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Solution-Phase Far-UV Photochemistry of Unsaturated Organosilanes: Dehydrosilylation, Dyotropic Rearrangement, and Protodesilylation

Mark G. Steinmetz,* Mark A. Langston, Richard T. Mayes, and B. S. Udayakumar

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233

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Photolysis of 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**1**) at 214 nm in methanol, 2,2,2-trifluoroethanol, or *tert*-butyl alcohol gave 5-alkoxy-3,3,5-trimethyl-3,5-disila-1-hexenes **4a** (RO = methoxy, 25% yield), **4b** (RO = 2,2,2-trifluoroethoxy, 30%), or **4c** (RO = *tert*-butoxy, 24%), 4–11% yields of 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclobutane (**2**), 5–7% yields of 2,4,4-trimethyl-2,4-disila-5-hexyne (**3**), and **1** recovered in 50%, 29%, and 24% yields, respectively. In *tert*-butyl alcohol 10% of 2-(*tert*-butoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**6**) and 5% 4-*tert*-butoxy-1,1,3,3-tetramethyl-1,3-disilacyclopentane (**5**) were also obtained. Both direct or xylene-sensitized photolyses of **1** in methanol-*O*-d_1 led to >98% C_1 monodeuteriation of **4a** with 94% (direct) or 87% (sensitized) of the label trans to the vinylsilicon, while opposite stereospecificity, i.e. cis deuteriation of the vinyl group, was observed on reflux in acidic methanol-*O*-d_1. Stereospecific (85%) trans deuteriation of the vinyl group of **4c**-d_1 was observed on direct photolysis in *tert*-butyl alcohol-*O*-d_1, and **5** was labeled at C_4 and **6** at the carbinyl carbon attached to C_2. The deuterium-labeling results imply two carbocation precursors to **5** and **6**. The occurence of photoprotonation in both the excited singlet and triplet states of a constrained cycloalkene such as **1** is highly exceptional and is interpretable in terms of potential reactivity of a 90° twisted, ionic ground-state intermediate or intramolecular charge-transfer $^{1,3}\sigma,\pi^*$ states.

The π,3s (R) state plays a central role in the photochemistry of alkenes,[1-5] particularly among the more heavily alkylated derivatives, which display weak, though distinct Rydberg transitions at the onset of π,π^* absorption in vapor-phase UV spectra.[1,4a,6,7] Since the 3s orbital is relatively large compared to the molecular "core", π,3s (R) transitions are subject to external perturbations by diluents, diminishing in intensity while shifting to shorter wavelengths in solution-phase compared to vapor-phase spectra.[7,8] Consistent with the involvement of Rydberg states in alkylethylene photochemistry, a radical cation like species is apparently trapped nucleophilically in photolyses in alcohol solvents,[4a] and there is additional evidence that scavengeable (loosely bound) electrons are produced under comparable conditions in the case of heavily alkylated ethylenes such as 2,3-dimethyl-2-butene.[4d] Rydberg states have also been proposed in alkylethylene photorearrangements involving carbenes produced through migration of an alkyl group across the double bond.[1-5] Such skeletal rearrangements are largely suppressed on photolysis in alcohols,[4a] which suggests that the carbene and nucleophilic addition pathways share a common excited state. Additional support for the intervention of carbenes in alkylethylene photochemistry is provided by theoretical calculations of ethylene potential surfaces,[9] which show the corresponding excited-state 1,2-H migration giving ethylidene as energetically feasible from the π,3s (R) state. An alternate route to ethylidene is available from the orthogonal π,π^* state as well.[9]

Unlike alkylethylenes, alkenes bearing two or more trimethylsilyl groups exhibit a moderately intense (ϵ 300–920) band at the onset of strong π,π^* absorption in solution,[10] which is thought to correspond to a transition primarily valence σ,π^* in character rather than Rydberg,[11] consistent with the ability of silicon to stabilize π, and especially π^*, orbitals relative to the σ manifold through σ^*,d–π^* interactions.[10-12] Robin has further noted that the term values of the long-wavelength bands of heavily silylated ethylenes are as much as 10 000 cm^{-1} too high to be π,3s (R) transitions,[11] which suggests that the π,3s (R) transitions might lie at shorter wavelengths. In view of the unusual spectroscopic characteristics of silylethylenes and the prospects for uncovering new photoreactivity unique to silicon, we embarked on a study of 1,1,3,3-tetramethyl-1,3-disilacyclopentane (**1**),[13] which in pentane displays a σ,π^* transition centered at 220 nm (ϵ 1120), tailing out to 254 nm (ϵ 13) in the ultraviolet (Figure 1). To our knowledge, no prior study of silylethylene photochemistry has been reported.

The photochemistry of **1** in pentane and a variety of alcohols as solvents at 185-, 214-, and 254-nm wavelengths proved to be quite diverse and mechanistically complex. Four categories of reactivity, depending on reaction conditions, were established: (1) dehydrosilylation, (2) dyotropic rearrangement, i.e. the exchange of position of a silyl group and a vicinal substituent;[14] (3) photochemical protodesilylation by a mechanism profoundly different from the ground-state version of this reaction; (4) photoaddition of alcohols, with and without accompanying skeletal rearrangement.

Results

Direct Photolyses of Disilacyclopentene 1 in Pentane. Preparative direct photolysis of 10^{-2} M solutions of disilacyclopentene **1** in deoxygenated pentane at 185 + 254 nm produced a ring-contraction product, 1,1,3,3-tetra-

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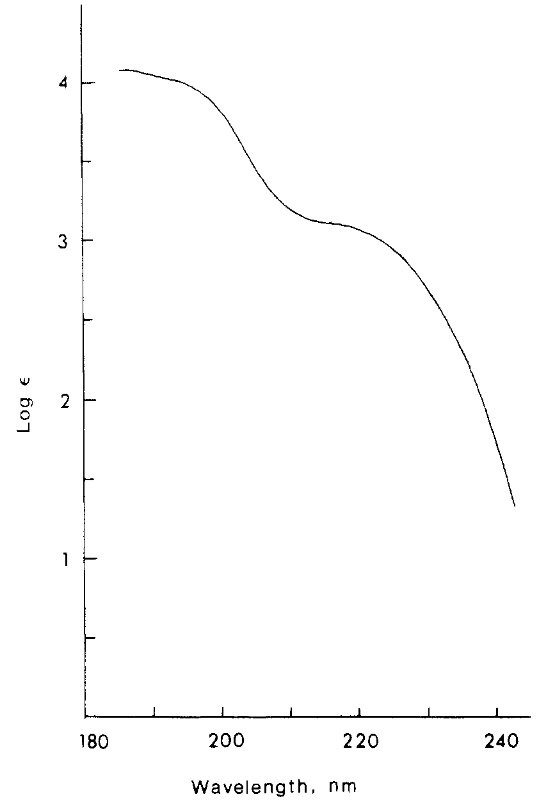
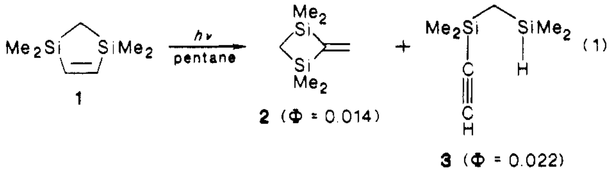


Figure 1. UV spectrum of disilacyclopentene 1 in pentane.

methyl-2-methylene-1,3-disilacyclobutane (2), and a cleavage product, 2,4,4-trimethyl-2,4-disilahex-5-yne (3), in absolute yields of 5–9% and 12%, respectively, at 40–60% conversions by GC analysis (eq 1). Each product



1

2 (Φ = 0.014)

3 (Φ = 0.022)

was isolated by preparative GC and identified by comparison of spectral data to literature data reported for 2[15] or by comparison of GC retention times and spectral data to an independently synthesized sample in the case of 3.

Low (<50% relative to 1 consumed) material balances were obtained in preparative runs taken to 40–60% conversions, which appeared to be partly attributable to secondary photolysis of products 2 and 3.[16] Degradation of products and/or reactant through additional reactions possibly involving free radicals could not be ruled out at 185 nm. While no additional products were detected by ^1H NMR or GC analysis of the photolysate, a colorless to pale yellow film had permanently deposited onto the inner glass sleeve of the photolysis apparatus during the preparative runs. Material balances markedly improved to 85–100% in quantitative runs taken to <11% conversions at 185 nm (entry 1, Table I) and 214 nm (entry 2, Table I). Here, yields of 2 and 3 relative to 1 consumed were obtained from rates, i.e. slopes of product formation and reactant disappearance derived from concentration vs. time profiles. Figure 2a depicts the concentration vs. time plot corresponding to the second entry in Table I.

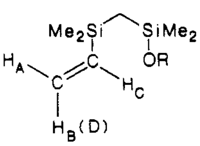
Table I. Rates of Product Formation of 185- and 214-nm Photolyses of Disilacyclopentene 1 in Pentane, Methanol, 2,2,2-Trifluoroethanol, and *tert*-Butyl Alcohol

		$k \times 10^5$,[a] M min^{-1} (% yield)[b]			
solvent	ϵ[c]	2	3	4	other
pentane (185 nm)[d]		0.11 (35)	0.15 (50)		
pentane (214 nm)[e]		0.56 (47)	0.63 (53)		
Photolyses Performed at Constant[f] Light Output at 214 nm[e]					
methanol (p*Ka* 15.5)	32.6	1.2 (14)	0.98 (12)	5.8 (71)	
CF_3CH_2OH (pK_a 12.4)	26.7	1.0 (11)	0.98 (11)	6.8 (73)	
t-BuOH (pK_a 18)	12.2	1.4 (19)	1.0 (13)	2.6 (35)	1.9 (25)[g]

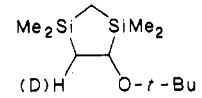
[a] Rates correspond to slopes of concentration vs. time profiles, average deviation 15%. [b] Product yields are normalized to rate of reactant disappearance. [c] Dielectric constants from ref 18. [d] Filtered output of a low-pressure mercury lamp used. [e] 15-W Philips zinc lamp used. [f] Average deviation in light output was 10%. [g] Individual rates (yields) for products 5 and 6 were 0.63 (8.3) and 1.3 (17), respectively.

Calibration of slopes (mmol min^{-1}) obtained from concentration vs. time plots against *cis*-cyclooctene actinometry[17] (Experimental Section) for three independent runs taken to low conversions gave quantum yields of products 2 and 3 representative of primary photochemistry at 185 nm that are summarized in eq 1. An interference filter excluded the 254-nm component of the low-pressure mercury lamp.

Direct Photolyses of Disilacyclopentene 1 in Methanol, 2,2,2-Trifluoroethanol, and *tert*-Butyl Alcohol. Photolyses of 1 in alcohols were conducted to trap potential ground- and excited-state intermediates and to ascertain whether photoreactivity paralleled that of alkylethylenes, particularly with regard to nucleophilic addition. On photolysis of 10^{-2} M 1 in deoxygenated methanol, solvent addition to 1 in fact occurred, but with concomitant cleavage of the vinyl Si–C bond (protodesilylation) to form 5-methoxy-3,3,5-disila-1-hexene (**4a**; R = CH_3) in 25% yield at 50% conversion by GC analysis. The silyl ether was accompanied by formation of 4% **2** and 5% **3**.



4a, R = CH_3
b, R = CH_2CF_3
c, R = $C(CH_3)_3$



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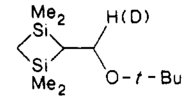

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With 2,2,2-trifluoroethanol as the solvent, direct photolysis of 0.04 M 1 gave 4% **2**, 5% **3**, and 30% 5-(2,2,2-trifluoroethoxy)-3,3,5-trimethyl-3,5-disila-1-hexene (**4b**; R = OCH_2CF_3) at 71% conversion. When photolyses of 1 (0.03 M) were conducted with the less acidic alcohol of lower dielectric constant, *tert*-butyl alcohol, two new products were formed in 5% and 10% yields, respectively (by GC analysis), 4-*tert*-butoxy-1,1,3,3-tetramethyl-1,3-disilacyclopentane (**5**) and 2-(*tert*-butoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**6**). Additional products were **2** (11%), **3** (7%), and 5-*tert*-butoxy-3,3,5-trimethyl-3,5-disila-1-hexene (**4c**; 24% yield) at 76% conversion.

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[15] Fritz, G.; Schober, P. *Z. Anorg. Allg. Chem.* **1969**, *368*, 337.

[16] (a) Product 2 is apparently destroyed on 185-nm photolysis in pentane. Alkyne 3 produces disilacyclopentene 1 and methylenedisilacyclobutene 2 with quantum yields of 0.10 and 0.12, respectively.[16b] (b) Steinmetz, M. G.; Mayes, R. T.; Langston, M. A., unpublished results.

