable secondary KIE.⁴⁵

The variation in the relative yields of 10 and 11 with substitution at trivalent silicon (Table 1) is intriguing. With the stereochemistry of siloxetane adduct 11c reasonably well established, we speculate that the observed inversion in the relative yields of siloxetane and silyl ether that occurs for reaction of 9 compared to 3 and 8 is due to unfavorable steric effects in the transition state for ether formation (see Scheme 1). Hydrogen abstraction in the biradical (leading to silyl ether 10) requires that the allylic hydrogen be in the pseudoaxial position,^{46,47} which necessitates that the trimethylsilyl group in the intermediate occupy a pseudoequatorial site. Increasing the steric bulk of the substituents on the adjacent silicon would

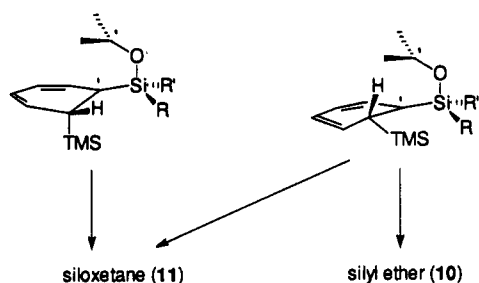
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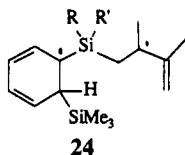
Scheme 1



clearly be expected to force the trimethylsilyl group into a pseudoaxial position and thus favor the formation of the 1,2-siloxetane adduct.

The variation in the rate constants for reaction of acetone with the three silatrienes in a single solvent may also be attributable to steric factors. In all three solvents, the rate constants decrease by a factor of 5–10 throughout the series $3 > 8 > 9$, consistent with the conclusion that increasing phenyl substitution at trivalent silicon retards the rate of attack of the carbonyl oxygen. Similar trends are observed for the reactions with DMB, oxygen, and carbon tetrachloride.

The complex product mixture formed in the reaction of DMB with **9** suggests that this reaction also proceeds in stepwise fashion. In all three cases, the major product is the formal ene adduct **13**; it is accompanied by small amounts of isomeric compounds which are due presumably to competing cyclization of the biradical intermediate (**24**).



Interestingly, these additional products are formed in particularly high yields in the reaction of DMB with the silatriene (**9**) derived from trimethyltriphenyldisilane (**7**). We attribute this to conformational/stereoelectronic effects in the biradical intermediate similar to those suggested above for the reaction of the silatrienes with acetone. Nonconcerted behavior is also observed in the reaction of dienes with simple silenes, in that both ene and [4 + 2] cycloaddition products are commonly observed.^{6,8,48,49}

Methoxytrimethylsilane (MTMS) is commonly used as a silene trapping reagent and reacts by addition across the Si=C bond.^{6,8,48,49} The complex mixtures of products obtained from photolysis of **1**, **6**, and **7** in neat MTMS are analogous to those obtained using methanol as the silatriene trap.^{17,50,51} NLFP experiments indicate that the rate constant for silatriene trapping by this reagent is too low to be measured (by conventional techniques) with our system; for **3**, the most reactive of the three silatrienes, an upper limit of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ has been estimated. It should be noted that this revises our earlier determination of the absolute rate constant for the reaction of MTMS with **3**;¹² product studies carried out as part of the present work, using the sample of MTMS employed in our earlier study, revealed that it contained significant amounts of methanol.

