The Far-UV Photochemistry of Five- and Six-Membered-Ring Monosilacycloalkenes in Alcohols: Stereospecific β-Cleavage to Silyl Ethers and Stereoselective Formation of Silacycloalkyl Ethers

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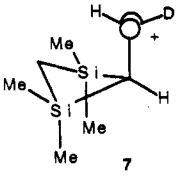
Photoalcoholysis of 1,1-dimethylsilacyclopent-2-ene (**9**) at 214 nm in methanol, 2,2,2-trifluoroethanol, and *tert*-butyl alcohol affords alkoxy(3-butenyl)dimethylsilanes **11** and 3-alkoxy-1,1-dimethylsilacyclopentanes **12**. Also formed are alkoxy(cyclopropylmethyl)silanes **13** from apparent 1,3-C migration. In pure, deuterated alcohols (CH_3OD and CF_3CD_2OD) adducts **11** and **12** become trans deuterated, whereas in dilute solutions of methanol-*O-d* in pentane, scrambling of deuterium between the trans and cis C-2 positions of **12** is observed without corresponding loss of stereospecificity for formation of silyl ether **11**. Silyl ether **11** is thus produced via a pathway which is mechanistically distinct from that giving **12**, for which the loss of stereoselectivity in dilute alcohols is ascribed to pseudorotational scrambling of deuterium in a silacyclopentyl cation intermediate. At high concentrations of alcohol the trans-stereoselective deuteration of **12** can be attributed to least hindered anti attack of the alcohol at C-3 of this hyperconjugatively stabilized cation. High cis-stereoselective deuteration of **12** is observed for photolysis in dilute CF_3CD_2OD in pentane, possibly reflecting the intermediacy of an ion pair or unsymmetrically solvated silacyclopentyl cation. Photoalcoholyses of the silacyclohex-2-ene were conducted for comparison.

We previously reported results of photolyses of disilacyclopentene **1**, which in alcohols as solvents produced high yields of adducts **4–6** and minor amounts of isomers **2** and **3** (Scheme I).[1] The formation of the photoalcoholysis products was attributed to the intermediacy of silyl cations **7** and **8**, generated through protonation of **1** by the solvent, either in the lowest singlet and triplet excited states, or in the ground state subsequent to cis–trans isomerization. With deuterated alcohols such as methanol-*O-d* and *tert*-butyl alcohol-*O-d* the β Si–C bond cleavage forming silyl ethers **4a–*d*** and **4c–*d*** was highly stereospecific. This trans-stereospecific outcome was ascribed to a barrier to free rotation imposed by hyperconjugation with the Si–C σ bonds[2–6] in disilacyclobutylmethyl cation **7**. Cation **7** was believed to play a more important role than **8** in silyl ether formation, because facile pseudorotation in disilacyclopentyl cation **8** would presumably have led to appreciable scrambling of deuterium in the vinyl group of these adducts. No stereochemical information was available on disilacyclopentyl ether **6** from our previous study, because the methylene protons vicinal to the *tert*-butoxy group were accidentally equivalent in the ^1H NMR spectrum.[1]



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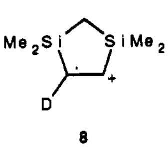

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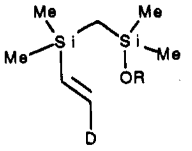

4a-*d* R=OMe

4c-*d* R=*t*-Bu

As part of a comprehensive study of the far-UV photochemistry of the more rigid[7] system, monosilacyclopentene **9** and, for comparison, silacyclohexene **10**, it was found that

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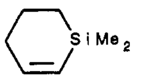

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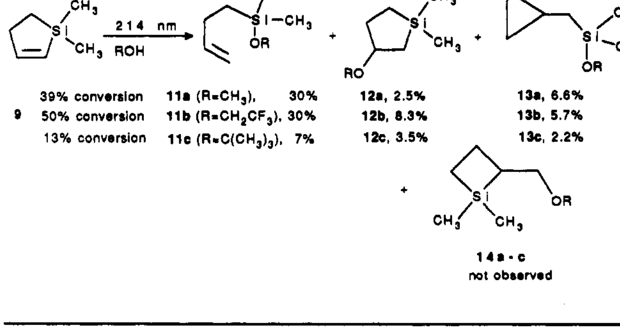
the stereoselectivity could be determined for incorporation of deuterium into the C-2 position of the monosilacycloalkyl ether analogues of **6-*d***. We now report the results of this study, which provide evidence against the common intermediacy of a 3-silacyclopentyl cation in the formation of both silacyclopentyl ethers and alkenylsilyl ether products analogous to **4-*d***.

Results

Direct Photolyses of Silacyclopent-2-ene 9 and Silacyclohex-2-ene 10 in Methanol, 2,2,2-Trifluoroethanol, and *tert*-Butyl Alcohol. Preparative direct photolyses of 10^{-2} M solutions of **9** and **10** in deoxygenated alcohols at 214 nm gave alkenylsilyl ethers **11a–c** and **17a–c** as the major products, along with silacycloalkyl ethers **12a–c** and **18a–c** (eqs 1 and 2). (Cyclopropylmethyl)silyl ethers **13a–c** were additional minor products of **9**, which were not observed in photolyses of **10**. In



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[1] Steinmetz, M. G.; Langston, M. A.; Mayes, R. T.; Udayakumar, B. S. *J. Org. Chem.* **1986**, *51*, 5051.

[2] For a review, see: Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

[3] (a) For primary silylcations the magnitude of the β-hyperconjugative effect from ab initio calculations is 38 kcal mol^{-1}[3b] and for secondary cations 22 kcal mol^{-1}.[3c] Experimentally determined gas phase values are 39 or 48 kcal mol^{-1} (primary)[4] and 28 kcal mol^{-1} (secondary).[4b] Profound rate accelerations are observed in solvolyses, depending on the orientation of the Si–C σ bond with respect to the vacant p-orbital of the incipient cation.[5,6] (b) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (c) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

[4] (a) Hajdasz, D.; Squires, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1212. (b) Li, X.; Stone, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5586.

[5] Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

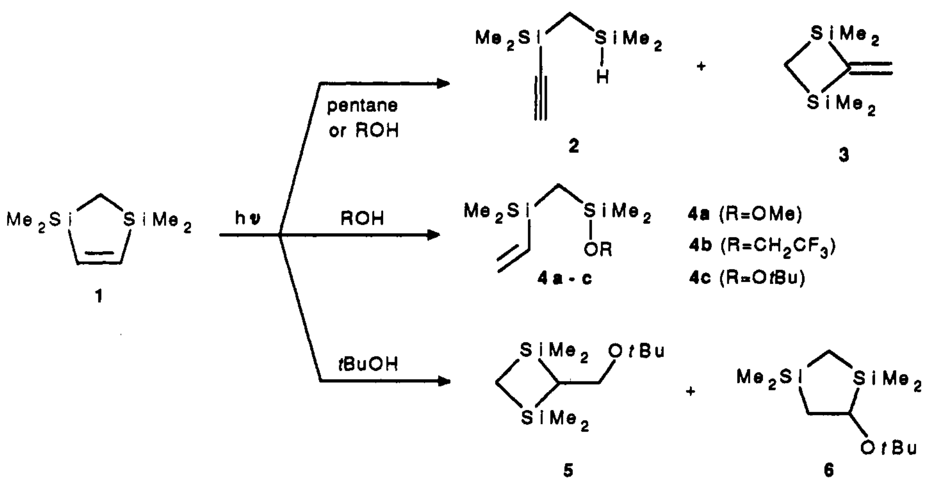
[6] Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120 and references cited therein.

[7] (a) Vibrational spectroscopy of silacyclopent-2-ene shows this ring system to be both planar and extremely rigid with respect to ring puckering.[7b] In contrast, 1,3-disilacyclopent-4-ene, though planar, is not nearly as rigid.[7c,d] (b) Kelly, M. B.; Laane, J. *J. Phys. Chem.* **1988**, *92*, 4056. (c) Colegrove, L. F.; Laane, J. *Abstracts of Papers*; 24th Organosilicon Symposium, El Paso, TX, April 12–13, 1991; Abstract No. 23. (d) Colegrove, L. F.; Laane, J. *J. Phys. Chem.* **1991**, *95*, 6494.

