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Synthesis and Isolation of Stable 1,2-Siloxetanes from Reaction of Transient Silenes with Acetone

Nicholas P. Toltl and William J. Leigh*

Department of Chemistry, McMaster University, 1280 Main Street West,
Hamilton, Ontario, Canada L8S 4M1

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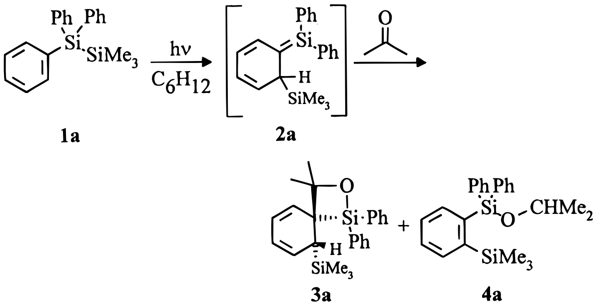
Direct irradiation of 1,1,1-trialkyl-2,2,2-triphenyldisilanes ($R_3Si{-}SiPh_3$; $SiR_3 = SiMe_3$, $SiEt_3$, $SiMe_2{}^tBu$) in hydrocarbon solution in the presence of acetone leads to the formation of 1,2-siloxetanes and silyl ethers, from reaction of the ketone with the 1,3,5-(1-sila)hexatriene resulting from photochemical [1,3]-trialkylsilyl migration into one of the aromatic rings of the disilane. The two products have been isolated in each case by low-temperature chromatography and identified on the basis of spectroscopic data. The siloxetane is the major product in each case, and its yield relative to silyl ether increases with increasing steric bulk of the $-SiR_3$ group. Photolysis of the three disilanes in the presence of di-*tert*-butylketone affords the corresponding silyl ether in nearly quantitative yield, to the exclusion of siloxetane. 1,1,1-Triisopropyl-2,2,2-triphenyldisilane yields an intractable mixture upon photolysis in the presence of acetone under the above conditions but shows clear evidence for the formation of the corresponding siloxetane and silyl ether (in addition to chlorotriphenyl- and chlorotriisopropylsilane) when photolyzed in the presence of acetone and chloroform. Nanosecond laser flash photolysis techniques have been employed to determine absolute rate constants for the reaction of acetone, pinacolone, and di-*tert*-butyl ketone with the silatriene intermediates. These experiments also show that the triisopropyl derivative undergoes Si−Si bond homolysis to yield silyl radicals in competition with rearrangement to silatriene. The yield of silyl radicals is substantially higher in acetonitrile solution than in cyclohexane solution.

Introduction

1,2-Siloxetanes are relatively reactive four-membered ring compounds that have been successfully isolated only in a few rather special cases.[1−4] It is generally accepted that they are the primary products in the reaction of silenes with nonenolizable ketones and aldehydes,[5−7] and in fact, this is the method employed for the syntheses of most of the analogs that have been reported. Most of these examples also contain the common feature of being derived from stable silenes; thus, they possess sterically bulky substituents at the silicon and carbon atoms of the ring system. It is generally assumed that this factor is primarily responsible for their stability.

Recently, we reported evidence for the formation of a 1,2-siloxetane derivative (**3a**) from photolysis of 1,1,1-trimethyl-2,2,2-triphenyldisilane (**1a**) in cyclohexane solution containing acetone.[8,9] Nanosecond laser flash photolysis results,[8,9] as well as a substantial amount of prior literature on the photochemistry of aryldisilanes,[10−15] provide strong evidence that **3a** is derived from the reaction of acetone with the transient 1,3,5-(1-sila)hexatriene (**2a**) resulting from photoinduced [1,3]-trimethylsilyl migration in **1a** (eq 1). The structural assignment for **3a** was based on ^1H, ^{13}C, and ^{29}Si NMR and infrared spectroscopic data recorded on crude reaction mixtures, since our initial attempts to isolate the compound by chromatographic methods failed owing to its apparently substantial thermal and hydrolytic reactivity.



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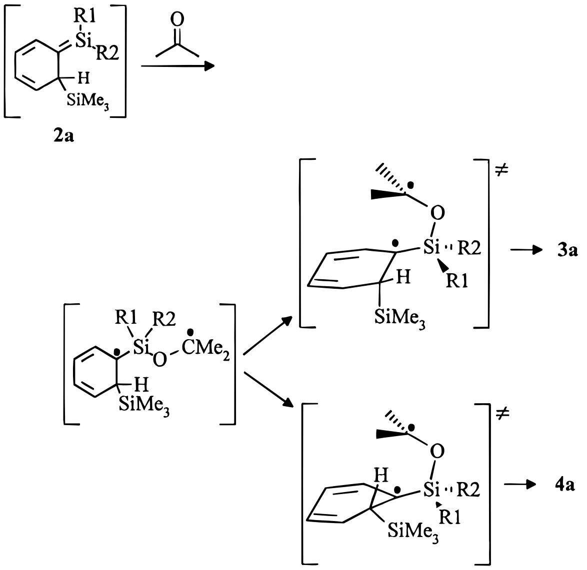
The relative yields of siloxetane and silyl ether in the reaction of acetone with a series of aryldisilane-derived silatrienes vary with the degree of aryl substitution at the silenic silicon atom,[9] the siloxetane being favored only when the silenic silicon atom bears *two* phenyl substituents. On the basis of this observation, a mechanism was proposed in which **3a** and **4a** are formed via collapse of a 1,4-biradical (or zwitterionic) intermediate resulting from attack of the carbonyl oxygen at the silenic silicon atom (eq 2). If silyl ether (**4a**) formation requires a pseudoaxial orientation of the allylic hydrogen atom (and hence a pseudoequatorial orientation of the allylic trimethylsilyl group), then one would expect siloxetane formation to be preferred when potential steric interactions between R1 and the allylic trimethylsilyl group are maximized.



(2)

The indication that steric effects control product selection in this reaction and, in general, increase the stability of strained and/or reactive small-ring compounds led us to examine the effects of increased steric bulk in both the (migrating) trialkylsilyl group in **1** and the carbonyl addend on the course of the reaction, in the hopes that these two factors might combine to allow isolation of an aryldisilane-derived 1,2-siloxetane in analytically pure form. In this paper, we report the results of a study of the photochemistry of the series of 1,1,1-trialkyl-2,2,2-triphenyldisilanes **1a-d** in solution at −78 and 25 °C, in the presence of acetone and di-*tert*-butyl ketone. The successful isolation of 1,2-siloxetanes derived from three of these compounds and acetone, is also reported.

$Ph_3Si{-}Si(CH_2CH_3)_3$ **1b**

$Ph_3Si{-}SiMe_2(CMe_3)$ **1c**

$Ph_3Si{-}Si(CHMe_2)_3$ **1d**

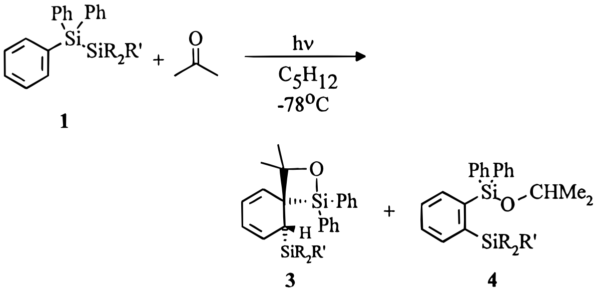
Results

Disilanes **1b**−**d** were synthesized by reaction of (triphenylsilyl)lithium with the appropriate chlorotrialkylsilane,[16] as employed previously for the synthesis of **1a**.[8,9] They exhibit spectral and analytical data consistent with their proposed structures in each case.

