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 PhRR'Si-SiMe₃ (R, R' = 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 dehydroisilylation, 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 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 studies1-9 and has been confirmed recently by transient spectroscopic methods.10-13


dienes,2,18 alkyynes,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 (eq 1).

$$\text{Me}_3\text{Si} \rightarrow \text{Me} \hspace{1cm} \text{Me} \hspace{1cm} \text{Me} \hspace{1cm} \text{SiMe}_3$$

1

$$\text{Ph} \hspace{1cm} \text{Si} \hspace{1cm} \text{Si} \hspace{1cm} \text{MePh}_2$$

2

$$\begin{array}{c}
\text{Ph} \\
\text{Si} \\
\text{Si} \\
\text{Ph}
\end{array} + \text{PhSiH} + \begin{array}{c}
\text{MeMe} \\
\text{Si} \\
\text{Si} \\
\text{MeMe}
\end{array} + \text{PhSi} \hspace{1cm} + \text{PhMeSi}$$

3

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 methyldiphenylsilyl radicals.12 The strong absorptions of these species in the 330-nm range obscure those due to the simpler silene 42 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 NLF 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 (DBM), 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, DBM, 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 silenes25,26,31 (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 the silatrienes 3, 8, and 9 with acetone, which yields 1,2-siloxetane products16 in addition to the one 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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trapping studies, employing chloroform
role of silyl free radicals in the formation of silenic products
for all three disilanes are blue-shifted by ca. 35 nm in
hydrocarbon solvents relative to those in acetonitrile.
determined using the phenyl-ds analog of
of our goals in undertaking this study was to evaluate the
values given in percent. Integrated against dichloromethane as internal
trap, have also been carried out.
d12 containing 0.05 M acetone yields the products shown
acetonitrile or isooctane solution at room temperature,
derium isotope effects on the rate constants for reaction
of silatriene 3 with each of these reagents have been
fluorescence from
exhibit weak fluorescence emission in
or isoctane 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-ds analog of 1 (1-ds). One of our goals in undertaking this study was to evaluate the role of silyl free radicals in the formation of silenic products from arylidisilane 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 isoctane 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-d12 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 photolyses; 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.41 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.

Table 1. Product Yields from Photolysis of 0.05 M Cyclohexane-d12 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 (DBaseq 4)  

<table>
<thead>
<tr>
<th>disilane products</th>
<th>acetone</th>
<th>DMB</th>
<th>HSiMe3</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>41</td>
<td>21</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>b</td>
<td>54</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>c</td>
<td>33</td>
<td>69</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

* 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%. Unidentified additional products, for which the combined yields and number are listed.

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 C6D6) 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 C6D6 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 photolyses after ca. 50% conversion. The chemical shifts of the protons in 11c proved to be very similar in C6D6 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.

of mixture from photolysis of a deoxygenated, 0.05 M solution conversion, after evaporation of solvent and redissolution in CDCl$_3$. Resonances due to protons in reveal the weak signals in the 2.9-6.0 region.

The infrared spectrum of the crude photolysate also contained minor amounts of trimethylsilane, characterized in the NMR spectrum by the Si-H multiplet at $\delta$ 4.00 ($J = 3.6$ Hz$^{-2}$) and the corresponding methyl doublet at $\delta$ 0.08. Minor amounts of other products were also formed in these photolyses, as evidenced by the presence of additional TMS peaks in the $^1$H 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 $^1$H 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 methoxytrisilane (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 identified by GC/MS, GC/FTIR, and $^1$H NMR analyses of the crude photolysis mixtures. Product yields are collected in Table 1. The $^1$H 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, as a 0.01 M deoxygenated solution 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

\[
\begin{align*}
1 (R=R'=Me) \\
6 (R=Ph; R'=Me) \\
7 (R=R'=Ph) \\
14a: R=R'=Me \\
14b: R=Ph; R'=Me \\
14c: R=R'=Ph
\end{align*}
\]

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 $^1$H NMR spectra of the crude photolysis mixtures in CD$_2$Cl$_2$ 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 $^1$H 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

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14a: R=R'=Me \\
14b: R=Ph; R'=Me \\
14c: R=R'=Ph
\end{align*}
\]

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 photolysis. The $^{13}$C NMR spectrum of 11c shows quaternary carbon resonances at $\delta$ 44.4 and $\delta$ 89.4. The latter is assigned to $C_9$ of the 1,2-siloxetane ring and should be compared to the value of $\delta$ 67.1 which is observed for the ketyl carbon in silyl ether 10c, while the $\delta$ 44.4 resonance can be assigned to $C_9$ of the siloxetane ring. The $^{29}$Si spectrum shows resonances at $\delta$ 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.$^{30}$ 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.$^{30}$