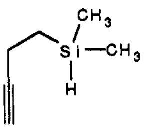
[8] Adam, W.; Oppenlander, T. *J. Am. Chem. Soc.* **1985**, *107*, 3924.

0022-3263/92/1957-3107$03.00/0

Scheme I



contrast to disilacyclopentene 1, none of the photolyses produced ring-contracted silacycloalkylmethyl ethers 14a–c or 20a–c, and neither 9 nor 10 underwent detectable photoisomerization to 16 or 22 or elimination to acetylenes 15 or 21.



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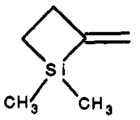

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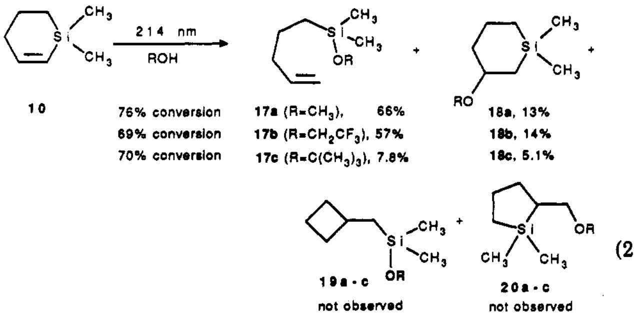
Chemical yields determined by GC analyses of photolysates are summarized in eqs 1 and 2. Given the generally satisfactory photochemical mass balances found, photolyses of silacyclohexene 10 in *tert*-butyl alcohol proved to be exceptional. The low mass balance of 43% in this alcohol was due to photochemical formation of three nonvolatile products in a 2:3:1 ratio of GC peak areas (FID detector) at long retention times. The ratio of nonvolatiles:17c plus 18c was 0.8:1. From GC–MS analyses these products appeared to be dimers of 10, since each exhibited a parent ion at m/z 252.



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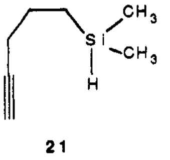

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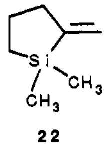

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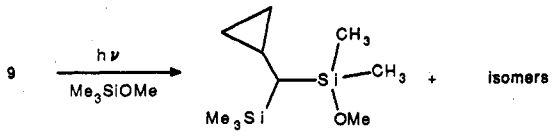
The photoproducts of 9 and 10 were all isolated by preparative GC and initially identified by ^{1}H and ^{13}C NMR, IR, and MS. Independent synthesis of the alkenylsilyl ethers 11a–c (eq 1) and 17a–c (eq 2) were routine (Experimental Section). In some cases the alkoxysilacycloalkyl ethers were obtainable through oxymercuration and reductive demercuration of the corresponding silacycloalkenes. This approach afforded 3-methoxysilacyclopentane 12a (eq 1) in 43% yield, but gave only 0.6% yield of 2,2,2-trifluoroethoxy ether 12b, along with 1.6% of 11b and unreacted starting material. Oxymercuration–demercuration of 9 was not attempted with *tert*-butyl alcohol because of the low yields experienced in the synthesis of *tert*-butyl ether 18c from silacyclohexene 10. 3-Methoxysilacyclohexane 18a was obtained in 77% yield by a similar procedure. Only β-cleavage to silyl ether 17b was observed in the attempted synthesis of 2,2,2-trifluoroethoxy derivative 18b.

Simmons–Smith cyclopropanation of alkoxy(2-propenyl)dimethylsilanes was used to synthesize (cyclopropylmethyl)silyl ethers 13a–c, which were obtained in isolated yields ranging from ca. 50–60% of 13a and 13b to 80% yield of *tert*-butoxy silyl ether 13c.

Photolyses of Silacycloalkenes in the Presence of Silene Traps. Initial attempts to scavenge potential silene intermediates, produced through excited state 1,3-shift of the silylmethylene group of 9, were made by performing 214-nm photolyses of 0.07 M substrate in pentane in the presence of 0.1 M methoxytrimethylsilane.[9] Three isomeric methoxytrimethylsilane adducts were formed, suggesting that trapping was accompanied by cleavage of the cyclopropane ring. Only adduct 23 could be isolated in pure form for spectroscopic characterization. Since numerous unidentified byproducts complicated the product isolation, further attempts at silene trapping were made with 0.02 M acetone in pentane.[9,10] Photolyses of 0.03 M 9 under these conditions gave a single product in 24.5% yield (assuming a detector response factor of unity) plus unreacted starting material at 32% conversion. No problems from competitive absorption of 214-nm light by the acetone were experienced as acetone has a UV absorption minimum in this wavelength region.[10c] After



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[9] Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

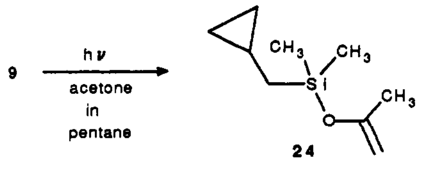
[10] (a) Wagner, G.; Wiberg, N. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005. (b) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (c) 1,1-Dimethyl-1-sila-1,3-butadiene can be generated by 214-nm photolysis of 0.1 M 1,1-dimethyl-1-silacyclobut-2-ene[10d] and trapped in high yield through ene reaction with 0.04 M acetone in deoxygenated pentane without significant photolysis of the trapping agent: Steinmetz, M. G.; Bai, H., unpublished results. (d) Steinmetz, M. G.; Udayakumar, B. S.; Gordon, M. S. *Organometallics* **1989**, *8*, 530.

Table I. Quantum Yields, Φ, and Rates of Product Formation in 214-nm Direct Photolyses of Silacycloalk-2-enes 9 and 10

reactant	solvent	products Φ ($k \times 10^5$, M min$^{-1\,a}$)			convn, %
		11	**12**	**13**	
9	CH_3OH	0.066 (2.08)	0.006 (0.20)	0.013 (0.46)	3.3
	CF_3CH_2OH	0.074 (1.92)	0.012 (0.44)	0.019 (0.42)	3.5
	$(CH_3)_3C$-OH	0.022 (0.24)	0.008 (0.09)	0.010 (0.13)	1.6
		17	**18**		
10	CH_3OH	0.176 (7.92)	0.030 (1.58)		5.4
	CF_3CH_2OH	0.271 (15.0)	0.065 (3.75)		9.4
	$(CH_3)_3C$-OH	0.043 (0.71)	0.021 (0.46)		1.7

[a] Rates from slopes of concentration vs time profiles.

preparative GC collection in benzene-d_6, the pure acetone adduct was identified by ^{1}H and ^{13}C NMR as enol ether **24**. Deuteriochloroform was unsuitable as a solvent because decomposition to give a complex mixture of products was observed within 15 min, probably due to the presence of trace acid. Even in benzene-d_6 some decomposition of **24** was evident after ca. 2 h and became more extensive after 48 h, as ascertained from ^{1}H and ^{13}C NMR and GC–MS analyses.



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Quantum Yields for Direct Photolyses in Alcohols. Quantum yields of product formation employing uranyl oxalate[11] as the actinometer are summarized in Table I. An interference filter excluded extraneous wavelengths of the 15-W Philips zinc lamp used in the 214-nm direct runs. That alcohol adducts **11a–c–13a–c** of silacyclopentene **9** were primary products was established from ratios of $\%P_i/\Sigma\%P_i$ versus time, which did not vary significantly ($\%P_i$ is the yield of each photoproduct and $\Sigma\%P_i$ is the total chemical yield of products). The average deviation of this ratio was generally less than 5% for **11a–c** and **13a–c** and less than 10% for **12a–c** over a 1–68% range of conversions.[12] In the case of silacyclohexene **10**, adducts **17a–c** and **18a–c** deviated by less than 10% over a 1–79% range of conversions. The data are tabulated in the supplementary material.

