Mechanistic Studies of the Far-UV Photochemical Ring-Opening and Cleavage Reactions of 1,1-Dimethyl-1-silacyclobut-2-ene

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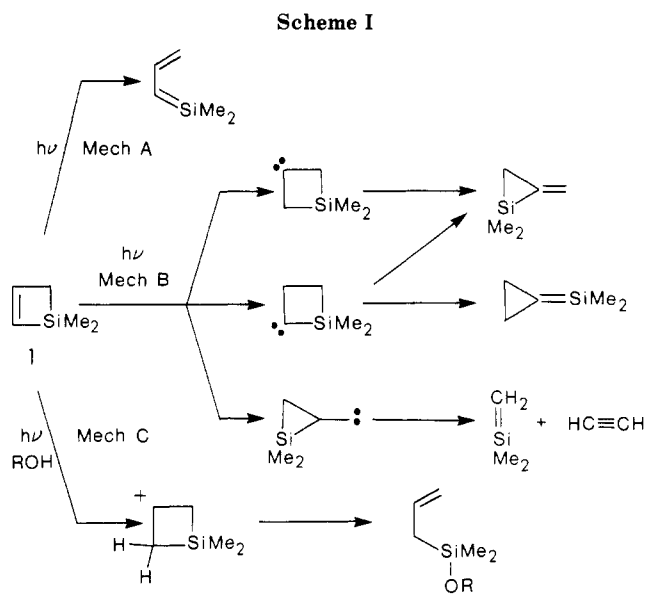
Direct photolyses of 1,1-dimethyl-1-silacyclobut-2-ene (1) at 214 nm in *tert*-butyl alcohol gave 29% *tert*-butoxydimethyl(2-propenyl)silane (2), 4.3% (Z)-*tert*-butoxydimethyl(1-propenyl)silane [(Z)-3], 6.9% (E)-*tert*-butoxydimethyl(1-propenyl)silane [(E)-3], and 5.9% *tert*-butoxytrimethylsilane (4) at 49% conversion. Products 2–4 were primary, and the total quantum yield of formation was 0.11. Use of *tert*-butyl alcohol-O-d led to >98% monodeuteration: $2\text{-}d_1$ had 93.5% of the label at C_1 and 6.5% at C_3 of the 2-propenyl group, (E)- and (Z)-$3\text{-}d_1$ [(E),(Z)-$3\text{-}d_1$] were labeled >95% at C_3 of the 1-propenyl group, and $4\text{-}d_1$ was deuterated at a silyl methyl. Cleavage of a silacyclopropylmethylene intermediate to 1,1-dimethyl-1-silaethene accounts for the labeling of $4\text{-}d_1$ and the deuteration of $2\text{-}d_1$ and (E),(Z)-$3\text{-}d_1$ suggests the intermediacy of 1,1-dimethyl-1-sila-1,3-butadiene, while the 13% contribution by a photoprotodesilylation pathway explains the partial C_3 labeling of 2. Additional evidence for silicon–carbon doubly bonded intermediates is the formation of 31% 2-methoxy-2,4,4-trimethyl-3-vinyl-2,4-disilapentane and 4.8% 2-methoxy-2,4,4-trimethyl-2,4-disilapentane upon 214 nm photolysis of 1 with 0.25 M methoxytrimethylsilane in pentane. Product yields versus *tert*-butyl alcohol concentration were determined to probe whether equilibrating, ground-state *s-cis* (gauche) and *s-trans* conformers of silabutadiene were involved in the formation of the 2 and (E),(Z)-3. Optimized geometries using the 6-31G(d) basis set were calculated for the cis, gauche, and *s-trans* structures of 1-sila-1,3-butadiene and 1,3-butadiene, as well as relative energies and barriers for interconversion of the gauche and trans species at the MP2/6-31G(d) level.

At least three types of photoreactivity are possible in the short wavelength photochemistry of 1,1-dimethyl-1-silacyclobut-2-ene (1) (Scheme I): π,π^* electrocyclic ring opening (mechanism A), carbene rearrangements (mechanism B) associated with $\pi,3s$ (R) reactivity,[1] and protodesilylation (mechanism C)[2] (mechanisms A–C labeled Mech A–C in Scheme I). The carbene component corresponding to the fragmentation of silacyclopropylmethylene in Scheme I is analogous to the mechanism proposed for formal retro 2 + 2 photofragmentations of cyclobutene derivatives,[3-5] whereas the silacyclobutylidene pathway follows from the reported photorearrangement of unsubstituted cyclobutene to methylenecyclopropane.[6] From the combined quantum yields of 0.23 for these two processes of cyclobutene and the predominance of electrocyclic opening to 1,3-butadiene ($\phi = 0.43$), one might anticipate a limited role for the third process in Scheme I, protodesilylation (mechanism C). While protodesilylation is the principal photoreaction in protic media of rigid disilacycloalkenes having lowest energy σ,π^* excited states,[2] attenuated σ,π^* reactivity for monosilacycloalkenes may be expected from the shift of this band to shorter wavelength as fewer silicon are attached to the double bond.[7] Similar implications regarding reactivity follow from comparison of UV spectra of 1 and 1,1,3,3-tetramethyl-1,3-disilacyclopentene (Figure 1). The less pronounced $\sigma,\pi^* - \pi,\pi^*$

Scheme I

energy difference[7] in the case of the silacyclobutene and the close proximity of two or more excited states thus suggested that the photochemistry of 1 could be complex.

1,1-Dimethyl-2-phenyl-1-silacyclobut-2-ene is the closest analogue of 1 which has been studied previously.[8] Its photolysis in methanol has been reported to yield three solvent adducts, as shown in eq 1. The results of a deuterium-labeling study with methanol-O-d as the solvent were consistent with the dimethylmethoxy(1-phenyl-2-propenyl)silane deriving from the addition of methanol to a 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene intermediate of π,π^* electrocyclic ring opening; the (E)- and (Z)-dimethylmethoxy(1-phenyl-1-propenyl)silane products were also observed upon photolysis of the 2-propenylsilane and

(1) (a) Kropp, P. J. Org. Photochem. **1979**, 5, 1. (b) Adam, W.; Oppenlander, T. Angew. Chem., Int. Ed., Engl. **1986**, 25, 661. (c) Steinmetz, M. G. Org. Photochem. **1987**, 8, 67. (d) Leigh, W. J.; Srinivasan, R. Acc. Chem. Res. **1987**, 20, 107. (e) Collin, G. J. Adv. Photochem. **1987**, 14, 135.

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(6) Adam, W.; Oppenlander, T.; Zang, G. J. Am. Chem. Soc. **1985**, 107, 3921.

(7) A similar comparison of UV spectra of successively silylated ethylenes has been made previously: Robin, M. B. Higher Excited States of Polyatomic Molecules; Academic: New York, 1974; Vol. 1, pp 311–314.

(8) (a) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. J. Organomet. Chem. **1981**, 219, 153. (b) Valkovich, P. B.; Weber, W. P. Tetrahedron Lett. **1975**, 2153.

thus could be secondary photoproducts.[8a] The intermediacy of 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene has also been implicated by the isolation of 2,2,6,6-tetramethyl-1-oxa-3-phenyl-2-sila-3-cyclohexene in 83% yield when photolyses were conducted in acetone.[8b] Attempts to characterize 1,1-dimethyl-1-sila-1,3-butadiene by pyrolytic generation followed by matrix isolation have not been successful.[9]

To assess the roles of mechanisms A–C in Scheme I, deuterium-labeling studies of the 214-nm photochemistry of 1,1-dimethyl-1-silacyclobut-2-ene (1) in *tert*-butyl alcohol-*O-d* as the solvent have been conducted. Our results are consistent with mechanism A as the principal photoreaction and mechanism B as a minor component corresponding to cleavage to 1,1-dimethylsilaethene at 214 nm. The contribution by mechanism C is 13% as an upper limit; interestingly, with methanol as the solvent a "dark" reaction of 1 is observed which is reminiscent of mechanism C. Among the four photochemical products observed are three *tert*-butyl alcohol adducts analogous to the methanol adducts of the 2-phenyl derivative of 1 shown in eq 1. The primary nature of these adducts was es-

$$\text{(1)}$$
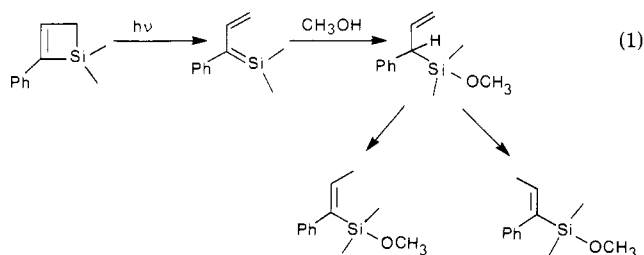
tablished by several criteria. Mechanistic studies and methoxytrimethylsilane trapping support the intermediacy of 1,1-dimethyl-1-sila-1,3-butadiene in the electrocylic ring opening of 1. The reactivity of the *s-cis* (gauche) and *s-trans* conformers was probed by varying *tert*-butyl alcohol concentration, and the results are discussed in terms of the ab initio calculated potential surfaces for interconversion of 1-sila-1,3-butadiene and 1,3-butadiene rotamers.

Results

Direct Photolyses of 1,1-Dimethylsilacyclobutene (1)[10] in *tert*-Butyl Alcohol. Preparative direct photolysis of a 10^{-2} M solution of 1 in deoxygenated *tert*-butyl alcohol at 214 nm produced 5.9% 1-*tert*-butoxytrimethylsilane (4), 6.9% (*E*)-*tert*-butoxydimethyl(1-propenyl)silane [(*E*)-3], 29% *tert*-butoxydimethyl(2-propenyl)silane (2), and 4.3% (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3] (eq 2).

$$\text{(2)}$$
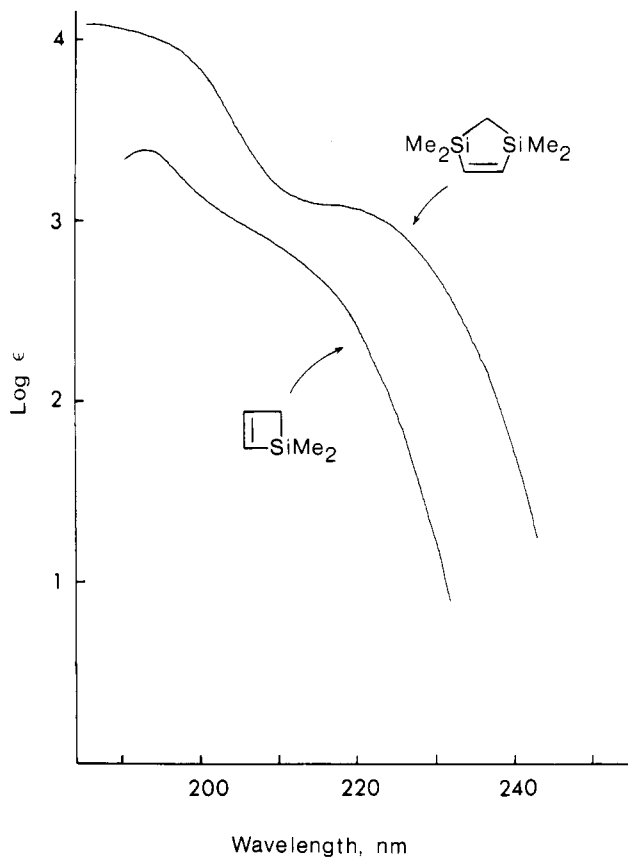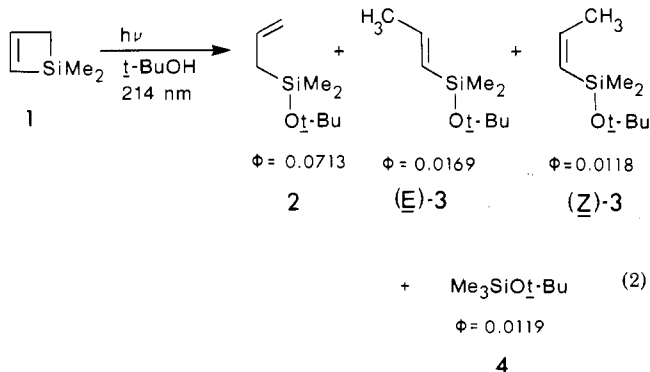
Figure 1. UV spectra of 1,1-dimethyl-1-silacyclobut-2-ene (1) and 1,1,3,3-tetramethyl-1,3-disilacyclopentene.