Photolysis (254 nm) of a deoxygenated 0.015 M solution of **1a** in 2-methylbutane containing acetone (0.05 M) at −78 °C led to the formation of two products, as revealed by the ^{1}H NMR spectrum of the crude photolysate after ~80% conversion of **1a**, evaporation of the solvent from an aliquot of the solution, and redissolution of the residue in deuteriochloroform. As reported previously,[8,9] the spectrum showed clear evidence of resonances assignable to siloxetane **3a** and silyl ether **4a**; the yield of **3a** is significantly higher in photolyses carried out at −78 °C than at ambient temperatures, however. Initial unsuccessful attempts to separate the components of the mixture by room-temperature column chromatography verified the substantial lability of **3a** toward hydrolytic decomposition. Success was ultimately achieved by use of rapid, low-temperature (~5 °C) radial chromatography on silica gel. This afforded a pure sample of **3a** as a colorless oil. Silyl ether **4a** was obtained as a mixture with **1a** but could be separated from the disilane by semipreparative gas chromatography and was identified on the basis of spectroscopic data.

^{1}H, ^{13}C, and ^{29}Si NMR spectra of **3a** matched those previously assigned to this compound on the basis of homo- and heteronuclear COSY experiments carried out on crude photolysis mixtures.[8,9] Similarly, the infrared spectrum of the compound as the neat liquid (included as Supporting Information) verified the presence of a strong absorption at 1112 cm^{-1}, which may be assigned to Si-O vibrations.

Irradiation of **1b**,**c** in 2-methylbutane containing acetone at −78 °C resulted in the formation of two major products in each case; these were isolated as crystalline solids using a procedure similar to that employed for **3a** and **4a** and were identified as **3b**,**c** and **4b**,**c** (see eq 3) on the basis of spectroscopic data. The basic features of the ^{1}H NMR spectra of **3b**,**c** in the region above δ ~0.7 are similar to those in the spectrum of **3a**. As expected, the regions below δ ~0.7 are considerably more complex, partly because the *tert*-butyldimethylsilyl methyl groups in **3c** and the triethylsilyl methylene hydrogens in **3b** are diastereotopic. As a result, the 500 MHz spectrum of **3b** shows two three-proton doublets-of-quartets (the AB part of an ABX_3 spin system) due to the triethylsilyl methylene hydrogens. In the case of **3c**, the ^{1}H NMR spectrum shows two three-proton singlets at δ −0.21 and 0.03 due to the *tert*-butyldimethylsilyl methyl protons.



(3)

a. R = R' = Me
b. R = R' = Et
c. R = Me; R' = *t*-Bu

Spectroscopic data for **3a**−**c** and **4a**−**c** are listed in the Experimental Section. Siloxetane **3c** was obtained

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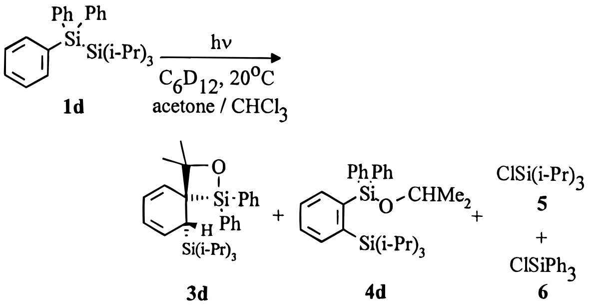
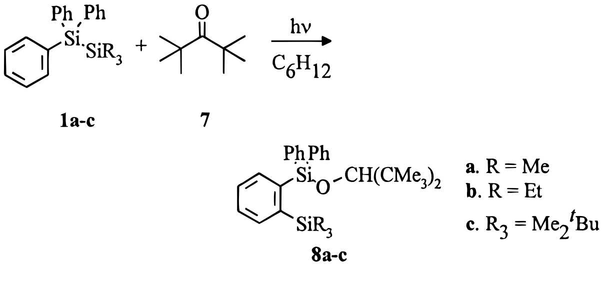
as a crystalline solid, but attempts to obtain crystals of suitable quality for X-ray crystallographic study were unsuccessful due to their slow decomposition during recrystallizations over prolonged periods of time.

Irradiation of a deoxygenated 0.015 M solution of **1d** in 0.05 M acetone/2-methylbutane at −78 or 25 °C gave rise to an intractable mixture of products. The ^{1}H NMR spectrum of the crude photolysate after ~80% conversion showed tentative indications of the presence of siloxetane and silyl ether products, but the spectrum was too complex to be analyzed reliably. Attempts to separate the components of the photolysate chromatographically failed. NMR spectra of the crude photolysis mixture from irradiation (25 °C) of a 0.05 M solution of **1d** in cyclohexane-d_{12} containing acetone (0.075 M) and chloroform (0.075 M) to various conversions between 10 and 50% were somewhat cleaner, showing clear indications of the formation of siloxetane **3d**, silyl ether **4d**, and 1,1,2,2-tetrachloroethane. GC/MS analysis verified the formation of **4d**, as well as chlorotriisopropylsilane (**5**), chlorotriphenylsilane (**6**), and several other minor products. The relative yields of **3d**/**4d** and tetrachloroethane/**3d** were estimated to be ~1.6 and ~2.0, respectively, by integration of the NMR spectrum of the crude photolysis mixture after ca. 5% conversion of **1d**, the lowest conversion at which relative yields could be measured with reasonable precision. The relative yield of **4d** and **6** was estimated to be **6**:**4d** ≈ 1.6 by GC/MS. The yield of **3d** diminished markedly at higher conversions; therefore, the value obtained after 5% conversion is assumed to be a lower limit. The course of this reaction is summarized in eq 4. The crude reaction mixture appeared to be stable to storage in the dark for several hours after the completion of the experiment, but compounds **3d** and **4d** were not isolated. The ^{1}H NMR spectrum of the crude photolysate after ~8% conversion of **1d** is available as Supporting Information.