Toluene-Sensitized Photolyses in Methanol. Preparative photolysis of 0.05 M silacyclohex-2-ene **10** with 4.5 M toluene as triplet[13] sensitizer in methanol with Vycor filtered light of a Rayonet photochemical reactor gave silyl ether **17a** and methyl ether **18a** in 50% and 13% yields according to GC analyses; 30% of the starting material remained unreacted. The photoproducts of **10** were isolated by preparative GC and identified by comparison of ^{1}H and ^{13}C NMR spectra and GC–MS data to authentic samples.

Table II. Stereochemistry of Deuterated Products 11a,b and 12a,b in Photolyses of Silacyclopentene 9 in Methanol-*O*-*d*, and 2,2,2-Trifluoroethanol-*d*$_3$

solvent	products, % *trans*-11	*cis*-11	*trans*-12	*cis*-12	convn, %
CH_3OD (neat)	93	7	94	6	70
1.0 M CH_3OD^a	92	8	81	19	52
0.2 M CH_3OD^a	85	15	70	30	61
0.2 M CH_3OD^a	93	7	72	28	10
CF_3CD_2OD (neat)	87	13	91	9	20
0.2 M $CF_3CD_2OD^a$	85	15	14	86	75
0.2 M $CF_3CD_2OD^a$	86	14	17	83	12

[a] Pentane as the solvent.

Analogous triplet-sensitized photolyses of silacyclopent-2-ene **9** in methanol were complicated by the formation of numerous byproducts from photoreactions of the toluene sensitizer. At least 10 of these products were consistent with reaction of the sensitizer with the methanol, but none corresponded to addition of toluene to silacyclopentene **9**, as would have been expected for toluene singlets.[14] Although silyl ether **11a** was isolated by preparative GC and characterized by ^{1}H NMR spectroscopy, adduct **12a** was obtained in insufficient yield and purity and was thus only identified from comparison of retention times and mass spectra to an authentic sample. (Cyclopropylmethyl)dimethylsilyl ether **13a** was absent, as confirmed by coinjection of an independently synthesized sample. No apparent increase in product yields was noted in a trial-sensitized photolysis with 2,2,2-trifluoroethanol as the solvent. GC–MS analyses showed a plethora of products including **11b** and **12b**; **13b** was not detected, as verified by co-injection of an authentic sample.

Quantum yields were determined utilizing uranyl oxalate as the actinometer at 254 nm. Concentrations of substrate and sensitizer were such that the toluene absorbed >99% of the incident light. Upon irradiation of 10^{-2} M silacyclohex-2-ene **10** and 0.085 M toluene in methanol, the quantum yields for formation of **17a** and **18a** were 0.12 and 0.02 at 16% conversion. In the case of silacyclopentene **9**, the quantum yields for sensitized formation of silyl ether **11a** and silacyclopentyl ether **12a** were 0.004 and 0.0009, respectively. Only a trace of a component possibly attributable to (cyclopropylmethyl)silyl ether **13a** was detected, and this product could not have exceeded 1% of product **11a** formed.

Direct Photolyses of Silacyclopent-2-ene 9 in Deuterated Methanol. Photolyses were performed in methanol-*O*-*d* (99.5+ atom % D) as the solvent to probe the stereochemistry of alcohol addition. From a preparative 214-nm photolysis of 0.05 M **9** in methanol-*O*-*d*, taken to 75% conversion, products **11a–13a**-*d* and unreacted starting material were each isolated by preparative GC and characterized by ^{1}H and ^{2}H NMR spectroscopy. From the integrated intensities in the ^{1}H NMR spectra it was clear that each of the methanol adducts was at least 95% monodeuterated; no detectable deuterium was incorporated into recovered **9**. GC–MS analyses confirmed that recovered reactant contained no detectable deuterium. The assignments of the positions labeled in each product are shown below, and the percentages of deuterium at each position are summarized in Table II.

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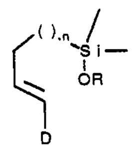
[11] (a) Forbes, G. S.; Heidt, L. J. *J. Am. Chem. Soc.* **1934**, *56*, 2363. (b) Leighton, W. G.; Forbes, G. S. *Ibid.* **1930**, *52*, 3139. (c) Pitts, J. N.; Margerum, J. D.; Taylor, R. P.; Brim, W. *Ibid.* **1955**, *77*, 5499.

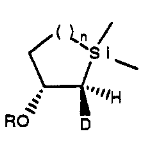
[12] Concern that silyl ethers **11** are formed from secondary photolysis of (cyclopropylmethyl)silyl ethers **13** is unwarranted. The ratio of **13**:total products would have strongly deviated, whereas observed average deviations were only 1.7% in methanol and <5% for the other alcohols (supplementary material). During 214-nm photolyses the fraction of light absorbed by <10^{-3} M **13a** (ϵ_{214} 6.9) formed in the presence of 10^{-2} M **9** (ϵ_{214} 1180) would have been insufficient (<0.001) to account for the quantum yield of **11a** at 3% conversion. Secondary photolysis of deuterated **13a,b** would not give **11a,b**-*d* labeled at the terminal position of the vinyl group.

[13] Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, P. J. *J. Org. Chem.* **1981**, *46*, 3609.

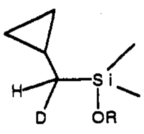
[14] (a) Kropp, P. J. *Org. Photochem.* **1979**, *5*, 1. (b) Wender, P. A.; Siggel, L.; Nuss, J. M. *Ibid.* **1989**, *10*, 357.



11a,b-*d* (n=1)
17a-*d* (n=2)



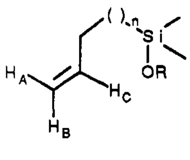
12a,b-*d* (n=1)
18a-*d* (n=2)



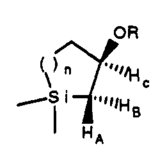
13a,b-*d*

(a) R=CH_3
(b) R=CD_2CF_3

The ^{2}H NMR spectrum of silyl ether of **11a-*d*** showed deuterium to be present only at δ 4.95, a chemical shift corresponding to the protons at the terminal position of the vinyl group in the undeuterated material. The chemical shift difference between H_A and H_B was not well-resolved by ^{2}H NMR spectroscopy, so the stereochemical assignment was based on ^{1}H NMR spectroscopy, which showed H_A at δ 4.99 as a doublet of triplets with a large coupling to H_C of 17.1 Hz; similarly H_B appeared at δ 4.89 coupled to H_C by 10.1 Hz. The 10- and 17-Hz coupling constants matched those obtained from the H_C portion of the spectrum of undeuterated material.[15] From the integrated intensities of H_A and H_B the ratio of trans:cis deuterium in the vinyl group was found to be 93:7.



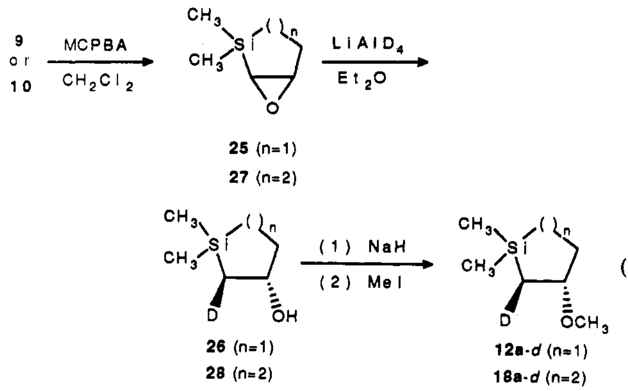
11a,b (n=1)
17a (n=2)



12a,b (n=1)
18a (n=2)

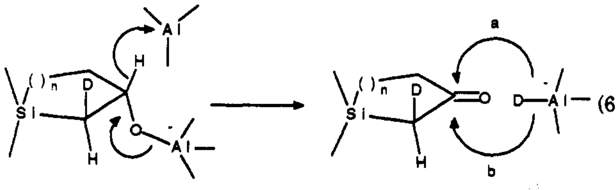
(a) R=Me
(b) R=CD_2CF_3

Careful examination of the ^{1}H NMR spectrum of the monodeuterated silacyclopentyl ether **12a-*d*** showed that this adduct was produced with incorporation of deuterium at C-2, predominantly trans to the methoxy group at C-3. ^{2}H NMR spectroscopy showed deuterium to be present almost exclusively at δ 0.98 rather than upfield at δ 0.66. This upfield chemical shift was found to correspond to the remaining cis C-2 methylene proton, which was observed in the ^{1}H NMR spectrum. The stereochemical assignments were confirmed by additional labeling experiments which scrambled deuterium into this upfield position (vide infra) and by independent synthesis of trans-deuterated **12a-*d*** (eq 5). The assignment of the upfield proton at C-2 as cis was also in accord with literature precedent for such shielding by hydroxy, methoxy, and halogen substituents in substituted cyclopentanes.[16] ^{2}H NMR spectroscopy showed that no detectable deuterium was present elsewhere in the molecule.