Table I. Ratio of Product Yield, $\%P_i$, to Total Yield, $\sum\%P_i$, for 214 nm Photolysis of 1,1-Dimethylsilacyclobutene (1) in *tert*-Butyl Alcohol

time, min	$\%P_i/\sum\%P_i^{a,b}$				
	2	(*E*)-3	(*Z*)-3	4	$\sum\%P_i$
10	0.72	0.11	0.12	0.061	1.59
20	0.67	0.14	0.11	0.073	3.07
30	0.67	0.12	0.11	0.10	6.70
40	0.69	0.11	0.11	0.081	8.25
50	0.66	0.13	0.11	0.11	12.0
60	0.66	0.12	0.12	0.11	15.5
80	0.67	0.12	0.11	0.11	20.0
100	0.66	0.12	0.11	0.10	24.1
125	0.64	0.13	0.10	0.12	28.8
av	0.67	0.12	0.11	0.10	
av dev[c]	0.014	0.008	0.004	0.015	
% av dev	2.1	6.6	3.6	16	

[a] $\%P_i$ is a product yield and $\sum\%P_i$ is the sum of all product yields. [b] Product yields were determined by GC analysis. [c] Average of absolute deviation from the mean.

The remainder of the material was 51% of unreacted 1. Each product and reactant 1 were isolated by preparative GC, and the products were identified by comparison of GC retention times and spectral data to those of authentic samples (Experimental Section). If samples were not subjected to a workup to remove *tert*-butyl alcohol prior to GC analysis, acetylene could be detected, although it was not quantified. No other products were detected by ¹H NMR or capillary GC–MS analyses. Controls established that silacyclobutene 1 was stable in the dark in *tert*-butyl alcohol as the solvent.

Products 2–4 were primary in nature, as evidenced by a constant ratio of $\%P_i/\sum\%P_i^{11}$ versus time, where $\%P_i$ is the yield of each product and $\sum\%P_i$ is the total product yield. The percent average deviation of $\%P_i$ of products 2, (*E*)-3, and (*Z*)-3 was 6.6% over a 1.6–29% range of

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(10) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978,** *100,* 1630.
(11) Adam, W.; Oppenlander, T. *J. Am. Chem. Soc.* **1985,** *107,* 3924.
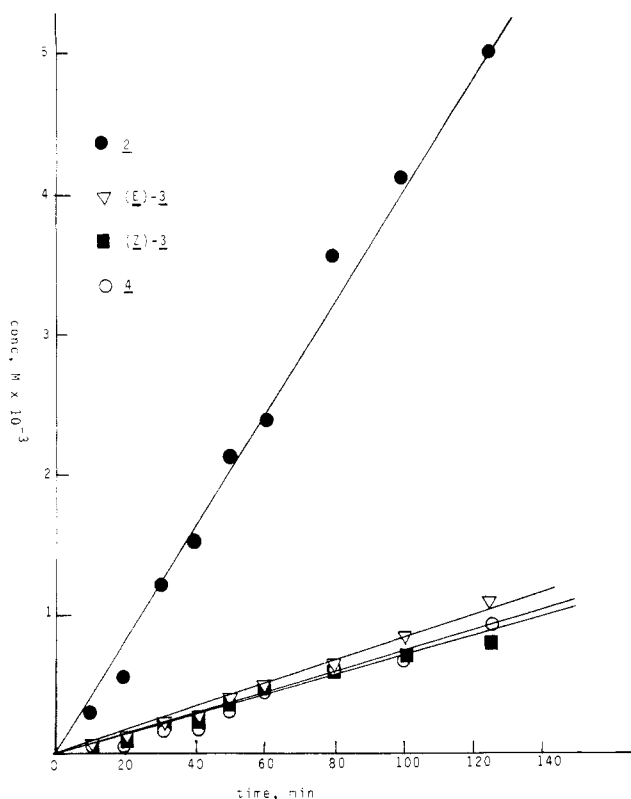
Figure 2. Concentration versus time profile for 214 nm photolysis of 1,1-dimethyl-1-silacyclobut-2-ene in *tert*-butyl alcohol at 27 °C.

Table II. 214 nm Product Yields of Silacyclobutene 1 as a Function of Concentration and Temperature

t-BuOH, M	time, min	yields, %				convn, %
		2	(*E*)-3	(*Z*)-3	4	
n-Pentane Runs[a]						
1.0	60	2.66	0.537	0.261	0.353	3.81
0.50	90	4.60	0.608	0.398	0.682	6.29
0.50	60	2.69	0.361	0.243	0.185	3.48
0.10	90	4.99	0.228	0.342	0.702	6.26
0.10	60	3.17	0.112	0.227	0.436	3.95
0.05	90	4.96	0.104	0.322	0.695	6.08
0.05	60	3.11	0.080	0.215	0.437	3.84
0.01	90	4.85	0.052	0.326	0.706	5.93
0.01	60	3.24	0.047	0.222	0.449	3.96
n-Hexane Runs[b]						
0.50 (1 °C)	30	12.8	1.05	0.995	1.94	16.8
0.50 (67 °C)	30	15.5	0.525	0.620	2.33	19.0
Pure *tert*-Butyl Alcohol[b] at 83 °C						
	10	3.44	0.410	0.363	0.614	4.83
	30	9.33	1.08	0.868	1.97	13.2

[a] Runs in *tert*-butyl alcohol in *n*-pentane were performed at 8–9 °C in a square cuvette with the quantum yield apparatus. [b] Both the *tert*-butyl alcohol in hexane and pure *tert*-butyl alcohol runs were performed with a double-walled immersion well apparatus.

conversions; 4 gave a higher value of 16% (Table I). The corresponding concentration versus time profile is shown in Figure 2. At conversions as low as 1.6%, GC analysis showed the presence of 0.10% 4, 0.17% (*E*)-3, 1.14% 2, and 0.18% (*Z*)-3.

The possibility that (*E*)-3 was produced by secondary photolysis of (*Z*)-3 had to be considered further, since irradiation of the Z isomer at 214 nm gave (*E*)-3 in 62% yield, in addition to traces of *tert*-butoxy(2-propenyl)silane 2; unreacted (*Z*)-3 was present to the extent of 33%. UV molar extinction coefficients of 1–4 at 214 nm were used to calculate the fraction of light absorbed by (*Z*)-3 for comparison to quantum yields of reaction to determine whether sufficient light could have been absorbed to convert (*Z*)-3 to its E isomer at 1.6% conversion, our lowest conversion run. From the quantum yield of appearance of (*E*)-3, ϕ = 0.0169, as determined by uranyl oxalate actinometry at 214 nm (vide infra), and the fraction of light absorbed by (*Z*)-3, 0.003, it was clear that the quantum yield for isomerization of (*Z*)-3 to (*E*)-3 would have to exceed unity for (*Z*)-3 to be a significant source of (*E*)-3.

A control showed that (*E*)-3 is not a secondary product of *tert*-butoxydimethyl(2-propenyl)silane (2), since this would have produced two other, unidentified products, at later retention times, that were not detected in photolysates of silacyclobutene 1, as shown by capillary GC retention times, GC–MS analysis, and ¹H NMR spectroscopy (Experimental Section).

Quantum yields of product formation are summarized in eq 2 and were determined at 214 nm with uranyl oxalate[12] as the actinometer (Experimental Section). An interference filter excluded the long wavelength output of the 15-W Philips zinc lamp used in the runs.

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Additional Mechanistic Studies. Photolyses of 10⁻² M silacyclobutene 1, performed at 185 nm with 0.10 M tert-butyl alcohol in pentane as the solvent at 9 °C, gave a ratio 2:(*E*)-3:(*Z*)-3:4 of 15:1.8:1.0:1.2 from the slopes of a concentration versus time profile over a 0–20% range of conversions (total rate of product formation was 1.12 × 10⁻⁴ M s⁻¹; for absolute yields, see the Experimental Section). This ratio differed from the 6.2:1.2:1.0:1.1 ratio obtained from product slopes of a 214-nm concentration versus time profile with pure tert-butyl alcohol as the solvent at 27 °C (Figure 2, 0–29% range of conversions; rate of total product formation was 6.49 × 10⁻⁵ M min⁻¹, and rate of reactant disappearance was 7.1 × 10⁻⁵ M min⁻¹). Comparison to the ratio of 15:0.68:1.0:2.05 obtained at 214 nm in 0.10 M tert-butyl alcohol in pentane at 9 °C (6% conversion) showed that this difference resulted in part from the decrease in alcohol concentration, which led to decreased yields of (*E*)-3 and (*Z*)-3 relative to 2 and 4, although the reduced yield of (*E*)-3 at 214 nm was apparently offset at 185 nm by a wavelength effect.

A study of 214 nm product yields and ratios at low conversions versus the concentration of tert-butyl alcohol in pentane at 9 °C was conducted for a 1.0–0.01 M range of concentrations (Table II). The product ratio 2:(*E*)-3:(*Z*)-3:4 varied from 11:1.5:1.0:1.7 at 0.5 M to 15:0.15:1.0:2.2 at 0.01 M. Thus, (*E*)-3 strongly depended upon tert-butyl alcohol concentration. GC–MS analyses did not show the presence of dimers of 1 and total mass balances were 83–104%.

When 214 nm photolyses in pure tert-butyl alcohol were conducted at 83 °C, the product ratio 2:(*E*)-3:(*Z*)-3:4 was 9.4:1.1:1.0:1.7 (yields are reported in Table II). Photolyses in 0.50 M tert-butyl alcohol in hexane showed a more pronounced decrease in yield of (*E*)- and (*Z*)-3 relative to 2, but only a small change in the (*E*)-3/(*Z*)-3 ratio with increasing temperature. The product ratio was 12:1.1:1.0:2.0 at 1 °C and 25:0.85:1.0:3.8 at 67 °C (yields are given in Table II). A control in which a solution of 1 in 0.50 M tert-butyl alcohol in hexane was heated at 67 °C gave no detectable products from dark reaction, and the photoproduct ratio of the 1 °C run remained unchanged upon heating of the mixture to 67 °C in the dark.

Deuterium-Labeling Results from Direct Photolyses of Silacyclobutene 1 in *tert*-Butyl Alcohol-*O*-*d*.

Deuterium-labeling studies of the 214 nm photochemistry of silacyclobutene 1 in *tert*-butyl alcohol-*O*-d_1 were conducted to obtain mechanistic information on potential intermediates. Each of products 2–4, isolated after the photolyses and analysed by GC–MS, 250-MHz ^{1}H NMR, and ^{2}H NMR spectroscopy, contained one deuterium to the extent of >95% (see Experimental Section), although further discussion is needed in the case of *tert*-butoxytrimethylsilane (vide infra). Recovered silacyclobutene 1 was found to be unlabeled by ^{1}H NMR analyses. Assignments of the positions which were deuterated in each of the products are shown below.

Only in the case of *tert*-butoxy(2-propenyl)silane 2 was deuterium detected at more than one position in the molecule. From the integrated intensities of the ^{2}H NMR spectrum, the ratio of C_1:C_3 deuteration was found to be 93.4:6.5. This result was in agreement with integrated intensities of the methylene and vinyl proton absorptions in the ^{1}H NMR spectrum of 2-d_1. The C_3 methyl groups of *tert*-butoxy(1-propenyl)silanes (*E*)-3-d_1 and (*Z*)-3-d_1 exhibited ^{2}H NMR signals at δ 1.68 for the *E* isomer and δ 1.72 for the *Z* isomer. These assignments were in complete accord with ^{1}H NMR spectral data.
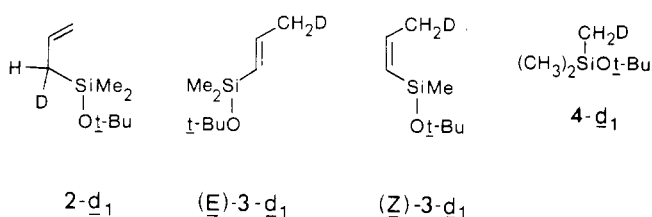
^{2}H NMR analysis of 1-*tert*-butoxytrimethylsilane (4-d_1) showed the presence of deuterium only at the trimethylsilyl group at δ −0.075, as opposed to the *tert*-butyl group, which would have givn an absorption at δ 1.19. ^{1}H NMR integrated intensities indicated at least 95% monodeuteration. The absence of a parent ion and complications due to fragmentation with loss of the CH$_2$D group precluded determination of the isotopic distribution by GC–MS analyses.