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The products of photolysis of **1**, **6**, and **7** in the presence of oxygen have not been reported previously, although the rate constant for quenching of silatriene **3** by O_2 has.^{11,12} Formally, the reaction involves loss of $\text{RR}'\text{Si}$: to yield phenyltrimethylsilane, although the reaction clearly does not proceed by this simple mechanism. NLFP experiments demonstrate that O_2 reacts with the silatrienes with rate constants in the $(2\text{--}9) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ range but has no effect on their initial yields. It can thus be concluded that the reaction involves one or more intermediates which arise from initial attack of O_2 on the silatrienes. On the basis of the indication that acetone and DMB quenching proceeds via stepwise processes, we formulate the reaction with oxygen as involving biradical **25** as the initially formed reactive intermediate (eq 10). The formation of an intermediate such as **25** is consistent with the fact that the silatrienes are substantially more reactive toward O_2 than simple silenes are;^{25,28} again, a biradical intermediate is expected to be strongly stabilized by conjugation of one of the radical centers with the cyclohexadienyl moiety. The observed lack of a substantial solvent effect on the rate constants is also consistent with the initial formation of a nonpolar reactive intermediate. The simplest route from **25** to the final products (**17** and **18**) would involve loss of the corresponding dioxasilirane⁵² (or silanone oxide⁵³) to yield a cyclohexadienyl-carbene intermediate (**26**) which gives **17** upon [1,2]-H or -trimethylsilyl migration. 1,1-Dimethyldioxasilirane has recently been detected as the product of reaction of dimethylsilylene with oxygen under matrix isolation conditions,⁵² but its subsequent thermal chemistry has not been reported. By analogy with the behavior of carbonyl oxides,⁵⁴ it might be expected to yield dimethylsilanone upon thermal decomposition, which would account for the ultimate formation of $(\text{R}_2\text{SiO})_n$ oligomers in the present case. Unfortunately, we have been unable to obtain direct evidence for the formation of any intermediates (other than **3**) or additional products in the reaction. Thus, we cannot rigorously rule out the possible involvement of additional intermediates such as the corresponding siladioxetane or hydroperoxide, although it does not seem likely that either of these compounds would yield **17** and silanone-derived products upon thermal decomposition.^{32,55} Furthermore, the reaction does not yield *p*-(trimethylsilyl)phenol in detectable amounts. Supporting evidence for the mechanism shown in eq 10 is derived from the fact that photolysis of **1-d**₅ under similar conditions yields **17-d**₅ with no loss of deuterium. This result rules out the possibility that **17** arises via solvent hydrogen abstraction by (trimethylsilyl)phenyl radicals.

It is pertinent to note that **17** and dimethylsilanone-derived oligomers are also formed as the major products of photolysis of **1** in the presence of dimethyl sulfoxide (eq 11).^{22,23} While a mechanism similar to that shown in eq 10 (i.e., involving the intermediacy of carbene **26**) has been considered for this reaction, it was ruled out in favor of one involving direct attack of the sulfoxide on the excited

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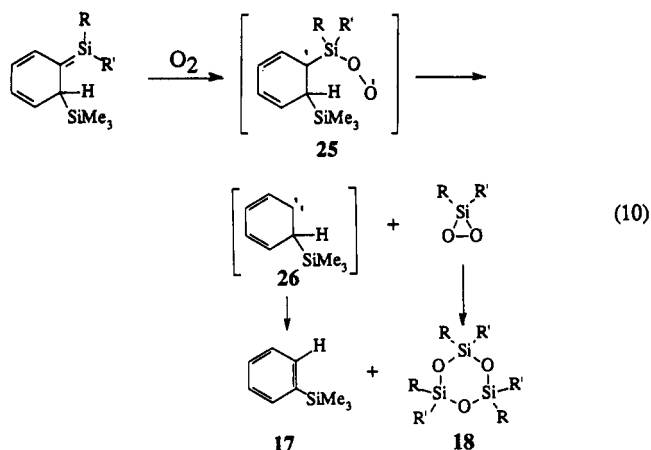
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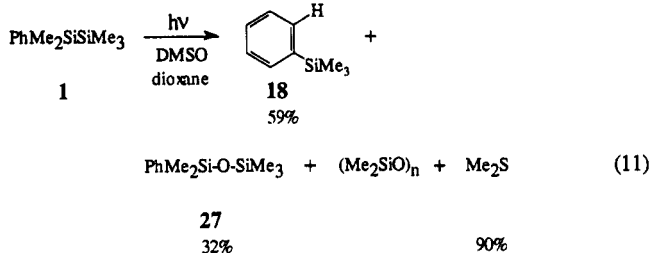
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singlet state of **1**.²² The mechanism involving carbene **26**