25 (n=1)
27 (n=2)
26 (n=1)
28 (n=2)
12a-*d* (n=1)
18a-*d* (n=2)

The relative stereochemistry of the labeled silacyclopentyl ether **12a-*d*** was established as trans by independent synthesis (eq 5). Fortunately, lithium aluminum deuteride reduction of epoxide **25** proceeded regioselectively with almost exclusive C–O cleavage at the C-2 rather than the C-3 position. In the ^{2}H NMR spectrum of alcohol **26** the deuterium appeared primarily at the trans C-2 position corresponding to δ 1.02, downfield from the cis C-2 proton at δ 0.65 in the ^{1}H NMR spectrum. However, small amounts of cis C-2 and C-3 deuterium were also detected at δ 0.65 and δ 4.18. In a separate, successful synthetic attempt to convert the alcohol to methyl ether **12a**, the observed ratio of deuterium at the cis C-2:trans C-2:C-3 positions of **12a** was 1:13:2.4. We assume that this ratio reflects the distribution of deuterium in alcohol **26**, as was found for silacyclohexanol **28** and silacyclohexyl methyl ether **18a** (vide infra). This ratio would then be explicable in terms of initial reduction of epoxide **25** with cleavage of the C-2 oxygen bond to give alkoxide, subsequent hydride abstraction from C-3, presumably by trivalent aluminum, and then further reduction of the ketone.[17] Reduction of the ketone by both paths a and b (eq 6) would ultimately result in approximately twice as much deuterium at C-3 as at the cis C-2 position in alcohol **26**, consistent with the above ratio determined for the methyl ether derivative. Furthermore, the total percentage of dideuterated **12a** should correspond to twice the percentage of cis C-2 deuterium plus the percentage of C-3 deuterium. This was found to be the case from GC–MS analyses of **12a**, which gave an isotopic composition of 0% d_0, 77.4% d_1, and 22.6% d_2; the M − 15 fragment ion of deuterated and undeuterated **12a** was used since the parent ion was extremely weak.



Direct Photolyses of Silacyclopent-2-ene 9 in Deuterated 2,2,2-Trifluoroethanol. Preparative photolyses of **9** in pure 2,2,2-trifluoroethanol-d_3 (CF_3CD_2OD, 99 atom % D), taken to 20% conversion, were performed with the unfiltered light of a 450-W medium-pressure mercury lamp with the argon-purged sample contained in an externally mounted quartz cuvette. This procedure was required for the three individual runs made, which were combined. The positional and stereochemical assignments of deuterium in adducts **11b-*d*$_3$** and **12b-*d*$_3$** were analogous to those of **11a-*d*** and **12a-*d*** and were made by utilizing the approach described above (Table II); an authentic sample of **12b-*d*$_3$** was not available. From integration of H_A and H_B at δ 4.99 and 4.91 in the ^{1}H NMR spectrum of **11b-*d*$_3$**, which was isolated by preparative GC, it was clear that 87% of the deuterium was trans on the vinyl group. The ^{2}H NMR spectrum of GC-isolated **12b-*d*$_3$** showed deuterium to be

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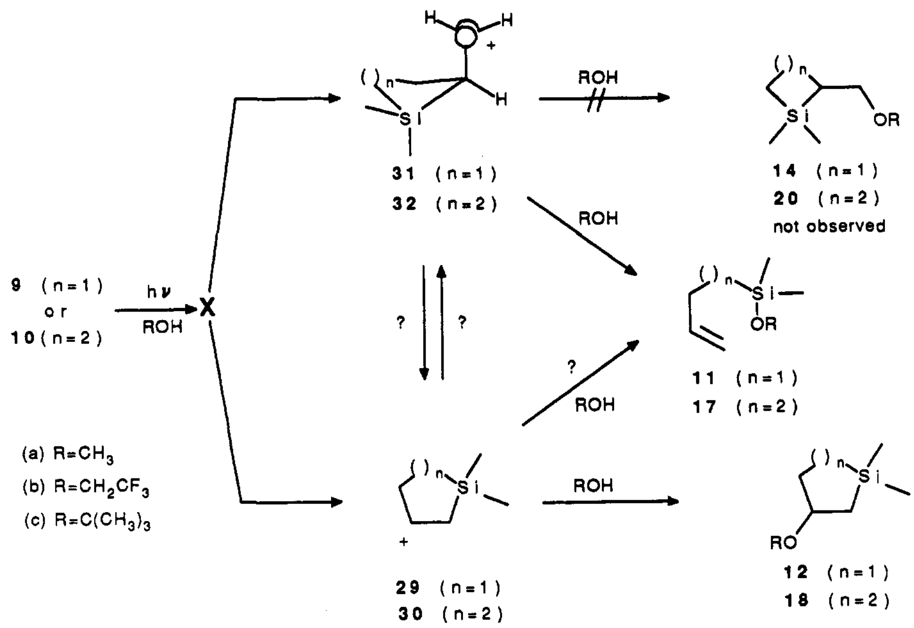
[15] In the case of undeuterated **11a–c**, the ddt pattern corresponding to H_C resembled the X part of an ABX spectrum with additional coupling by the allylic methylene group superimposed. Approximate coupling constants J_{AC} and J_{BC} were assigned by direct inspection, as discussed in the following: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 205.

[16] (a) Hunter, G.; Miller, J. A.; Moore, M.; Ullah, G. M. *Org. Magn. Reson.* **1983**, *21*, 275. (b) Anteunis, M.; Daneels, D. *Ibid.* **1975**, *7*, 345. (c) Fay, C. K.; Grutzner, J. B.; Johnson, L. F.; Sternhell, S.; Westermann, P. W. *J. Org. Chem.* **1973**, *38*, 3122. (d) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730. (e) Trost, B. M.; Molander, G. A. *Ibid.* **1981**, *103*, 5969.

[17] (a) Thyagarajan, B. S. *Selective Organic Transformations*; Wiley: New York, 1972; Vol. 2, pp 37–38. (b) Eisch, J. J.; Trainor, J. T. *J. Org. Chem.* **1963**, *28*, 2870.

Scheme II



present in the alkoxy group and at the C-2 methylene position. Aside from the CD_2CF_3 group, 91% of the deuterium was at δ 0.93, trans to the trifluoroethoxy group, and the balance was at δ 0.76 or cis. These assignments were consistent with integrated intensities in the ^{1}H NMR spectrum.

Direct Photolyses of Silacyclopent-2-ene 9 in Dilute Solutions of Deuterated Alcohol in Pentane. Direct photolyses were also conducted at 1.0 and 0.2 M methanol-*O-d* in pentane as the solvent. ^{1,2}H NMR analyses of monodeuterated alcohol adducts **11a**–**13a** indicated that deuterium was significantly scrambled between the cis and trans positions at C-2 in **12a**-*d*, and the extent of the scrambling increased with decreasing concentration of the alcohol (entries 1–4, Table II). As for adduct **11a**-*d*, the stereospecificity was >90% trans, regardless of the concentration of the methanol. Low conversions were required to minimize scrambling of deuterium in **11a**-*d* in these runs (entries 3 and 4, Table II). A 0.0066 M pentane solution of 93% trans-deuterated **11a**-*d*, which was isolated by preparative GC from the run corresponding to entry 4 (Table II), cleanly photoisomerized to a 63:37 ratio of trans:cis-deuterated **11a**-*d* upon irradiation at 214 nm (no attempt was made to reach a photostationary state). The above scrambling thus appeared to be due to secondary photolysis of **11a**-*d*.