Dark Reaction of Silacyclobutene 1 with Methanol and Methanol-*O*-*d*. Reaction of silacyclobutene 1 with methanol for 4 h at room temperature in the dark led to the complete disappearance of starting material and the formation of methoxy(2-propenyl)silane 5 and the *Z* isomer of methoxy(1-propenyl)silane 6 in 55% and 33% yields, respectively (eq 3). After preparative GC isolation, the
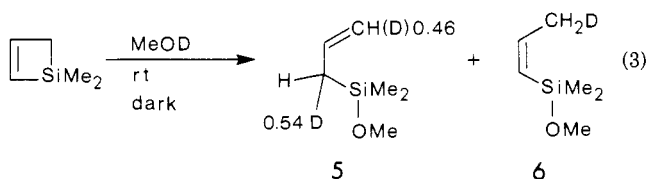
product structures were established by comparison of spectral data to those of authentic samples prepared by independent synthesis (Experimental Section). The *E* isomer of 6 was not detected by ^{1}H NMR spectroscopy; nor were any additional products detected in the crude reaction mixture prior to preparative GC.

The reaction of 1 at ambient temperature in methanol which was distilled from magnesium methoxide followed first-order kinetics, giving a 1.4:1 ratio of 5:6 in 98% total yield. With 1 mol % sulfuric acid as additive, this ratio was 4.5:1 (102% mass balance), and a threefold rate retardation was observed, whereas the presence of 1 mol % sodium methoxide led to a >50-fold rate increase and a

ratio of 5:6 of 1.4:1 (88% total yield).

Reaction of 1 with untreated methanol-*O*-*d* gave 5-*d* and 6-*d* monodeuterated to the extent of ca. 99% by GC–MS analysis; recovered 1 was undeuterated. ^{1}H NMR spectroscopy showed the deuterium label to be almost completely scrambled between the C_1 methylene and C_3 vinyl positions of methoxy(2-propenyl)silane 5-d_1, and the C_1:C_3 ratio of one deuterium was 54:46 by ^{2}H NMR. The deuterium was incorporated only at the C_3 methyl group of methoxy(1-propenyl)silane 6-d_1.

Photolyses of Silacyclobutene 1 in the Presence of Silene Trapping Agents. Preparative direct photolysis of silacyclobutene 1 with 0.25 M methoxytrimethylsilane in pentane at 214 nm produced 2-methoxy-2,4,4-trimethyl-3-vinyl-2,4-disilapentane (7) in 31% yield and 2-methoxy-2,4,4-trimethyl-2,4-disilapentane (8) in 4.8% yield, along with 51% unreacted 1 by GC analyses (eq 4).
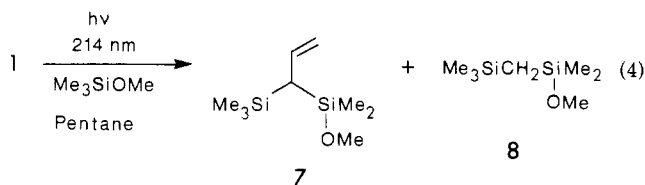
The products were isolated by preparative GC and identified by NMR, IR, and GC–MS analyses. Small amounts (<2% each) of five additional products were detected by capillary GC–MS analyses, four of which were isomers of 7 and one which exhibited a parent ion at *m/z* 200; the low yields precluded further characterization.

Computational Results. The geometries and relative energies have been determined for several rotational structures of 1-silabutadiene. Analogous calculations were performed for the parent hydrocarbon 1,3-butadiene for comparison. For both molecules, the global minimum on the potential energy surface is the planar, all trans structure. At the SCF level of theory for both species, the planar cis structure is a transition state, rather than a minimum, on the surface, the second (gauche) minimum occurring at a twist angle about the central CC single bond of 39.6° (38.2°) for butadiene (silabutadiene).[13a,b] The transition state for rotation from gauche to trans occurs at a twist angle of 102.0° (104.2°) for butadiene (silabutadiene).

Pertinent structural information and the relative MP2/6-31G(d) energies are listed in Table III. The

Table III. Key Bond Lengths^a (Å) and Relative Energies^b (kcal mol^{-1})

| rotamer	1,3-butadiene			1-sila-1,3-butadiene			
	C=C	C—C	E	Si=C	C—C	C=C	E
trans	1.323	1.468	0.0	1.710	1.460	1.327	0.0
gauche	1.321	1.478	2.7	1.707	1.469	1.325	2.3
cis	1.322	1.480	3.6	1.709	1.468	1.326	3.3
tr state	1.319	1.490	5.9	1.701	1.489	1.320	6.2

^{a}Calculated at the SCF/6-31G(d) level. ^{b}Calculated at the MP2/6-31G(d) level.

(13) (a) For a comprehensive summary of previous experimental and theoretical studies of 1,3-butadiene conformers, see ref 13b–f. (b) Calculations employing DZ polarization basis sets also indicate the gauche form of 1,3-butadiene (37.8° of twist) is lower in energy than the planar *s*-*cis* form by 0.7 kcal mol^{-1}: Breulet, J.; Lee, T. J.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1984**, *106*, 6250. (c) The planar *s*-*cis* form is slightly more stable than the gauche rotamer according to MCSCF split valence calculations: Feller, D.; Davidson, E. R. *Theor. Chim. Acta* **1985**, *68*, 57. (d) Squillacote, M. E.; Semple, T. C.; Mui, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 6842. (e) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *Ibid.* **1979**, *101*, 3657. (f) Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 1056.

Scheme II
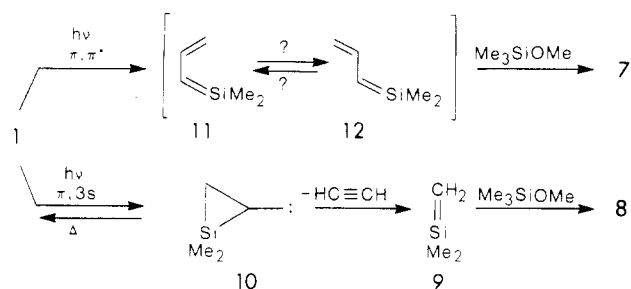
variation in the bond lengths reflects the decrease in delocalization across the central CC bond when either molecule is twisted about that bond. The difference between the two minima in butadiene is 2.7 kcal mol^{-1}, and this energy difference decreases slightly to 2.3 kcal mol^{-1} when a silicon is substituted at the 1-position. For both molecules the cis structure is about 1 kcal mol^{-1} higher than the gauche conformer at the correlated level. The latter is 2.7 (2.3) kcal mol^{-1} above the trans minimum in butadiene (1-silabutadiene). The MP2/6-31G(d) gauche-to-trans barrier is 3.2 and 3.9 kcal mol^{-1} for butadiene and 1-silabutadiene, respectively. Computed free energy differences (282 K) between gauche and trans species and for the barriers are within 0.1 kcal mol^{-1} of the energy differences cited above. Although the computed energies of the parent butadiene rotamers are consistent with experiment,[13d,e] UV[13d,e] and polarized matrix IR[13f] spectroscopy indicate an essentially planar structure for the *s-cis* form, in contrast to the present study.

Discussion

Evidence for Unsaturated Organosilane Intermediates through Trapping Studies with Methoxytrimethylsilane. Evidence for silene intermediates in photochemical and thermal reactions of organosilanes is often obtained through trapping studies with alkoxysilanes and various other reagents, including alcohols, HCl, HBr, O$_2$, and ketones.[14] Methoxytrimethylsilane does not absorb appreciably above 200 nm[15] and thus appeared to be a good choice of trapping agent for far-UV work. Methoxytrimethylsilane also undergoes 1,2-addition across silicon-carbon double bonds in a syn stereospecific manner, possibly indicative of a concerted mechanism.[16] Two methoxytrimethylsilane adducts are formed in 214 nm photolyses of 1 (eq 4). The structure of the major adduct 7 is consistent with the trapping of an intermediate 1,1-dimethyl-1-sila-1,3-butadiene, whereas 8 apparently results from photofragmentation to 1,1-dimethylsilaethene 9 and acetylene (Scheme II). 1,4-Addition is of minimal importance (<3% by GC analysis), possibly due to a propensity for delivery of the trimethylsilyl group of the alkoxysilane to the site of highest charge density, which would be the carbon α rather than γ to silicon according to ab initio calculations.[17]

The formal retro 2 + 2 product 8, corresponding to 1,1-dimethylsilaethene (Scheme II), most likely results from cleavage of silacyclopropylmethylene 10, an intermediate expected from 1,2-Si shift in the π,3s (R) state,[1] by analogy to cyclobutene (vide supra).[6] A potential source

of inefficiency is reversion of the intermediate to 1, given the high migratory aptitude of silicon[18] and the recent finding that 1,3,4,4- and 1,3,3,4-tetramethylcyclobutenes interconvert via a cyclopropylmethylene species upon photolysis at 185 nm.[4b]

Potential Mechanisms for the Photochemical Reactivity of Silacyclobutene 1 in Alcohols. The formation of *tert*-butyl alcohol adducts (*E*)-3 and (*Z*)-3 as primary products can be rationalized by mechanism A, as shown in Scheme III, whereas product 2 can be ascribed, a priori, to any combination of mechanisms A–C (Schemes III and IV). The 93.5:6.5 experimental ratio of C$_1$:C$_3$ deuterium labeling of the 2-propenyl group, however, indicates that at least 87% of 2-d_1 derives from the electrocyclic ring-opening mechanism originally proposed for the 2-phenyl derivative of 1 by Weber and co-workers (eq 1).[8a] This value assumes that the deuterium at C$_3$ comes from the symmetrical intermediate of mechanism C (photoprotonation). Mechanism B could be an alternate source, although the similarity in the ratio of quantum yields $(\phi(2) + \phi(3))/\phi(4) = 5$ compared to the ratio of 7/8 = 6 from methoxysilane trapping suggests that the postulated silacyclopropylmethylene 10 undergoes fragmentation at a faster rate than protonation. Here product 4 is ascribed to the trapping of silaethene 9 by *tert*-butyl alcohol, consistent with deuterium-labeling studies with *tert*-butyl alcohol-*O-d* as the solvent, showing the incorporation of one deuterium into the silylmethyls of 4-d_1. Protonation of silacyclobutylidenes 17 and 18 (Scheme IV) can be ruled out by the absence of detectable deuterium at C$_2$ of the 2-propenyl group of 2-d_1, and although competing cyclobutylidene–methylenecyclopropane rearrangements[6,19] 17 → 22 or 18 → 23 (eq 5) could be the reason for this, the corresponding products 24 and 25 were not detected; 25 could also derive from α-silacyclobutyl cation 19 rearrangement or from rearrangement of 21 or 16, disregarding labeling.[20]

(5)
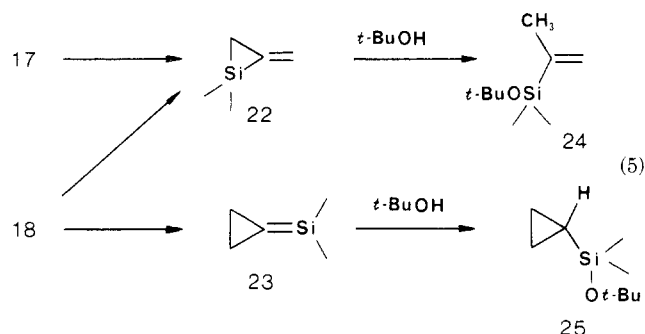
It is reasonable to expect that photoprotonation of 1 by mechanism C in *tert*-butyl alcohol would have led to scrambling of deuterium between the C$_1$ and C$_3$ positions of 2 via the symmetrical intermediate 15. A similar mechanism is apparently operative in the ground-state reaction of 1 in untreated methanol and methanol-*O-d*, as evidenced by the 54:46 ratio of C$_1$:C$_3$ deuterium labeling

(14) (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(15) Reference 7, p 269.

(16) Jones, P. R.; Bates, T. F.; Cowley, A. F.; Arif, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 3122.

(17) Trinquier, G.; Malrieu, J. *J. Am. Chem. Soc.* **1981**, *103*, 6313.

(18) (a) Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 7221. (b) Brook, A. G.; Bassindale, A. R. *Org. Chem.* **1980**, *42-2*, 149.