was ruled out on the basis of the observation that photolysis of pentamethyl(4-tolyl)disilane (**28**) under similar conditions yields 4-(trimethylsilyl)toluene (**29**), and not the meta-substituted isomer expected if collapse of the carbene occurs by hydrogen migration in preference to trimethylsilyl migration. Whether this expectation is valid or not is evidently still unknown. However, [1,2]-silyl migrations are known to occur in carbenes as well as radicals,⁵⁶ so the possibility that collapse of carbene **26** occurs preferentially by [1,2]-silyl migration is a reasonable one. At the very least, a mechanism involving reaction of DMSO with the disilane excited singlet state can be ruled out, given that the excited singlet state lifetime of **1** is only ~ 30 ps in solution at room temperature.¹⁰ Indeed, DMSO quenches silatriene **3** at nearly the diffusion-controlled rate in dioxane solution at room temperature ($k_q = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), with no reduction in its initial yield. We are unable to account definitively for the reported formation of pentamethylphenylsiloxane (**27**) in these experiments.^{22,23} While we initially suspected that **27** might result from reaction of the sulfoxide with dimethylphenylsilyl and trimethylsilyl radicals,⁵⁷ we have found that this reaction is quite slow in the case of *tert*-butyldiphenylsilyl radicals ($k < 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

Our discovery of the reaction of carbon tetrachloride with the silatrienes was quite accidental and arose as a result of our observation that chloroform quenches **3** at a measurable (though relatively slow) rate. Indeed, all three silatrienes are quenched at substantial rates by carbon tetrachloride, and the trend of decreasing reactivity with increasing phenyl substitution is the same as observed for the other quenchers examined in this study. This reaction is unprecedented in silene chemistry. Unfortunately, the product mixtures observed are so complex that we have been unable to determine the course of the reaction. However, since the yields of chlorotrimethylsilane and **21** in these experiments are similar to those obtained in the presence of acetone and chloroform, we

can at least conclude that these products are formed from reaction of the corresponding silyl radicals with carbon tetrachloride and not from reaction of the silatrienes with the halocarbon. Further study of this intriguing reaction is the subject of future work.

Summary and Conclusions

It is instructive to compare the reactivity of the 1,3,5-(1-sila)hexatrienes investigated in the present work with that of 1,1-diphenylsilene (**4**), whose reactivity toward carbonyl compounds, 2,3-dimethyl-1,3-butadiene, and oxygen has recently been reported.²⁵ The reactivity of the silatrienes toward these reagents differs in many important respects from that of **4**, and indeed, it has been remarked previously that arylidene-derived silatrienes do not exhibit "normal" silene reactivity.⁴⁹ In fact, our results show that the 1,3,5-(1-sila)hexatrienes exhibit reactivity which is quite consistent with what is known of silene behavior, if the silatriene moiety is viewed as a silene with an especially good radical-stabilizing substituent on the silylic carbon atom.

We have previously concluded that 1,1-diphenylsilene (**4**) undergoes ene reactions with carbonyl compounds by a concerted, asynchronous mechanism in which the silene plays the role of the enophile, and solvent and deuterium kinetic isotope effect studies suggest that, in the transition state for the reaction, Si-O bond formation is more advanced than hydrogen transfer.²⁵ One might then expect that if the silylic carbon in **4** were substituted with a radical-stabilizing group such as the cyclohexadienyl moiety present in **9**, the mechanism might change to a nonconcerted one in which initial Si-O bond formation leads to a discrete biradical intermediate. This accounts nicely for the apparent differences in the reactivity of silatrienes and simpler silenes toward acetone. The presence of the allylic (cyclohexadienyl) hydrogen—whose transfer to the ketyl carbon in the biradical is driven by aromatization of the cyclohexadienyl ring—is responsible for the different course of the formal ene additions of the silatrienes compared to that obtained with **4**. Presumably, similar factors are also responsible for their increased reactivity (compared to that of simpler silenes) toward oxygen and carbon tetrachloride. Thus, our results for **4**²⁵ and the silatrienes reported in this paper are illustrative of the spectrum of silene reactivity which is observable depending on the nature of the substituents on the Si=C carbon.