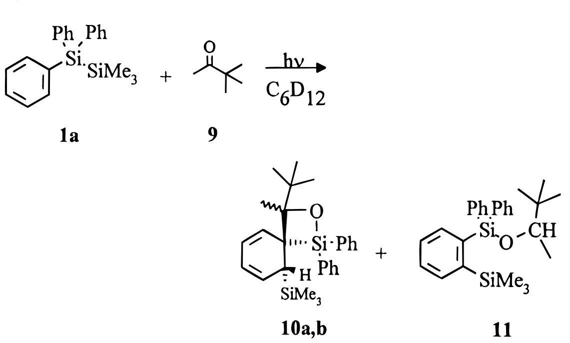
(4)

Irradiation of deoxygenated cyclohexane solutions of **1a-c** (0.05 M) containing di-*tert*-butyl ketone (**7**, 0.075 M) at 25 °C resulted in the formation of a single product in each case. These were isolated as crystalline solids and identified as the silyl ethers **8a−c** on the basis of spectroscopic data (see eq 5). In the case of **8c**, the structural assignment was confirmed by X-ray crystallography, details of which are published elsewhere.[17] No evidence for the formation of the corresponding siloxetane could be obtained in these cases, even in runs carried out in cyclohexane-d_{12} solution and monitored directly by NMR at low (10−30%) conversions. The material balances in these experiments were estimated to be >90% by NMR analysis of crude photolysis mixtures containing hexamethyldisilane as an internal standard.



(5)

Irradiation of a deoxygenated cyclohexane-d_{12} solution of **1a** (0.05 M) containing pinacolone (**9**, 0.075 M) at 25 °C resulted in the formation of three major products, as evidenced by inspection of the ^{1}H NMR spectra of the crude photolysis mixture at 15−25% conversion of **1a**. The spectra contained two doublets at δ 2.95 and 3.25 of total intensity ca. one-fourth of that due to a complex pattern of resonances in the vinylic region, which were tentatively attributed to the stereoisomeric siloxetanes (**10a/10b**), and a quartet at δ 3.68, which was tentatively assigned to the silyl ether **11** (see eq 6). At ca. 6% conversion, the relative intensities of the three signals were **10a:10b:11** ≈ (2.2):(2.2):(1.0). With increased conversion, the spectrum grew more complex and the relative yields of **10** and **11** changed; for example, at 25% conversion, the ratio was **10a:10b:11** ≈ (0.24):(0.9):(1.0). No attempts were made to isolate the products of this reaction. The ^{1}H NMR spectrum of the crude photolysate after ~12% conversion of **1a** is available as Supporting Information.



(6)

Thermolysis of a 0.05 M solution of **3c** in benzene-d_6 at 70 °C over several days led to slow disappearance of the ^{1}H NMR resonances due to the siloxetane and the concomitant growth of a complex series of resonances between 0.5 and 3 ppm. The NMR spectrum of the reaction mixture at high conversions of **3c** was so complex that no attempt was made to separate and isolate the components of the mixture.

Nanosecond laser flash photolysis of deoxygenated 5 × 10^{-4} M solutions of **1a−d** in *n*-hexane led to readily detectable transient absorptions in the 400−550 nm region, which decayed with mixed first- and second-order kinetics and estimated lifetimes in excess of 10 μs. The transient absorption spectrum recorded ~1−2 μs after laser excitation of **1a** was identical with that reported previously for this compound in isooctane solution and was assigned as silene **2a**.[8,9] Transient absorption spectra recorded for **1b,c** were similar to that from **1a**, exhibiting single absorption bands with λ_{max} 488 nm in both cases. The spectrum recorded for **1b** is shown in Figure 1a.

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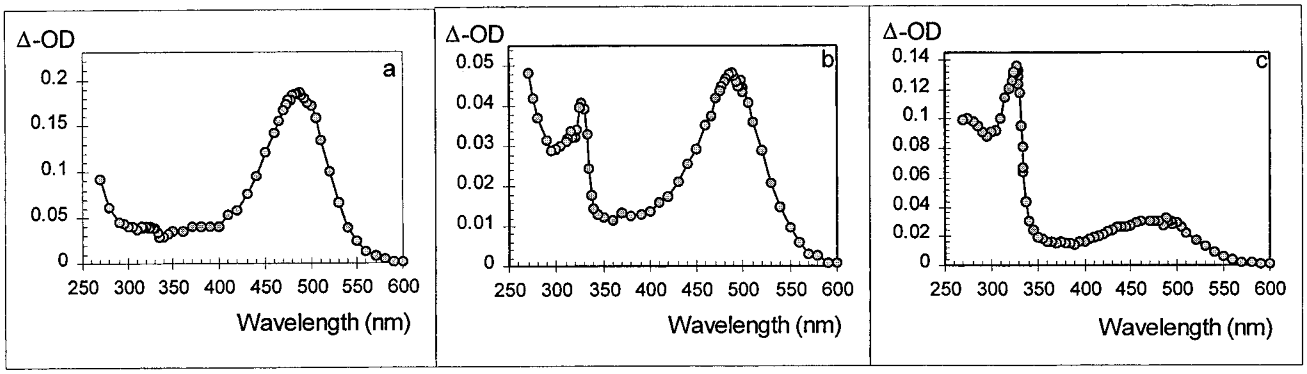

Figure 1. Transient absorption spectra recorded at 23 °C by 248 nm nanosecond laser flash photolysis of deoxygenated, ca. 2×10^{-4} M solutions of (a) **1b** in hexane, (b) **1d** in hexane, and (c) **1d** in acetonitrile.

The transient absorption spectrum recorded for *n*-hexane solutions of **1d** under conditions similar to those employed for **1a**–**c** is shown in Figure 1b. It exhibits two absorption bands of similar intensities: one centered at 488-nm (assignable to silene **2d**) and another centered at 328 nm (assigned to the triphenylsilyl radical[18–20]). As expected, transient decay traces recorded at the two absorption maxima exhibited markedly different decay kinetics. Furthermore, addition of chloroform to the solution resulted in shortening of the lifetime of the 328-nm transient but had no appreciable effect on the lifetime at 488 nm. Laser flash photolysis of a deoxygenated 5×10^{-4} M solution of **1d** in dried acetonitrile (Figure 1c) gives rise to a spectrum consisting largely of that of the triphenylsilyl radical;[21] in this case, the longer wavelength silyl radical absorption band at $\lambda_{max} = 450$ nm is clearly evident, superimposed on a very weak band due to silene **2d**.

In the presence of acetone, the 488-nm transient absorptions from **1a**–**d** are shorter lived and their decay follows clean pseudo-first-order kinetics. Rate constants for reaction of the transients with acetone (k_q) were obtained from plots of transient decay rate constant (k_{decay}) *versus* acetone concentration according to eq 7, in which $k_d°$ is the pseudo-first-order rate constant for decay of the transient in the absence of acetone. Representative plots from experiments with **1b**–**d** in hexane solution (23 °C) are shown in Figure 2.

$$k_{decay} = k_d° + k_q[\text{acetone}] \qquad (7)$$

Addition of di-*tert*-butyl ketone (**7**) to solutions of **1a** in hexane had no detectable effect on transient lifetime, within experimental error, allowing an upper limit of $\sim 10^6$ M^{-1} s^{-1} to be estimated for the rate constant for quenching of **2a** by this ketone. The rate constant for quenching of **2a** by pinacolone (**9**) was determined to be $k_q = (6.7 \pm 0.2) \times 10^8$ M^{-1} s^{-1} in hexane solution at 23 °C.

Table 1 lists the absolute rate constants for reaction of silatrienes **2a-d** with acetone, along with the product ratios ([**3**]/[**4**]) obtained by ^{1}H NMR analysis of crude mixtures from photolysis (to <15% conversion) of **1a**–**d** in cyclohexane-d_{12} containing 0.075 M acetone at 23 °C.