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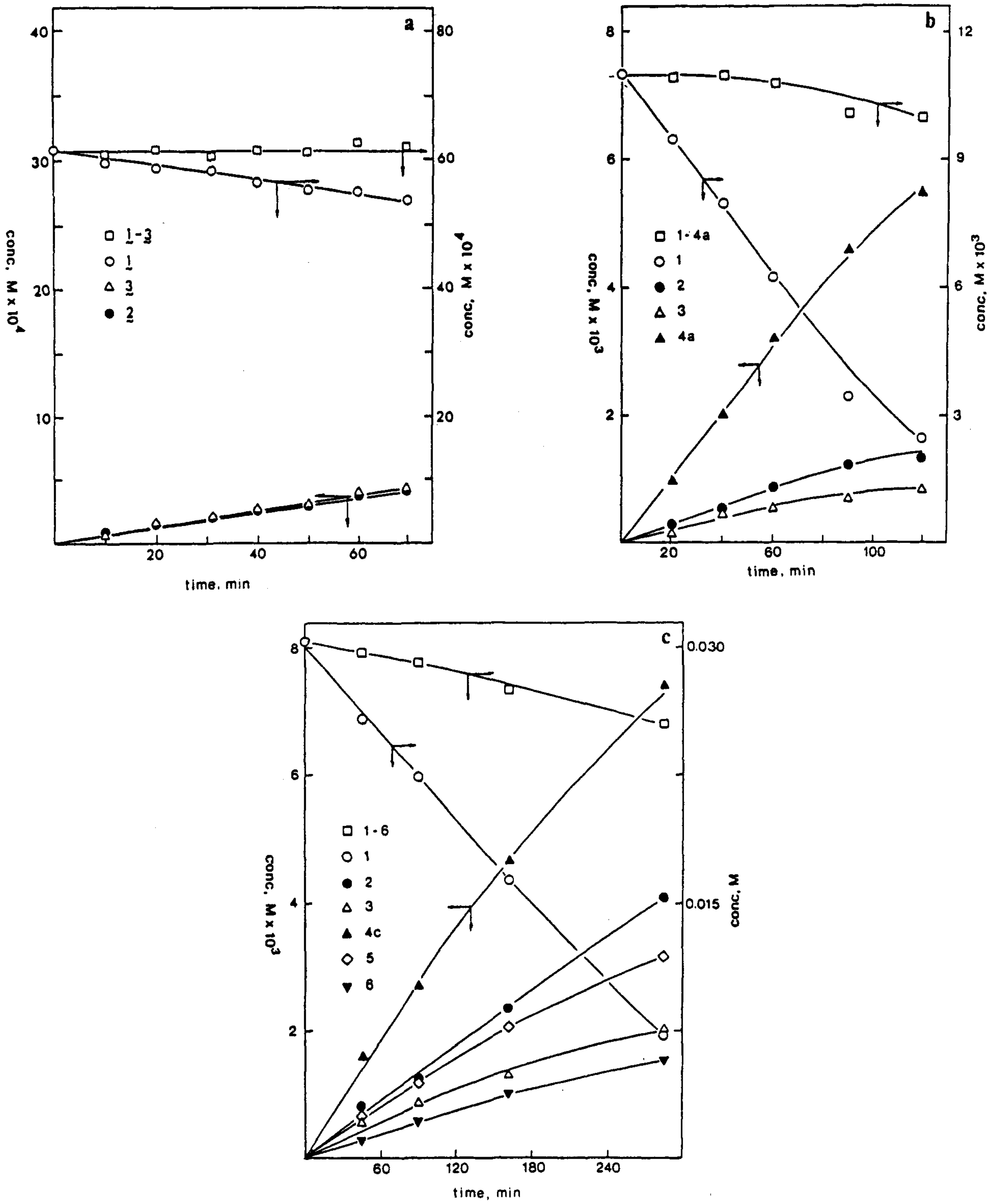

Figure 2. Concentration vs. time profiles for photolysis of disilacyclopentene 1 in (a) pentane, (b) methanol, and (c) *tert*-butyl alcohol at 214 nm.

For each of the preparative photolyses described above, products 2 and 3 along with reactant 1 were isolated by preparative GC as a mixture, which was characterized by GC-MS analysis and ^{1}H NMR spectroscopy and by comparison of GC retention times to independently synthesized 3 and to product 2 isolated from preparative photolyses in pentane (vide supra). Each of silyl ethers 4a-c was isolated by preparative GC and identified by GC-MS analysis and by comparison of ^{1}H NMR and IR spectral data and GC retention times to those of authentic samples.

The ^{1}H and ^{13}C NMR, IR, and GC-MS data were fully consistent with the structural assignments for products 5 and 6 (Experimental Section). The ^{13}C NMR spectrum of 5 was particularly diagnostic in exhibiting nine absorptions corresponding to each carbon in the molecule, four of which represented nonequivalent methyls as observed in the 250-MHz ^{1}H NMR spectrum of 5. The ^{1}H NMR spectrum of product 5 exhibited a doublet at δ 0.82 (J = 7 Hz) and a triplet (J = 7 Hz) at δ 3.45 corresponding to methylene and methine (CHOR) protons, respectively. The methylene (CH_2OR) group of product 6 was a doublet at δ 3.47 (J = 9 Hz) while the disilacyclobutane methine proton appeared upfield as a triplet at δ 0.82 (J = 9 Hz). These absorptions assumed considerable importance as likely sites for incorporation of deuterium from *tert*-butyl alcohol-O-d_1 in the deuterium-labeling studies described below.

It is important to note that while products **4c** and **5** were not difficult to handle, **6** was not stable under certain conditions. Neat **6** gave 46% **4c** and 33% **5** along with 18% unreacted **6** after 10 days. However, dilute solutions of **6** in pentane or CCl_4 remained unchanged for weeks. Careful controls (Experimental Section) with a highly purified sample of **6** showed that (1) no significant error (<5%) would have been introduced during quantitative determination of **4c**–**6** by GC analysis of photolysates, (2) no more than 7–14% of **5** or 5% of **4c** isolated from photolysates could have derived from **6**, and (3) products **4c**–**6** could be converted to **4a** on reflux in methanol containing a catalytic amount of *p*-toluenesulfonic acid.

The 214-nm rates of product formation (M min^{-1}) and yields relative to **1** consumed were not markedly sensitive to pK_a or dielectric constant of the solvent, as seen from Table I. A slight enhancement in the rate of ether **4b** formation in the more acidic alcohol, trifluoroethanol, relative to **4a** in methanol, is noteworthy, as well as the diminished rates of **4c** + **5** + **6** formation in *tert*-butyl alcohol. The rates were obtained from concentration vs. time profiles at constant light intensity (10% average deviation of light output for all runs; Experimental Section). Representative runs with methanol and *tert*-butyl alcohol are shown in Figure 2, parts b and c.

Sensitized Photolyses of Disilacyclopentene 1. Alkylbenzenes have been shown to be effective triplet sensitizers for simple alkyl-substituted olefins having triplet energies E_T in excess of 95 kcal mol^{-1}.[19] No reaction of **1** was observed on 254-nm irradiation in pentane with toluene as triplet sensitizer, however. GC–MS analysis of the photolysate showed only **1** and toluene (E_T = 82.5 kcal mol^{-1} [19]), no detectable amounts of **2** or **3**, and no other products in other than trace quantities.

Photolysis of 0.00862 M **1** and 0.85 M *p*-xylene (E_T = 80.4 kcal mol^{-1} [19]) in methanol at 254 nm with Vycor-filtered light of a Rayonet photochemical reactor gave a 48% yield of silyl ether **4a** as the sole product at 48% conversion by GC analysis. No trace of products **2** or **3** was found by GC analysis. A control run to check the stabilities of **2** and **3** showed that respective concentrations no higher than 1.13×10^{-4} and 1.76×10^{-4} M would have been photostable in the presence of 0.01–0.004 M **1**, 0.003–0.009 M **4a**, and 0.85 M *p*-xylene (Experimental Section). Nonetheless, a careful check revealed that these concentrations of **2** and **3** would certainly have been detected by GC in the sensitized photolysis of highly purified (>99.5%) samples of **1**. Further efforts focused on quantitative Stern–Volmer quenching studies to determine the triplet efficiency and ensure that formation of **4a** was not due to direct absorption of light by **1**. This seemed unlikely in any case, since at all concentrations of substrate and sensitizer employed the *p*-xylene absorbed >99% of the incident light.

A linear Stern–Volmer quenching plot for runs 0.85 M in xylene at a series of concentrations of **1** in methanol was obtained, as shown in Figure 3. Data over a 0.00239–0.0508 M range of concentrations of **4a** gave an average slope of 0.0464 M^{-1} and an intercept of 4.80 ± 0.24. Thus, the limiting quantum yield for formation of **4a** was 0.21, and $k_q\tau$ from the ratio of intercept to slope was 105.[20] Given the magnitude of the measured efficiencies, 0.07–0.17 over the entire concentration range of substrate, formation of **4a** in the presence of xylene can not be an artifact of direct absorption of a small fraction (<0.01) of the incident light in competition with sensitizer.

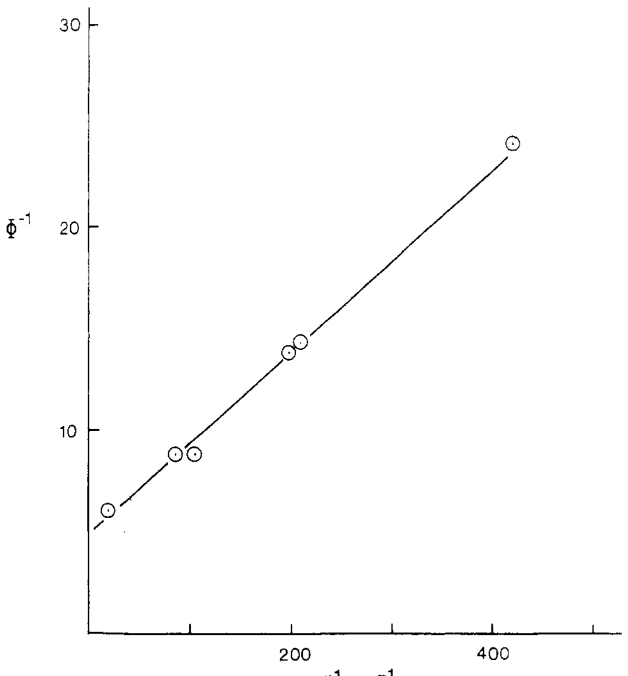

Figure 3. Stern–Volmer plot for *p*-xylene-sensitized reaction of disilacyclopentene **1** in methanol.

Stern–Volmer quenching of *p*-xylene fluorescence showed that triplet rather than singlet energy transfer to **1** most likely accounts for the Stern–Volmer kinetics of Figure 3. Slopes of plots of I_0/I vs. **1** concentration, where I and I_0 correspond to fluorescence intensities with and without quencher, for aerated or nitrogen-purged solutions of 0.85 M *p*-xylene in methanol, were insensitive to **1** concentration (0.01–0.05 M). Thus, $k_q\tau$ = 2.3–3.6 M^{-1} was found, far less than required to account for sensitized photoreaction of **1**,[21] consistent with the expected endothermicity of the singlet energy transfer from *p*-xylene (E_S = 104 kcal mol^{-1} [22]) to **1** (E_S > 110 kcal mol^{-1}, nonvertical; E_S = 130 kcal mol^{-1}, vertical).

Sensitized photolysis of 0.063 M **1** and 0.88 M *p*-xylene in *tert*-butyl alcohol at 254 nm produced 20% of silyl ether **4c**, 5.8% of **5**, and 10% of **6**, along with 44% unreacted **1** after 28 h. As with xylene-sensitized runs in methanol (vide supra), neither **2** nor **3** was found in detectable amounts by GC analysis. Product ratios of **4c**:**5**:**6** of 3.7:1:2.0 at 24% conversion (the lowest conversion measured) were comparable to the 4.1:1:2.1 ratio of direct runs extrapolated to 0% conversion (Table I). This similarity in product ratios, independent of multiplicity, suggests the possibility that products **4c**, **5**, and **6** share a common excited state.

Direct Photolyses in Deuteriated Alcohols. Photolyses of **1** in methanol-O-d_1 (99% + atom % D) led to >99% incorporation of one deuterium into silyl ether **4a**, exclusively at the C_1 vinyl position, with stereospecificity

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[19] Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, P. J. *J. Org. Chem.* **1981**, *46*, 3609 and references cited therein.