Experimental Section

²⁹Si NMR spectra were recorded at 59.6 MHz on a Bruker AC300 spectrometer using the DEPT pulse sequence. Mass spectra were recorded on a VG ZABE mass spectrometer. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and Hewlett-Packard 3396A integrator, and an HP-1 megabore capillary column (12 m \times 0.53 mm; Hewlett-Packard, Inc.) with a conventional (heated) injector or a DB-1 capillary column (60 m \times 0.2 mm; Chromatographic Specialties, Inc.) with cold on-column injection. 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 \times 0.2 mm; Chromatographic Specialties, Inc.). GC/FTIR analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with an HP-1 megabore capillary column (5 m \times 0.53 mm; Hewlett-Packard, Inc.) and a Bio-Rad GC/C 32 interface attached to a Bio-Rad FTS-40 FT infrared

spectrometer. Semipreparative VPC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and an OV-101 stainless steel column (6 ft \times 1/4 in; Chromatographic Specialties, Inc.). 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), methyl-diphenylsilyl chloride (Aldrich), dimethylphenylsilyl chloride (Aldrich), chlorotrimethylsilane (Aldrich), (trimethylsilyl)benzene (Aldrich), hexamethyldisilane (Aldrich), and hexamethylsiloxane (Aldrich) were all used as received from the suppliers. Acetonitrile (BDH Omnisolv) and tetrahydrofuran (Caledon HPLC) were distilled under nitrogen after refluxing over calcium hydride or sodium, respectively, 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). Dioxane (BDH Reagent) was refluxed over sodium and distilled under nitrogen. Dimethyl sulfoxide (BDH Reagent) was distilled twice after refluxing over calcium hydride. Methoxytrimethylsilane (Aldrich) was stored over activated molecular sieves (4 Å). 2,3-Dimethyl-1,3-butadiene (Aldrich) was passed through activated alumina prior to use. Acetonitrile- d_3 and cyclohexane- d_{12} were used as received from Isotec, Inc. The concentration of water (presumably as D_2O) present in the former was estimated to be ca. 0.005 M from the lifetime of 1,1-diphenylsilene (4) in an oxygenated acetonitrile- d_3 solution. This experiment was carried out by nanosecond laser flash photolysis and employed 1,1-diphenylsilylacetylene as the precursor of 4. The rate constant for quenching of 4 by D_2O in acetonitrile solution is ca. $10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁵⁸

Pentamethylphenyldisilane (1),⁵⁹ pentamethyl(pentadeuteriophenyl)disilane (1- d_5),⁶⁰ 1,1,1,2-tetramethyl-2,2-diphenylsilane (6),⁵⁹ and 1,1,1-trimethyl-2,2,2-triphenyldisilane (7)⁶¹ were prepared according to the published procedures and exhibited melting and boiling points and spectral data that agreed satisfactorily with those reported in each case.

Steady-state photolysis experiments were carried out in a Rayonet photochemical reactor equipped with a merry-go-round and 8–10 RPR-254 (254 nm) lamps. Photolysis solutions were contained in 9 \times 100 mm or 5 mm NMR tubes, constructed from fused quartz, which were sealed with rubber septa and deoxygenated prior to photolysis with a stream of dry nitrogen. Photoproducts 10a–c were isolated by semipreparative VPC and were fully characterized. Siloxetanes 11a–c were identified by NMR analysis of the crude photolysates. Silyl enol ethers 12a,b were identified by spectral comparisons to literature data³⁴ and an authentic sample, respectively. ^1H NMR data, including those from NOE experiments, are listed for these compounds below. ^{13}C chemical shift data are also listed. For 11b,c, the ^{13}C NMR data were obtained from heteronuclear spin correlation spectra of the crude mixtures, while for 11a, these were obtained from the conventional ^{13}C NMR spectrum after subtraction of the signals due to 1 and 10a. The other photoproducts were identified by GC/MS, GC/FTIR, and ^1H NMR spectroscopy and/or by GC coinjection of the photolysates with authentic samples. Chemical yields were determined by integration of the ^1H NMR (300 MHz) spectra of the crude photolysates from small-scale (ca. 10 mg disilane) runs in deuterated solvents and are listed in Tables 1 and 2. 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.

Dimethyl(2-(trimethylsilyl)phenyl)(2-propoxy)silane (10a). ^1H NMR (300 MHz; C_6D_{12}): δ (multiplicity; integral;

identification) 0.375 (s; 9H; Si(CH₃)₃), 0.380 (s; 6H; Si(CH₃)₂), 1.22 (d, $J = 6.1$ Hz; 6H; CH₃), 4.13 (sept, $J = 6.1$ Hz; 1H; OCHMe₂), 7.20–7.60 (m; 4H; Ph). ^{13}C NMR (75.5 MHz; C_6D_{12}): δ 1.4 (Si(CH₃)₂), 1.9 (Si(CH₃)₃), 26.1 (CH₃), 66.2 (OCHMe₂), 127.9, 128.5, 134.9, 135.5, 145.1, 146.6 (Ph). GC/FTIR: 3077 (w), 3055 (m), 2979 (s), 2890 (m), 1385 (m), 1256 (m), 1172 (m), 1129 (s), 1022 (s), 846 (s), 738 (m) cm^{-1} . MS: m/z (I) 266 (2), 251 (2), 209 (30), 193 (100), 147 (14), 116 (12), 75 (15).