(19) See footnote 8, ref 6, and the following: Kirmse, W. *Carbene Chemistry*; Bloomquist, A. T., Wasserman, H., Eds.; Academic: New York, 1974; pp 467–475.
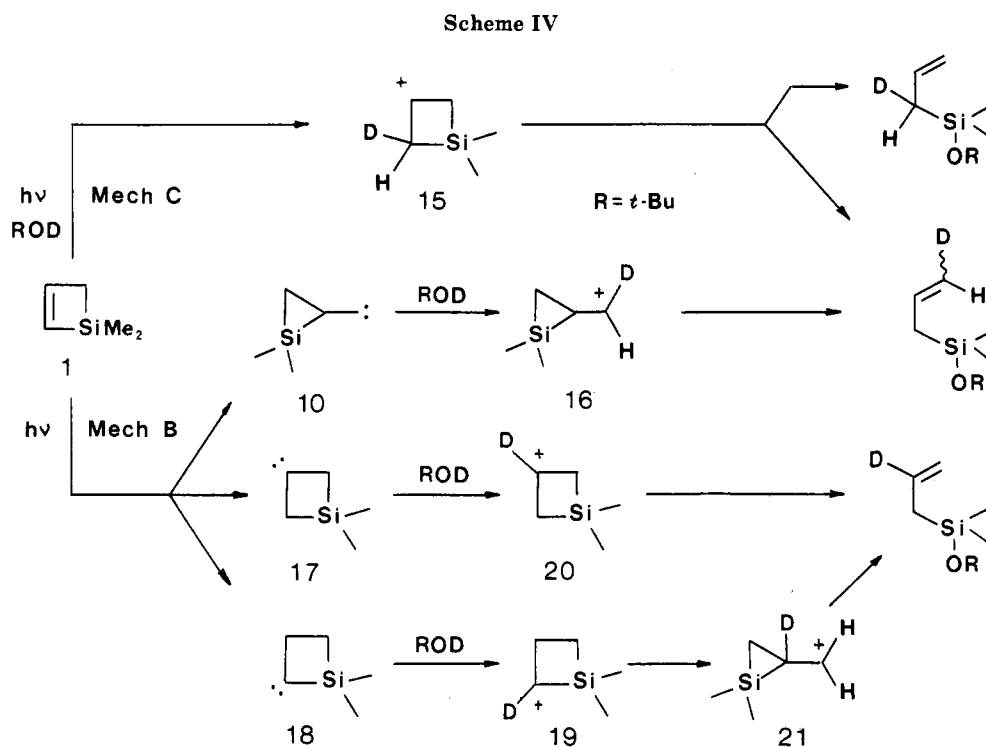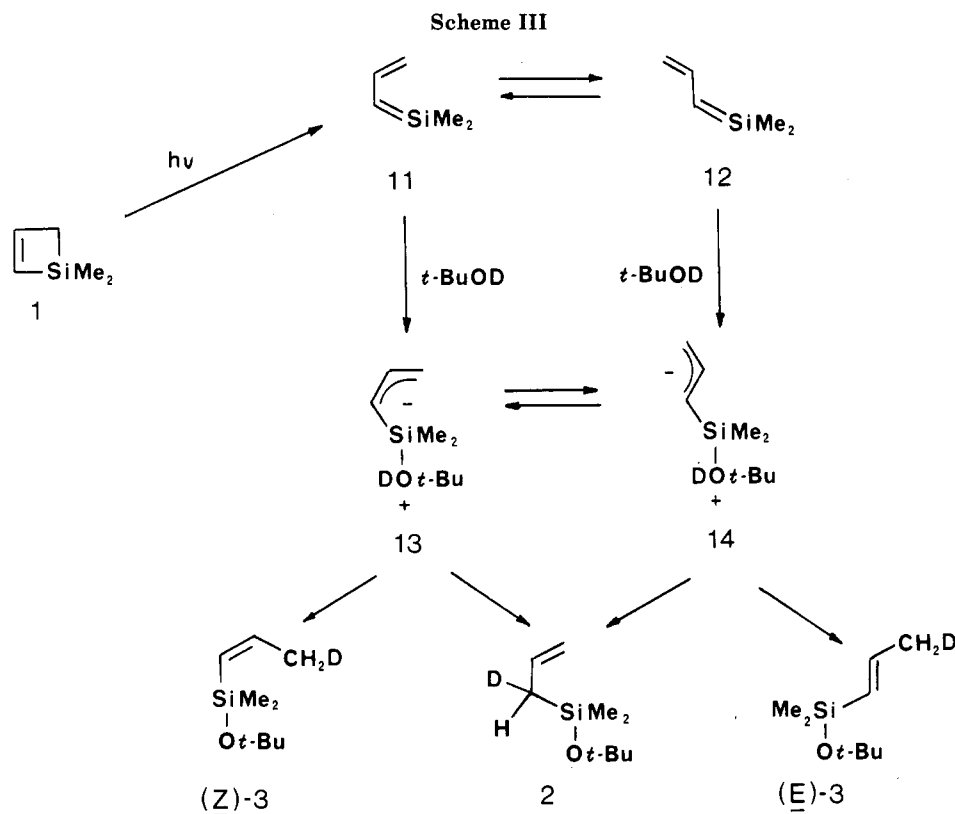
(20) (a) A mixture of chloro- and bromosilane products analogous to 25 are observed, however, in the reaction of 2-bromo-2-phenyl-1,1-dimethyl-1-silacyclobutane with AlCl$_3$.[20b] This reaction as well as those of a variety[20b,c] of (chloromethyl)vinylsilanes with AlCl$_3$ appear to proceed via the intermediacy of silacyclopropylcarbinyl and cyclopropylsilylenium cations. (b) Robinson, L. R.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935. (c) Tamao, K.; Nakajima, T.; Kumada, M. *Organometallics* **1984**, *3*, 1655.

Scheme III

Scheme IV

of the 2-propenyl group of 5-d_1. The excess of deuterium at the allylic methylene is consistent with a secondary deuterium isotope effect of 1.17 for the ring opening step. Such isotope effects normally range from 1.12 to 1.25 per deuterium.[21] This reaction likely results, in part, from acidic impurities in the methanol, since the ratio of 5:6 increases upon addition of 1 mol % sulfuric acid.

The formation of methanol adduct 6-d_1 containing deuterium exclusively at the allylic methyl group presumably results from methoxide anion attack at silicon of 1 via a pentavalent intermediate (vide infra).[22,23]

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(21) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row, New York, 1981; p 211.

(22) Other pyramidal structures are possible, as for example, the methoxy group could be equatorial. Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* 1984, *15*, 43.

(23) Nucleophilic cleavage of small rings containing silicon by base does not require participation by a double bond, since the reaction occurs with a variety of silacyclobutanes: Damrauer, R. *Organomet. Chem. Rev., A* 1972, *8*, 67.

SiMe₃

/ —H

//   \ =SiMe₂
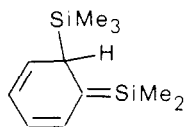
26

An analogous mechanism was proposed by Eaborn and co-workers[24] for the cleavage of 1,1-dimethyl-2,3-benzo-1-silacyclobutene in neutral methanol with autoprotolysis serving as the source of methoxide, whereas protonation of the benzo group under acidic conditions gave rise to a second product by a pathway closely resembling the protonation reaction forming 5. The strong rate increase in the reaction of 1 under basic conditions plus the absence of a concomitant decrease in the ratio of 5:6 suggests that the initially formed pentavalent intermediate may partition to both products.

In the electrocyclic mechanism for ring opening of Scheme III the s-cis (gauche, vide infra) and s-trans forms of 1-sila-1,3-butadiene, 11 and 12, respectively, possibly account for the formation of both the Z and E isomers of 3 as primary products. The mechanism also accommodates the exclusive C_3 monodeuteration of the 1-propenyl group of 3. The addition of alcohol to 11 and 12 can proceed either concertedly or as a stepwise process[14a] envisioned as involving an irreversible, rate-determining nucleophilic addition followed by a second, ultrafast proton-transfer step. In the case of unconjugated silenes, both mechanisms are consistent with (1) the dependence of rates on steric effects and Lewis basicity of the nucleophile in additions to nonconjugated silenes[14] and (2) the syn stereospecific outcome for methanol addition to (E)- and (Z)-1-phenyl-1-methyl-2-neopentyl-2-(trimethylsilyl)silene,[25] although the stepwise mechanism accounts for the reported absence of an isotope effect in the addition of methanol and methanol-O-d to $Me_2Si=C(SiMe_3)_2$[26a] and is further supported by reports[26] that hindered, unconjugated silenes form stable complexes with THF, amines, and the F^- ion. While comparison of the X-ray structure of the THF adduct[26b,d] to that of the F^- adduct[26d] indicates only partial dipolar character, for purposes of discussion (vide infra) stepwise addition of alcohol will be depicted as involving zwitterionic complexes 13 and 14 in Scheme III. Since partial equilibration of 13 to 14 must compete with proton transfer to form products (vide infra), such a process would seem a doubtful source of (E)-3. Furthermore, complexation by alcohol is likely to increase the C_2-C_3 rotational barrier, depending on the extent of dipolar character in the complex. A limiting case is the allyl anion (Cs counterion), which has a rotational barrier of $\Delta G^\ddagger = 18$ kcal mol⁻¹.[27] For similar reasons, attack of tert-butyl alcohol on electronically excited silacyclobutene 1 to form complex 13 followed by equilibration to 14 seems an unlikely source of (E)-3.

The proton transfers to form the final products of 13 and 14 may be mediated[28] by the alcohol solvent, especially

with (E)-3, where the distance involved likely precludes intramolecular transfer. Solvent mediation accounts for the strong decrease in yield of (E)-3 with decrease in tert-butyl alcohol concentration, whereas the less pronounced effect on yields (Z)-3 and 2 implies intramolecular proton transfer or concerted addition. Given the ΔpK_a between fully formed, dipolar complexes and solvent of ca. 19 pK units, proton transfer to solvent should be rapid (ca. 10^{10} M⁻¹ s⁻¹ [29]) or even concerted with addition via a termolecular complex.[30] Product formation would then involve two, single proton transfers or a simultaneous two proton transfer.[31]

Gauche and s-trans-1,1-Dimethyl-1,3-silabutadienes as Potential Intermediates in the Formation of Alcohol Adducts. The computational results at the highest level of theory employed, MP2/6-31G(d), indicate a rotational barrier of 3.9 kcal mol⁻¹ for the conversion of gauche 1-sila-1,3-butadiene to its s-trans rotamer, which has a 6.2 kcal mol⁻¹ C_2-C_3 rotational barrier in the reverse direction. Incorporation of zero-point vibrational energy (ZPE) corrections produces 0 K activation energies of 3.8 and 5.8 kcal mol⁻¹, respectively. Because of the very small ZPE correction, these energy differences are expected to have only a slight temperature dependence.[32]

Extrapolating the computational results to the methyl-substituted analogues, selective trapping of gauche 11 becomes possible only if alcohol addition occurs at diffusion-controlled rates. Even then, pseudo-first-order rates of alcohol addition in pentane as the solvent would be slower than or comparable to rotation, ranging from 2.4 $\times$ 10⁸ s⁻¹ at 0.01 M tert-butyl alcohol to 2.4 $\times$ 10¹⁰ s⁻¹ at 1.0 M tert-butyl alcohol.[33] Trapping rates may actually be slower than diffusion-controlled. The bimolecular rate constant for reaction of a transient postulated as silene 26

┌─┐
│ │   ⁻ ‖‖‖ Me
└─ Si
    │   ⁀Me
   OMe
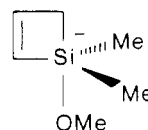
with ethanol has recently been found by laser flash photolysis techniques to be 2.5 $\times$ 10⁸ M⁻¹ s⁻¹,[34] and tert-butyl alcohol is half as reactive toward hindered silenes as ethanol.[14b,26a] Yields of (Z)-3 remain almost constant as tert-butyl alcohol concentration varies (Table II), and only with pure tert-butyl alcohol as the solvent is selective trapping of 11 manifested as a slightly enhanced yield of (Z)-3 relative to the other tert-butyl alcohol adducts of 1. That (Z)-3 does not strongly decrease with decreasing

(24) Eaborn, C.; Walton, D. R. M.; Chan, M. *J. Organomet. Chem.* 1967, 9, 251.

(25) (a) Nonstereospecific addition of methanol to certain silenes has also been observed.[25c] (b) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* 1987, 109, 913. (c) Brook, A. G.; Safa, K. D.; Lickiss, P. D.; Baines, K. M. *J. Am. Chem. Soc.* 1985, 107, 4338.

(26) (a) Wiberg, N. *Ibid.* 1984, 273, 141. (c) Wiberg, N.; Kopf, H. *Ibid.* 1986, 315, 9. (b) Wiberg, N.; Wagner, G.; Muller, G.; Riede, J. *J. Organomet. Chem.* 1984, 271, 381. (c) Wiberg, N.; Wagner, G.; Riede, J.; Muller, G. *Organometallics* 1987, 6, 32. (d) Wiberg, N.; Wagner, G.; Reber, G.; Riede, J.; Muller, G. *Ibid.* 1987, 6, 35.

(27) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* 1979, 101, 5459.

(28) Menger, F. M. *Tetrahedron* 1983, 39, 1013.