[20] The kinetic derivation of $k_q\tau$ is given by: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

[21] Our first trial gave a somewhat higher Stern–Volmer slope $k_q\tau$ = 13 M^{-1}. However, subsequent work with samples of **1** freshly prepared from pyrolysis of disilane followed by careful GC purification failed to uncover signs of significant quenching beyond the results cited in the text. We suspect that an impurity led to spurious quenching in the initial trial.

[22] E_S value taken from the 0–0 band of *p*-xylene: Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: New York, 1971; p 148.

favoring label at H_B, trans to the silyl group at C_2 (vide supra). Reactant **1** and products **2** and **3** were unlabeled on completion of the photolyses and contained <2% deuterium, as an upper limit, by GC–MS analysis (Experimental Section). Although no parent ion was observed for **4a** or **4a**-d_1 by electron-impact mass spectroscopy, GC–MS did show a characteristic fragment ion at m/e 174 (relative intensity 100) corresponding to loss of a methyl group of **4a**-d_1, but no detectable m/e 173 fragment ion attributable to the undeuteriated silyl ether. The extent of di- and trideuteriation was negligible, <1%. In the ^{13}C NMR spectrum of **4a** the terminal carbon of the vinyl group appeared at 130.6 ppm as a 1:1:1 triplet due to coupling with deuterium, whereas a single peak was observed for the vinyl carbon bearing silicon at 140.8 ppm, thus establishing the position of the label as H_A and/or H_B. The 250-MHz ^1H NMR spectrum of **4a**-d_1 showed H_A and H_B as doublets at δ 5.63 (J_{AC} = 20 Hz) and δ 5.89 (J_{BC} = 15 Hz) and a multiplet corresponding to H_C at δ 6.19, which appeared as a partially resolved doublet of triplets (J_{AC} = 20 Hz, J_{HD} = 2.1 Hz) superimposed on a multiplet due to H_C coupling to H_B. The intensity ratio of H_A:H_B immediately established H_B as the site preferentially labeled by deuterium. This assignment was confirmed by ^2H NMR, which also showed the C_2 position as unlabeled. A high degree of stereospecificity was achievable if conversions were kept low. Thus, the ratio H_B:H_A was 15:1 at 15% conversion, but dropped to 2.5:1 at 50% conversion, most likely due to secondary photolysis of **4a** and resultant scrambling between H_A and H_B vinyl positions.

Photolyses in *tert*-butyl alcohol-*O*-d_1 (98+ atom % D) as the solvent were performed to obtain mechanistic information concerning possible precursors to products **5** and **6**. As in the above methanol-*O*-d_1 runs, reactant **1** and products **2** and **3** were essentially unlabeled by deuterium. Silyl ether **4c** was labeled to the extent of 91–99% by mass spectroscopy (Experimental Section) with 85% of the label at H_B (δ 5.86) and 15% of the label at H_A (δ 5.60). Deuterium was not detected at H_C (δ 6.17) or elsewhere in the molecule. Considering the high (50–60%) percent conversion achieved in this run as compared to runs in methanol, the high degree of stereospecificity for incorporation of deuterium into **4c** implies a lower efficiency for photoisomerization about the double bond in the case of silyl ether **4c**-d_1 and **4a**-d_1. Products **5** and **6** were >99% and >90%, respectively, monodeuteriated by mass spectroscopy. ^2H NMR showed that **5** was exclusively labeled at the δ 0.82 methylene group and that **6** had at least 87% of the deuterium at the δ 3.47 methylene position; the appearance of 13% of the deuterium at the δ 0.82 methine position was no doubt due to the presence of **5**-d_1 as a contaminant to the extent of 12–13% from the integrated intensities of the respective *tert*-butyl absorptions and GC analysis. The 250-MHz ^1H NMR spectra of **5** and **6** were consistent with the above labeling assignments. Thus, it was clear from the integrated intensity and the appearance of the δ 3.47 absorption, which remained to a doublet (J = 9 Hz), and from the collapse of the δ 0.82 methine triplet to a doublet (J = 9 Hz), that the methylene position of product **6** contained the deuterium. The collapse of the δ 3.45 methine triplet of **5** to a doublet (J = 7 Hz) and presence of a corresponding doublet at δ 0.82 (J = 7 Hz) were indicative of deuterium labeling of the methylene position.

Table II. Rates of Product Formation (Relative Yields) and Rates of Reactant Disappearance for Photolyses of 1 in Methanol at 214 vs. 254 nm

		$k \times 10^5$,[a] M min^{-1} (% yield)[b]				conversion,
λ, nm	concn, M	**1**	**2**	**3**	**4a**	%
214[c]	0.0110	−7.9	1.39 (18)	0.94 (12)	5.3 (67)	0–41
214[c]	0.00840	−4.7	0.59 (12)	0.65 (14)	3.1 (67)	0–40
254[d,e]	0.0169	−2.08	0.14 (6.7)	0.18 (8.6)	1.8 (86)	0–26
254[d,f]	0.0144	−2.30	0.16 (7.0)	0.14 (6.9)	1.9 (83)	0–40

[a] Rates correspond to slopes of concentration vs. time profiles. [b] Product yields are normalized to rate of disappearance of reactant. [c] Output of a 15-W Philips zinc lamp used. [d] Rayonet photolysis apparatus was used (Experimental Section). [e] Temperature was 3 °C. [f] Temperature was 65 °C.

Sensitized Photolyses of 1 in Methanol-*O*-d_1. Stereospecific incorporation of deuterium at H_B of **4a** was effected by *p*-xylene-sensitized photolysis of **1** in methanol-*O*-d_1. Analysis of GC-isolated silyl ether **4a**-d_1 by $^{1,2}H$ NMR and GC–MS showed >98% incorporation of one deuterium exclusively at the terminal vinyl position, 74% of the label at H_B and the balance at H_A at 18% conversion of **1**. Scrambling of label between H_A and H_B of **4a**, presumably from triplet-sensitized isomerization about the double bond, was a function of conversion as in direct runs (vide supra). Extrapolation of 18%, 31%, and 48% conversion runs to 0% conversion gave 84–87% stereospecificity favoring labeling of H_B. The extrapolation was required due to difficulty in separating large amounts of xylene from **4a** at conversions lower than 18%.

Reaction of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Acidic Methanol-*O*-d_1. To determine whether the stereospecificity for incorporation of deuterium into **4a** followed the usual course of protodesilylation in the ground state, i.e. retention of configuration with respect to the silyl group lost from the double bond, reaction of **1** in methanol-*O*-d_1 with 6% by weight sulfuric acid-d_2 (99.5+ atom % D) was conducted. The rate of formation of **4a** was sluggish, and at best, only 11% maximum yields of **4a**-d_1 could be achieved after 91-h reflux. Nonetheless, the reaction was highly stereospecific. Practically exclusive (95 ± 5%) labeling of the H_A position of **4a**-d_1 by deuterium was found by 250-MHz ^1H NMR spectroscopy, parallel to labeling results reported for reaction of β-trimethylstyrenes with DCl.[23]

Wavelength Effects. The rates of formation of **2** and **3**, relative to **1** consumed, appeared to be wavelength dependent, as shown by comparison of entries 1 and 2 of Table II, obtained at 214 nm, to entries 3 and 4, which correspond to runs at 254 nm, conducted at two temperatures, 3 and 65 °C. The 67% relative yield of **4a** of the 214-nm runs increased to 83–86% at the expense of products **2** and **3** on going to the longer wavelength, 254 nm, while the mass balance, i.e. total relative yield of **2** + **3** + **4a**, essentially remained constant at 93–99%. The corresponding change in ratios of **2** or **3**:**4a** was 1:4–5 at 214 nm, as compared to 1:10–13 at 254 nm. These ratios remained constant within the specified limits over a range of conversions as low as 6–7% to as high as 40–41%.

While a higher electronic state than S_1, or a vibrationally excited state of S_1, accounts for the wavelength effect on yields of **2** or **3**, the interpretation of wavelength effects requires caution,[24] particularly since the Table II effects are small. The most obvious alternate interpretation, secondary photolysis of **2** or **3** at the longer wavelength, was ruled out by a control. Thus, a photomixture con-

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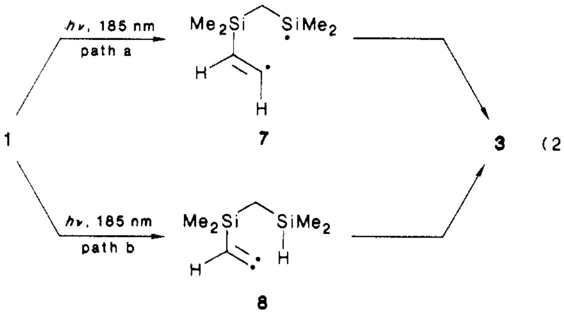
[23] (a) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416; *Tetrahedron Lett.* **1973**, 2523. (b) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: Boston, 1981; pp 62–66.

[24] (a) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1967; p 659. (b) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

taining 5.23×10^{-4} M product **2**, 6.14×10^{-3} M reactant **1**, 4.40×10^{-4} M alkyne **3**, and 2.89×10^{-3} M silyl ether **4a** was irradiated at 254 nm while being monitored by GC analysis. No decrease in concentration of **2** or **3** was observed after 30 min. Instead, products **2**, **3**, and **4a** increased in concentration at respective rates (M min^{-1}) of 1.3×10^{-6}, 1.2×10^{-6}, and 2.0×10^{-5} for a 2-h period. These rates do not differ markedly from the 254-nm rates of Table II.

Discussion

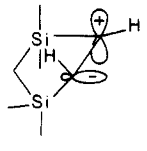
Photochemical Dehydrosilylation. At least two mechanisms are possible in the elimination of an SiH group of **1** to produce alkyne **3** (eq 2): cleavage to diradical **7** followed by hydrogen transfer (path a) or 1,1-elimination (path b).[9,25,26] 1,2-Elimination by nonplanar transition states resembling carbenes **10** and/or **11**,[9,27,28] or directly via a retro 2s + 2s pathway analogous to photochemical cycloreversion of cyclobutane to ethylene,[9] is also conceivable. However, 1,2-elimination has not been observed in 185-nm photolyses of *cis*-2-octene, which instead undergoes cis–trans isomerization and double-bond migration,[29,30a] although both 1,1- and 1,2-elimination have been reported for 185-nm photolyses of a γ,δ-unsaturated ketone that has 1,2-disubstitution at the double bond.[30b] 1,1-Elimination predominates among 1,1-dialkylethylenes,[30] and interestingly, a vinylidene intermediate is apparently trapped through intramolecular CH insertion in competition with 1,2-alkyl migration in the case of 2-methyl-1-pentene.[30a] The various modes of elimination are not experimentally distinguishable in the case of **1**.



(2)

The π,π^* state of mono- and dialkylethylenes is thought to be involved in 1,1- and 1,2-elimination,[30] since alternate modes of reactivity, e.g. skeletal rearrangement and "nucleophilic trapping", become more important as the π,3s (R) state is stabilized relative to the π,π^* state on successive alkylation of the double bond. Such an assignment for dehydrosilylation would require reaction via the higher energy π,π^* state of **1** as opposed to the S_1 σ,π^* state, which would explain why **3** is subject to wavelength effects similar to those for the loss of molecular hydrogen from 1-octene at 185 nm vs. longer wavelengths.[30a]

1,1-Elimination equivalent to path b has been treated theoretically in the case of ethylene.[9,27,28] The calculated ground- and excited-state potential surfaces show that vinylidene is accessible on twisting in the π,π^* state, with pyramidalization of an sp^2 center required to minimize the excited-state barrier to 1,1-elimination of molecular hydrogen.[9] Pyramidalization concomitant with rotation about the π system would open up this channel to geometrically constrained olefins such as **1**, although the full perpendicular geometry of species **9** might not be reached prior to attainment of the transition state for hydrogen loss. Species **9** is consistent with the concept of sudden polarization in π–π^* states.[31]



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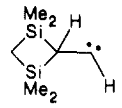
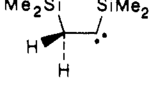


10



11

Theoretical calculations also suggest that the twisted π,π^* state or the π,3s (R) state of ethylene[9] can undergo 1,2-elimination by a high-energy pathway topologically related to ethylidene.[9,27,28] While photochemical scrambling of deuterium in dideuteriated ethylenes is consistent with reversible 1,2 H(D) shifts via ethylidene,[32a,b] competitive molecular elimination is thought[9] to be predissociative to account for the lack of quenching of acetylene formation on going from vapor to condensed phase. Analogous disengagement of an SiH group in concert with or subsequent to rearrangement of **1** to carbenes **10** and/or **11** competitive with 1,2 H or 1,2 Si shifts, forming **2** (vide infra), would appear to be unlikely in solution[28] but nonetheless has a potential counterpart in the 1,2-elimination of γ,δ-unsaturated ketones at 185 nm.