Methylphenyl(2-(trimethylsilyl)phenyl)(2-propoxy)silane (10b). ^1H NMR (300 MHz; C_6D_{12}): δ (multiplicity; integral; identification) 0.32 (s; 9H; Si(CH₃)₃), 0.63 (s; 3H; SiCH₃), 1.09 (d, $J = 6.1$ Hz; 3H; CH₃), 1.21 (d, $J = 6.1$ Hz; 3H; CH₃), 4.07 (sept, $J = 6.1$ Hz; 1H; OCHMe₂), 7.10–7.70 (m; 9H; Ph). ^{13}C NMR (75.5 MHz; C_6D_{12}): δ -0.3 (SiCH₃), 1.9 (Si(CH₃)₃), 25.7 (CH₃), 26.0 (CH₃), 66.8 (OCHMe₂), 127.7, 128.1, 128.7, 129.8, 135.2, 135.5, 136.5, 139.3, 143.1, 147.5 (Ph). GC/FTIR: 3116 (w), 3076 (m), 3057 (s), 2978 (s), 2907 (m), 1430 (m), 1376 (m), 1255 (s), 1019 (s), 843 (s), 796 (s) cm^{-1} . MS: m/z (I) = 328 (2), 313 (2), 271 (12), 255 (11), 209 (21), 193 (100), 178 (45), 137 (33), 105 (6), 73 (6). Exact mass: calcd for $\text{C}_{19}\text{H}_{28}\text{OSi}_2$ 328.1679, found 328.1686.

Diphenyl(2-(trimethylsilyl)phenyl)(2-propoxy)silane (10c). ^1H NMR (500 MHz; CDCl_3): δ (multiplicity; integral; identification) 0.30 (s; 9H; Si(CH₃)₃), 1.20 (d, $J = 6.1$ Hz; 6H; CH₃), 4.25 (sept, $J = 6.1$ Hz; 1H; OCHMe₂), 7.20–7.70 (m; 14H; Ph). ^{13}C NMR (50.3 MHz; CDCl_3): δ 1.6 (Si(CH₃)₃), 25.5 (CH₃), 67.1 (OCHMe₂), 127.1, 127.6, 128.4, 129.7, 135.1, 135.9, 136.4, 137.2, 140.7 (Ph). ^{29}Si NMR (59.6 MHz; CDCl_3): δ -2.1 (SiMe₃), -12.2 (OSiPh₂Ar). GC/FTIR: 3074 (m), 3058 (s), 2978 (m), 2904 (w), 1429 (m), 1386 (m), 1252 (m), 1116 (s), 1021 (s), 843 (s), 791 (s), 765 (s) cm^{-1} . MS: m/z (I) 390 (5), 375 (3), 333 (10), 317 (16), 271 (20), 255 (100), 240 (72), 199 (78), 165 (10), 135 (15), 105 (23), 73 (60). Exact mass: calcd for $\text{C}_{24}\text{H}_{30}\text{OSi}_2$ 390.1835, found 390.1853.

1,1,3,3-Tetramethyl-2-oxa-1-sila-9-(trimethylsilyl)spiro[3.5]nona-5,7-diene (11a). ^1H NMR (500 MHz; C_6D_{12}): δ (multiplicity; integral; identification; NOE enhancements) 0.03 (s; 9H; Si(CH₃)₃), 0.41 (s; 6H; Si(CH₃)₂), 1.26 (s; 3H; CH₃; δ 5.97), 1.47 (s; 3H; CH₃; δ 1.26, 2.57, 5.77, 7.2–7.4), 2.57 (d; $J = 6.3$ Hz; allyl; δ 1.47, 5.77, 7.3–7.4), 5.7–6.0 (cmplx m; 4H; vinyl). ^{13}C NMR (125 MHz; C_6D_{12}): δ 0.6 (Si(CH₃)₃), 1.3 (Si(CH₃)₂), 30.4 (allyl), 31.8 (CH₃), 33.4 (CH₃), 41.4 (C4), 87.2 (C3).