With 0.2 M trifluoroethanol-d_3 in pentane, 214-nm photolysis of 0.04 M **9** gave adducts **11b**-d_3 and **12b**-d_3. In contrast to the run with the pure alcohol (vide supra), the stereochemistry for incorporation of deuterium at the C-2 position of **12b**-d_3 was predominantly cis to the C-3 2,2,2-trifluorethoxy group (Table II). This reversal in stereochemistry in **12b** was not accompanied by a corresponding loss of trans stereospecificity in silyl ether **11b**-d_3, which remained 85–87% trans-deuterated at all concentrations of 2,2,2-trifluoroethanol-d_3 employed.

Deuterated (Cyclopropylmethyl)dimethylsilanes 13a-*d* and 13b-d_3. Each of the above photolyses also gave deuterated (cyclopropylmethyl)silyl ethers **13a**-*d* and **13b**-d_3. ^{1}H NMR spectroscopy indicated that each product was essentially monodeuterated, and ^{2}H NMR spectroscopy showed label present at δ 0.59 in **13a**-*d* and at δ 0.63 in **13b**-d_3, but not elsewhere in these molecules. The ^{13}C NMR spectrum of one of the samples of **13a**-*d* exhibited a single 1:1:1 triplet at δ 20.88 or downfield from the two equivalent cyclopropyl methylenes at δ 6.34 and the methine carbon at δ 5.25. The deuterated carbon was assigned to the methylene group α to silicon on the basis of its downfield chemical shift relative to the cyclopropylmethylene groups and the ^{13}C APT spectrum.

Direct Photolyses of Silacyclohex-2-ene 10 in Deuterated Methanol. Photolyses at 214 nm were performed with 10^{-2} M silacyclohexene **10** in pure methanol-*O-d* and in dilute 0.2 M methanol-*O-d* in pentane. The positions labeled in the deuterated photoproducts (vide infra) were established by a combination of ^{1}H and ^{2}H NMR spectroscopy of the preparative GC-isolated products, as described above for **9**. In all of the runs, silyl ether **17a**-*d* was found to be stereospecifically trans-deuterated from integration of the vinyl protons at δ 4.98 and 4.93 (Table III). In contrast to silacyclopentyl ethers **12a**-*d*, trans-deuterated silacyclohexyl ethers **18a**-*d* were produced with high stereoselectivity, regardless of the concentration of the methanol (Table III).

The ^{2}H NMR spectrum of silacyclohexyl ether **18a**-*d*, produced in pure methanol and in dilute methanol in pentane, showed deuterium incorporation exclusively at the trans C-2 position at δ 1.2. No deuterium was detected at δ 0.6 corresponding to the cis C-2 proton. As with silacyclopentyl ether **12a**-*d*, the cis C-2 proton was upfield from the trans C-2 proton. An independently synthesized sample of *trans*-**18a**-*d* (eq 5) exhibited deuterium primarily at δ 1.24. Due to the aforementioned exchange during lithium aluminum deuteride reduction of epoxide **27** (eq 6), alcohol **28** and ether **18a** also contained smaller amounts of deuterium at the cis C-2 methylene and C-3 methine positions; in each case the ratio of cis C-2:trans C-2:C-3 deuterium was 1:5:2.3.

Discussion

Mechanisms for Protodesilylation and Alcohol Addition in Direct Photolyses of Silacycloalkenes 9 and 10. In direct photolyses of **9** (*n* = 1) and **10** (*n* = 2) in alcohols as solvents, the major photoproducts, **11a**–**c** (*n* = 1) and **17a**–**c** (*n* = 2), result from formal addition of alcohol across the vinyl Si–C σ bond (Scheme II). The observed deuterium labeling of the terminal position of the vinyl groups of these silyl ethers can be attributed to

Scheme III

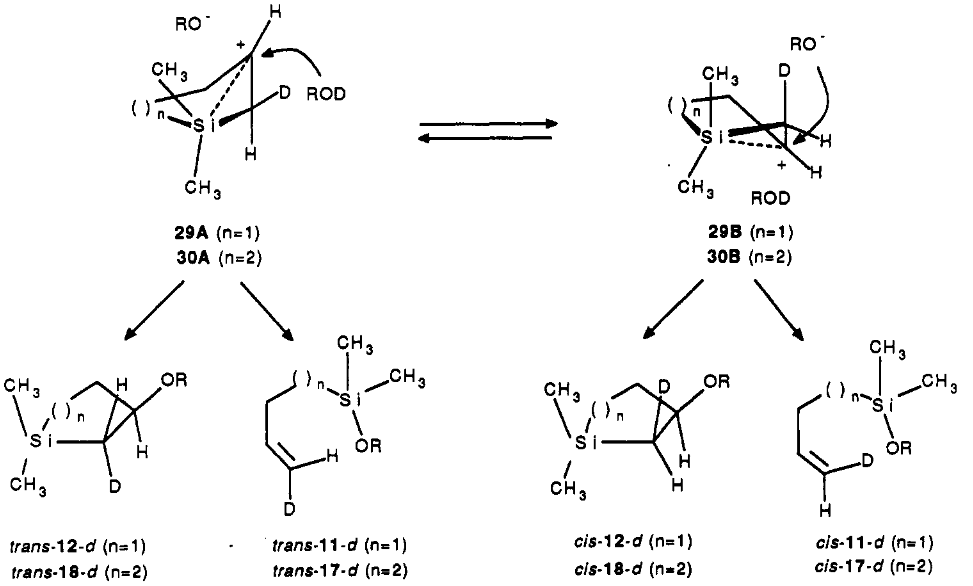
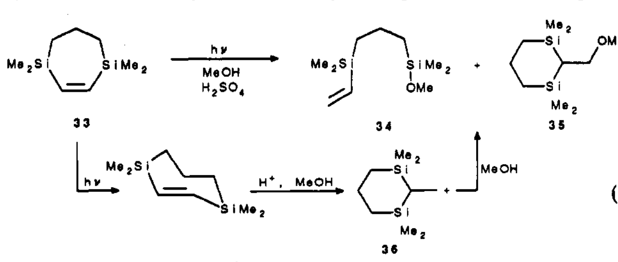


Table III. Stereochemistry of Deuterated Products 17a and 18a in Photolyses of Silacyclohexene 10 in Methanol-*O*-d_1

solvent	products, %				convn, %
	trans-17a	*cis*-17a	*trans*-18a	*cis*-18a	
CH_3OD (neat)	97	3	100	0	75
0.2 M CH_3OD^a	94	6	100	0	81
0.2 M CH_3OD^a	94	6	100	0	23

[a] Pentane as solvent.

protonation at the C-2 position (vide infra), α to Si of the silacycloalkenes, followed by cleavage of the Si–C bond at the β position of the resultant carbocations. The obvious intermediates to propose for this β-cleavage process are cations 29 and 30, since the silyl ethers are accompanied by formation of the corresponding alcohol adducts 12a–c (n = 1) and 18a–c (n = 2) as minor products. On the basis of these products alone, no additional intermediates, such as ring contracted cations 31 (n = 1) and 32 (n = 2), need to be postulated. The absence of products 14a–c (n = 1) and 20a–c (n = 2) in photolyses of 9 and 10 notwithstanding, alcohol adducts corresponding to analogous disilacycloalkylcarbinyl cations, i.e., 7 and 36, have been observed previously in photolyses of 1 (Scheme I)[1] and 1,1,4,4-tetramethyl-1,4-disilacyclohept-2-ene (33) (eq 7).[18]



(7)

As noted previously,[1] preferential β-cleavage of disilacyclobutylmethyl cation 7 also minimizes the possibility of pseudorotational scrambling of deuterium in cation 8 and accompanying loss of stereospecificity in the formation of trans-deuterated 4-*d*.