The diradical route, path a, is analogous to simple α-cleavage of alkenes to radicals, which is normally observed on photolysis in the vapor phase.[32] Path a might be anticipated to play only a minor role in solution,[32b] since bond dissociation energies suggest that **1** should be unexceptional with regard to homolytic Si–C bond cleavage.[33,34] Such a cleavage has no counterpart in the solution-phase photochemistry of carbocyclic alkenes.[1-5] Nonetheless, selective weakening of a Si–C bond might be a manifestation of electronic properties of the σ,π^* configuration,[35] which is dominant in the lowest spectroscopic state. A high-energy vibronic state of S_1 would then be needed to account for wavelength effects on yields of **3**.

Dyotropic Rearrangement. Precedent for formation of carbene-derived products through migration of a substituent across the double bond of alkylethylenes strongly supports a mechanism whereby carbene **10** plays a dominant role in the formation of **2**, which would be consistent

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[25] (a) Gilbert, J. C.; Luo, T. *J. Org. Chem.* **1981**, *46*, 5237. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

[26] (a) Theoretical calculations indicate that the transformation of vinylidene to acetylene is unactivated,[26b] and that 1,1-elimination probably proceeds by a transition-state species 12.2 kcal mol^{-1} further above vinylidene.[27] (b) Krishnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *79*, 408.

[27] Krishnan, R.; Frisch, M. J.; Pople, J. A. *Chem. Phys. Lett.* **1982**, *85*, 145.

[28] McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1985**, *107*, 5191.

[29] Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1983**, 1665.

[30] (a) Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1984**, 1725. (b) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1982**, *104*, 4424.

[31] (a) Salem, L. *Science (Washington, D.C.)* **1976**, *191*, 822. (b) Petsalakis, I. D.; Theodorakopoulos, G.; Nicolaides, C. A.; Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1984**, *81*, 3161. (c) Buenker, R. J.; Bonacic-Koutecky, V.; Pogliani, L. *J. Chem. Phys.* **1980**, *73*, 1836. (d) Trinquier, G.; Malrieu, J.-P. *Chem.* Phys. *Lett.* **1980**, *72*, 328. (e) Brooks, B. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1979**, *101*, 307.

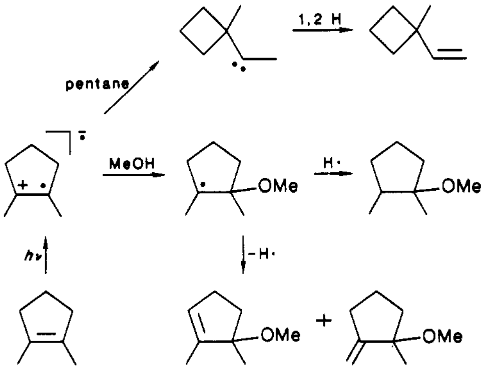
[32] (a) McNesby, J. R.; Okabe, H. *Adv. Photochem.* **1964**, *3*, 157. (b) Hirokami, S.; Cvetanovic, R. *J. Phys. Chem.* **1974**, *78*, 1254 and references cited therein. (c) Wieckowski, A.; Collin, G. J. *J. Phys. Chem.* **1977**, *81*, 2592. (d) Collin, G. J.; Deslauriers, H.; Wieckowski, A. *J. Phys. Chem.* **1981**, *85*, 944 and references cited therein.

[33] Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

[34] Dehydrosilylation has no analogue in the 185-nm solution-phase photochemistry of cyclopentene,[2,3d,5a] cyclohexene,[2,3c] cycloheptene,[2,3a,c] or cyclooctene.[2,3c]

[35] Modified CNDO/2 calculations of vinylsilane as a model show that σ–π^* excitation would involve promotion of an electron from a second highest occupied MO involving the vinylsilicon σ bond, suggesting scission in the lowest excited singlet of silylethylenes. See: Mollere, P.; Bock, H.; Becker, G.; Fritz, G. *J. Organomet. Chem.* **1972**, *46*, 89.

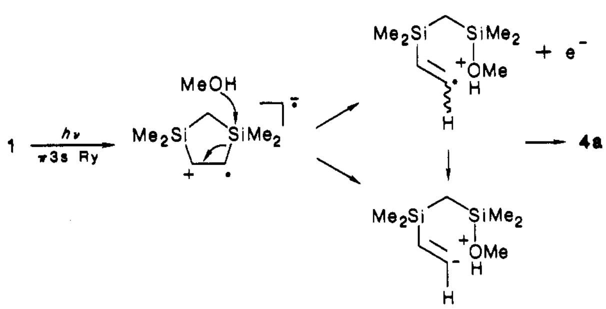
Scheme I



with the high migratory aptitude of silicon relative to hydrogen or carbon, at least in ground-state rearrangements.[36] While 1,2 H shift competitive with 1,2 alkyl migration is not observed in 185-nm photolyses of cyclopentene, the occurrence of 1,2 H migration resulting in products of trappable carbenes in the photochemistry of hindered *tert*-butylethylenes suggests,[37] as an alternate route to **2**, the reversed sequence of migrations involving carbene **11**. If reversion of carbene **10** to **1** is particularly facile, **2** might instead derive from **11**.[38]

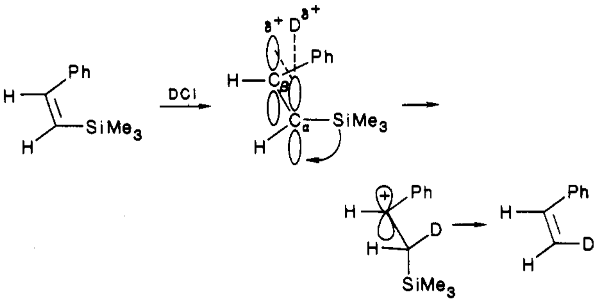
As noted earlier, the π,3s (R) state has become closely associated with alkylethylene photorearrangements via carbenes and would seem to be the most likely assignment of the vertical state in the photorearrangement of **1** giving **2**. The wavelength effects on product **3**, though small, would then suggest that this state lies at higher energy than the σ,π^* state, in line with term value estimates (vide supra). Vapor-phase spectroscopic studies of **1** are needed to confirm this. Photorearrangement via the π,π^* state, which for alkylethylenes crosses the π,3s (R) state on twisting,[9,40] still remains a possibility in light of the ethylene theoretical calculations,[9] although counterarguments[29] have been made noting a correlation between wavelength effects on yields of carbene-derived products and fluorescence efficiencies of the Rydberg state[41] of 2,3-dimethyl-2-butene.

Protodesilylation and Alcohol Addition. Protodesilylation does not appear to be related to nucleophilic addition of alcohols associated with radical cation like Rydberg states of tetraalkyl-substituted alkenes, e.g. dimethylcyclopentene[4a] (Scheme I). Although the eq 3 mechanism accounts for incorporation of deuterium at the terminal position of the double bond of **4a** or **4c** on photolysis of **1** in methanol-*O*-d_1 or *tert*-butyl alcohol-*O*-d_1, the observed stereospecificity favoring deuteriation trans to the dimethylsilyl group does not necessarily follow from the intermediates of eq 3. Moreover, the extent of monodeuteriation of **4a**,**c** (>90%) is atypical of alkylolefins, which give distributions of nondeuteriated, monodeuteriated, and dideuteriated products.[4a] Finally, the rates of formation of silyl ethers **4a–c** are not markedly sensitive to polarity of the medium, in contrast to the more than fivefold enhancement of ether yields going from butanol to methanol in photolyses of tetramethylethylene.[4a]



(3)

Photochemical protodesilylation of **1** producing silyl ethers **4a–c** superficially resembles the ground-state version of this reaction and, in principle, could involve simple protonation of the double bond of **1** followed by cleavage of the β-silyl cation, i.e. the usual mechanism proposed for ground-state protodesilylation. In the case of β-trimethylsilyl-substituted styrenes (eq 4),[23a] as well as other silyl-substituted alkenes,[23b] protodesilylation is stereospecific, leading to retention of configuration with respect to the silyl group lost on addition of an electrophile to the double bond. Ground-state desilylation of **1** also proceeds with retention of configuration in giving cis-deuteriated silyl ether **4a**-d_1 on reaction with D_2SO_4 in methanol-*O*-d_1, opposite to the photochemical outcome in the absence of strong acid.



(4)

The appearance of solvent addition products **5** and **6** on photolysis of **1** in *tert*-butyl alcohol implicates a mechanism (Scheme II) whereby carbenes **10** and **11** undergo OH insertion in alcohols, presumably through protonation followed by addition via a tight ion pair,[42] analogous to the formation of cation-derived ethers and rearranged products in the photochemistry of *tert*-butylethylenes in methanol.[37] The stereospecific incorporation of deuterium into **4a**,**c**-d_1 from deuteriated alcohols can be explained by least hindered protonation of carbene **10** with cleavage of the C–Si bond β to positive charge of cation **13** to avoid scrambling of label through bond rotation. Each of intermediates **10** and **13** would presumably achieve maximum hyperconjugative stabilization[43] by assuming a bisected conformation with respect to the vacant p orbital,[44] which further implies a barrier to rotation of the bond to the divalent carbon.

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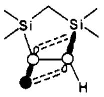
[36] In ground-state reactivity, trimethylsilyl groups are said to be "superb" in migratory aptitude: Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 7221.

[37] Kropp, P. J.; Tise, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 7293.

[38] A third possibility is photochemically allowed[39] concerted $\sigma^2a + \sigma^2a$ rearrangement as depicted below:



[39] (a) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272. (b) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: GmbH, Weinheim, 1971.

[40] Buenker, R. J.; Peyerimhoff, S. D.; Hsu, H. L. *Chem. Phys. Lett.* **1971**, *11*, 65.

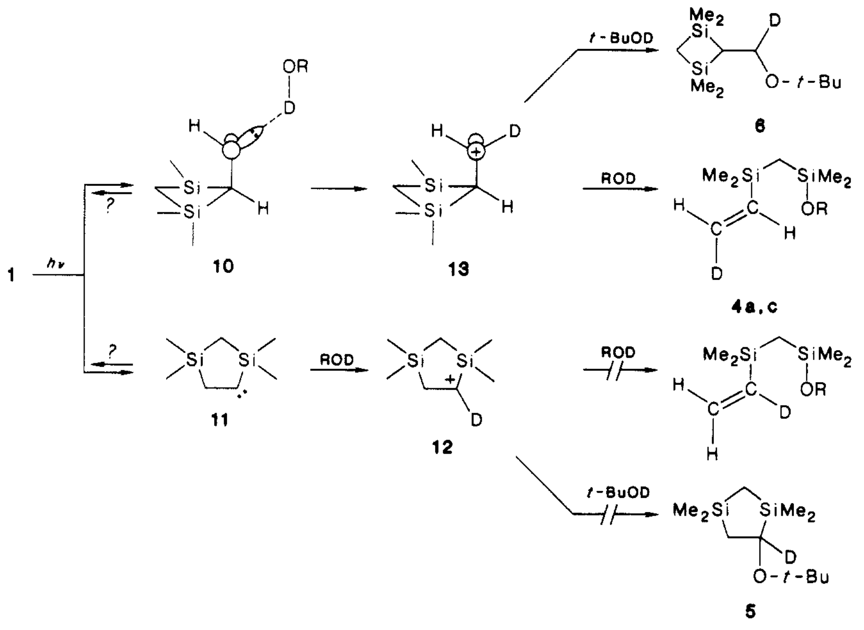
[41] Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1975**, *62*, 576.

[42] See ref 37 for a discussion of modes of alkyl carbene OH insertion.

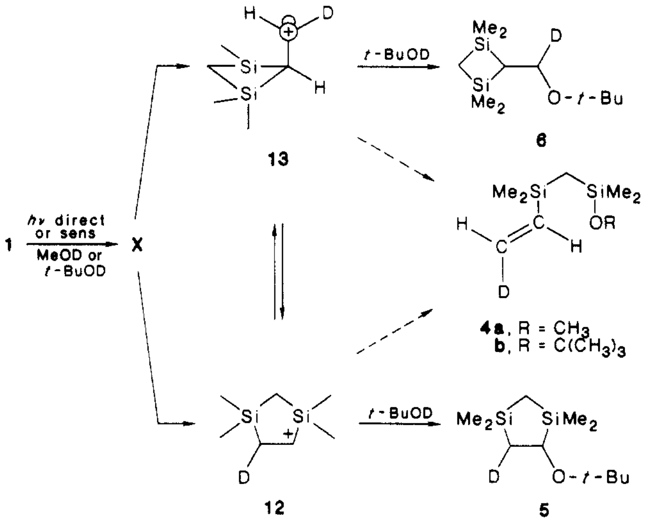
[43] (a) However, in contrast to theory,[43b] a recent solvolysis study of 2-(trimethylsilyl)cyclohexyl trifluoroacetates indicates a strong rate enhancement for β-silyl stabilization of the incipient carbenium ion while exhibiting only a marginal dependence on coplanarity of the β-C–Si σ bond and vacant p orbital.[43c] (b) Wierschke, S. C.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (c) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

[44] The analogy is to the cyclobutyl carbinyl cation: Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

Scheme II

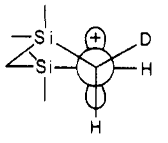


Scheme III

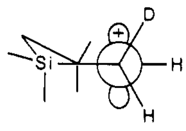


The cleavage of **13** to give **4a** (Scheme II) is further consistent with the formation of **4a** on acid-catalyzed reaction of ether **6** in methanol.