(29) (a) The bimolecular rate constant for proton transfer between methyloxonium ions and methanol is 8.8 $\times$ 10¹⁰ M⁻¹ s⁻¹ and the $\Delta H^\ddagger = 2$ kcal mol⁻¹.[29b] Comparable barriers are obtained from ab initio molecular orbital calculations of the $(CH_3OH-H-HOCH_3)^+$ system, depending on the interoxygen distance and the angular deformation of the H bonds.[29c] (b) Grunwald, E.; Jumper, C. F.; Meiboom, S. *J. Am. Chem. Soc.* 1962, 84, 4664. (c) Hillenbrand, E. A., Scheiner, S. *Ibid.* 1984, 106, 6266.

(30) This situation appears analogous to the fast proton transfer regime of the n–f class of reactions described by: Jencks, W. P. *Acc. Chem. Res.* 1976, 9, 425.

(31) Scheiner, S. *J. Am. Chem. Soc.* 1981, 103, 315.

(32) The 3.8 kcal mol⁻¹ barrier to rotation of the gauche form corresponds to a rate constant 7.1 $\times$ 10⁹ s⁻¹, as calculated from transition-state theory. The rate constant for the reverse direction ($\Delta G^\ddagger = 5.8$ kcal mol⁻¹) is 2.0 $\times$ 10⁸ s⁻¹.

(33) (a) The bimolecular rate constant for diffusion in pure pentane is 2.4 $\times$ 10¹⁰ M⁻¹ s⁻¹ at 282 K; the corresponding value for tert-butyl alcohol is 1.8 $\times$ 10⁹ M⁻¹ s⁻¹ at 300 K. These values were calculated from the Debye equation making use of viscosities tabulated by Wagner.[33b] (b) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* 1969, 90, 2232.

(34) Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* 1987, 20, 329.

alcohol concentration is apparently indicative of a preequilibrium of 11 and 12 that is at least competitive with, if not faster than, trapping, particularly at low alcohol concentrations.

The MP2/6-31G(d) calculations indicate a significant, 2.3 kcal mol^{-1} difference in stability between gauche and *s-trans* forms of the parent silabutadiene, and this difference is expected to be accentuated by the presence of the terminal methyl groups of 11 and 12. Competitive preequilibrium of the two forms of silabutadiene would thus heavily favor the *s-trans* form and lead to a predominance of alcohol addition products of 12 at all concentrations of *tert*-butyl alcohol employed. The predominance is not reflected by the (E)-3/(Z)-3 ratios of Table II but rather by the ratio $(2 + (E)$-3)/(Z)-3 of 13–18, which suggests that 1,2-addition giving 2 occurs almost exclusively from the *s-trans* side of Scheme III. A faster rate of alcohol addition to 11 than to 12 as a consequence of an asynchronous, concerted mechanism is also conceivable. Direct formation of 13 or (Z)-3 through trapping of excited 1 seems unlikely given the nearly concentration independent yields of (Z)-3.

As noted above, the strong decrease in (E)-3 yield with decreasing alcohol concentration may be attributable to differences in partitioning of 14 to products as a result of solvent mediation in the proton transfer step. The absolute yield of $2 + (E)$-3 is surprisingly constant over 0.01–1.0 M *tert*-butyl alcohol, although relative yields vary significantly (Table II). As for the decrease in yield of (E)-3 and (Z)-3 relative to 2 at 67 °C compared to 1 °C with 0.50 M *tert*-butyl alcohol in hexane as solvent, we can only speculate that the yield of 2 from 12 increases at the expense of both products, presumably as a result of a temperature effect on partitioning of 14 through disruption of hydrogen bonding in solvent mediated proton transfer forming (E)-3. A smaller, though similar effect of temperature was observed with pure *tert*-butyl alcohol as the solvent.

Conclusions

While our deuterium-labeling, trapping, and product studies of 1,1-dimethyl-1-silacyclobut-2-ene (1) have shown that it is possible to assess the contributions of electrocyclic opening, Rydberg carbene processes, and protodesilylation to the overall photochemistry, further elucidation of the mechanistic details of the major component, electrocyclic opening, has proven difficult, particularly regarding the role of the *s-cis* or gauche and *s-trans* conformers of 1,1-dimethyl-1-sila-1,3-butadiene. For the most part our results are consistent with both the *s-cis* or gauche and *s-trans* rotamers as the precursors to products 2 and (Z),-(E)-3, and studies of product ratios as a function of *tert*-butyl alcohol concentration suggest that conformational interconversion effectively competes with solvent addition to the 1-sila-1,3-butadienes at low concentrations. Optimized geometries using the 6-31G(d) basis set were calculated for the *cis*, gauche, and *s-trans* structures of 1-sila-1,3-butadiene and 1,3-butadiene, as well as relative energies and barriers for interconversion of the gauche and trans species at the MP2/6-31G(d) level.

Experimental Section

Spectra were recorded with the following spectrometers: Varian EM360L (60MHz, ^{1}H NMR), Bruker WM-250 or GE QE-300 (^{1,2}H NMR), Analect FX-6200 (FTIR), Perkin-Elmer 320 (UV). A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC-MS analyses, which were performed at 70 eV with the following columns: either a 0.25 mm × 30 m DB-1 capillary column programmed at 50 °C for 4 min and then 200

°C at 10 °C min^{-1} or a 0.25 mm × 30 m, 50:50 Superox:OV-1 capillary column programmed at 40 °C for 4 min and then 80 °C at 5 °C min^{-1} (only for selected ion monitoring studies).

Preparative GC separations were performed on a HP (FM Scientific 700) gas chromatograph with He as carrier gas at 30 mL min^{-1} flow rate on the following columns: column A, 17 ft × $^1/_4$ in. 15% OV-101 on 100/120 mesh Supelcoport; column B, 17 ft × $^1/_4$ in. 20% DC-550 on 60/80 mesh Chromosorb PAW; column C, 15 ft × $^1/_4$ in. 15% QF-1 on 60/80 mesh Chromosorb W; column D, 10 ft × $^1/_4$ in. 15% didecyl phthalate on 80/100 mesh Chromosorb P.

A Varian 1400 gas chromatograph equipped with a flame ionization detector and an HP 3390A electronic integrating recorder was 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, 22 ft × $^1/_8$ in. 10% OV-101 on 100/120 mesh Supelcoport; column F, 12 ft × $^1/_8$ in. 10% QF-1 on 100/120 Supelcoport; column G, 12 ft × $^1/_8$ in. 10% didecyl phthalate on 100/120 mesh Supelcoport.

tert-Butyl alcohol (Alfa, 99.9%, distilled from CaH$_2$), *tert*-butyl alcohol-*O-d* (99 atom % D, ICN Biomedicals), pentane (EM Omnisolv), methanol (Fisher Scientific), and methanol-*O-d* (Aldrich, 99.5 atom % D) were used as solvents in photolyses. Hexane was purified by the method of Morgan and Lowry,[35] as described by Riddick and Bunger.[36] *tert*-Butoxytrimethylsilane is commercially available through Huls-Petrarch; it was purified by preparative GC on column D.

1,1-Dimethyl-1-silacyclobut-2-ene (1). The silacyclobut-2-ene was synthesized in crude yields of 25–30% from flash vacuum pyrolysis at 800 °C of diallyldimethylsilane following the procedure of Block and Revelle.[10] The apparatus was an unpacked quartz tube (25 mm × 335 mm) mounted in a Lindberg tube furnace which was connected to a liquid-nitrogen trap evacuated to 0.05 mm. The crude product, obtained as a yellow liquid, was distilled (6 in. Vigreaux column) at 70–71 °C and then purified by preparative GC using column A (50 °C) or column B (50 °C). The ^{1}H NMR spectrum was as reported previously.[10] IR (CCl$_4$): 3.27, 3.31, 6.61, 7.03, 7.85, 8.63, 9.71 μm. GC–MS: retention time 2.1 min, m/z (relative intensity) 98 (71), 83 (100), 72 (32), 59 (29), 43 (95). UV (pentane): λ_{max} 193 nm (ϵ 2637); see Figure 1.

(E)- and (Z)-*tert*-Butoxydimethyl(1-propenyl)silanes (3). To 4.1 g (0.59 mol) of finely cut lithium wire and 140 mL of anhydrous ether in a Morton flask equipped with a high speed stirrer was added, dropwise under nitrogen, a solution of 8.1 mL (11 g, 0.094 mol) of a mixture of (E)- and (Z)-1-bromo-1-propenes in 40 mL of dry ether over a 1-h period at −28 °C (dry ice, carbon tetrachloride–acetone bath).[37] After an additional 1 h a solution of 11 mL (12 g, 0.094 mol) of dichlorodimethylsilane in 20 mL of dry ether was added, dropwise, while cooling the mixture to 0 °C. The reaction mixture was stirred overnight followed by suction filtration of the salts. After distillation of the ether 9.7 g of (E)- and (Z)-1-chloro-1,1-dimethyl(1-propenyl)silanes was distilled (6 in. Vigreaux column) at 100–105 °C (760 mm) to obtain 8.0 g (64% yield) of a colorless liquid. The ^{1}H NMR data were as follows: (CCl$_4$) δ 0.33 (s, 6 H, methyl), 1.69–1.79 (d, J = 5.5 Hz, 3 H, methyl), 5.19–6.56 (m, 2 H, vinyl). The chlorosilanes were converted to *tert*-butoxy derivatives without further purification.

To a mixture of 12 mL (13 g, 0.10 mol) of quinoline and 9.6 mL (7.5 g, 0.10 mol) of *tert*-butyl alcohol (distilled from CaH$_2$) in 50 mL of pentane was added, dropwise with stirring, 8.0 g (0.060 mol) of a mixture of (E)- and (Z)-1-chloro-1,1-dimethyl-(1-propenyl)silanes. The reaction mixture was refluxed 22 h followed by cooling and suction filtration of the salts. The filtrate was washed several times with water, once with 5% hydrochloric acid, and then with saturated sodium chloride solution, followed by drying over anhydrous sodium sulfate. The pentane was distilled giving 8.1 g (78% crude yield) of a mixture of (E)- and (Z)-*tert*-butoxydimethyl(1-propenyl)silanes 3 as a colorless liquid. The

(35) Morgan, S. O.; Lowry, H. H. *J. Phys. Chem.* **1930**, *34*, 2385.
(36) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1970; Vol. II, p 595.
(37) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379.

E and *Z* isomers were separated by preparative GC on column B at 110 °C.

The spectral data for (*E*)-*tert*-butoxydimethyl(1-propenyl)silane [(*E*)-3] were as follows: ^{1}H NMR (CCl$_4$) δ 0.14 (s, 6 H, methyl), 1.24 (s, 9 H, *tert*-butoxy), 1.77–1.81 (d, *J* = 5.5 Hz, 3 H, methyl), 5.4–5.8 (d, *J* = 19 Hz, 1 H, vinyl), 5.8–6.4 (d of quartets, *J* = 5.5, 19 Hz, 1 H, vinyl); IR (CCl$_4$) 3.35, 6.14, 7.28, 7.94, 9.50, 11.69, 12.27 μm; UV (pentane) λ$_{max}$ 190 nm (ε 11 500); GC–MS, retention time 6.2 min, *m/z* (relative intensity) 172 (0.15), 157 (38), 115 (2.3), 101 (100), 99 (39.4), 85 (2.2), 83 (3.1), 75 (39), 73 (9), 61 (27), 59 (17), 47 (8), 45 (19), 43 (14); high resolution MS-EI calcd for C$_9$H$_{20}$OSi (M$^+$) 172.1284, found 172.1280.

The spectral data for (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3] were as follows: ^{1}H NMR (CCl$_4$) δ 0.2 (s, 6 H, methyl), 1.24 (s, 9 H, *tert*-butoxy), 1.7–1.9 (dd, *J* = 1.5, 7 Hz, 3 H, methyl), 5.27–5.61 (d of quartets, *J* = 1.5, 14.5 Hz, 1 H, vinyl), 6.04–6.64 (m, *J* = 7, 14.5 Hz, 1 H, vinyl); IR (CCl$_4$) 3.36, 6.19, 7.33, 8.0, 9.3, 9.5, 9.6, 9.73, 11.9, 12.3, 13.3 μm; UV (pentane) λ$_{max}$ 189 nm (ε 15 700); GC–MS, retention time 6.5 min, *m/z* (relative intensity), 172 (0.15), 157 (33), 116 (7), 101 (100), 99 (36), 85 (2.5), 83 (3.3), 75 (39), 61 (26), 45 (19); high-resolution MS-EI calcd for C$_9$H$_{20}$OSi (M$^+$) 172.1284, found 172.1281.