Mechanistic Implications of Deuterium Labeling Studies with Silacyclopent-2-ene 9. Although 12a,b-*d* are produced with high trans stereoselectivity in pure methanol or 2,2,2-trifluoroethanol, scrambling of deuterium (entries 2–4, Table II) and high cis stereoselectivity (entries 6 and 7, Table II) are observed in dilute solutions of these alcohols in pentane. These stereochemical outcomes are difficult to reconcile with the high stereospecificity observed in the formation of the corresponding trans-deuterated silyl ethers 11a,b-*d*, if 3-silacyclopentyl cation 29 serves as a common intermediate. In principle, β-cleavage of initially formed cation 29A (Scheme III) could give *trans*-11a,b-*d*, while both 29A and 29B could be invoked to account for varying degrees of stereoselectivity in 12a,b-*d*. However, in order to accommodate stereospecific formation of 11a,b-*d* in the face of modest amounts of *cis*-12a,b-*d* as a product, strongly attenuated reactivity toward β-cleavage would be required on the part of 29B, as compared to 29A. In addition, 29B would have to display correspondingly higher selectivity for capture by alcohol than 29A (vide infra). Given the predominance of β-cleavage over capture by solvent, indicated by the 5–6:1 ratios of 11:12 observed for photolyses in dilute alcohols, the reluctant β-cleavage of 29B seems unreasonable. Thus, although β-cleavage of silacyclopentyl cation 29-*d* probably contributes to some extent to the formation of silyl ether 11a-*d*, it does not appear to be the sole precursor to product. The bulk of silyl ether 11 most likely forms by a mechanistically distinct pathway from cation 29-*d*, possibly involving silacyclobutylmethyl cation 31-*d* (Scheme IV). However, direct cleavage to a silylenium ion 37[19] or to silyl ether 11-*d* cannot be excluded on the basis of our results.

The high trans stereoselectivity for the formation of silacyclopentyl ethers 12a-*d* and 12b-d_3 in pure methanol-*O*-*d* and 2,2,2-trifluoromethanol-d_3 implies that attack by alcohol at the C-3 carbocation center of 29 proceeds from an anti direction, as shown in Scheme III. This approach could be favored if the "top" face of the ring is sterically hindered due to distortion of the ring to improve

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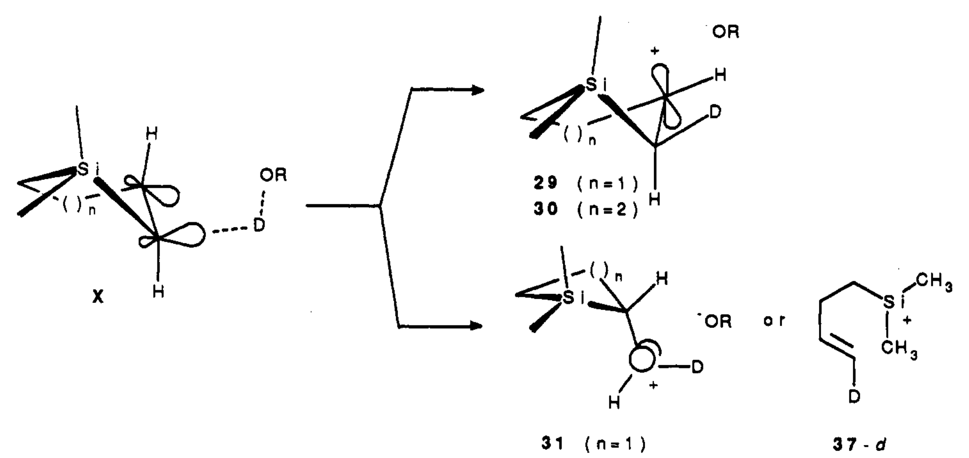
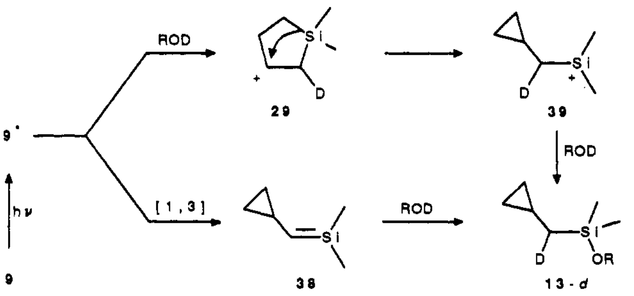
[18] Steinmetz, M. G.; Seguin, K. J.; Udayakumar, B. S.; Behnke, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 6601.

[19] (a) There is evidence for the generation of silylenium ions via 1,2-methyl shifts of α trimethylsilyl cations in solvolyses of silyladamantyl esters.[19b] More persistent examples produced by hydride abstraction in solution have been recently reported.[19c] (b) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272 and references cited therein. (c) Lambert, J. B.; Schulz, W. J.; McConnell, J. A.; Schilf, W. *Ibid.* **1988**, *108*, 2482. (d) For an opposing view, see: Olah, G. A. *Abstracts of Papers*, 25th Organosilicon Symposium, Los Angeles, CA, April 3, 4, 1992; p 52.

Scheme IV



Scheme V



hyperconjugative overlap of the carbocation p-orbital with the Si-C_2 bond. The dotted lines in **29A** and **29B** are not intended to imply bridging, however. Ab initio calculations[3c] of the 2-silylpropyl cation suggest that a vertical or hyperconjugative mechanism is involved in stabilization with some nuclear motion on the part of silicon to improve overlap with the vacant p-orbital. In solvolyses of *endo*-3-(trimethylsilyl)-*endo*-2-norbornyl esters,[6] steric hindrance by the leaving group appears to interfere with the achievement of optimal vertical overlap between the trimethylsilyl group and the developing carbocation center. The rate acceleration for this synperiplanar orientation of the leaving group and silicon is 10^5, compared to 10^{12} found for the optimal antiperiplanar geometry.[5,6] Hyperconjugation accounts for 10^{10} of the latter rate acceleration, and the contribution by induction is 10^2.[5,6] Considering that the photoalcoholyses correspond to the microscopic reverse process, the stereoselective formation of trans-deuterated **12a,b** is consistent with an antiperiplanar approach of alcohol or alkoxide with respect to the Si–C_2 bond and cation center of **29**.

The increased yields of cis-deuterated **12a**-*d* observed for photolyses in dilute solutions of methanol-*O*-*d* in pentane probably reflects an attenuated rate of anti capture of the initially formed carbocation **29A** through effective reduction in the number of proximate free alcohol molecules or clusters. Due to unsymmetrical solvation on the "top" face from which proton (or deuteron) transfer occurs, nucleophilic attack from an anti direction would require pseudorotation[20,21] to **29B** or tumbling of the molecule relative to the solvent. Subsequent anti capture of **29B** would result in overall syn addition to give the cis isomer of **12**. Further retardation of anti attack at C-3 of **29A** in less nucleophilic media such as 2,2,2-trifluoroethanol in pentane could account for the strong predominance of *cis*-**12b**-d_3.

Deuterium Labeling Studies with Silacyclohex-2-ene 10. Given the almost exclusive formation of the trans stereoisomers of **17a**-*d* and **18a**-*d*, regardless of the concentration of methanol in pentane (Table III), a mechanism involving cation **30** as a common intermediate (Scheme III) is not distinguishable from the mechanism of Schemes II and IV. The trans-stereoselective deuteration of **18a** does implicate anti attack by alcohol in the initially formed silacyclohexyl cation **30A**.[22] The lack of scrambling in dilute alcohol could reflect a relatively slower rate of chair conformational interconversion due to more favorable overlap between the Si–C_2 bond and C-3 cation center, and consequently, a stronger β effect in cation **30A** than in silacyclopentyl cation **29A**.[22] A higher barrier is also known to be associated with chair interconversion in silacyclohexane than pseudorotation in silacyclopentane.[23]

Mechanisms for Formation of Alkoxy(cyclopropylmethyl)dimethylsilanes 13a–c. These products, in principle, can be formed by a protolytic mechanism involving 1,3-rearrangement[24] of cation **29** (Scheme V), as suggested by the 2-fold increase in quantum yield with 2,2,2-trifluoroethanol versus methanol as solvents (Table I). However, trapping experiments with methoxytrimethylsilane and acetone implicate[9,10] silene **38** as an intermediate, produced through 1,3-C shift in the singlet excited state of **9** (eq 8). Triplet photoexcited **9** is not involved, because virtually no trace of **13a** was observed in toluene sensitized photolyses. An analogous [1,3] shift

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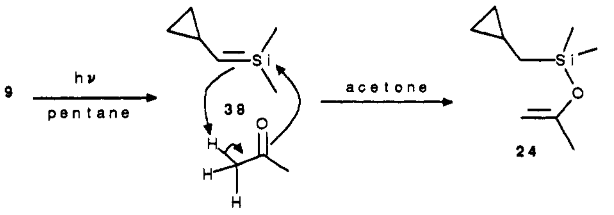
(20) (a) Experimentally, the barrier corresponding to interconversion of the C_2 symmetric twist silacyclopentane conformers via the C_s symmetric envelope form as the transition state is 3.89 kcal mol^{-1}.[20b] The molecular mechanics calculated barrier is 3.93 kcal mol^{-1}.[20c] (b) Laane, J. *J. Chem. Phys.* **1969**, *50*, 1946. (c) Tribble, M. T.; Allinger, N. L. *Tetrahedron* **1972**, *28*, 2147.