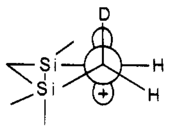
The positions actually labeled by deuterium in the case of products **4a,c**-d_1, **5**-d_1, and **6**-d_1, on photolysis of **1** in deuteriated methanol or *tert*-butyl alcohol, are consistent with the intermediacy of carbene **10** and labeled cation **13** of Scheme II. However, the experimentally observed labeling of **5**-d_1 requires carbocation **12**, labeled as in Scheme III instead of as in Scheme II, thus ruling out carbene **11** as a precursor. Protonation of carbene **11** followed by cleavage of a β-silyl group is also not a significant pathway (Scheme II), since no detectable deuterium is observed by ^{2}H NMR at the vinyl carbon α to the SiMe$_2$ group of **4a,c**-d_1. If carbene **10** is species **X** in Scheme III, formation of cation **12** would require 1,2 Si shift in concert with or subsequent to protonation.[45] An indication that rearrangement of **13** to **12** is possible, assuming ion pairs are involved is the observed conversion of neat **6** to **4c** and **5**.



12a



12b

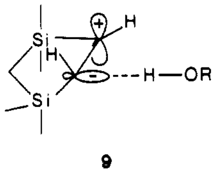


12c

While the existence of some species **X** common to **4c**, **5**, and **6** follows from the similarity in product ratios of direct and sensitized photolyses of **1**, a number of problems arise if carbene **10** serves as **X**. It is unlikely that product **2** and ethers **4a,c**, **5**, and **6** share a common intermediate, since (1) **2** is not quenched on going from hydrocarbon solvents to alcohols, (2) at least detectable amounts of **2** should have accompanied the ethers on photosensitization, and (3) yields of **4a** increase at the expense of **2** (and **3**) on going to longer wavelength. These results are consistent with involvement of a higher energy pathway in the formation of **2** as compared to **4a–c**, **5**, and **6**. It is thus tempting to invoke reaction via the π,3s (R) state and carbenes **10** and/or **11** to form **2**, the π,π^* state in **3** formation, and the lowest σ,π^* state or a zwitterionic species (as a ground-state intermediate, vide infra) in the formation of **4a,c**, **5**, and **6**.

Before turning to other possibilities for species **X**, it is necessary to consider the potential role of cation **12** in Scheme III. To avoid extensive loss of stereospecificity in the cleavage of **12**-d_1 to form **4a,c**-d_1, which could be important, two conditions must be potentially met. Species **X** must undergo protonation to give **12a**-d_1 in preference to **12c**-d_1, and the rate of β-cleavage would need to be faster than interconversion of conformers **12a–c** (vide supra). It seems possible that **4a,c**-d_1 could derive from protonation of **X** in concert with cleavage of a β-silyl group.

The $^{1,3}\sigma,\pi^*$ excited states themselves or, under special circumstances, the Z state represented by species **9** could



9

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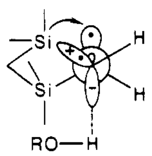
[45] Cleavage of a silyl group β to a cation center appears to be facile and faster than rearrangement of the silanorbornyl cation.[45a] However, rearrangements of silacyclopropyl carbinyl and silacyclobutyl carbinyl cations have been reported:[45b,c] (a) Pierce, R. A.; Cheng, A. H. B. *Organometallics* **1983**, *2*, 12. (b) Tamao, K.; Nakajima, T.; Kumada, M. *Ibid.* **1984**, *3*, 1655. (c) Robinson, L. R.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935.

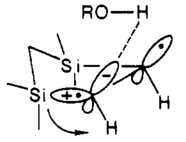
serve as species **X** in Scheme III. Species **X** must account for the exceptional behavior of **1** on photosensitization, in that the efficient formation of ether product **4a** ($\Phi = 0.21$) in methanol rather than radical-derived products of hydrogen abstraction such as 1,1,3,3-tetramethyl-1,3-disilacyclopentane is unprecedented among diradicaloid π,π^* triplets of constrained carbocyclic systems,[1,46] which undergo photoreduction and solvent addition via free radicals generated by hydrogen abstraction from solvent. The triplet photochemistry of **1** is reminiscent of ether formation on protonation of strained *trans*-cycloalkene intermediates, produced through π,π^* singlet and triplet photoisomerization of cyclohexenes[1,47a-d] and cycloheptenes.[1,3c,47d]

Framework molecular models show that disilacyclopentene **1** can twist up to 90° without incurring undue strain if one of the sp^2 carbons is permitted to pyramidalize on going to species **9**. This suggests that the Z_1 and Z_2 π,π^* states on pyramidalization would not be subject to the same constraint on twisting as the diradicaloid S_0 state. A "type B" avoided crossing[31a,48] in the region of 90° of twist then becomes conceivable.[49] As a result of mixing of excited-state ionic character and S_0 covalent character in the crossing region, there could be a secondary minimum on the ground-state surface corresponding to a 90° twisted zwitterionic intermediate, species **9**. Since there is no evidence for such a species in the case of cyclopentene in the form of unusual triplet behavior, i.e. photoprotonation to produce ether products,[1,46] the Z state appears to be an unlikely intermediate, barring the possibility of unusual stability conferred by silicon.

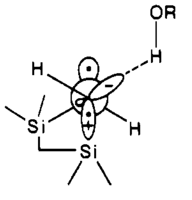
The increase in rate of ether formation (Table I) with increasing acidity of the solvent is suggestive of enhanced basicity of the double bond on photoexcitation of **1**, which in turn implicates protonation of the σ,π^* excited state as species **X** in Scheme III. Enhanced basicity in the σ,π^* state is anticipated from the intramolecular charge-transfer nature of the electronic promotion as illustrated by structures **14a**–**c**. Each structure is shown as being pyramidalized at both carbons of the double bond consistent with theoretical calculations of ethylene and fluoroethylene radical anions. Only those conformers twisted >30° from strict anti geometry, represented in the limit of twist by structure **14c**, are believed to have the requisite geometry for least hindered protonation and accompanying electron demotion to give deuteriated silyl ethers **4a**,**c**-d_1 with the correct stereospecificity. Bridging or 1,2 Si migration to give cation **13** would also seem possible with conformer **14c**. However, the most stable conformers would be expected to be the anti or syn forms from ab initio calculations of ethylene and fluoroethylene radical anions,[50a] although two points have been made regarding MNDO calculated potential surfaces of ethylene radical cations and anions:[50b] (1) that the torsional potential is "soft"; (2) that the radical anion of ethylene should exhibit a similar, though attenuated, tendency to undergo twisting from coplanarity due to hyperconjugative effects. Given the strongly twisted conformation of silylethylene radical cations[51] and the recently established directional effect for hyperconjugative σ^* stabilization of silyl radicals, twisted structures such as **14c** do not appear to be an unreasonable pictorial description of the σ,π^* excited state of **1**. Theoretical calculations are needed to elucidate the potential surfaces for twisting.



anti-**14a**



syn-**14b**



14c

A final point is that the vertical diradicaloid π,π^* triplet might be lower in energy than the σ,π^* triplet on the basis of exchange integral considerations.[53] T_1–T_2 equilibration of these states would then be required for photoprotonation.

Experimental Section

Spectra were recorded with the following spectrometers: Varian EM360L (60-MHz ^{1}H NMR), Bruker WM-250 (250-MHz ^{1}H NMR), JOEL FX60Q (^{13}C), Perkin-Elmer 700 and Analect FX-6200 (IR, FTIR), Perkin-Elmer 320 (UV), and Perkin-Elmer LS-5 (fluorescence). A Finnigan 9610 system equipped with a 0.25 mm × 30 m DB-1 capillary column programmed at 35 °C for 4 min and then 150 °C at 5 °C min^{-1} was used for GC–MS analyses, which were performed at 70 eV.

Preparative GC separations were performed on a Hewlett-Packard (FM Scientific 700) gas chromatograph with He as carrier gas at 30 mL min^{-1} flow rate on the following columns: column A, 10 ft × $^1/_4$ in. 15% didecyl phthalate on 80/100 mesh Chromosorb P; column B, 10 ft × $^1/_4$ in. 10% didecyl phthalate on 60/80 mesh Supelcoport; column C, 17 ft × $^1/_4$ in. 15% OV101 on 100/120 mesh Supelcoport; column D, 10 ft × $^1/_4$ in. 20% DOPN on 100/120 mesh Supelcoport.

HP 5710A or Varian 1400 gas chromatographs equipped with flame ionization detectors and HP 3380A or HP 3390A electronic integrating recorders were used for analytical separations. Nitrogen was the carrier gas at a flow rate of 30 mL min^{-1}. Detector response was calibrated against standard mixtures. The following columns were used: column E, 10% didecyl phthalate on 100/120 mesh Supelcoport (12 ft × $^1/_8$ in.); column F, 20% DOPN on 100/120 Supelcoport (12 ft × $^1/_8$ in.); column G, 10% OV101 on 100/120 Supelcoport (22 ft × $^1/_8$ in.).

Pentane (Baker Photrex), methanol (Baker photrex), 2,2,2-trifluoroethanol (Aldrich gold label), and *tert*-butyl alcohol (Alfa 99.9%, distilled from CaH_2) were used as solvents in photolyses.

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(49) (a) It is well-known that energy minima are located on the T_1 and S_1 potential surfaces of unconstrained ethylene at 90° of twist about the double bond. For the triplet, the minimum is practically degenerate with the transition state for ground-state cis–trans isomerization whereas the S_1 minimum, depending on the theoretical calculation,[31c] is poised another ca. 73–85 kcal mol^{-1} above the ground-state maximum and corresponds to the ionic Z state. Zimmerman and co-workers[49b] have simulated the effect of ring constraint for twisting of styrene in these states by superimposing a Hooke's law potential corresponding to weak, moderate, and large constraint on the electronic energy. In the extreme case of constraint the S_1 minimum at 90° of twist was completely lost in S_1 and T_1, and no minimum was present on the S_0 surface except at 0°. Using Zimmerman's case D potential to simulate constraint, it is possible that a constrained diradicaloid S_0 state would cross the essentially *unconstrained*, pyramidalized, ionic Z state at 90° of twist. (b) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

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(53) The lowest triplet might be π,π^* since a smaller exchange integral for out-of-plane promotion of an electron would lead to a smaller singlet–triplet splitting in the case of the σ,π^* configuration: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing: Menlo Park, CA, 1978; p 28.

1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1). The disilacyclopentene was synthesized in crude yields of 50–60% from vacuum flow pyrolysis at 800 °C of 1,2-diallyl-1,1,2,2-tetramethyldisilane.[13] The apparatus consisted of an unpacked quartz tube (25 mm × 335 mm) mounted in a Lindberg tube furnace and connected to a liquid nitrogen trap evacuated to 0.05 mm. The crude product, obtained as a yellow oil, was distilled at 33 °C (1 mm) and then purified by preparative GC using column C at 90 °C. The ^{1}H NMR spectrum was as reported previously:[54] IR (CCl_4) 3.39, 7.19, 7.44, 7.75, 8.13, 10.4, 11.8, and 12.3 μm; GC–MS, retention time 6.4 min, m/z (relative intensity) 156 (12), 142 (16), 141 (100), 113 (10), 73 (12), 63 (11), 59 (9.4).