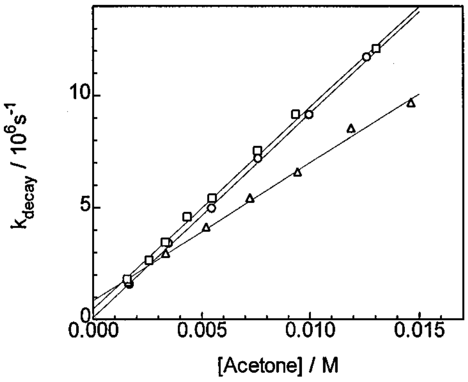

Figure 2. Plots of k_{decay} vs acetone concentration from nanosecond laser flash photolysis of **1b** (△), **1c** (□), and **1d** (○) as ca. 2×10^{-4} M solutions in deoxygenated hexane in the presence of acetone. Transient decay was monitored at 490 nm in each case.

Table 1. Absolute Rate Constants for Reaction of Acetone with Silenes 2a–e (k_q) in Deoxygenated *n*-Hexane Solution at 22 °C, and Product Ratios Determined by ^{1}H NMR Analysis of Crude Photolysis Mixtures[a]

silene	$-SiR_2R'$	$k_q \times 10^{-8}$ M s	**3**:**4** product ratio
2a	$-SiMe_3$	6.0 ± 0.2	2.7 ± 0.2
2b	$-SiEt_3$	6.2 ± 0.3	4.7 ± 0.5
2c	$-SiMe_2{}^tBu$	8.7 ± 0.2	6.4 ± 0.4
2d	$-Si^iPr_3$	9.2 ± 0.3	(1.6)[c]
2e[b]	$-SiPh_2Me$	7.6 ± 0.3	7.1 ± 0.5

[a] Errors are reported as twice the standard deviation in the slope of plots of silatriene decay rate *versus* acetone concentration. Product ratios were determined by ^{1}H NMR analysis of crude photolysis mixtures (see Experimental Section). [b] Data from reference 18. [c] Lower limit (see text). The products were not isolated in this case.

Discussion

The ^{1}H and ^{13}C NMR spectra of 1,2-siloxetane **3a** were initially assigned on the basis of 1D and 2D NMR experiments carried out on the crude mixture from photolysis of **1a** in cyclohexane-d_{12} containing acetone.[9] This is straightforward since at relatively high conversions of **1a**, the siloxetane is the major component of the reaction mixture and the spectra of the other components (**1a** and **4a**) are relatively simple. The stereochemistry of the molecule was assigned on the basis of ^{1}H NOE experiments, in which irradiation of the methyl group at δ 1.84 caused enhancement in the allylic proton resonance (δ 2.93), while irradiation of the TMS singlet at δ −0.17 caused enhancements in the aromatic proton resonances. The ^{1}H and ^{13}C NMR

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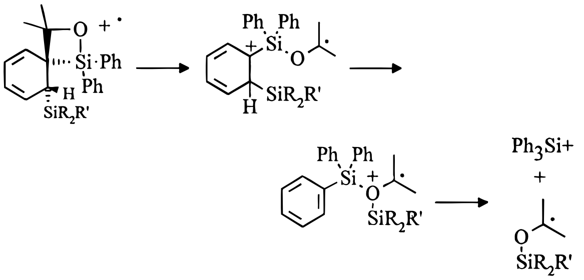
(18) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1994**, *13*, 1005.
(19) Sluggett, G. W.; Leigh, W. J. *Organometallics* **1992**, *11*, 3731.
(20) Ito, O.; Hoteiya, K.; Watanabe, A.; Matsuda, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 962.
(21) Chatgilialoglu, C. In *CRC Handbook of Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, pp 3–11.

spectra of an isolated sample of **3a** verify all of the assignments made in the previous study and allow further identification of the aromatic ^{1}H and ^{13}C resonances belonging to the molecule.

The ^{13}C spectrum of **3a** shows quaternary carbon resonances at δ 44.4 and 89.4, which are assignable to the C_4 and C_3 carbons, respectively, of the 1,2-siloxetane ring. The ^{29}Si NMR spectrum shows resonances at δ 2.2 and 12.4; the latter is assignable to the siloxetane ring silicon atom. Except for differences due to the different trialkylsilyl groups in **3b,c**, the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of these analogs are very similar to those of **3a**; in all three derivatives, the ^{29}Si NMR spectrum shows a singlet at ~12 ppm, while the ^{13}C spectra show resonances at ~44 and ~89 ppm. The ^{1}H NMR spectra of the three compounds are also diagnostic, particularly the four-proton multiplet in the vinylic region, part of which is coupled to a single-proton doublet at δ ~2.9 due to the allylic proton of the cyclohexadienyl ring. The IR spectra of all three derivatives show a prominent absorption at ~1110 cm^{-1}, as do those of other 1,2-siloxetanes for which IR data have been reported.[1c]

The electron impact mass spectra of neither the siloxetanes (**3**) nor the alkoxysilanes (**4** and **9**) exhibit molecular ions, even at low (<15 eV) impact energies; the highest molecular weight ions observable in the mass spectra of all three sets of compounds are those corresponding to loss of the heaviest alkyl group on the trialkylsilyl substituent. However, ammonia chemical ionization spectra were recorded in several cases, and all show the expected M + 18 ions corresponding to addition of ammonium ion to the proposed structures. The base peak in the EI spectrum of all three siloxetane derivatives is *m/z* 259, which is most probably assignable to the triphenylsilyl cation, formed by the fragmentation pathway shown in eq 8. A peak at *m/z* 317, corresponding to loss of the trialkylsilyl group, is also prominent in the EI spectra of the three compounds.



(8)

The difficulties which we originally experienced in the isolation of **3a** were ascribed to substantial thermal and hydrolytic reactivity of the molecule.[8,9] Indeed, none of the three compounds survive gas chromatographic injection or attempts to isolate them by vacuum distillation, but experience gained in the present work suggests that this may be due to a high propensity for *catalytic* thermal decomposition. For example, purified samples of **3c** proved to be quite resilient to thermolysis at 70 °C in benzene-d_6 solution. Heating at this temperature for several days did result in significant decomposition of the compound but yielded an intractable mixture of several products which could not be easily identified. Similar experiments with **3a** indicated it to be slightly more reactive than **3c**, but the product mixture obtained was no more straightforward to deduce. In this regard, it is worth noting that the siloxetanes appear to be much more stable *after* chromatographic purification than they are in the crude reaction mixtures. The siloxetanes also react readily with methanol in benzene solution at 40−70 °C to yield a mixture of several products, only some of which have yet been identified.[22]

The results presented in Table 1 verify our initial assessment that the selectivity of the reaction of **2** with carbonyl compounds should be sensitive to substitution at the allylic trialkylsilyl group of the silatriene. The variation in product distribution throughout the series **1a**−**c**, though not large, shows a distinct increase in the relative yield of siloxetane **3** relative to silyl ether **4** with increasing steric bulk at the trialkylsilyl group. The increase in the **3**/**4** ratio throughout the series of three compounds (from ~3 for **1a** to ~6 for **1c**) indicates an increase of about 0.5 kcal/mol in the relative free energy of activation for formation of the two products from collapse of the presumed biradical/zwitterion intermediate shown in eq 2. The relative yield of siloxetane is even higher for that derived from methylpentaphenyldisilane (**12**),[18] data for which are also included in Table 1. The silatriene derived from this compound contains an allylic methyldiphenylsilyl substituent, which is presumably even bulkier than the *tert*-butyldimethylsilyl group in **2c**.