***tert*-Butoxydimethyl(2-propenyl)silane (2).** To 12 mL (13 g, 0.10 mol) of dichlorodimethylsilane was added 110 mL (0.11 mol) of allylmagnesium bromide (Aldrich, 1 M solution in ether) while stirring under a nitrogen atmosphere. The reaction mixture was refluxed for 5 h, followed by cooling and suction filtration of the salts. After distillation of the ether the crude product was distilled (6 in. Vigreaux column, 78 °C at 220 mm) to obtain 3.9 g (29% yield) of 1-chloro-1,1-dimethyl(2-propenyl)silane as a colorless liquid. The ^{1}H NMR (CCl$_4$) data were as follows: δ 0.42 (s, 6 H, methyl), 1.7–1.9 (d, *J* = 7 Hz, 2 H, methylene), 4.6–5.00 (m, 2 H, vinyl), 5.35–6.10 (m, 1 H, vinyl). The chlorosilane was converted to its *tert*-butoxy derivative without further purification.

The *tert*-butoxy derivative of 2 was prepared by the same procedure used for 3 (vide supra) from 20 mL (26 g, 0.17 mol) of quinoline, 16 mL (12.6 g, 0.170 mol) of *tert*-butyl alcohol (distilled from CaH$_2$), and 2.3 g (0.017 mol) of 1-chloro-1,1-dimethyl(2-propenyl)silane in 50 mL of pentane. Thus, 1.7 g (59% yield) of crude *tert*-butoxydimethyl(2-propenyl)silane was obtained as a colorless oil, which was purified by preparative GC on column A at 95 °C. The spectral data were as follows: ^{1}H NMR (CCl$_4$) δ 0.10 (s, 6 H, methyl), 1.23 (s, 9 H, *tert*-butoxy), 1.46–1.6 (d, *J* = 8 Hz, 2 H, methylene), 4.53–5.00 (m, 2 H, vinyl), 5.33–6.10 (m, 1 H, vinyl); IR (CCl$_4$) 3.23, 3.36, 6.15, 7.31, 7.94, 8.33, 8.65, 9.42, 10.67, 11.04, 11.84, 13.36 μm; UV (pentane) λ$_{max}$ 194 nm (ε 9000), GC–MS, retention time 6.3 min, *m/z* (relative intensity), 172 (0.08), 157 (3.5), 131 (11), 101 (7), 99 (8), 75 (100), 61 (8), 59 (7), 47 (7), 45 (12); high-resolution MS-EI for C$_9$H$_{20}$OSi, (relative intensity, empirical formula, deviation from calculated *m/z*), no parent, 157.1048 (4.3, C$_8$H$_{17}$OSi, −0.5 ppm), 131.089 (17.4, C$_6$-H$_{15}$OSi, 1.9 ppm), 101.0425 (8.76, C$_4$H$_9$OSi, 1.8 ppm). Anal. Calcd for C$_9$H$_{20}$OSi: C, 62.72; H, 11.70. Found: C, 62.60; H, 11.75.

Synthesis of (*E*)- and (*Z*)-Methoxydimethyl(1-propenyl)silanes. The isomeric 1-propenylsilanes, bp 85–87 °C (760 mm), were prepared in 57% yield from the reaction of 25.3 g (0.188 mol) of a mixture of (*E*)- and (*Z*)-1-chloro-1,1-dimethyl(1-propenyl)silanes (vide supra), 22.2 mL (24.3 g, 0.188 mol) of quinoline, and 7.6 mL (6.0 g, 0.19 mol) of methanol in 50 mL of pentane following the procedure described above for the preparation of the corresponding *tert*-butyldimethyl(1-propenyl)silanes. The mixture was purified by preparative GC on a 10 ft × $^1/_4$ in. column of 10% OV-7 on 60/80 mesh Chromosorb PAW at 60 °C; attempts to separate the two isomers preparatively on columns A–D and OV-7 were unsuccessful. The spectral data of the mixture of *E* and *Z* isomers were as follows: ^{1}H NMR (CCl$_4$) δ 0.09 and 0.156 (overlapping singlets, 6 H, methyl), 1.72–1.87 (m, 3 H, methyl), 3.30 and 3.32 (overlapping singlets, 3 H, methoxy), 5.19–5.66 (m, 1 H, vinyl), 5.92–6.67 (m, 1 H, vinyl); IR (CCl$_4$) 3.37, 3.40, 3.53, 6.17, 6.94, 7.96, 8.40, 9.17, 11.91, 12.65, 13.59, 13.77 μm; GC–MS, *m/z* (relative intensity) 130 (2.4), 115 (100), 99 (2.1), 89 (19), 85 (9), 83 (2.5), 75 (67), 69 (2.8), 59 (47); high-resolution MS-EI calcd for C$_6$H$_{14}$OSi (M$^+$) 130.0814, found 130.0811.

Synthesis of Methoxydimethyl(2-propenyl)silane (5). The 2-propenylsilane was prepared in 86% yield, bp 97–98 °C (760

mm), from the reaction of 26.5 g (0.199 mol) of 1-chloro-1,1-dimethyl(2-propenyl)silane (vide supra), 30 mL (32 g, 0.24 mol) of quinoline and 9.9 mL (7.8 g, 0.24 mol) of methanol in 50 mL of pentane following the procedure described above for the synthesis of *tert*-butoxydimethyl(2-propenyl)silane (2). The product was purified by preparative GC on a 10 ft × $^1/_4$ in. column of 10% OV-7 on 60/80 mesh Chromosorb PAW at 60 °C. The spectral data were as follows: ^{1}H NMR (CCl$_4$) δ 0.056 (s, 6 H, methyl), 1.54 (d, *J* = 8 Hz, 2 H, methylene), 3.34 (s, 3 H, methoxy), 4.59–4.99 (m, 2 H, vinyl), 5.35–6.05 (m, 1 H, vinyl); IR (CCl$_4$) 3.24, 3.38, 3.53, 6.12, 7.03, 7.96, 8.40, 8.65, 9.13, 9.67, 10.07, 11.15, 11.84, 13.35 μm; GC–MS, *m/z* (relative intensity) 130 (1.3), 115 (6.6), 89 (100), 87 (15), 75 (8.0), 71 (1.1), 59 (88), 55 (2.0), 45 (13), 43 (17), 41 (6), 39 (9.5). Anal. Calcd for C$_6$H$_{14}$OSi: C, 55.33; H, 10.83. Found: C, 55.30; H, 10.92.

General Procedure for Preparative Direct Photolyses. Unless noted otherwise, photolyses were performed with an immersion well apparatus of either 40 or 48 mL volume. Runs with *tert*-butyl alcohol as the solvent were conducted at 27 °C with a Philips zinc lamp (214 nm), which was cooled by a stream of air. All photolysates were purged with nitrogen 1 h prior to and during photolyses.

Determination of Photochemical Product Yields of Photolyses Conducted in *tert*-Butyl Alcohol. Solutions of 0.01–0.03 M 1,1-dimethyl-1-silacyclo-but-2-ene (1) and *n*-decane as internal standard in *tert*-butyl alcohol were irradiated following the above procedure for direct photolyses. Aliquots were taken at time intervals for GC analysis and were diluted with 0.5 mL of pentane, washed five times with 1 mL of water, and dried over anhydrous sodium sulfate. Column E (40 °C for 30 min and then at 90 °C) was used to quantify unreacted silacyclobutene 1, *tert*-butoxytrimethylsilane (4) (retention time 45 min), and (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3] (retention time 73 min); (*E*)-*tert*-butoxydimethyl(1-propenyl) silane [(*E*)-3] (71 min) overlapped with *tert*-butoxydimethyl(2-propenyl)silane (2) and was thus quantified on column F (32 °C, nitrogen flow rate 24 mL min^{-1}). The retention times on column F were 18 min for (*E*)-3 and 22 min for 2 and (*Z*)-3. The amount of 2-propenylsilane 2 was then obtained by subtraction. This procedure was used to obtain photochemical yields and concentration versus time profiles (Figure 2), and the data are summarized in Tables I and II (vide infra).

Identification of Photoproducts from Direct Photolyses of 1,1-Dimethyl-1-silacyclobut-2-ene (1) in *tert*-Butyl Alcohol at 214 nm. A 0.0314 M solution of 123 mg (1.26 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene in 40 mL of *tert*-butyl alcohol was irradiated at 214 nm for 2 h following the general procedure described above. GC and GC–MS analyses of aliquots after workup (Determination of Product Yields, vide supra) showed only four peaks with retention times and mass spectra corresponding to authentic samples of 1–4 by GC coinjection. After 40 mL of pentane was added, the photolysate was washed six times with 150 mL of water and then dried over anhydrous sodium sulfate. The bulk of the pentane was distilled, and the reactant and products were isolated by preparative GC on column B at 85 °C. Starting material, *tert*-butoxytrimethylsilane (4), and (*Z*)-*tert*-butoxy(1-propenyl)silane (*Z*)-3 were obtained as pure compounds, whereas *tert*-butoxy(2-propenyl)silane 2 and (*E*)-*tert*-butoxy(1-propenyl)silane (*E*)-3 were isolated as a mixture and thus were subjected to preparative GC on column C (80 °C) to effect separation. Each of the products were identified by ^{1}H NMR, IR, GC–MS, and capillary GC–MS coinjection with authentic samples.

Direct Photolyses of 1,1-Dimethyl-1-silacyclobut-2-ene (1) in *tert*-Butyl Alcohol-*O-d* at 214 nm. The general procedure described above was used. Two 214 nm direct photolyses of 400 mg (4.08 mmol) and 412 mg (4.20 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene (1), each in 40 mL of *tert*-butyl alcohol-*O-d*, were taken to 40% conversion. After 40 mL of pentane was added, the photolysate was washed six times with 150 mL of water and then dried over anhydrous sodium sulfate. The bulk of the pentane was distilled, and the reactant and products were isolated by preparative GC (columns B and C), followed by ^{1}H NMR, ^{2}H NMR, and GC–MS analyses.

GC–MS data obtained under identical experimental conditions for products of *tert*-butyl alcohol and *tert*-butyl alcohol-*O-d* were

compared to determine the extent of deuterium incorporation. Thus reactant silacyclobutene was found to be >99% unlabeled as calculated[38] from contributions of each isotopic species to the m/z 83, 84, and 85 peak intensities (M − 15 ion used). On the basis of m/z 131, 132, and 133 (M − 15) fragment ion intensities 1-*tert*-butoxytrimethylsilane was found to be 84.4% mono-deuterated, 0% dideuterated, and 15.6% undeuterated (see Results for further discussion). The calculated isotopic composition of (*E*)-*tert*-butoxydimethyl(1-propenyl)silane, based on the M − 15 fragment ions, m/z 157, 158, and 159, was as follows: 97.5% monodeuterated and 2.5% dideuterated. The isotopic composition, calculated from M − 15 (m/z 157, 158, and 159) peak intensities of *tert*-butoxydimethyl(2-propenyl)silane, was as follows: 4.4% undeuterated, 94.4% monodeuterated, and 12% dideuterated. The calculated isotopic composition of (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane based on fragment ions m/z 157, 158, and 159 was as follows: 99.4% monodeuterated and 0.6% dideuterated. Thus all the products were found to be >95% monodeuterated.

^{1}H NMR and ^{2}H NMR data identified the positions and distribution of deuterium in the photoproducts. The 250-MHz ^{1}H NMR (CCl$_4$) of monodeuterated *tert*-butoxytrimethylsilane was as follows: δ 0.040 (s, 5 H, methyl) 1.19 (s, 9 H, *tert*-butoxy). ^{2}H NMR (CCl$_4$) showed a single peak at δ −0.075, confirming that the methyl group bonded to silicon contained the deuterium.

(*E*)-*tert*-Butoxydimethyl(1-propenyl)silane-d_1 showed the following 250-MHz ^{1}H NMR (CCl$_4$) spectrum: δ 0.03 (s, 6 H, methyl), 1.14 (s, 9 H, *tert*-butoxy), 1.73 (m, 2 H, methyl), 5.50–5.58 (d of triplets, J = 1.7, 19 Hz, 1 H, vinyl), 5.86–6.01 (d of triplets, J = 6.1, 19 Hz, 1 H, vinyl). The ^{2}H NMR spectrum (CCl$_4$) showed only one peak at δ 1.68 corresponding to C$_3$ of the 1-propenyl group as the deuterated site.

The 250-MHz ^{1}H NMR (CCl$_4$) spectrum of *tert*-butoxydimethyl(2-propenyl)silane-d_1 was as follows: δ 0.10 (s, 6 H, methyl), 1.20 (s, 9 H, *tert*-butoxy), 1.46–1.53 (m, 1 H, methylene), 4.70–4.77 (m, 2 H, vinyl), 5.58–5.72 (m, 1 H, vinyl). ^{2}H NMR showed two peaks at δ 1.39 (methylene) and 4.68 (vinyl) with intensities corresponding to a 93.4:6.54 ratio of deuterium at C$_1$ and C$_3$ of the 2-propenyl group.