2,4,4-Trimethyl-2,4-disila-5-hexyne (3). Commercial acetylene was passed through a 100 cm × 2 cm column of activated alumina and bubbled into 50 mL of dry THF (distilled from sodium benzophenone ketyl) at 5 °C for 30 min. A solution of 60 mmol of ethylmagnesium bromide in 40 mL of dry THF was then added dropwise with mechanical stirring over a period of 45 min while the slow introduction of acetylene into the mixture was continued. After 30 min of additional stirring and bubbling of acetylene, 8.1 g (49 mmol) of 4-chloro-2,4,4-trimethyl-2,4-disilapentane[55] in 20 mL of dry THF was added dropwise over a 25-min period, followed by heating the reaction mixture at 40–43 °C for 3 h. The acetylene flow was discontinued and the mixture stirred 17 h at room temperature after which a colorless precipitate had fully formed. The mixture was decanted into 100 mL of ice and water and ether extracted. The combined extracts were water-washed, treated with saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated by distilling the volatiles of bp <50 °C. The THF was distilled at reduced pressure followed by microdistillation to give 3.8 g (47% yield) of crude alkyne, bp 80–85 °C (106 mm), as a colorless liquid. Analytically pure samples were obtained by preparative GC using column A at 90 °C. The spectral data follow: ^{1}H NMR (CCl_4) δ −0.025 (d, J = 3.7 Hz, 2 H, methylene), 0.20 (d, J = 3.5 Hz, 6 H, methyl, partially obscured by 4,4-dimethyl singlet), 0.23 (s, 6 H, methyl), 2.27 (s, 1 H, alkynyl), 4.02 (nonet, J = 3.5 Hz, SiH); IR (CCl_4) 3.08, 3.34, 3.39, 4.63, 4.81, 7.95, 9.46, 11.11 μm; GC–MS, retention time 6.3 min, m/z (relative intensity) 156 (2.1), 155 (8.2), 142 (16), 141 (100), 115 (8.7), 113 (14), 95 (8.3), 83 (16), 73 (25), 59 (12). Anal. Calcd for $C_7H_{16}Si_2$: C, 53.77; H, 10.31. Found: C, 53.52; H, 10.13.

5-Methoxy-3,3,5-trimethyl-3,5-disila-1-hexene (4a). To 1.85 g (0.074 mol) of magnesium was added a portion of a solution of 10 g (0.074 mol) (chloromethyl)dimethylvinylsilane in 40 mL of dry tetrahydrofuran (distilled from CaH_2) with stirring under nitrogen. After initiation, the remainder of the chloromethyldimethylvinylsilane solution was added dropwise, and the reaction mixture was then refluxed 1.5 h. A solution of 18 g (19 mL, 0.14 mol) of dichlorodimethylsilane in 30 mL of dry tetrahydrofuran was added to the reaction mixture, which was refluxed while stirring overnight. The bulk of the tetrahydrofuran was removed by distillation, benzene was added to precipitate the magnesium salts, which were removed by suction filtration, and the supernatant was concentrated by distillation of the benzene. Short-path distillation of the residue at 59–62 °C (15 mm) gave 6.9 g (48% yield) of 5-chloro-3,3,5-trimethyl-3,5-disila-1-hexene, as a colorless liquid: The ^{1}H NMR spectrum was as follows: (CCl_4) δ 0.18 (s, 6 H, methyl), 0.25 (s, 2 H, methylene), 0.45 (s, 6 H, methyl), 5.3–6.6 (m, 3 H, vinyl). The chlorosilane was further characterized as the methoxysilane derivative **4a**.

To a mixture of 1.0 mL (0.83 g, 0.026 mol) of methanol and 3.1 mL (3.4 g, 0.026 mol) of quinoline in 20 mL of pentane was added dropwise with stirring 5.0 g (0.026 mol) of 5-chloro-3,3,5-trimethyl-3,5-disila-1-hexene. The mixture was refluxed 22 h followed by cooling and suction filtration of the salts. The pentane was distilled from the supernatant, and the residue was distilled at 62–66 °C (17 mm) to yield 3.51 g (72% yield) of 5-methoxy-3,3,5-trimethyl-3,5-disila-1-hexene (**4a**) as a colorless liquid, which was 98.5% pure by GC analysis on column E at 80 °C. Further purification was effected by preparative GC on column B at 90 °C. The spectral data were as follows: 250-MHz ^{1}H NMR ($CDCl_3$) δ 6.19 (dd, 1 H, J_{AC} = 20, J_{BC} = 15 Hz, vinyl), 5.89 (dd, 1 H, J_{BC} = 15, J_{AB} = 3.8 Hz, vinyl), 5.63 (dd, 1 H, J_{AC} = 20, J_{AB} = 3.8 Hz, vinyl), 3.37 (s, 3 H, methoxy), 0.12 (s, 6 H, methyl), 0.09 (s, 6 H, methyl), −0.06 (s, 2 H, methylene); IR (neat) 3.24, 3.34, 3.50, 6.25, 7.09, 7.97, 8.37, 9.13, 9.48, 9.85, 10.5, 12.0, 13.1, 13.8, 14.4 μm; ^{13}C NMR ($CDCl_3$, ppm) 140.8, 130.6, 49.9, 2.79, 0.064, −0.746; GC–MS, retention time 11 min, m/z (relative intensity), no parent, 174 (17), 173 (100), 162 (9), 161 (49), 143 (39), 141 (10), 131 (25), 117 (8.2), 115 (28), 89 (14), 73 (22), 59 (59); MS-CI $C_8H_{20}OSi_2$ (M + H)$^+$, calcd 189.1131, found 189.1129, 189.1133.

5-(2,2,2-Trifluoroethoxy)-3,3,5-trimethyl-3,5-disila-1-hexene (4b). To a solution of 23.1 mL (23.1 mmol) of 1.0 M vinylmagnesium bromide in tetrahydrofuran under nitrogen was added dropwise 4.65 g (23.1 mmol) of 2,4-dichloro-2,4-dimethyl-2,4-disilapentane[56] in 50 mL of tetrahydrofuran with stirring over a period of 2 h. After 2-h reflux the solvent was removed by distillation. Distillation of the residue gave 2.67 g of material, bp 76 °C (19 mm), which ^{1}H NMR analysis revealed to be a 2.3:1 mixture of 5-chloro-3,3,5-trimethyl-3,5-disila-1-hexene and a product tentatively identified as 3,3,5,5-tetramethyl-3,5-disila-1,6-heptadiene.

Without further purification, the above mixture in 50 mL of pentane was refluxed for 20 h with 1.3 g (9.9 mmol) of quinoline and 0.99 g (9.9 mmol) of 2,2,2-trifluoroethanol. After suction filtration of the salts, the pentane was removed by distillation. Distillation of the residue at 43 °C (0.1 mm) gave 1.64 g of a colorless liquid, which ^{1}H NMR analysis showed to be the trifluoroethoxy compound contaminated with ca. 25% of the aforementioned divinyldisilane. The trifluoroethoxydisilane was purified by preparative GC on columns D (50 °C) and then B (100 °C). The spectral data were as follows: ^{1}H NMR ($CDCl_3$) δ 6.49–5.37 (m, ABC pattern, 3 H, vinyl), 3.86 (q, J = 8 Hz, 2 H, ethoxy methylene), 0.17 (s, 6 H, methyl), 0.12 (s, 6 H, methyl), −0.027 (s, 2 H, methylene); IR (neat) 3.21, 3.31, 6.25, 7.04, 7.63, 7.72, 7.91, 8.55. 9.39, 9.80, 10.3, 11.8, 14.3 μm; ^{13}C NMR ($CDCl_3$, ppm) 140.4, 130.9, 124.2 (q, J = 278 Hz), 61.1 (q, J = 35.6 Hz), 3.21, 0.291, −0.876; MS m/z (relative intensity), no parent, 229 (23), 163 (100), 162 (23), 161 (100), 157 (13), 153 (44), 150 (13), 149 (80), 135 (25), 134 (11), 133 (75), 121 (12), 85 (12), 77 (38), 73 (26), 69 (11), 63 (10), 59 (30), 58 (10); MS-CI for $C_9H_{19}OSi_2F_3$ (M + H)$^+$, calcd 257.1004, found 257.1005, 257.1008.

5-*tert*-Butoxy-3,3,5-trimethyl-3,5-disila-1-hexene (4c). To a mixture of 2.88 g (0.039 mol) of *tert*-butyl alcohol and 4.21 g (0.0326 mol) of quinoline in 20 mL of pentane was added 5.0 g (0.026 mol) of 5-chloro-3,3,5-trimethyl-3,5-disila-1-hexene, prepared as described in the synthesis of 5-methoxy-3,3,5-trimethyl-3,5-disila-1-hexene (**4a**). The mixture was refluxed 24 h followed by cooling to −15 °C and suction filtration of the salts. The pentane was distilled from the supernatant followed by short-path distillation of the residue at 87–95 °C (22 mm) to yield 2.78 g (46.5%) of NMR-pure 5-*tert*-butoxy-3,3,5-trimethyl-3,5-disila-1-hexene (**4c**) as a colorless liquid. Final purification was effected by preparative GC on column B at 103 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$) δ 6.17 (dd, 1 H, J_{AC} = 20, J_{BC} = 15 Hz, vinyl), 5.86 (dd, 1 H, J_{BC} = 15, J_{AB} = 4 Hz, vinyl), 5.63 (dd, 1 H, J_{AC} = 20, J_{AB} = 4 Hz, vinyl), 1.23 (s, 9 H, *tert*-butoxy), 0.13 (s, 6 H, methyl), 0.10 (s, 6 H, methyl), −0.15 (s, 2 H, methylene); IR (CCl_4) 3.27, 3.36, 3.45, 6.27, 6.85, 7.09, 7.17, 7.30, 7.94, 8.31, 9.43, 9.66, 10.36, 11.94 μm; ^{13}C NMR ($CDCl_3$, ppm) 141.4, 129.9, 72.1, 32.1, 5.54, 4.18, −0.582; GC–MS, retention time 16 min, m/z (relative intensity) no parent, 215 (1.7), 159 (100), 147 (27), 131 (39), 117 (10), 75 (42), 73 (23), 59 (31), 57 (52); high-resolution MS, m/z (relative intensity, empirical formula, deviation from calculated m/z), no parent, 215.1285 (1.3%, $C_{10}H_{23}OSi_2$, 1.3 ppm), 159.0661 (72%, $C_6H_{15}OSi_2$, 0.2 ppm), 157.0869 (12%, $C_7H_{17}Si_2$, 0.1 ppm). Anal. Calcd for $C_{11}H_{26}OSi_2$: C, 57.32; H, 11.37. Found: C, 57.32; H, 11.49.

General Procedure for Direct Photolyses. Unless noted otherwise, photolyses were performed with a Suprasil immersion well apparatus of either 33-, 48-, or 104-mL volume maintained at 0–5 °C, except for runs in *tert*-butyl alcohol as the solvent, which were conducted at 31 °C. The light sources were either an unfiltered Osram HNS 10 W/U oz. low-pressure mercury lamp (185 + 254 nm) or Philips zinc lamp (214 nm). A stream of air

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cooled the lamps. All photolysates were purged with nitrogen 1 h prior to and during photolyses.

Determination of Product Yields. Solutions 0.01–0.02 M in disilacyclopentene 1 were irradiated following the general procedure for direct photolyses (vide supra). Aliquots were taken at time intervals and analyzed by GC with column E (80 °C unless noted otherwise) to determine product yields and to construct concentration vs. time profiles from which the rates of product formation and reactant disappearance of Table I were obtained. Nonane was the internal standard. When methanol was the solvent, each aliquot (0.5 mL) was diluted with 0.5 mL of pentane and washed three times with water prior to analysis. When *tert*-butyl alcohol was the solvent, aliquots were analyzed first at 102 °C for high-boiling products and then at 80 °C after diluting with 0.5 mL of pentane and washing six times with water.

Rates of product formation at essentially constant light output at 214 nm (vide infra) were determined with methanol, 2,2,2-trifluoroethanol, and *tert*-butyl alcohol as solvents (entries 3–5, Table I). The general procedure for direct photolyses was performed with solutions 0.01 M in substrate in 33 mL of solvent. Each photolysis in a solvent was paired against a photolysis in methanol without turning off the lamp or cooling nitrogen. The rate of disappearance of disilacyclopentene 1 in methanol, which was used to check variation in light output from run to run, varied from -7.4×10^{-5} to 9.1×10^{-5} M min^{-1}, or ca. 10%. The average deviation in rate of product formation of duplicate runs was 14–16% for each solvent.

Direct Photolyses (185 + 254 nm) of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Pentane. A 0.024 M solution of 400 mg (2.56 mmol) of 1 in 104 mL of pentane (Baker Photrex) in an annular Suprasil reaction vessel was purged 45 min with nitrogen and then irradiated under nitrogen for 7 h with an unfiltered Osram HNS 10W/U oz. low-pressure mercury lamp (185 + 254 nm). A stream of air was used to cool the lamp. GC analysis of aliquots taken at time intervals with column E at 68 °C showed only three components with the following retention times: product A, 10 min; reactant 1, 11 min; product B, 14 min. No additional GC peaks were observed. The photolysate was concentrated by distillation of the pentane followed by ^{1}H NMR analysis of the residue. Products A and B in addition to 1 were then isolated by preparative GC with column A at 90 °C and further identified by ^{1}H NMR and IR spectral data. Product B was identical with authentic 2,4,4-trimethyl-2,4-disila-5-hexyne (3), vide supra, as confirmed by GC coinjection. The ^{1}H NMR spectrum of product A matched the literature data[15] for 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclobutane (2); additional spectral data were as follows: IR (CCl_4) 3.36, 3.38, 6.19, 7.99, 10.7 μm; GC–MS, retention time 6.1 min, 156 (33), 142 (17), 141 (100), 115 (13), 113 (22), 95 (9.3), 83 (10), 73 (32), 63 (12), 59 (18).