We do not attach much significance to the anomalously low **3/4** ratio obtained for **1d**. In this case, formation of silyl free radicals (triphenyl- and triisopropylsilyl) competes significantly with the formation of silatriene **2d** in the initial photolytic event. Judging from the complexity of the reaction mixture obtained in this case, we conclude that the competing formation of radicals ultimately reduces the observable yield of silatriene adducts, presumably through secondary reactions. Photolysis of the **1d**/acetone mixture in the presence of enough chloroform to quantitatively trap the radicals allows the two silatriene/acetone adducts to be observed, but the apparent yield of **3d** is reduced proportionately at conversions higher than ~5%, the lowest at which product yields can be estimated by our ^{1}H NMR method. The **3d**/**4d** ratio of ~1.6 obtained at 5% conversion can thus be considered to be a lower limit.

Laser flash photolysis of **1b**−**d** in hexane solution produces transient absorptions in the 450−550 nm region which are similar (spectrally and temporally) to those previously reported for **1a**[8,9] and **12**.[18] The transient species giving rise to the prominent absorption band with λ_{max} ~490 nm has been assigned to the silatriene **2** (**2a** from **1a**; $SiR_3 = SiMePh_2$ from **12**) on the basis of its reactivity toward various "classic" silene traps (and nonreactivity toward classic silyl radical and silylene traps), along with the identity of the products isolated from or identified in steady-state trapping experiments.[8,9,13,15] In the present cases, the ~490 nm transient absorptions are all quenched by acetone and oxygen but not by chloroform, allowing their assignment to the corresponding silatrienes **2b**−**d** to be made with a reasonable degree of certainty.

The flash photolysis behavior of **1b,c** (see Figure 1a) is virtually indistinguishable from that of **1a**, in that there is clear evidence for the formation of only a single

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(22) Toltl, N. P.; Leigh, W. J. Unpublished results.

transient product which absorbs in the 270−600-nm spectral range—the corresponding silatriene **2b,c**. In contrast, flash photolysis of **1d** (Figure 1b) gives evidence for the formation of significant yields of triphenylsilyl radicals (λ_{max} 328 nm[21]) in addition to the corresponding silatriene **2d**.

There is a slight (~30%) variation in the rate constant for silatriene quenching by acetone throughout the series, with the rate constant *increasing* slightly with increasing size of the allylic trialkylsilyl group. This trend could result if the allylic trialkylsilyl group causes some degree of distortion of the Si═C bond, increasing its reactivity toward nucleophiles. The rate constant for reaction of **2a** with pinacolone (**9**) is similar to that with acetone; this and the fact that the product distributions are similar for the two ketones (at low conversions) suggest identical reaction mechanisms.

The reaction of the silatrienes **2a**−**c** with di-*tert*-butyl ketone (**7**) yields only a single detectable product in each case, the corresponding silyl ethers **8a**−**c**. These reactions appear to proceed cleanly; although the isolated chemical yields of the products are only in the 20−60% range, the material balances determined by NMR after 5−10% conversion were >90%. Our failure to detect the corresponding siloxetanes in the product mixtures may be due to their having lower thermodynamic stability than those obtained from acetone addition, or it may indicate a change in mechanism for addition of the bulkier ketone. The former is suggested by the results obtained with pinacolone (**9**) as the carbonyl addend; in this case, inspection of the product mixture at short photolysis times indicates the presence of two stereoisomeric siloxetane derivatives (**10a,b**) and silyl ether **11**, in a ratio of ~2:2:1. The product ratio changes with increased conversion of **1a**, however, to a value of ~0.2:0.9:1.0 at ~25% conversion. This suggests that **10a,b** are prone to decomposition under the reaction conditions; furthermore, one of the isomeric siloxetanes (that with the lower field allylic proton doublet, which can probably be assigned to the isomer with the *tert*-butyl substituent *syn* to the allylic proton) is clearly less stable than the other. However, no evidence for siloxetane formation could be obtained by NMR analysis of the crude reaction mixtures from photolysis of **1a**−**c** in the presence of **7**, even at low (≤5%) conversion, and the material balances are quite high.

The possibility that the formation of ether **8** from reaction of **7** proceeds by a different mechanism thus seems a very good one, especially in light of the fact that the rate constant for reaction of this ketone with **2a** is at least 2 orders of magnitude slower than those for acetone and pinacolone (**9**). The most reasonable explanation for this is that the bulky alkyl substituents on the ketone effectively shield the carbonyl n orbital from electrophilic attack, slowing the rate of formation of the proposed biradical/zwitterionic intermediate (eq 2) markedly. If this steric protection is complete enough, the reaction mechanism could change to a concerted ene addition, in which the carbonyl π orbital is the active MO involved in the transformation, and abstraction of the cyclohexadienyl hydrogen occurs in concert with Si−O bond formation.

The photochemical behavior of **1d** is distinctly different from that of **1a**−**c**, in that silyl free radicals (triphenylsilyl and triisopropylsilyl) are formed competitively with silatriene **2d** in hexane solution, presumably owing to an increase in the yield of disilane triplets as the (singlet-derived) [1,3]-silyl migration is slowed due to the increased size of the triisopropyl substituent.[18,19] Steady-state photolysis of **1d** in the presence of both acetone (to trap **2d**) and chloroform (to trap silyl radicals) indicate that radical-derived products account for ca. 40% of photolyzed disilane in hexane solution at room temperature. As expected,[8,9,13,18] the yield of radicals is increased markedly in acetonitrile solution due to enhanced intersystem crossing in the more polar solvent.[8,23] While product studies were not carried out in this solvent, comparison of the transient absorption spectra recorded in the two solvents (Figure 1b,c) suggests that silyl radical formation accounts for at least 90% of the primary transient product mixture in acetonitrile. This compound exhibits photobehavior in nonpolar solvents that is intermediate between **1a** (which undergoes predominant singlet state photochemistry[8]) and more heavily arylated disilanes (which react predominantly via the triplet state[18,19]). This duality may be useful for further studies of medium effects on the photochemistry and photophysics of aryldisilanes.

Summary and Conclusions

The reaction of aryldisilane-derived silatrienes with aliphatic ketones is markedly affected by steric effects of substituents at the silenic silicon atom, the allylic trialkylsilyl group, and the ketone. Reaction of methyl ketones proceeds in stepwise fashion via a biradical or zwitterionic intermediate which is formed by attack of the carbonyl oxygen at the silenic silicon atom. This is the rate-determining step for the reaction, and the rate increases slightly with increasing steric size of the substituents on the allylic trialkylsilyl group, presumably due to minor, sterically induced distortions of the Si═C bond. The intermediate collapses to form mixtures of siloxetane and silyl ether, with the yield of siloxetane increasing with increasing substituent size at either the silenic or trialkylsilyl silicon atoms. Extremely bulky ketones such as di-*tert*-butyl ketone react orders of magnitude slower than methyl ketones with the silatriene and yield only the corresponding silyl ether. It is proposed that, in this case, the mechanism changes to a concerted ene addition, since attack at the carbonyl oxygen n orbital is prevented by steric factors.