The 250-MHz ^{1}H NMR (CCl$_4$) data of (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane-d_1 follows: δ 0.13 (s, 6 H, methyl), 1.20 (s, *tert*-butoxy), 1.70–1.79 (m, 2 H, methyl), 5.36–5.43 (d of triplets, J = ca. 1, 14.5 Hz, 1 H, vinyl), 6.17–6.30 (d of triplets, J = 7.3, 14.5 Hz, 1 H, vinyl). The integration intensities showed a single deuterium at C$_3$ of the 1-propenyl group, which was further confirmed by ^{2}H NMR (CCl$_4$) which showed a single peak at δ 1.72.

Direct Photolyses of 1,1-Dimethyl-1-silacyclobut-2-ene (1) in 0.10 M *tert*-Butyl Alcohol in Pentane at 185 + 254 nm. A 0.0119 M solution of 46.6 mg (0.476 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene (1) in 40 mL 0.10 M *tert*-butyl alcohol in pentane with 10.2 mg of *n*-decane internal standard was irradiated 2 h at 5 °C following the general procedure described above, except that the lamp was an Osram HNS 10W/U oz with a light output at 185 + 254 nm. After workup (Determination of Product Yields, vide supra), aliquots taken at time intervals were analyzed by GC on columns E and F. The product ratio and rates of product formation from a concentration versus time profile are given in the Results. In addition to unreacted silacyclobutene, 1-*tert*-butoxytrimethylsilane (4) (4.1% yield), (*E*)-*tert*-butoxydimethyl(1-propenyl)silane [(*E*)-3] (6.1% yield), *tert*-butoxydimethyl(2-propenyl)silane (2) (27% yield), and (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3] (2.2% yield) were found. No other products were observed. GC-MS and coinjection studies with authentic samples verified the product assignments.

A second run with 49.3 mg (0.503 mmol) of 1 and 13.5 mg of decane in 38 mL of 0.10 M *tert*-butyl alcohol in pentane was performed to quantify reactant 1 consumed as well as the product yields. After 10 min photolysis GC analysis, as above, gave 88.8% of 1, 0.86% of 4, 0.88% (*E*)-3, 8.59% of 2, and 0.72% of (*Z*)-3.

Direct Photolysis of (*Z*)-*tert*-Butoxydimethyl(1-propenyl)silane [(*Z*)-3] in *tert*-Butyl Alcohol at 214 nm. The

general procedure for photolyses described above was used. A solution of 79.2 mg (0.460 mmol) of (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3] in 40 mL of *tert*-butyl alcohol was irradiated for 11 h at 214 nm. A known amount of decane standard was added to aliquots taken at time intervals. Each aliquot was diluted with 0.5 mL of pentane and washed six times with 2 mL of water prior to GC analyses (column E at 80 °C and column F at 32 °C), which showed the formation of 62.0% of (*E*)-*tert*-butoxydimethyl(1-propenyl)silane [(*E*)-3] and 33.1% of unreacted (*Z*)-*tert*-butoxydimethyl(1-propenyl)silane [(*Z*)-3]. No other products were detected. The identity of the components was determined by capillary GC-MS and by comparison of retention times to authentic samples on columns E and F.

GC-MS selected ion monitoring (SIM) experiments using a 25 m × 0.25 mm capillary column of 50% Superox 50% OV-1 (40 °C for 4 min and then 5 °C min^{-1} to 80 °C) gave 61% (*E*)-*tert*-butoxydimethyl(1-propenyl)silane [(*E*)-3] and 0.16% *tert*-butoxydimethyl(2-propenyl)silane (2). The characteristic m/z 131 ion was used to quantify *tert*-butoxy(2-propenyl)silane 2, which overlapped with the (*E*)-*tert*-butoxydimethyl(1-propenyl)silane chromatographic peak, whereas the m/z 101 ion was used to quantify the latter silane, correcting for the trace amount of allylic silane. Both ions were calibrated against m/z 57 of decane standard.

Direct Photolysis of *tert*-Butoxydimethyl(2-propenyl)-silane (2) at 214 nm in *tert*-Butyl Alcohol. A 0.015 M solution of 104 mg (0.605 mmol) of 2-propenylsilane 2 and 23.3 mg of decane standard in 40 mL of *tert*-butyl alcohol was irradiated for 25 h at 214 nm following the general procedure for photolyses described above. Aliquots taken at time intervals were worked up to remove *tert*-butyl alcohol (vide supra) and analyzed by GC on column E at 80 °C and by GC-MS on a DB-1 column and on a 50:50 Superox:OV-1 column (vide supra). Two unknown products appeared at longer retention times than 2 in approximately a 2:1 ratio. The estimated, combined yield of the two major photoproducts was 24% after photolysis, and 29% of 2 remained unreacted. While no more than 1% of (*Z*)-3 could have been present at any stage in the photolysis, the yield of (*E*)-3 after 25 h was 4% on column F at 32 °C. The presence of (*E*)-3 was detected in the ^{1}H NMR spectrum of 2 recovered by preparative GC. Each component of the photolysate was isolated by preparative GC on column B at 100 °C. The spectral data of the major unknown photoproduct follow: ^{1}H NMR (CCl$_4$) δ −0.14 (s, 6 H), −0.043–0.37 (m, 5 H), 1.12 (s, 9 H); IR (CCl$_4$) 3.25, 3.36, 3.41, 3.44, 3.48, 4.19, 4.58, 5.18, 6.84, 7.19, 7.33, 7.75, 7.98, 8.33, 9.76, 11.10, 12.62, 14.51 μm; GC-MS, m/z (relative intensity) no parent, 157 (50), 131 (2.5), 115 (4.4), 101 (100), 99 (43), 75 (75), 61 (34), 59 (22), 57 (7.6), 55 (4.0), 47 (15), 45 (39), 43 (22), 41 (13). The spectral data of the minor unknown photoproduct follow: ^{1}H NMR (CCl$_4$) δ 0.24 (s), 1.42 (s), intensity ratio 1:3; IR (CCl$_4$) 3.36, 7.33, 7.96, 8.08, 8.38, 9.49, 9.76, 11.81, 12.70, 12.87, 13.17, 13.40, 13.63 μm; GC-MS, m/z (relative intensity) no parent, 189 (22), 134 (5.9), 133 (49.9), 115 (2.7), 101 (3.4), 87 (7.2), 77 (64), 75 (100), 61 (5.9), 59 (6.4), 57 (17), 47 (9.4), 45 (13), 43 (6.5), 41 (7.4).

Dark Reaction of 1,1-Dimethyl-1-silacyclobut-2-ene (1) with Methanol. A solution of 78.8 mg (0.804 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene (1) in 20 mL of methanol was stirred under nitrogen for 4 h at 25 °C. After 50 mL of pentane was added, the reaction mixture was washed six times with 150 mL of water and then dried over anhydrous sodium sulfate. GC-MS analysis showed two peaks. The component with a retention time of 4.6 min [m/z (relative intensity) 130 (1), 115 (7), 89 (100), 75 (9), 61 (5), 59 (80), 45 (11), 43 (14)] was identified as methoxydimethyl(2-propenyl)silane (5). The peak with retention time 4.8 min [m/z (relative intensity) 130 (1), 115 (100), 99 (2), 89 (29), 85 (10), 75 (60), 69 (3), 61 (11), 59 (55), 45 (20)] was identified as (*Z*)-methoxydimethyl(1-propenyl)silane (6). Comparison of retention times of authentic samples on column E and capillary GC-MS supported the above assignments. GC analysis of a duplicate run on column E (50 °C for 40 min and then at 90 °C) showed complete disappearance of reactant 1 and the formation of 5 and 6 in 55% and 33% yields, respectively. A separate run was performed on a 200-mg (2.04-mmol) scale followed by preparative GC (column B) to characterize the products by ^{1}H NMR. The *E* isomer of 6 was not detected in the ^{1}H NMR spectrum of (*Z*)-6.

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

Three reactions were performed with 1 on a 50-mg (0.51-mmol) scale at room temperature under nitrogen with methanol that was distilled from magnesium methoxide, containing 2.5×10^{-4} M of either sulfuric acid or sodium methoxide, or no additive. In the acid-catalyzed run the silacyclobutene had a half-life of ca. 14 h and after 24 h gave 5 and 6 in 59% and 13% yields, respectively, along the 30% unreacted 1, by GC analysis. When purified methanol without acid or base was used as solvent, an excellent fit to first-order kinetics for the disappearance of 1 was obtained, which gave a pseudo-first-order rate constant for reaction of 4.18×10^{-5} s^{-1}. The product yields after 24 h were 58% 5 and 40% 6. With sodium methoxide as the additive, reactant 1 was consumed within 10 min to give 52% of 5 and 36% of 6. At 0.001 M sodium methoxide, the yields of 5 and 6 were 60% and 40%, respectively. Control runs showed that 0.025 M 5 was stable in the presence of 0.001 M sodium methoxide in methanol for 17 h at room temperature, whereas 5 was found to be 97.4% unreacted along with 0.7% yield of 6 after 17 h under identical conditions.

Reaction of 1,1-Dimethyl-1-silacyclobut-2-ene (1) with Methanol-O-d_1. A solution of 86.7 mg (0.885 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene in 20 mL of methanol-O-d (99.5 atom % D) was stirred for a total of 12 h under nitrogen at 25 °C. An aliquot of 0.5 mL taken after 2 h of reaction was added to 0.5 mL of pentane and washed three times with 1 mL of water. GC analysis on column E (50 °C for 40 min and then at 90 °C) showed three peaks with retention times of 14 min (silacyclobutene, 20% yield), 36 min (methoxydimethyl(2-propenyl)silane (5), 56% yield), and 38 min ((Z)-methoxydimethyl(1-propenyl)-silane (6), 23% yield). After 12 h the reaction mixture was added to 30 mL of pentane and washed four times with 30 mL of water. The pentane solution was dried over anhydrous sodium sulfate. After the pentane was distilled, the products were isolated by preparative GC on column B (110 °C) and characterized by ^{1}H NMR, IR, and GC-MS.

The spectra data for methoxydimethyl(2-propenyl)silane (5-d_1) were as follows: ^{1}H NMR (CCl$_4$) δ 0.07 (s, 6 H, methyl) 1.50–1.64 (d, 1.44 H, methylene), 3.37 (s, 3 H, methoxy), 4.64–5.00 (m, 1.56 H, vinyl), 5.44–5.94 (m, 1 H, vinyl); IR (CCl$_4$), 3.25, 3.28, 3.38, 3.40, 3.44, 3.53, 4.44, 4.64, 5.55, 6.14, 6.22, 6.87, 7.08, 7.39, 8.60, 8.77, 10.00, 10.31, 10.57, 11.29, 12.40, 16.52 μm; GC-MS, retention time 4.6 min, m/z (relative intensity) 131 (1.3), 116 (7), 100 (0.5), 90 (8.5), 88 (100), 84 (1.25), 76 (1.3), 75 (8), 59 (83), 55 (1.6), 45 (10), 43 (15).

The spectral data for (Z)-methoxydimethyl(1-propenyl)silane (6-d_1) were as follows: ^{1}H NMR (CCl$_4$) δ 0.16 (s, 6 H, methyl), 1.69–1.92 (m, 2 H, methyl), 3.29 (s, 3 H, methoxy), 5.19–5.49 (m, J = 14 Hz, 1 H, vinyl), 6.12–6.65 (m, J = 14 Hz, 1 H, vinyl); IR (CCl$_4$), 3.37, 3.43, 6.21, 7.97, 9.49, 11.87, 12.78, 12.91, 13.09, 13.31, 14.77, 15.70 μm; GC-MS, retention time 4.8 min, m/z (relative intensity) 131 (1.85), 116 (100), 100 (1.6), 89 (39), 86 (11), 75 (64), 59 (68), 53 (3), 45 (21), 43 (20). GC-MS data obtained under identical experimental conditions for methanol and methanol-O-d runs were compared to determine the extent of deuterium incorporation in the products. Thus dimethylmethoxy(2-propenyl)silane was found to be 99.88% monodeuterated and 0.12% dideuterated and (Z)-dimethylmethoxy(1-propenyl)silane was 100% monodeuterated, based on M − 15, m/z 115, 116, and 117, fragment ion intensities in the methanol-O-d runs.

Analysis of ^{1}H NMR and ^{2}H NMR data identified the positions and distribution of deuterium in the products. For methoxydimethyl(2-propenyl)silane ^{1}H NMR integration showed the scrambling of deuterium between C$_1$ and C$_3$ of the 2-propenyl group: ^{2}H NMR (CCl$_4$) δ 1.42 (methylene) and 4.74 (vinyl) with intensities corresponding to a 54:46 ratio of deuterium at C$_1$ and C$_3$ of the 2-propenyl group.