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 $^1$H NMR spectra of the crude photolysis mixtures in CD$_2$Cl$_2$ 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 $^1$H 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

\[
\begin{align*}
1 (R=R'=Me) \\
6 (R=Ph; R'=Me) \\
7 (R=R'=Ph) \\
14a: R=R'=Me \\
14b: R=Ph; R'=Me \\
14c: R=R'=Ph
\end{align*}
\]
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-d12) solutions of 1 (0.005 M) yields phenyltrimethylsilane (17) and hexamethyl-1,3,5-cyclosiloxane (18) as the major products (eq 6). The photolyzate also contained at least eight other relatively minor products, of which cyclohexanol, cyclohexanone, dimethylphenylsilanol, and octamethyl-1,3,5,7-cyclosiloxane 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-d5 under identical conditions led to the formation of 17-d5 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 hexamethylsilane 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, unidentified products. The photolysis of 7 under these conditions, which has been reported previously, 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-d12 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;
chlorotriphenylsilane (21c) and chlorotrimethylsilane were formed in yields of ca. 5% each, according to $^1$H NMR analysis.

\[
\begin{align*}
\text{PhRR'SCl} & \quad \text{a: } R = R' = \text{Me} \\
& \quad \text{b: } R = \text{Me}; R' = \text{Ph} \\
& \quad \text{c: } R = R' = \text{Ph}
\end{align*}
\]

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. 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 270–650-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. 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
transient decay in the absence of quencher and 
 wider range of concentration (up to 0.21 M) than that 
 the case of DMB, data were actually collected over a much 
 identical to those measured for acetone under the same conditions.

The second-order rate constant for transient quenching by the 
 quencher Q-are collected in Table 3. The rate constant 
 was determined to be $k_d = 0.02 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$
 in isooctane solution, the transients decay with clean pseudo-
 reduction in the initial yield of the transient), and in 
 solvent deuterium and chlorine abstraction by silyl rad-
 solution results in competitive 
 photolysis of the disilanes 
 contain trace amounts of methanol.

Addition of up to 0.6 M MTMS (purified over dry 4-A 
 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. $10^4 \text{ M}^{-1} \text{s}^{-1}$ 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 ($k_2 = (3.0 \pm 0.2) \times 10^9 
 \text{ M}^{-1} \text{s}^{-1}$) and with tert-butylidiphenylsilyl radicals13 ($k_3 < 
 10^9 \text{ M}^{-1} \text{s}^{-1}$), 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-

![Figure 4](image-url)
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,\textsuperscript{13,38,41} while silatriene formation is distinguished by the strong absorptions in the 420–500-nm region.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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, \(\approx 3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}\)),\textsuperscript{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 aryldisilanes 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.\textsuperscript{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 deuterosilanes and, in the presence of chloroform, chlorosilanes.\textsuperscript{16} We have shown that the formation of silyl free radicals is triplet-derived;\textsuperscript{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.\textsuperscript{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 (\(\sim 35\%\)) 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.\textsuperscript{19,23,24} 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 silatrienes 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\textsubscript{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 deuteron atom abstraction from MeCN-d\textsubscript{3} (k \(< 7 \times 10^5 \text{ M}^{-1} \text{s}^{-1}\); estimated from the lifetime of the triphenylsilyl radical in MeCN) in the presence of 0.05 M chloroform (k \(\approx 3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}\)).\textsuperscript{13,38,41} Furthermore, the formation of these products due to reaction of the disilane excited singlet or triplet states with traces of D\textsubscript{2}O\textsuperscript{20} can also be ruled out, since the concentration of water in the acetonitrile employed in these experiments (\(< 0.005 \text{ M}\)) is too low for excited-state quenching to occur to any significant extent.


(43) We thank a reviewer for bringing this possible mechanism for the formation of deuterosilanes to our attention.
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-\( \text{D}_2 \) 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, \( \lambda_{\text{max}} \) 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 complexity with the solvent,44 on the basis of the observation that spectra recorded in THF/McCN 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/McCN 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 (\( \lambda_{\text{max}} = 470 \) 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 arylsilane-derived silatrienes with acetone and DMB have been reported previously by a number of workers.21,18,21 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.21,14 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-\( \text{D}_2 \) (\( k_D/k_H = 1.0 \pm 0.1 \) 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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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 trimethyltriphenylsilane (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.\(^{6,8,48}\)

Methoxytrimethylsilane (MTMS) is commonly used as a silene trapping reagent and reacts by addition across the \( \text{Si}=\text{C} \) bond.\(^{6,8,48}\) 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.\(^{17,51}\) NLF 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 \( 10^8 \text{M}^{-1} \text{s}^{-1} \) 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.