Experimental Section

^{1}H NMR spectra were recorded on Bruker AC200 or AM500 (where noted) spectrometers, ^{13}C NMR spectra were recorded on Bruker AC200 or AC300 spectrometers, and ^{29}Si NMR spectra were recorded on the Bruker AC300 using the DEPT pulse sequence; all were recorded in deuteriochloroform solution and are referenced to tetramethylsilane. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer and are referenced relative to the 1601.9 cm^{-1} polystyrene absorption. Mass spectra were recorded on a VGH ZABE mass spectrometer. Ultraviolet absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer interfaced to an IBM PS/2-286 microcomputer, or on a Hewlett-Packard HP8451 UV spectrometer. Gas chromatographic (GC) analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and an HP-1 mega-

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(23) Shizuka, H.; Hiratsuka, H. *Res. Chem. Intermed.* **1992**, *18*, 131.

bore capillary column (12 m × 0.53 mm; Hewlett-Packard Inc.). Semipreparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and an OV-101 stainless steel column (6 ft × $^1/_4$ in.; Chromatographic Specialties, Inc.). Radial chromatography was carried out using a Chromatotron (Harrison Research, Palo Alto, CA) and 2 or 4 mm silica gel 60 thick-layer plates. 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. Elemental analyses were performed by Galbraith Laboratories, Inc.

Triphenylsilyl chloride (Lancaster), trimethylsilyl chloride (Aldrich), dimethyl-*tert*-butylsilyl chloride (Lancaster), triethylsilyl chloride (Aldrich), triisopropylsilyl chloride (Aldrich), and 2-methylbutane (Fisher) were used as received from the suppliers. Reagent grade cyclohexane, *n*-hexane, and methanol were used as received from Caledon. Acetone (Baker Reagent) was distilled from potassium carbonate. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone after refluxing for several days. Cyclohexane-d_{12} and benzene-d_6 were used as received from Isotec, Inc.

Analytical-scale photolyses were carried out in a Rayonet photochemical reactor equipped with a merry-go-round and eight RPR-254 (254 nm) lamps. Photolysis solutions were contained in quartz NMR tubes sealed with rubber septa and were deoxygenated prior to photolysis with a steady stream of dry nitrogen.

1,1,1-Trimethyl-2,2,2-triphenyldisilane (**1a**), 1,1,1-triethyl-2,2,2-triphenyldisilane (**1b**), 1,1-dimethyl-1-*tert*-butyl-2,2,2-triphenyldisilane (**1c**), and 1,1,1-triisopropyl-2,2,2-triphenyldisilane (**1d**) were prepared by the procedure of Gilman.[16] Compound **1a** exhibited spectral data and melting points similar to those previously reported.[9,16]

1,1,1-Triethyl-2,2,2-triphenyldisilane (1b): mp = 94−95 °C; ^{1}H NMR δ 0.88 (cplx m, 15H), 7.36 (m, 9H), 7.50 (m, 6H); ^{13}C NMR δ 4.40, 8.40, 127.85, 128.84, 136.07; ^{29}Si NMR δ −9.31, −21.55; IR (KBr) 3069.2 (m), 2956.1 (s), 2874.9 (s), 1958.0 (w), 1896.6 (w), 1823.9 (w), 1483.9 (m), 1427.6 (m), 1100.6 (s), 1004.9 (m), 972.7 (w), 808.6 (m) cm^{-1}; MS *m/z* (*I*) 374 (30), 345 (10), 317 (4), 289 (7), 259 (100), 181 (5); exact mass calcd for $C_{24}H_{30}Si_2$ 374.1886, found 374.1880. Anal. Calcd for $C_{24}H_{30}Si_2$: C 76.94, H 8.07. Found: C 76.78, H 8.18.

1,1-Dimethyl-1-*tert*-butyl-2,2,2-triphenyldisilane (1c): mp = 82−83 °C; ^{1}H NMR δ 0.24 (s, 6H), 0.84 (s, 9H), 7.35 (m, 9H), 7.52 (m, 6H); ^{13}C NMR δ −3.9, 18.45, 28.05, 127.79, 128.86, 136.08, 136.22; ^{29}Si NMR δ −8.53, −21.08; IR (KBr) 3069.9 (s), 2956.2 (s), 2929.5 (s), 2856.7 (s), 1958.6 (w), 1900.0 (w), 1824.8 (w), 1428.0 (s), 1247.2 (m), 1100.1 (s), 1005.3 (m), 806.5 (s) cm^{-1}; MS *m/z* (*I*) 374 (20), 359 (18), 317 (100), 259 (55), 197 (15); exact mass calcd. for $C_{24}H_{30}Si_2$ 374.1886, found 374.1873. Anal. Calcd for $C_{24}H_{30}Si_2$: C 76.94, H 8.07. Found: C 76.47, H 8.23.

1,1,1-Triisopropyl-2,2,2-triphenyldisilane (1d): mp = 101−102 °C; ^{1}H NMR δ 1.02 (d, 8H), 1.35 (septet, 3H), 7.33 (m, 9H), 7.52 (m, 6H); ^{13}C NMR δ 12.53, 19.90, 127.74, 128.73, 136.44; ^{29}Si NMR δ −3.10, −20.64; IR (KBr), 3070.4 (w), 3052.8 (w), 2946.3 (s), 2866.4 (s), 1959.0 (w), 1897.6 (w), 1824.9 (w), 1464.7 (m), 1427.8 (s), 1097.1 (s), 998.6 (w), 803.7 (m), 774.7 (m) cm^{-1}; MS *m/z* (*I*) 416 (14), 373 (25), 331 (20), 289 (30), 259 (100), 197 (7), 157 (28), 115 (22), 59 (12); exact mass calcd for $C_{27}H_{36}Si_2$ 416.2356, found 416.2340. Anal. Calcd for $C_{27}H_{36}Si_2$: C 77.81, H 8.71. Found: C 77.62, H 8.79.