Direct Photolyses of 1,1,3,3-Tetramethyl-1,3-disilacyclopentane (1) in Methanol and Methanol-*O*-d_1 at 214 nm. A solution of 146 mg (0.936 mmol) of 1 in 31 mL of methanol was irradiated for 5 h following the general procedure outlined above. GC analysis (vide supra) showed, in addition to 50% unreacted disilacyclopentene 1 at a retention time of 10 min, 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclobutane (2) in 4% yield at a retention time of 9 min, 2,2,3-trimethyl-2,4-disila-5-hexyne (3) in 5% yield at 11 min, and 5-methoxy-3,3,5-trimethyl-3,5-disila-1-hexene (4a) in 25% yield at 26 min. To the photolysate was added 30 mL of pentane followed by a wash with 30 mL of water. The aqueous phase was extracted with 30 mL of pentane, and the combined pentane extracts were dried over anhydrous magnesium sulfate. After distillation of the pentane, the products were isolated by preparative GC (column B, 90 °C) and further identified by ^{1}H NMR analysis and GC–MS. Compounds 1–3 were obtained as a mixture with this column.

A solution of 81.4 mg (0.522 mmol) of disilacyclopentane 1 in 30 mL of deoxygenated methanol-*O*-d_1 was irradiated at 214 nm as above for 3 h (50% conversion by GC analysis). The photolysate was worked up as described above, and silyl ether 4a was isolated by preparative GC on a 10 ft × $^1/_4$ in. column of 10% OV-101 on 100/120 mesh Supelcoport at 90 °C. The site of deuterium incorporation was determined by 250-MHz ^{1}H and ^{2}H NMR as described in the Results. The following ^{13}C NMR data were obtained: ($CDCl_3$, ppm) 140.6, 130.3 (1:1:1, $J_{^{13}C-^2H} = 24$ Hz), 49.9, 2.76, 0.031, −0.778. The 250-MHz NMR data for photolysis of 232 mg (1.49 mmol) of disilacyclopentene 1 in 80 mL of methanol-d_1 for 1 h (15% conversion GC analysis) is described in the Results.

Two photolyses of 150 mg (0.962 mmol) of disilacyclopentene 1 in 30 mL of methanol or methanol-*O*-d_1 were taken to 60% conversion, and then aliquots were diluted with pentane and washed with water. GC–MS data obtained under identical experimental conditions for the two runs were compared to determine the extent of deuterium incorporation in products 2–4a and reactant 1. Reactant 1 and product 2 were found to be >99% unlabeled, <1.0% singly labeled, and <0.3% doubly labeled as ascertained by calculating contributions[57] of each isotopic species to the *m*/*z* 156, 157, and 158 ions. The same distributions were obtained on the basis of the *m*/*z* 141 (loss of methyl), 142, and 143 fragment ions. Alkyne 3 had an intense M − 1 ion at *m*/*e* 155 and a weak parent; the calculated distribution based on the *m*/*z* 141 (loss of methyl), 142, and 143 fragment ions was >98.2% unlabeled, <1.1% singly labeled, and <0.7% doubly labeled. Silyl ether 4a exhibited no parent ion; the calculated distribution based on fragment ions of *m*/*z* 173 (loss of methyl), 174, 175, and 176 were as follows: 0% unlabeled; >99.3% singly labeled; <0.3% doubly or triply labeled.

Direct Photolyses of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Methanol at 254 nm. A Rayonet photochemical reactor containing 16 RPR 2537 A low-pressure mercury lamps were used. Photolysates were contained in Vycor tubes that were immersed in a quartz-jacketed water bath thermostated at 65 °C by circulating water or at 3 °C by circulating methanol–water. Aliquots of 0.25-mL volume taken at time intervals were assayed as described above. The rates of product formation and reactant disappearance for runs conducted at 3 and 65 °C are summarized in Table II.

Direct Photolyses of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in 2,2,2-Trifluoroethanol at 214 nm. The general procedure described above was used. GC analysis (vide supra) after a 6-h photolysis of 285 mg (1.83 mmol) of disilacyclopentene 1 in 46 mL of nitrogen-purged 2,2,2-trifluoroethanol showed formation of 3.6% methylenedisilacyclobutane 2, retention time 10.8 min, 4.9% alkyne 3, retention time 14.2 min, and 30% 5-(2,2,2-trifluoroethoxy)-3,3,5-trimethyl-3,5-disila-1-hexene (4b), retention time 49.8 min, in addition to 29% disilacyclopentene 1, retention time 12.3 min. The identities of all components were initially established by GC–MS. When the photolysate was distilled, compounds 1–3 and most of silyl ether 4b codistilled with the solvent at 70 °C. The distillate was extracted twice with 40- and 25-mL portions of pentane, and the combined extracts were washed four times with 40 mL of water. After distillation of the pentane, compounds 1–4b were isolated by preparative GC on column B (90 °C). Compounds 1–3, obtained as a mixture, were further identified by GC retention times and ^{1}H NMR spectroscopy. Silyl ether 4b was characterized by ^{1}H and ^{13}C NMR and IR spectroscopies.

Direct Photolyses of Disilacyclopentene 1 at 214 nm in *tert*-Butyl Alcohol. The general procedure described above was used. A solution of 450 mg (2.88 mmol) of disilacyclopentene 1 in 50 mL of *tert*-butyl alcohol (distilled from CaH_2) was irradiated for 13 h. GC analysis (vide supra) showed the presence of the following components: methylenedisilacyclobutane 2, retention time 9.6 min; starting disilacyclopentene 1, retention time 10.8 min; disilahexyne 3, retention time 12.2 min; silyl ether 4c, retention time 70.2 min; unknown product **A**, retention time 81.5 min; unknown product **B**, retention time 99.3 min. GC–MS analysis was consistent with the presence of products 2–4c. The GC–MS data, *m*/*z* (relative intensity) for unknown products **A** and **B**, were as follows: unknown **A**, retention time 16 min, no parent, 173 (86), 159 (8), 157 (6), 147 (9), 133 (48), 131 (100), 117 (9), 115 (12), 85 (8), 75 (15), 73 (44), 59 (50), 57 (43); unknown B, retention time 17 min, no parent, 173 (2), 159 (27), 147 (6), 133 (6), 131 (24), 117 (7), 87 (6), 85 (5), 75 (100), 59 (22), 57 (44). To the photolysate was added 50 mL of pentane. After it was washed eight times with 50 mL of water, the photolysate was concentrated by distillation of the pentane and each of the com-

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(57) Biemann, K. *Mass Spectrometry*; McGraw-Hill: New York, 1962; p 209.

ponents of the mixture was isolated by preparative GC on column B at 102 °C. The photolysis, workup, and product isolation were repeated as described above to obtain more of each component. Methylenedisilacyclobutane **2**, disilacyclopentene **1**, and disilahexyne **3**, obtained as a mixture, were identified by ^{1}H NMR spectroscopy and GC–MS data. The identity of silyl ether **4c** was confirmed by comparison of ^{1}H and ^{13}C NMR and IR spectral data to that of an authentic sample. Unknowns **A** and **B** were found to be, respectively, 4-*tert*-butoxy-1,1,3,3-tetramethyl-1,3-disilacyclopentane (**5**) and 2-(*tert*-butoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**6**) from spectral data (vide infra).

The spectral data for 4-*tert*-butoxy-1,1,3,3-tetramethyl-1,3-disilacyclopentane (**5**) were as follows: ^{1}H NMR (CCl$_4$) δ 3.45 (t, 1 H, methine), 1.12 (s, 9 H, *tert*-butoxy), 0.82 (d, 2 H, methylene), 0.12 (s, 3 H, methyl), 0.07 (br s, 9 H, methyl), −0.42 (center of AB q, J = 14 Hz, 2 H, methylene); IR (CCl$_4$) 3.35, 3.44, 6.83, 7.19, 7.30, 7.97, 8.33, 8.73, 9.62, 9.90, 10.15, 11.63, 12.00 μm; ^{13}C NMR (CDCl$_3$, ppm) 69.7, 64.7, 28.6, 23.3, 0.892, 0.567, −1.54, −3.16, −3.73; high-resolution MS, m/z (relative intensity, empirical formula, deviation from calculated m/z) no parent, 173.0819 (100%, $C_7H_{17}OSi_2$, 0.6 ppm), 159.0658 (16%, $C_6H_{15}OSi_2$, 2.3 ppm). Anal. Calcd for $C_{11}H_{26}OSi_2$: C, 57.32; H, 11.37. Found: C, 56.79; H, 11.55.

The spectral data for 2-(*tert*-butoxymethyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**6**) were as follows: ^{1}H NMR (CDCl$_3$) δ 3.47 (d, J = 9 Hz, 2 H, methylene), 1.12 (s, 9 H, *tert*-butoxy), 0.82 (t, J = 9 Hz, 1 H, methine), 0.22 (s, 6 H, methyl), 0.18 (s, 6 H, methyl), −0.067 (s, 2 H, methylene); IR (CCl$_4$) 3.34, 3.44, 7.17, 7.27, 7.94, 8.26, 9.05, 9.39, 9.68, 10.05, 10.31, 10.64, 11.55, 11.98 μm; ^{13}C NMR (CDCl$_3$, ppm) 71.9, 59.3, 27.9, 22.4, 2.99, 2.04, −1.23.

Product yields after 285-min photolysis (76% conversion), determined by the general procedure described above, were as follows: methylenedisilacyclobutane **2**, 11%; disilahexyne **3**, 7%; silyl ether **4c**, 24%; *tert*-butyl ether **5**, 5%; *tert*-butyl ether **6**, 10%. Total mass balance including remaining reactant **1** was 82%.

Product **6** was not stable to handling as shown by the following control. A 15.6-mg (0.0678-mmol) sample of >99% **6**, purified by preparative GC on column B (100 °C), was dissolved in 25 mL of *tert*-butyl alcohol along with nonane as an internal standard. GC analysis on column E (100 °C) initially showed only **6**. After 26 h at 31 °C GC analysis revealed the presence of 4.5% **4c**. After 32 h, the mixture was diluted with 25 mL of pentane and washed several times with water, at which point GC analysis showed 5.6% **4c** and 5.3% **5**. After distillation of the pentane, the mixture contained 11% **4c**, 7% **5**, and 82% remaining **6**. Reflux of this mixture in 20 mL of methanol containing ca. 1 mg of *p*-toluenesulfonic acid for 1 h gave 5-methoxy-3,3,5-trimethyl-3,5-disila-1-hexene (**4a**) in >95% yield, based on 0.0678 mmol of starting **6**, by GC analysis of an aliquot after workup in pentane (vide supra). The identity of silyl ether **4a** was confirmed by ^{1}H NMR analysis after isolation by preparative GC on column B.

Product **5** was recovered in >98% yield after the same stability check described for product **6** was performed. The behavior of pure **5** in acidic methanol was not studied.

Direct Photolyses of Disilacyclopentene 1 in *tert*-Butyl Alcohol-*O*-d_1. As described above for runs in *tert*-butyl alcohol three direct photolyses of 390, 350, and 405 mg of disilacyclopentene **1**, each in 33 mL of *tert*-butyl alcohol-*O*-d_1 (98+ atom % D), were taken to 50–60% conversion, followed by workup, and then preparative GC isolation of products and unreacted **1**. The products of each of the runs were combined and analyzed by ^{1}H and ^{2}H NMR spectroscopies and by GC–MS. The NMR data are summarized in the Results. The samples of **4c**-d_1, **5**-d_1, and **6**-d_1 in CCl$_4$ remained unchanged by ^{1}H NMR and GC analysis after 2 weeks at −15 °C and 1 week at room temperature.