1,3,3-Trimethyl-1-phenyl-2-oxa-1-sila-9-(trimethylsilyl)spiro[3.5]nona-5,7-diene (11b). ^1H NMR (500 MHz; C_6D_{12}): δ (multiplicity; integral; identification; NOE enhancements) 0.05 (s; 9H; Si(CH₃)₃), 0.68 (s; 3H; SiCH₃), 1.40 (s; 3H; CH₃), 1.61, 5.74, 7.7), 1.61 (s; 3H; CH₃; δ 2.68, 5.79, 7.2–7.4), 2.69 (d; $J = 6.3$ Hz; allyl; 1.61, 5.79), 5.7–6.0 (cmplx m; 4H; vinyl). ^{13}C NMR (125 MHz; C_6D_{12}): δ 1.2 (Si(CH₃)₃), 1.8 (SiCH₃), 30.7 (allyl), 31.7 (CH₃), 33.8 (CH₃), 42.4 (C4), 87.7 (C3), 123.5, 126.4, 130.0, 130.3 (C5–C8).

syn-3,3-Dimethyl-1,1-diphenyl-2-oxa-1-sila-9-(trimethylsilyl)spiro[3.5]nona-5,7-diene (11c). ^1H NMR (500 MHz; CDCl_3): δ (multiplicity; integral; identification; NOE enhancements) -0.17 (s; 9H; Si(CH₃)₃), δ 2.93, 5.7–5.9, phenyl), 1.41 (s; 3H; CH₃; δ 1.84, 5.74, phenyl), 1.84 (s; 3H; CH₃; δ 1.41, 2.93, 5.89, phenyl), 2.93 (d; $J = 6.3$ Hz; allyl), 5.74 (d; 1H; $J = 9.3$ Hz; H5), 5.78 (dd; 1 H; $J = 4.9$; 9.15 Hz; H7), 5.84 (dd; 1H; $J = 4.9$, 9.3 Hz; H6), 5.89 (dd; 1H; $J = 6.3$, 9.15 Hz; H8). ^{13}C NMR (125 MHz; CDCl_3): δ 1.3 (Si(CH₃)₃), 29.9 (allyl), 31.8 (CH₃), 33.2 (CH₃), 44.4 (C4), 89.4 (C3), 122.0 (C7), 125.7 (C6), 129.0 (C5), 131.0 (C8). ^{29}Si NMR (59.6 MHz; CDCl_3): δ 2.2 (SiMe₃), 12.4 (siloxetane Si). IR (CDCl_3): 3071 (m), 2930 (s), 2853 (s), 1590 (m), 1429 (s), 1248 (s), 1122 (s), 1057 (s) cm^{-1} .

2-(Diphenylmethylsiloxy)propene (12b). ^1H NMR (500 MHz; CDCl_3): δ 0.72 (s; 3H), 1.79 (s; 3H), 4.02 (d, $J = 6.8$ Hz; 2H), 7.4–7.6 (m; 10H). ^{13}C NMR (125 MHz; CDCl_3): δ -2.7, 22.8, 92.3, 127.9, 129.9, 134.2, 135.8, 155.7. GC/IR: 3062 (m), 2970 (w), 1638 (w), 1376 (w), 1273 (s), 1116 (s), 1056 (s), 934 (w), 894 (w), 795 (s) cm^{-1} . GC/MS: m/z (I) = 254 (10), 239 (50), 197 (70), 161 (15), 137 (100), 105 (25), 91 (15), 51 (14).