The siloxetanes **3a**−**c** and silyl ethers **4a**−**c** were prepared and isolated by essentially identical procedures. For example, a solution of **1c** (0.85 g, 0.0023 mol) and acetone (0.76 g, 0.013 mol) in 2-methylbutane (175 mL) was placed in a 200 mL capacity photochemical reactor consisting of a Pyrex outer vessel equipped with magnetic stirrer, reflux condenser, and gas inlet, a quartz immersion well, and an Osram HNS10U/OZ low-pressure mercury lamp surrounded by a Vycor sleeve. Dry nitrogen was bubbled through the solution for 15 min prior to and continuously throughout photolysis. The entire vessel was placed in a Dewar containing CO_2/2-propanol, and the solution was cooled to −78 °C. The solution was irradiated for 100 min, with aliquots being removed periodically for the purposes of monitoring the course of photolysis by GC. The solution was transferred to a round-bottom flask, and the solvent was distilled on the rotary evaporator to yield a colorless oil (0.90 g). The mass was dissolved in chloroform (3 mL). The separation procedure involved thick-layer radial chromatography, performed in a cold room at 4 °C; all solvents were cooled to 4 °C before use. After equilibration of the plate with hexanes, the sample was injected and the first band was eluted using a 70/30 hexanes/chloroform mixture. The first fraction (0.5 g after evaporation of solvent) was shown to consist of a mixture of **1c** and **4c** by ^{1}H NMR spectroscopy. A portion of the solid was dissolved in chloroform, and the components were separated by repeated semipreparative GC separations. The first component to elute was **1c**, as verified by coinjection with an authentic sample. The second component was difficult to obtain in pure form because of contamination with **1c**. Repeated collection and reinjection of the sample finally afforded a sample of **4c** contaminated with ~2% of the disilane. It was identified on the basis of the following data:

Diphenyl(2-(dimethyl-*tert*-butylsilyl)phenyl)(2-propoxy)silane (4c): colorless oil; ^{1}H NMR δ 0.19 (s, 6H), 0.90 (s, 9H), 1.18 (d, 6H), 4.20 (septet, 1H), 7.12−7.46 (cplx m, 9H), 7.50 (cplx d, 4H), 7.72 (d, 1H); ^{13}C NMR δ −2.13, 17.72, 25.45, 27.75, 67.20, 126.87, 127.55, 129.49, 135.89, 136.76, 136.99, 137.72, 140.99, 145.78; ^{29}Si NMR δ 4.51, −11.77; IR (neat) 3051.2 (s), 2971.2 (m), 2855.9 (w), 1468.6 (w), 1427.9 (w), 1367.4 (w), 1256.2 (w), 1113.6 (m), 1016.6 (m), 908.0 (m), 835.9 (m), 733.9 (w) cm^{-1}; MS (EI) *m/z* (*I*) 375 (10), 333 (17), 255 (100), 195 (27), 105 (8); MS [NH_3 CI] *m/z* (*I*) 431 (10), 375 (10), 272 (15), 258 (100); exact mass calcd for $C_{23}H_{27}Si_2O$ (M − 57) 375.1600, found 375.1587.

After the removal of the first band, the elution solvent was changed to 100% chloroform. Evaporation of solvent from the second fraction yielded a colorless solid, which was identified as **3c** on the basis of the following spectroscopic data.

***syn*-3,3-Dimethyl-1,1-diphenyl-9-(dimethyl-*tert*-butylsilyl)-2-oxa-1-silaspiro[3.5]nona-5,7-diene (3c):** 0.2 g, 27% isolated yield; mp 127−139 °C dec; ^{1}H NMR δ −0.21 (s, 3H), 0.03 (s, 3H), 0.60 (s, 9H), 1.39 (s, 3H), 1.86 (s, 3H), 2.98 (d, 1H), 5.72−5.86 (m, 4H), 7.28−7.50 (cplx m, 6H), 7.76−7.88 (m, 4H); ^{13}C NMR δ −4.07, 0.44, 17.15, 26.25, 26.83, 32.32, 33.58, 43.95, 89.42, 122.35, 126.77, 127.92, 128.12, 128.23, 130.12, 130.73, 131.70, 133.92, 134.74, 134.94, 136.20; ^{29}Si NMR δ 11.82, 9.25; IR (KBr) 2954.2 (m), 2927.8 (m), 1714.4 (s), 1431.7 (m), 1363.2 (s), 1223.9 (m), 1108.1 (s), 1006.3 (w), 855.5 (s), 801.3 (s), 705.0 (s) cm^{-1}; MS (EI) *m/z* (*I*) 375 (3), 317 (27), 259 (100), 240 (12), 199 (20), 181 (12), 105 (8), 73 (35); MS [NH_3 CI] *m/z* (*I*) 450 (5), 392 (8), 372 (35), 355 (30), 330 (100), 276 (32), 252 (15), 132 (22), 90 (15); exact mass calcd for $C_{23}H_{27}Si_2O$ (M − 57) 375.1600, found 375.1601.

Compounds **3a,b** and **4a,b** were prepared and isolated in a similar fashion and in similar chemical yields. Spectroscopic data for **diphenyl(2-(trimethylsilyl)phenyl)(2-propoxy)silane** (**4a**) were similar to those previously reported.[9] Spectroscopic data for the other three compounds are as follows.

***syn*-3,3-Dimethyl-1,1-diphenyl-9-(trimethylsilyl)-2-oxa-1-silaspiro[3.5]nona-5,7-diene (3a):** oil; ^{1}H NMR δ −0.19 (s, 9H), 1.38 (s, 3H), 1.80 (s, 3H), 2.90 (d, 1H), 5.71−5.83 (m, 4H), 7.33−7.50 (cplx m, 6H), 7.72−7.84 (m, 4H); ^{13}C NMR δ 1.27, 31.81, 33.12, 43.36, 89.33, 122.00, 125.61, 127.91, 128.08, 128.49, 130.14, 130.81, 130.95, 133.59, 134.63, 135.16, 135.96; ^{29}Si NMR δ 2.20, 12.40; IR (neat) 3025.5 (m), 2970.1 (m), 1739.6 (m), 1589.3 (m), 1428.9 (s), 1363.5 (m), 1246.3 (s), 1191.6 (w), 1112.3 (s), 931.5 (m), 840.3 (s), 740.1 (s), 699.2 (s), 648.8 (m) cm^{-1}; MS (EI) *m/z* (*I*) 375 (5), 317 (12), 271 (75), 259 (100), 199 (75), 181 (20), 73 (22); MS [NH_3 CI] *m/z* (*I*) 408 (33), 391

(10), 330 (90), 288 (100), 258 (60), 216 (40), 119 (15), 90 (85); exact mass calcd for $C_{23}H_{27}Si_2O$ (M − 15) 375.1600, found 375.1603.

***syn*-3,3-Dimethyl-1,1-diphenyl-9-(triethylsilyl)-2-oxa-1-silaspiro[3.5]nona-5,7-diene (3b):** oil; ^1H NMR (500 MHz), $\delta = 0.21$ (dq, 3H), 0.35 (dq, 3H), 0.76 (t, 9H), 1.38 (s, 3H), 1.81 (s, 3H), 2.94 (d, 1H), 5.86−5.71 (m, 4H), 7.35−7.43 (cplx m, 4H), 7.47 (m, 2H), 7.60 (m, 2H), 7.82 (m, 2H); ^{13}C NMR δ 5.52, 7.84, 27.30, 32.00, 33.21, 43.52, 89.39, 121.45, 125.44, 127.90, 128.10, 130.11, 130.78, 131.18, 133.96, 134.58, 135.16, 135.86; ^{29}Si NMR δ 11.24, 7.52; IR (neat) 2952.9 (s), 1741.0 (s), 1461.2 (m), 1374.4 (m), 1240.9 (s), 1111.3 (s), 1047.1 (m), 1007.9 (m), 860.8 (s), 699.5 (s) cm^{-1}; MS (EI) *m/z* (*I*) 403 (7), 375 (3), 347 (3), 317 (20), 300 (7), 285 (10), 259 (100), 240 (20), 212 (5), 199 (57), 181 (15); MS [NH_3 CI] *m/z* (*I*) 450 (5), 372 (35), 336 (53), 330 (100), 276 (15), 258 (30), 233 (28), 216 (20), 156 (7), 132 (90), 119 (12); exact mass calcd for $C_{25}H_{31}Si_2O$ (M − 29) 403.1913, found 403.1899.