(21) (a) The lowest energy conformer of silyl-substituted cyclopentyl cations is the twist form, and the envelope and planar forms are close in energy.[21b] Although pseudorotation in cyclopentane is barrierless,[21c] a substituent attached to the ring or incorporated within the ring will lead to hindered pseudorotation,[21d] whereas incorporation of an sp^2 center within the ring should reduced the barrier.[21b,c] (b) Wang, G.; Li, D.; Chelius, E. C.; Lambert, J. B. *J. Chem. Soc., Perkin Trans. 2* **1988**, 169. (c) Legon, A. C. *Chem. Rev.* **1980**, *80*, 231. (d) Pitzer, K. S.; Donath, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3213.

(22) (a) We speculate that hyperconjugation is more effective in the larger six-membered ring. Recently, NMR evidence and equilibrium isotope effects have been reported[22a,b] for the 1-methylcyclohexyl cation which support a pair of equilibrating chair conformers; the β carbons of the more stable form appear at unusually low field chemical shifts. This was attributed to extensive C_α–C_β hyperconjugation. (b) Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7811. (c) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *Ibid.* **1987**, *109*, 7816.

(23) See ref 20 and the following: Jensen, F. R.; Bushweller, C. H. *Tetrahedron Lett.* **1968**, 2825.

(24) The reverse ring expansion of the cyclopropylethyl cation occurs with relief of strain: Dewar, M. J. S.; Harris, J. M. *J. Am. Chem. Soc.* **1970**, *92*, 6557. The forward reaction in our case would be facilitated by formation of a relatively stable incipient silylenium ion.[19]



(8)

is observed for disilacycloheptene **33**, provided the methanol used as solvent is distilled from magnesium methoxide to remove adventitious acid.[18]

Excited-State vs Ground-State *trans*-Silacycloalkene Intermediates in Protonation. *trans*-Cyclohexenes have experimental support as intermediates in photoalcoholyses of cyclohexene and 4,5-dihydropyran.[14a,23-27] In addition, GVB calculations have been reported[28] which indicate that *trans*-cyclohexene exists as a local minimum with an activation energy for isomerization to the cis isomer of 15 kcal mol^{-1}. The calculations give CC_1C_2C and HC_1C_2H torsional angles of 81° and 177°, respectively, implicating rehybridization of the olefinic carbons. A fascimile of this structure is shown as species X in Scheme IV, and such a species could account for the similarities in photoreactivity of silacyclohexene **10** and other six-membered-ring cycloalkenes.

Photoalcoholysis of cyclohexene requires the presence of strong acid.[25] Under neutral conditions, its trans isomer does not undergo appreciable protonation, but instead cyclodimerizes with a second molecule of *trans*-cyclohexene.[14a] The putative trans isomer of **10** appears to be more reactive, forming alcohol adducts **17** and **18** in "acid-free" methanol, which has been distilled from magnesium methoxide.[18] Dimerization does not compete until the alcohol is as weakly acidic as *tert*-butyl alcohol. Even then, photoalcoholysis remains a significant process, occurring with a quantum yield of 0.06. The greater apparent proton acceptor ability of *trans*-**10** is possibly due to stabilization of the resultant cation intermediates through hyperconjugation. The effect of replacing carbon by silicon in the six-membered ring is roughly equivalent to replacement by a conjugating oxygen. 4,5-Dihydropyran displays a remarkably similar profile of photoalcoholysis yields versus pK_a of the alcohol.[26] The intermediacy of *trans*-**10** as species X (Schemes II and IV) is also consistent with the similarity of quantum yields of **17** and **18** for both direct and toluene sensitized photolyses. Among medium-ring cycloalkenes, such a correspondence usually follows from the common intermediacy of the *trans*-cycloalkene, populated through rotational decay of both the singlet and triplet excited states.[26,27,29]

The photoreactivity silacyclopentene **9** in methanol, 2,2,2-trifluoroethanol, and *tert*-butyl alcohol bears a closer resemblance to that of **10** than it does to the photoreactivity of five-membered-ring carbocyclic alkenes[14a,25,30,31] such as 1-methylcyclopentene, which instead photoisomerizes by a radical mechanism, giving no detectable ether products of ionic addition of alcohol.[25] In the case of **9** a short-lived *trans*-silacyclopentene intermediate as species X (Schemes II and IV) could account for the reduced efficiencies and less pronounced dependence of quantum yields on pK_a of the alcohol relative to **10**. Furthermore, replacement of carbon by silicon in cycloheptene derivatives has recently been shown to lead to substantial stabilization of the *trans*-cycloalkene with respect to trans–cis isomerization.[18,32] Additional experimental evidence for *trans*-**9** is lacking, however, since a meaningful comparison of quantum efficiencies as a function of alcohol pK_a for direct and toluene-sensitized photolyses was not possible, due to a 10-fold reduction in efficiency for the latter photoreaction. The low quantum yields for sensitization probably result from inefficient triplet energy transfer, although other causes are conceivable. Thus, while it is still unclear whether the photoalcoholysis of five-membered-ring mono- and disilacycloalkenes involves a ground-state intermediate or, alternatively, protonation of $^{1,3}\sigma,\pi^*$ excited states,[1,33] the species undergoing proton transfer must be highly twisted about the double bond (Scheme IV) in order to account for the observed stereochemical results.

Experimental Section

Spectra were recorded with the following spectrometers: GE GN300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 46 MHz, ^{2}H NMR), Analect FX6200 (FTIR), Mattson 4020 Galaxy Series (FTIR), Perkin-Elmer 320 (UV). A Hewlett-Packard 5890 GC and HP 5970 mass selective detector were used for GC–MS analysis, which were performed at 70 eV with a 0.25-mm × 30-m DB-1 capillary column programmed at 40 °C for 4 min and then 280 °C at 10 °C min^{-1}. The silanized glass-lined, capillary direct interface was at 260 °C.

Preparative GC separations were performed on a Gow-Mac (Series 580) gas chromatograph with He as carrier gas at 30 mL/min flow rate on the following columns: column A, 15 ft × $^1/_4$ in. 15% OV101 on 60/80-mesh Chromosorb W; column B, 15 ft × $^1/_4$ in. 15% QF-1 on 60/80-mesh Chromosorb W AW; column C, 17 ft × $^1/_4$ in. 20% DC550 on 60/80-mesh Chromosorb W AW; column D, 10 ft × $^1/_4$ in. 10% OV101 in 60/80-mesh Chromosorb W; column E, 17 ft × $^1/_4$ in. 15% didecyl phthalate on 60/80-mesh Chromosorb W; column F, 7 ft × $^1/_4$ in. 10% OV101 on 60/80-mesh Chromosorb W.

Varian 1400 and HP 5710 gas chromatographs equipped with flame ionization detectors and a HP 3390 A electronic integrating recorder were used for analytical separations. Nitrogen was the carrier gas at a flow rate of 30 mL/min. The silanized glass-lined injectors were at 250 °C. Detector response was calibrated against standard mixtures of all reactants and products utilizing column G: 23 ft × $^1/_8$ in. 10% OV101 on 100/120-mesh Chromosorb W HP. Each of the reactants and products gave a single peak, and the corresponding response factors were frequently checked to insure against decomposition during quantitative GC analyses.

tert-Butyl alcohol (Alfa 95%) was freshly distilled from CaH_2 for use in photolyses. Methyl alcohol (EM Omnisolv) was freshly distilled from magnesium under nitrogen to remove adventitious acid; previous work[18] had shown this treatment to be effective. 2,2,2-Trifluoroethanol (Aldrich Gold Label) was used without further treatment. When the 2,2,2-trifluoroethanol was refluxed for 3 h over anhyd $CaSO_4$ plus $NaHCO_3$ and then fractionally

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(25) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783.