1-(Trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)dimethylsilyl)benzene (14a).¹⁹ ^1H NMR (300 MHz; C_6D_{12}): δ (mul-

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tiplicity; integral; identification) 0.37 (s; 9H; Si(CH₃)₃), 0.39 (s; 3H; Si(CH₃)₃), 0.41 (s; 3H; Si(CH₃)₃), 0.91 (dd, $J = 7.5, 14.9$ Hz; 1H; CH₂), 1.07 (dd, $J = 6.8, 14.9$ Hz; 1H; CH₂), 1.00 (d, $J = 6.8$ Hz; 3H; CH₃), 1.63 (s; 3H; CH₃), 2.39 (m; 1H; allyl), 4.60 (m; 2H; vinyl). GC/MS: m/e (I) 290 (2), 275 (5), 217 (29), 207 (18), 191 (100), 160 (36), 135 (32), 73 (64), 59 (20). GC/FTIR: 3077 (m), 3054 (m), 2968 (s), 2909 (m), 1646 (m), 1454 (m), 1415 (m), 1377 (m), 1255 (s), 1117 (m), 1040 (m), 891 (m), 840 (s), 734 (s) cm⁻¹.

1-(Trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)methylphenylsilyl)benzene (14b).¹⁹ ¹H NMR (300 MHz; C₆D₁₂): δ (multiplicity; integral; identification) 0.108 (s; 4.5H; Si(CH₃)₃), 0.113 (s; 4.5H; Si(CH₃)₃), 0.615 (s; 1.5H; Si(CH₃)₃), 0.627 (s; 1.5H; Si(CH₃)₃), 0.93 (d, $J = 6.8$ Hz; 1.5H; CH₃), 0.95 (d, $J = 6.8$ Hz; 1.5H; CH₃), 1.21 (cmplx m; 2H; CH₂), 1.60 (s; 1.5H; CH₃), 1.61 (s; 1.5H; CH₃), 2.40 (m; $J = 6.8$ Hz; 1H; allyl), 4.61 (m; 2H; vinyl). GC/MS: m/z (I) 352 (2), 337 (1), 279 (31), 269 (62), 253 (24), 191 (100), 160 (33), 135 (55), 121 (31), 73 (44), 59 (7), 55 (16). GC/FTIR: 3116 (w), 3075 (m), 3057 (s), 2968 (s), 2907 (m), 1646 (m), 1454 (m), 1430 (m), 1376 (m), 1255 (s), 1109 (s), 1053 (m), 891 (m), 843 (s), 796 (s), 734 (s) cm⁻¹.

1-(Trimethylsilyl)-2-((2,3-dimethyl-1-buten-4-yl)diphenylsilyl)benzene (14c). ¹H NMR (300 MHz; C₆D₁₂): δ (multiplicity; integral; identification) -0.02 (s; 9H; Si(CH₃)₃), 0.87 (d, $J = 6.8$ Hz; 3H; CH₃), 1.35 (m; 2H; CH₂), 1.62 (s; 3H; CH₃), 2.40 (m; 1H; allyl), 4.56 (m; 2H; vinyl). GC/MS: m/z (I) 414 (12), 399 (2), 341 (24), 331 (76), 315 (10), 301 (11), 253 (100), 222 (39), 195 (42), 135 (25), 105 (32), 73 (32), 55 (16). GC/FTIR: 3075 (s), 3058 (s), 2966 (s), 2905 (m), 1644 (m), 1429 (m), 1375 (m), 1264 (s), 1108 (s), 890 (m), 842 (s), 735 (s) cm⁻¹.

Photolysis of 1 in Methoxytrimethylsilane. A deoxygenated solution of 1 (0.01 M) in distilled methoxytrimethylsilane was photolyzed to ca. 80% conversion with 254-nm light. GC and GC/MS analysis revealed the formation of five major products. The one with the shortest retention time is identified as 16 on the basis of its mass spectrum: m/z (I) 238 (1), 223 (100), 191 (18), 177 (9), 151 (10), 135 (11), 121 (19), 105 (9), 73 (10), 59

(16), 43 (9). The other four products eluted within 0.6 min of each other (but 3–4 min after 16) under the same conditions and were identified as isomers of 15 on the basis of their virtually identical mass spectra: m/z (I) = 312 (1), 297 (3), 239 (28), 209 (7), 193 (7), 151 (30), 135 (100), 121 (12), 89 (43), 73 (67), 59 (12), 45 (22).

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ca. 16 ns) from a Lumonics 510 excimer laser filled with F₂/Kr/He mixtures, and a microcomputer-controlled detection system.^{12,13,62} Disilane solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (10⁻⁴–10⁻³ M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100-mL reservoir. The solutions were deoxygenated continuously in the reservoir with a stream of dry nitrogen. Quenchers were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (6–10 points) which spanned at least 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least squares analysis in each case.

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