Diphenyl(2-(triethylsilyl)phenyl)(2-propoxy)silane (4b): colorless oil; ^1H NMR δ 0.95−0.75 (m, 15H), 1.15 (d, 6H), 4.20 (septet, 1H), 7.11−7.81 (cplx m, 14H); ^{13}C NMR δ 4.35, 7.61, 25.32, 67.12, 126.91, 127.59, 128.10, 129.56, 135.86, 136.10, 136.45, 137.45, 141.26, 144.85; ^{29}Si NMR δ 5.17, −12.42; IR (neat) 3050.6 (s), 2956.1 (m), 2874.3 (w), 1646.8 (s), 1461.8 (w), 1427.5 (w), 1381.4 (w), 1113.5 (s), 1017.0 (s), 702.2 (s) cm^{-1}; MS (EI) *m/z* (*I*) 415 (12), 403 (12), 361 (40), 331 (15), 303 (33), 283 (100), 255 (40), 227 (60), 181 (35), 105 (32), 87 (12); MS [NH_3 CI] *m/z* (*I*) 450 (5), 431 (10), 403 (20), 361 (45), 330 (12), 300 (60), 258 (100); Exact mass calcd for $C_{25}H_{31}Si_2O$ (M − 29) 403.1913, found 403.1907.

Irradiation of continuously deoxygenated 2-methylbutane solutions of **1a**−**c** (0.015 M) containing 2,2,4,4-tetramethyl-3-pentanone (0.075 M) under conditions similar to those employed above led to the formation of a single product, according to ^1H NMR analysis of the crude photolysates at various stages of conversion of **1**. The photolysis was taken to ∼90% conversion, the mixture was stripped of solvent on the rotary evaporator, and the residue was dissolved in absolute ethanol (ca. 2 mL) and this solution left in the freezer overnight. The resulting colorless solid was recrystallized from ethanol/diethyl ether mixtures.

Diphenyl(2-(trimethylsilyl)phenyl)(2,2,4,4-tetramethyl-3-pentoxy)silane (9a): 16.5% isolated yield; mp 139−140 °C; ^1H NMR δ −0.09 (s, 9H), 0.87 (s, 18H), 3.44 (s, 1H), 7.28−7.40 (cplx m, 8H), 7.59 (cplx d, 4H), 7.69 (d, 1H), 8.07 (d, 1H); ^{13}C NMR δ 1.70, 29.69, 38.04, 88.81, 126.86, 127.46, 128.15, 129.49, 135.98, 136.19, 136.68, 137.25, 141.73, 148.31; ^{29}Si NMR δ −3.246, −14.809; IR (KBr) 2958.2 (m), 2873.1 (m), 1715.2 (m), 1480.6 (m), 1427.2 (m), 1364.6 (m), 1246.0 (m), 1109.4 (s), 1055.3 (s), 1019.7 (s), 838.0 (s), 704.1 (s), 652.7 (w) cm^{-1}; MS (EI) *m/z* (*I*) 459 (5), 417 (30), 331 (100), 253 (30), 199 (30), 135 (10), 57 (32); exact mass calcd for $C_{29}H_{39}Si_2O$ (M − 15) 459.2539, found 459.2539.

Diphenyl(2-(triethylsilyl)phenyl)(2,2,4,4-tetramethyl-3-pentoxy))silane (9b): isolated yield 55%; mp 97−98 °C; ^1H NMR δ 0.75−0.45 (m, 15H), 0.93 (s, 18H), 3.45 (s, 1H), 7.29−7.39 (cplx m, 8H), 7.58 (cplx d, 4H), 7.64 (d, 1H), 8.16 (d, 1H); ^{13}C NMR, δ 4.60, 7.63, 29.66, 37.97, 88.79, 126.81, 127.38, 127.78, 129.40, 135.87, 136.65, 137.68, 142.89, 145.08; ^{29}Si NMR δ 4.202, −14.798; IR (KBr) 2960.8 (m), 2871.7 (m), 1714.9 (m), 1462.7 (m), 1427.5 (m), 1396.4 (m), 1364.6 (m), 1223.0 (w), 1113.5 (s), 1062.7 (s), 1023.1 (s), 822.7 (s), 735.5 (s), 699.6 (s) cm^{-1}; MS (EI) *m/z* (*I*) 487 (50), 439 (5), 373 (100), 361 (45), 325 (23), 283 (10), 199 (20), 71 (12), 57 (45); exact mass calcd for $C_{31}H_{43}Si_2O$ (M − 29) 487.2852, found 487.2871.

Diphenyl(2-(dimethyl-*tert*-butylsilyl)phenyl)(2,2,4,4-tetramethyl-3-pentoxy))silane (9c): isolated yield 55%; mp 172−173 °C; ^1H NMR δ 0.13 (s, 6H), 0.45 (s, 9H), 0.84 (s, 18H), 3.32 (s, 1H), 7.29−7.38 (cplx m, 8H), 7.60 (cplx d, 4H), 7.69 (d, 1H), 8.11 (d, 1H); ^{13}C NMR δ −2.13, 18.16, 27.29, 29.67, 37.98, 88.89, 126.79, 127.07, 127.35, 129.36, 135.94, 136.77, 137.27, 137.65, 142.16, 145.77; ^{29}Si NMR δ 2.508, −14.036; IR (KBr) 2957.4 (m), 2866.2 (m), 1715.2 (m), 1471.1 (m), 1429.3 (m), 1396.7 (m), 1363.2 (m), 1254.2 (m), 1221.9 (m), 1114.9 (s), 1053.5 (s), 1022.2 (s), 810.3 (s), 770.1 (m), 703.3 (s) cm^{-1}; MS (EI), *m/z*(*I*) = 501 (2), 459 (5), 373 (10), 333 (15), 255 (30), 195 (15), 135 (10), 71 (20), 57 (100); exact mass calcd for $C_{32}H_{45}Si_2O$ (M − 15) 501.3009, found 501.3007. Anal. Calcd for $C_{33}H_{48}Si_2O$: C, 76.69, H, 9.36. Found: C 76.50, H 9.60.

Nanosecond Laser Flash Photolysis. Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ca. 16 ns) from a Lumonics 510 excimer laser filled with F_2/Kr/He mixtures and a microcomputer-controlled detection system. 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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Supporting Information Available: Figures giving ^1H NMR spectra of **1a** and **1d** and the FTIR spectrum of **3a** (4 pages). Ordering information is given on any current masthead page.

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