GC–MS data obtained under identical experimental conditions for deuteriated and undeuteriated samples were compared to determine the extent of deuterium incorporation in products **2**–**6** and reactant **1**. Reactant **1** and product **2** were found to be, respectively, >99% unlabeled and 97% unlabeled plus 3% singly labeled, as calculated from contributions[57] of each isotopic species to the m/z 156, 157, and 158 ions. On the basis of the m/z 141 (M − 15), 142, 143, 144 fragment ions, product **2** was 94% unlabeled and 6% singly labeled while **1** was >99% unlabeled. Since alkyne **3** had a significant M − 1 ion at m/z 155, the isotopic distribution was calculated from the 141 (M − 15), 142, 143, and 144 fragment ions and was found to be >98% unlabeled, <2% singly labeled. Silyl ether **4c** and *tert*-butyl ethers **5** and **6** exhibited no parent. The calculated isotopic composition of **4c**-d_1 based on fragment ions was as follows: m/z 215, 216, 217, 8.6% unlabeled, 91.4% singly labeled; m/z 159, 160, 161, 162, 163, >99% singly labeled. The calculated isotopic composition of **5** based on fragment ions was as follows: m/z 173, 174, 175, 176, >99% singly labeled; m/z 159, 160, 161, 162, >99% singly labeled. The calculated composition of **6** based on fragment ions was as follows: m/z 173, 174, 175, 176, 8% unlabeled, 90% singly labeled, 2% doubly labeled; m/z 159, 160, 161, 162, 163, >99% singly labeled.

Toluene-Sensitized Photolysis of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Pentane. A solution of 152 mg (0.974 mmol) of disilacyclopentene **1** and 500 mg (5.43 mmol) of toluene in 50 mL pentane in a Vycor tube was purged with nitrogen 1.5 h and then irradiated 5 h with a Rayonet reactor fitted with 16 254-nm mercury lamps. GC analysis (vide supra) of aliquots taken at time intervals showed that no conversion to 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclobutane (**2**) or 2,2,4-trimethyl-2,4-disilahex-5-yne (**3**) or other products had occurred within a limit of detection of 0.25%. Only toluene and disilacyclopentene **1** were present in the photolysate by GC–MS analysis, the latter to the extent of 98% by GC analysis on column G at 90 °C.

***p*-Xylene-Sensitized Photolysis of Disilacyclopentene 1 in Methanol-*O*-d_1.** A solution of 195 mg (1.25 mmol) of 1,1,3,3-tetramethyl-1,3-disilacyclopentane (**1**) and 866 mg (8.17 mmol) of *p*-xylene in 10 mL of methanol-*O*-d_1 in a Vycor tube inserted inside a Vycor filter sleeve (2-mm wall) was purged with nitrogen for 1 h and then irradiated with a Rayonet photochemical reactor fitted with 16 RPR 2537 A low-pressure mercury lamps. After 9 h, GC analysis as described by the general procedure showed 32.7 mg (14% yield) of silyl ether **4a** in addition to 132 mg (69%) of unreacted starting material. GC–MS analysis as described above for direct photolyses in methanol-*O*-d_1 showed **4a**-d_1 to be >98% monodeuteriated. Neither 2-methylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane (**2**) nor 2,4,4-trimethyl-2,4-disila-5-hexyne (**3**) was found in the photolysate by GC analysis. The photolysate was poured into ca. 20 mL of pentane, which was then washed with an equal volume of water. The aqueous phase was extracted with 20 mL of pentane, and the combined organic phases were washed several times with an equal volume of water. After being over anhydrous magnesium sulfate, the pentane was distilled, and disilacyclopentane **1** and silyl ether **4a**-d_1 were isolated by preparative GC on column B (90 °C). The identities of GC-isolated **1** and **4a**-d_1 were confirmed by ^{1}H NMR and comparison of retention times to those of authentic samples on column E. The 250-MHz ^{1}H NMR spectral data of **4a**-d_1 were as follows: (CCl$_4$) δ 6.19 (m, 1 H, vinyl, H_C), 5.89 (d, J_{BC} = 15 Hz, 0.35 H, vinyl, H_B), 5.63 (d, J_{AC} = 20 Hz, 0.65 H, vinyl, H_A), 3.37 (s, 3 H, methoxy), 0.12 (s, 6 H, methyl), 0.09 (s, 6 H, methyl), −0.06 (s, 2 H, methylene). The ^{2}H NMR spectrum showed labeling of only the H_A and H_B protons of the vinyl group of silyl ether **4a**-d_1 in a ratio H_A:H_B of 1.00:1.88.

A second photolysis of 188 mg (1.20 mmol) of disilacyclopentene **1** in 10 mL of methanol-*O*-d_1 with 866 mg (8.17 mmol) of xylene sensitizer for 19 h was performed. GC analysis showed 48% conversion of reactant **1** to 19% of silyl ether **4a**. A 250-MHz ^{1}H NMR analysis of GC-isolated **4a** showed incorporation of one deuterium, 54% of the label at H_B and 46% at H_A.

Photolysis of 239 mg (1.54 mmol) of **1** in 29 mL of methanol-*O*-d_1 with 2.51 g (23.7 mmol) of xylene for 0.75 h resulted in 18% conversion of reactant **1** to 6.5% of **4a** labeled with one deuterium. The distribution of deuterium was 74% at H_B and 26% at H_A by 250-MHz ^{1}H NMR analysis of GC-isolated **4a**-d_1.

Stability of 2-Methylene-1,1,3,3-tetramethyl-1,3-disilacyclobutane (2) and 2,4,4-Trimethyl-2,4-disila-5-hexyne (3) on Xylene-Sensitized Photolysis of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Methanol. A solution of 1.03 mg (0.00662 mmol) of **2**, 48.6 mg (0.311 mmol) of **1**, 1.03 mg (0.00662 mmol) of **3**, and 20.1 mg (0.107 mmol) of silyl ether **4a**, nonane internal standard, in 28.4 mL of 0.85 M *p*-xylene in methanol was irradiated for 7 h. At hourly intervals 0.25-mL aliquots were taken and assayed following the general procedure described above to construct a concentration vs. time profile of each component in the mixture. Within 2 h the amounts of **2** and **3** had declined to 0.003 50 and 0.005 22 mmol, respectively, but were still present in respective amounts of 0.0032 and 0.004 99 mmol after 7-h irradiation. A total of 0.264 mmol of silyl ether **4a** and 0.121 mmol of unreacted **1** were observed by GC on completion of the run.

Stern–Volmer Plot for Xylene-Sensitized Photolysis of Disilacyclopentene 1 in Methanol. A Rayonet reactor containing 16 RPR 2537 A lamps was used. In the center was mounted a cylindrical Vycor filter with a 2-mm wall into which Vycor tubes containing 10 mL of photolysate could be inserted one at a time. Samples of 0.85 M xylene in methanol, each varying in the concentration of **1**, were photolyzed for 30 min and then analyzed by GC (column E, 80 °C) for product **4a** with nonane as the internal standard. Relative quantum yields based on silyl ether **4a** formed were thus obtained.

The absolute quantum yield for formation of silyl ether **4a** was found to be 0.113 ± 0.009 for solutions containing 0.0096 M reactant **1** and 0.85 M xylene in methanol. The photolyses were performed as described above for the Stern–Volmer runs, and the light output of the Rayonet reactor was determined before and after each photolysis of **1** by ferrioxalate actinometery.[58] Quantum yields for formation of **4a** at two light intensities with 8 or 16 RPR 2537 A lamps mounted were identical within experimental error.

Xylene-Sensitized Photolysis of Disilacyclopentene 1 in *tert*-Butyl Alcohol. A solution of 247 mg (1.58 mmol) of 1,1,3,3-tetramethyl-1,3-disilacyclopentene (**1**) and 2.70 mL (2.34 g, 22.1 mmol) of *p*-xylene in 22 mL of *tert*-butyl alcohol (distilled from CaH) in a Vycor tube was purged with nitrogen for 1 h and then irradiated inside a Rayonet photochemical reactor fitted with 16 RPR 2537 A low-pressure mecury lamps. After 28.2 h, GC analysis of an aliquot following the general procedure described above showed 44.5% reactant **1**, 19.5% silyl ether **4c**, 5.8% ether **5**, and 10.2% ether **6** (80% mass balance). Mass balances were improved at lower conversions; after 7.5-h photolysis, GC analysis showed 76.3% of **1**, 8.5% of **4c**, 2.3% of **5**, and 4.6% of **6** (91.7% mass balance). After workup, as described for direct runs in *tert*-butyl alcohol each of products **4c**, **5**, and **6**, as well as reactant **1**, were tentatively identified (vide supra) by GC–MS analysis. Neither 2-methylenedisilacyclobutane **4** nor alkyne **3** were observed by GC or GC–MS analysis. The identities of each of the components of the mixture were confirmed by NMR analysis after separation by preparative GC on column B (100 °C).

Reaction 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1) in Acidic Methanol-*O*-d_1. A solution of 138 mg (0.885 mmol) of disilacyclopentene **1** and 0.5 mL of 98% D_2SO_4 (99.5+ atom % D) in 15 mL of methanol-*O*-d_1 was refluxed while aliquots were monitored by GC analysis following the general procedure (vide supra). Each aliquot was diluted with pentane and washed with water. After 91 h, 20 mg (11% yield) of silyl ether **4a** was found along with 12 mg (8.7%) of unreacted **1**. GC–MS analysis as described above for direct photolyses in methanol-*O*-d_1 showed that 10.1% of the silyl ether **4a** was unlabeled and 89.9% singly labeled; unreacted disilacyclopentene **1** was not labeled with deuterium. The solution was poured into 20 mL of pentane and washed with an equal portion of water. The aqueous phase was extracted with 20 mL of pentane, and the combined extracts were washed several times with water and then dried over anhydrous magnesium sulfate. After distillation of the pentane, disilacyclopentane **1** and silyl ether **4a** were isolated by preparative GC on column B (90 °C) and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectral data of **4a**-d_1 showed 95 ± 5% incorporation of one deuterium at the vinyl group of **4a**-d_1; the 250-MHz spectrum appeared as follows: (CCl_4) δ 6.19 (dt, $J_{BC} = 15$, $J_{HD} = 3.0$ Hz, 1 H, vinyl, H_C), 5.89 (d, $J_{BC} = 15$ Hz, ca. 0.96 H, vinyl, H_B), 5.63 (dd, $J_{AC} = 20$, $J_{AB} = 3.8$ Hz, ca. 0.04 H, vinyl), 3.37 (s, 3 H, methoxy), 0.12 (s, 6 H, methyl), 0.09 (s, 6 H, methyl), –0.06 (s, 2 H, methylene).

Procedure for Quantum Yield Determinations. A jacketed aluminum cell holder and lamp enclosure were constructed for quantum yield determinations. Light from an Osram HNS 10 W/U oz. low-pressure mercury lamp was passed through a 25-mm-diameter Acton 185 WHR interference filter (metal film, 43% transmittance at 185 nm, 1.4% at 254 nm) unless noted otherwise. The lamp enclosure including filter and sample cell was flushed at a constant metered 25 mL min^{-1} flow rate with nitrogen before and during the photolyses to maintain constant light intensity. A 1 cm × 1 cm Suprasil cuvette with a 2-cm neck and 4-mL volume contained the photolysate, and sample temperature was maintained at –5 °C by circulating methanol–water from a –15 °C constant-temperature bath.

The cis to trans isomerization of *cis*-cyclooctene was used as actinometer at 185 nm following the procedure previously described.[17] GC analyses for actinometry were performed with column F at 60 °C.

Photolyses employed pentane (Baker Photrex) as solvent unless noted otherwise. All solutions were purged with nitrogen for 45 min before and during the irradiations.

Aliquots taken at time intervals were analyzed by GC following the general procedure for product assay. Data are reported for initial concentration of reactant, rates of product formation, quantum yield, and, additionally, rate of disappearance of reactant and quantum yield. Rates (mmol min^{-1}) were calculated from slopes of concentration vs. time profiles over the percent conversion range specified for each run.

Quantum Yields for Direct Photolysis of 1,1,3,3-Tetramethyl-1,3-disilacyclopentene (1). The interference filter was used to exclude 254-nm light. Light absorbed at 185 nm averaged 2.98 ± 0.03 × 10^{-4} mEinsteins min^{-1}.

Run 1: Disilacyclopentene **1** reactant, 0.0100 M, -1.2×10^{-5} mmol min^{-1}, $\Phi = 0.040$; methylenedisilacyclobutane **2**, 4.28×10^{-6} mmol min^{-1}, $\Phi = 0.0142$; alkyne **3**, 6.04×10^{-6} mmol min^{-1}, $\Phi = 0.0203$, 0–6.6% conversion.

Run 2: Disilacyclopentene **1** reactant, 0.009 97 M, methylenedisilacyclobutane **2**, 4.24×10^{-6} mmol/min, $\Phi = 0.0142$; alkyne **3**, 7.44×10^{-6} mmol min^{-1}, $\Phi = 0.0250$, 0–12% conversion.

Run 3: Disilacyclopentene **1** reactant, 0.008 29 M, methylenedisilacyclobutane **2**, 4.48×10^{-6} mmol min^{-1}, $\Phi = 0.0150$; alkyne **3**, 6.36×10^{-6} mmol min^{-1}, $\Phi = 0.0213$, 0–13% conversion.

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