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 \( \text{O}_2 \) has.\(^{11,12}\) Formally, the reaction involves loss of \( \text{RR}'\text{Si} \) to yield phenyltrimethylsilanol, although the reaction clearly does not proceed by this simple mechanism. NLF experiments demonstrate that \( \text{O}_2 \) reacts with the silatrienes with rate constants in the \( (2-9) \times 10^8 \text{M}^{-1} \text{s}^{-1} \) 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 \( \text{O}_2 \) on the silatriene. 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 \( \text{O}_2 \) than simple silenes are.\(^{26,28}\) 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 dioxasilirane (52) or silanol oxide (53) to yield a cyclohexadienyl-carbene intermediate (26) which gives 17 upon \([1,2]-\text{H} \) or -trimethylsilyl migration. 1,1-Dimethyldioxa silirane has recently been detected as the product of reaction of dimethylsilane with oxygen under matrix isolation conditions.\(^{52}\) But its subsequent thermal chemistry has not been reported. By analogy with the behavior of carbonyl oxides,\(^{24}\) it might be expected to yield dimethylsilylamine upon thermal decomposition, which would account for the ultimate formation of \( (\text{R}_3\text{Si})_n \) 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 silanol-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 \( (\text{trimethylsilyl})\)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).\(^{22}\) While a mechanism similar to that shown in eq 10 (i.e., involving the intermediary 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

\(^{11}(51)\) Leigh, W. J.; Sluggett, G. W., unpublished results.


hfylsilyl radicals

result of our observation that chloroform quenches 3 at
three silatrienes are quenched at substantial rates by

\begin{equation}
\text{PhMe}_{2}\text{SiO-SiPh}_{2} + (\text{Me}_{2}\text{Si})_{2} + \text{Me}_{3}\text{S}
\end{equation}

(11)

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 trimeth-
ylsilyl 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,\textsuperscript{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 of 1.\textsuperscript{22} The mechanism involving carbene 26

was initially suspected that 27 might result from
reaction of the sulfoxide with dimethylphen-
ylsilyl and trimethylsilyl radicals,\textsuperscript{57} we have found that
this reaction is quite slow in the case of tert-butylidiphos-
henylsilyl 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 chlorofluorines quench 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. Unfortu-
nately, the product mixtures observed are so complex that
we have been unable to determine the course of the
reaction. However, since the yields of chlorotrimethyl-
silane 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.\textsuperscript{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 arylsilane-derived silatrienes
do not exhibit "normal" silene reactivity.\textsuperscript{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 silenic 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.\textsuperscript{26} One might then expect
that if the silenic carbon in 4 were substituted with a
radical-stabilizing group such as the cyclohexadieny1
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(cyclohexadieny1) hydrogen—whose
transfer to the ketyl carbon in the biradical is driven by
aromatization of the cyclohexadieny1 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
\(4^{27}\) 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**

\(^{29}\)Si NMR spectra were recorded at 59.6 MHz on a Bruker
AC300 spectrometer using the DEPT pulse sequence. Mass
spectra were recorded on a VGH 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 \(\times\) 0.2 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
spectrum. Semipreparative VPC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and an OV-101 stainless steel column (6 ft × 1/8 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.

Cycloheptane (BDH Omnisoil), 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 Omnisoil) and tetrahydrofuran (Caledon HPLC) were distilled under nitrogen after refluxing over calcium hydride. Methanol (BDH Reagent), chlorotrimethylsilane (Aldrich), (trimethylsilyl)benzene (Aldrich), hexamethyldisilane (Aldrich), and hexamethylsiloxane (Aldrich) were all used as received from the suppliers. Acetonitrile (BDH Omnisoil) and tetrahydrofuran (Caledon HPLC) were distilled under nitrogen. Dimethyl sulfoxide (BDH Reagent), chloroform (BDH Omnisoil), and carbon tetrachloride (BDH Reagent) were refluxed over sodium and 2.2,4trimethylpentane (BDH Omnisoil). 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 Omnisoil), 2,2,4trimethylpentane (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 Omnisoil) and tetrahydrofuran (Caledon HPLC) were distilled under nitrogen after refluxing over calcium hydride or sodium, respectively, for several days. Acetone (Baker Reagent), chloroform (BDH Omnisoil), and carbon tetrachloride (BDH Reagent), chloroform (BDH Omnisoil), and carbon tetrachloride (BDH Reagent) were refluxed over sodium and 2.2,4trimethylpentane (BDH Omnisoil). 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.
tiplicity; integral; identification) 0.37 (s; 9H; Si(CH₃)₃), 0.39 (s; 3H; Si(CH₃)₂), 0.41 (s; 3H; Si(CH₃)), 0.91 (dd, J = 7.5, 14.9 Hz; 1H; CH₃), 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), 2.59 (m; 1H; allyl), 4.60 (m; 2H; vinyl). GC/MS: m/z (I) 290 (2), 275 (5), 217 (29), 207 (18), 191 (100), 160 (38), 135 (32), 73 (64), 58 (20). GC/FTIR: 3077 (m), 3054 (m), 2968 (s), 2909 (m), 1646 (m), 1454 (m), 1345 (m), 1277 (m), 1265 (s), 1117 (m), 1040 (m), 891 (m), 840 (s), 754 (cm⁻¹).

Aryldisilane Photochemistry

was photolyzed to ca. 80% conversion with 254-nm light. GCatsd solution of
producte. The one with the shortest retention time is identified
on the basis of its mass
spectrum: m/z (I) 352 (2), 337 (1), 279 (31), 269 (62), 253 (24), 191 (151), 135 (30), 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 18) 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 experimenta 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.12,13,14 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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