For (Z)-methoxydimethyl(1-propenyl)silane-d_1 ^{1}H NMR integration indicated two protons at C$_3$ of the 1-propenyl group. ^{2}H NMR (CCl$_4$) gave a single peak at δ 1.76 corresponding to deuterium at C$_3$, confirming the ^{1}H NMR results.

Direct Photolysis of 1,1-Dimethyl-1-silacyclobut-2-ene (1) with 0.25 M Methoxytrimethylsilane in Pentane at 214 nm. A 0.0255 M solution of 100 mg (1.03 mmol) of 1,1-dimethyl-1-silacyclobut-2-ene (1) and 1.07 g (10.3 mmol) of methoxytrimethylsilane in 40 mL of pentane was irradiated at 214 nm for 12 h (56% conversion). GC analysis on column E at 90 °C showed

only two product peaks with retention times of 58.3 (product A) and 66.6 min (product B) in addition to peaks corresponding to reactants. Products A and B were isolated by preparative GC on column D (at 80 °C) after the pentane solvent was distilled off. The products were identified by ^{1}H NMR, IR, and GC-MS. The minor product A was found to be 2-methoxy-2,4,4-trimethyl-2,4-disilapentane (8). The major product B was 2-methoxy-2,4,4-trimethyl-3-vinyl-2,4-disilapentane (7). A second run with 203 mg (2.07 mmol) of 1 and 2.16 g (20.8 mmol) of methoxytrimethylsilane in 40 mL of pentane was analyzed by GC on column G (40 °C for 12 min and then 10 °C min^{-1} to 90 °C), which showed the presence of 52% 1, 30% 7, and 4.8% 8 after 11 h irradiation; the response factors were determined relative to decane as internal standard with samples isolated by preparative GC (vide infra). The rates of product formation from concentration versus time profiles were 2.3×10^{-7} M s^{-1} for product 8 and 9.2×10^{-7} M s^{-1} for 7 over a 0–12% range of conversions.

The spectral data for 2-methoxy-2,4,4-trimethyl-2,4-disilapentane (8)[39] were as follows: ^{1}H NMR (CCl$_4$) δ −0.12 (s, 2 H, methylene), 0.07 (s, 9 H, methyl), 0.12 (s, 6 H, methyl), 3.36 (s, 3 H, methoxy); IR (CCl$_4$) 3.38, 3.45, 3.53, 7.98, 8.40, 9.15, 9.52, 11.12, 11.85, 12.45, 12.61, 12.70, 12.90, 13.35, 13.54, 13.88, 14.49 μm; GC-MS retention time 6.56 min, m/z (relative intensity) no parent, 161 (100), 145 (2.24), 131 (67), 115 (5), 89 (8), 73 (24), 59 (34), 58 (6), 45 (14).

The spectral data for 2-methoxy-2,4,4-trimethyl-3-vinyl-2,4-disilapentane (7) were as follows: ^{1}H NMR (CCl$_4$) δ 0.076 (s, 9 H, methyl), 0.14 (s, 6 H, methyl), 1.22 (d, J = 10.2 Hz, 1 H, methylene), 3.41 (s, 3 H, methoxy), 4.57–4.89 (m, 2 H, vinyl), 5.37–6.01 (m, 1 H, vinyl); IR (CCl$_4$) 3.25, 3.29, 3.45, 3.53, 6.18, 6.89, 7.11, 7.68, 8.40, 10.02, 13.78, 15.10 μm; GC-MS, retention time 9.49 min, m/z (relative intensity) 202 (5.7), 187 (18), 160 (1), 157 (1), 147 (2), 133 (3), 114 (9), 99 (12), 98 (57), 89 (100), 83 (19), 75 (6), 73 (49), 69 (4), 59 (69), 45 (29); high-resolution MS-EI calcd for C$_9$H$_{22}$Si$_2$O (M$^+$) 202.1210, found 202.1207.

Procedure for Quantum Yield Determinations. A jacketed aluminum cell holder and lamp enclosure was constructed as described previously.[2] Light from a 15-W Philips zinc lamp was passed through a 25 mm diameter Acton 214-IB interference filter (42.5% transmittance at 214 nm, 410 Å bandwidth). The lamp enclosure including filter and sample cell was flushed at a constant, metered flow of air during photolyses to maintain constant light intensity from run to run. A 10 mm path W240 quartz cylindrical cell of 3 mL volume contained the photolysate, and the sample temperature was maintained at 28 °C by circulating methanol–water from a constant-temperature bath. Solutions of 1,1-dimethyl-1-silacyclobut-2-ene (1) in 3.0 mL of tert-butyl alcohol were purged with nitrogen 45 min prior to and during the photolyses.

Procedure B as described by Pitts, Margerum, Taylor, and Brim was used for uranyl oxalate actinometry, the only modification being that a dilution was required for UV analysis of the final actinometer solution.[12a] Quantum yields for actinometry at 210–214 nm have been reported by Forbes and Heidt.[12b] Actinometry was performed before and after each photolysis of 1,1-dimethyl-1-silacyclobut-2-ene (1); average deviation of light output for the entire set of quantum yield runs was 4.7%.

The photolysates were diluted with an equal volume of pentane, washed six times with water, and dried over anhydrous sodium sulfate prior to GC analyses. The general procedure for product analyses (vide supra) was used. Data are reported for initial concentration of reactant (M); light absorbed at 214 nm (mEinsteins); mmol of tert-butoxydimethyl(2-propenyl)silane (2), quantum yield; mmol of (E)-tert-butoxydimethyl(1-propenyl)-silane [(E)-3], quantum yield; mmol of (Z)-tert-butoxydimethyl(1-propenyl)silane [(Z)-3], quantum yield; mmol of tert-butoxytrimethylsilane (4), quantum yield; percent conversion.

Runs 1 and 2: silacyclobutene 1, 0.006 90 M; 0.0111 mEinsteins; $(8.50 \pm 0.40) \times 10^{-4}$ mmol of product 2, ϕ = 0.0764 ± 0.0036; $(1.84 \pm 0.04) \times 10^{-4}$ mmol of product (E)-3, ϕ = 0.0166 ± 0.0003; $(1.38 \pm 0.04) \times 10^{-4}$ mmol of product (Z)-3, ϕ = 0.0124 ± 0.0004; $(1.31 \pm 0.001) \times 10^{-4}$ mmol of product 4, ϕ = 0.0118 ± 0.0001; 6.3% conversion.

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Runs 3 and 4: silacyclobutene 1, 0.006 90 M; 0.0167 mEinsteins; $(1.18 \pm 0.04) \times 10^{-3}$ mmol of product 2, $\phi = 0.0710 \pm 0.0027$; $(2.64 \pm 0.18) \times 10^{-4}$ mmol of product (E)-3, $\phi = 0.0158 \pm 0.0011$; $(1.94 \pm 0.06) \times 10^{-4}$ mmol of product (Z)-3, $\phi = 0.0166 \pm 0.0004$; $(2.12 \pm 0.16) \times 10^{-4}$ mmol of product 4, $\phi = 0.0127 \pm 0.0009$; 9.0% conversion.

Run 5: silacyclobutene 1, 0.006 90 M; 0.0334 mEinsteins; 2.05 $\times 10^{-3}$ mmol of product 2, $\phi = 0.0614$; 6.52×10^{-4} mmol of product (E)-3, $\phi = 0.0195$; 3.62×10^{-4} mmol of product (Z)-3, $\phi = 0.0108$; 3.49×10^{-4} mmol of product 4, $\phi = 0.0104$; 16% conversion.

214 nm Product Yields of 1,1-Dimethyl-1-silacyclobut-2-ene (1) as a Function of *tert*-Butyl Alcohol Concentration and Temperature. The quantum yield apparatus and procedure described above were used; actinometry was not performed. Solutions of 3.0 mL of 0.0340 M silacyclobutene 1 in *n*-pentane containing decane standard and varying in concentration of *tert*-butyl alcohol over the range 0.010–1.0 M were purged with nitrogen 45 min prior to and during photolysis; the temperature was 8–9 °C. Aliquots were taken at time zero, 60 min, and 90 min and analyzed by GC following the general procedure described above. GC analyses showed the presence of 91 ± 8% unreacted 1 in addition to the product yields reported in Table II.

Two runs of 0.0104 M 1 plus decane standard were performed with the immersion well apparatus at 1 and 67 °C with 51 mL of 0.50 M *tert*-butyl alcohol in purified hexane (vide supra) as the solvent; a similar run was performed with pure *tert*-butyl alcohol as the solvent at 83 °C. Unreacted 1 was obscured by solvent in the hexane runs, whereas the amounts were low (82% after 10 min and 65% after 30 min) in refluxing *tert*-butyl alcohol due to evaporation. All data are reported in Table II.

Controls. Stability of Silacyclobutene 1 under Reaction Conditions. The stability of 0.010–0.030 M solutions of silacyclobutene 1 in *tert*-butyl alcohol and mixtures of *tert*-butyl alcohol in *n*-pentane or *n*-hexane were checked with an unirradiated aliquot on column E with the analytical conditions employed for each photolysis, in most cases for a week after the photolysis was performed. No sign of decomposition or reaction of 1 in the dark was ever observed, even in the case of a *tert*-butyl alcohol solution of 1 which was monitored for a month at room temperature. In another case, aliquots were taken from a solution of 33.8 mg (0.345 mmol) of 1 in 50 mL of *tert*-butyl alcohol with decane as standard, subjected to a workup (vide supra) to remove *tert*-butyl alcohol, and then analyzed on column E (70 °C) over a period of a week, after which time 1 was present to the extent of 100 ± 3%.

Refluxing a nitrogen purged solution of 52.6 mg (0.537 mmol) of silacyclobutene 1 in 51 mL of *tert*-butyl alcohol with decane as standard for 90 min gave a 0.094% yield of 2 after workup (vide supra) by GC analysis on column E (70 °C) and by GC–MS analysis. Refluxing a 52.6 mg (0.537 mmol) solution of 1 and decane in 0.50 M *tert*-butyl alcohol in *n*-hexane gave no detectable products after 90 min. A nitrogen-purged solution of 52.8 mg (0.539 mmol) of 1 and decane in 0.50 M *tert*-butyl alcohol in *n*-hexane was irradiated with 214 nm light at 1 °C for 90 min and

analyzed on columns E and F to quantify the photoproducts and then refluxed for 90 min. The product yields were unchanged before and after reflux within the limits shown: 28.05 ± 0.15% 2, 3.06 ± 0.13% (E)-3, 1.96 ± (0.005% (Z)-3, and 4.42 ± 0.02% 4.

Computational Methods. Geometries were fully optimized with the 6-31G(d) basis set[40] at the self-consistent field (SCF) level, using the analytical gradient techniques in GAUSSIAN86.[41] All structures were verified as minima (transition states) by determining that the matrix of energy second derivatives has zero (one) negative eigenvalue. Final energy comparisons were obtained at the second-order perturbation theory (MP2[42]) level with the same basis set. Complete geometries and total energies of all structures are available from MSG upon request.

Registry No. 1, 66222-35-3; 2, 7087-22-1; 2-d_1 (1-*d*-2-propenyl isomer), 118319-23-6; 2-d_1 (3-*d*-2-propenyl isomer), 118319-24-7; (E)-3, 118319-19-0; (Z)-3, 118319-18-9; (E)-3-d_1, 118319-22-5; (Z)-3-d_1, 118319-25-8; 4, 13058-24-7; 5, 30535-30-9; 5-d_1 (1-*d*-2-propenyl isomer), 118319-26-9; 5-d_1 (3-*d*-2-propenyl isomer), 118319-27-0; 6, 80252-75-1; 6-d_1, 118319-28-1; 7, 118319-29-2; 8, 5180-93-8; $(CH_2=CHCH_2)_2SiMe_2$, 1113-12-8; (E)-BrCH=CHCH$_3$, 590-15-8; (Z)-BrCH=CHCH$_3$, 590-13-6; Cl_2SiMe_2, 75-78-5; (E)-$(CH_3CH=CH)(MeO)SiMe_2$, 80252-58-0; (Z)-$(CH_3CH=CH)(MeO)SiMe_2$, 80252-75-1; (E)-$(CH_3CH=CH)ClSiMe_2$, 118319-20-3; (Z)-$(CH_3CH=CH)ClSiMe_2$, 118319-21-4; MeOSiMe$_3$, 1825-61-2; $(CH_2=CHCH_2)ClSiMe_2$, 4028-23-3; 1-sila, 1,3-butadiene, 79650-23-0; 1,3-butadiene, 106-99-0.

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