(26) Inoue, Y.; Matsumoto, N.; Hakushi, T.; Srinivasan, R. *J. Org. Chem.* **1981**, *46*, 3609.

(27) Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 6383.

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distilled,[34] relative quantum yields for formation of products from silacyclopent-2-ene **9** were within 8% of the values reported under entry 2 in Table I for the untreated alcohol.

1,1-Dimethylsilacyclopent-2-ene (9). The silacyclopent-2-ene was prepared from 1,1-dichloro-1-silacyclopent-2-ene[35] following the procedure of Zuckermann and co-workers.[36] Silacyclopentene **9** was purified by preparative GC on column A at 71 °C. The NMR and IR spectral data were as reported previously:[37] GC–MS *m/z* (relative intensity) 112 (9), 97 (100), 95 (32), 69 (11), 55 (9), 43 (32); UV λ_{max} (methanol) 203 nm (ϵ 4570).

1,1-Dimethylsilacyclohex-2-ene (10). The silacyclohex-2-ene was synthesized following the procedure of Rosenberg and Zuckerman[36] and then purified by preparative GC on column D (110 °C). Spectral data were as reported previously: UV λ_{max} (methanol) 203 nm (ϵ 5820).

(3-Butenyl)methoxydimethylsilane (11a). To 0.96 g (0.0300 mol) of methyl alcohol (distilled from magnesium), 2.78 g (0.0215 mol) of quinoline, and 40 mL of pentane was added, dropwise with stirring under nitrogen, 3.20 g (0.0182 mmol) of (3-butenyl)chlorodimethylsilane (supplementary material) in 20 mL of pentane. The reaction mixture was refluxed 7 h, cooled, and filtered. The pentane was distilled, and the residue was fractionated through a 6-in. Vigreux column to give 2.0 g (64% yield) of silyl ether **11a**, bp 49–55 °C (140 mm), which was further purified by preparative GC on column D (91 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 6 H, methyl), 0.68–0.74 (m, 2 H, methylene), 2.06–2.15 (m, 2 H, methylene), 3.43 (s, 3 H, methoxy), 4.88–5.04 (m, 2 H, vinyl), 5.88 (ddt, J = 17.0 Hz, 10.3 Hz, 6.3 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.61, 15.00, 27.16, 50.23, 112.88, 141.23; IR (CCl_4) 3.25, 3.38, 3.41, 3.43, 3.53, 6.09, 6.92, 7.07, 7.98, 8.40, 9.15, 10.07, 11.03, 11.95, 12.30, 12.49 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 129 (11), 101 (4), 97 (15), 89 (100), 75 (23), 59 (56), 55 (3), 47 (2), 45 (12), 43 (13). Anal. Calcd for $C_7H_{16}SiO$: C, 58.28; H, 11.18. Found: C, 58.16, H, 11.09.

(3-Butenyl)(2,2,2-trifluoroethoxy)dimethylsilane (11b). The 2,2,2-trifluoroethoxy derivative of (3-butenyl)chlorodimethylsilane was prepared in 58% yield, bp 59–66 °C (45 mm), by the procedure to synthesize the methoxy derivative (vide supra) and purified by preparative GC on column A (64 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 6 H, methyl), 0.73–0.78 (m, 2 H, methylene), 2.07–2.15 (m, 2 H, methylene), 3.91 (q, J = 8.7 Hz, 2 H, trifluoroethoxy), 4.92 (ddt, J = 10.2, 1.5, 1.0 Hz, 1 H, vinyl), 5.01 (ddt, J = 17.1, 1.7, 1.0 Hz, 1 H, vinyl), 5.87 (ddt, J = 17.1, 10.7, 6.3 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −2.34, 15.01, 26.76, 61.16 (q, J = 30 Hz), 113.27, 123.93, (q, J = 276 Hz), 140.38; IR (CCl_4) 3.25, 3.38, 3.41, 6.09, 6.85, 6.92, 7.07, 7.67, 7.77, 7.96, 8.48, 8.61, 10.07, 10.34, 10.99, 11.84, 12.37 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 177 (1), 158 (2), 157 (16), 156 (6), 138 (1), 117 (3), 107 (6), 97 (3), 93 (2), 89 (22), 85 (3), 79 (9), 78 (8), 77 (100), 64 (3), 63 (12), 61 (14), 59 (6), 55 (11), 49 (8), 47 (11), 43 (8), 41 (9). Anal. Calcd for $C_8H_{15}SiOF_3$: C, 45.20; H, 7.12. Found: C, 45.06; H, 7.28.

(3-Butenyl)(*tert*-butoxy)dimethylsilane (11c). The *tert*-butoxy derivative of (3-butenyl)chlorodimethylsilane was prepared in 35% yield, bp 76–84 °C (20 mm), by the procedure to synthesize the methoxy derivative (vide supra) and purified by preparative GC on column D (126 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.11 (s, 6 H, methyl), 0.61–0.67 (m, 2 H, methylene), 1.25 (s, 9 H, *tert*-butoxy), 2.05–2.09 (m, 2 H, methylene), 4.83–4.99 (m, 2 H, vinyl), 5.84 (ddt, J = 16.8, 10.3, 1.0 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ 1.01, 17.61, 27.47, 31.99, 71.77, 112.58, 141.30; IR (CCl_4), 3.25, 3.36, 3.42, 3.44, 6.09, 6.84, 6.92, 7.07, 7.19, 7.33, 7.98, 8.33, 9.52, 9.76, 10.68, 11.03, 11.95, 12.41 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 171 (6), 131 (16), 117 (3), 115 (9), 113 (12), 97 (11), 87 (8), 85 (9), 76 (7), 75 (100), 59 (14), 47 (7), 4 (12), 43 (8). Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.19; H, 11.83.

Synthesis of 3-Methoxy-1,1-dimethylsilacyclopentane (12a). To a vigorously stirred suspension of 2.90 g (9.10 mmol) of mercuric acetate and 15 mL of methyl alcohol was added 0.90 g (8.02 mmol) of silacyclopent-2-ene **9**. After 10 min of stirring at room temperature, 9.0 mL of 3 M aqueous NaOH and 9.0 mL of 0.5 M sodium borohydride in 3 M aqueous NaOH were added. The mixture was stirred for 2 h until the mercury coagulated and then extracted three times with pentane. The combined extracts were dried over anhyd Na_2SO_4 and concentrated by distillation. Short-path distillation of the residue at 39–45 °C (40 mm) gave 0.50 g (43.2% yield) of methoxysilacyclopentane **12a**, which was purified by preparative GC on column A (114 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 3 H, methyl), 0.16 (s, 3 H, methyl), 0.42–0.53 (m, 1 H, methylene), 0.62–0.75 (m, 2 H, methylene), 0.86–0.98 (m, 1 H, methylene), 1.62–1.86 (m, 2 H, methylene), 3.25 (s, 3 H, methoxy), 3.05–3.69 (m, 1 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −1.05, −0.89, 9.06, 19.51, 31.50, 55.43, 82.68; IR (CCl_4) 3.39, 3.47, 3.55, 6.85, 7.11, 7.43, 8.00, 8.26, 8.48, 8.67, 8.96, 9.17, 9.47, 9.71, 9.84, 10.33, 10.49, 10.90, 11.59, 11.88, 12.22 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 129 (12), 116 (12), 102 (9), 101 (85), 99 (6), 97 (16), 90 (8), 89 (100), 86 (18), 85 (8), 75 (26), 73 (7), 71 (8), 61 (6), 60 (7), 59 (70), 58 (51), 54 (7), 45 (23), 44 (10), 43 (39), 42 (9). Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18. Found: C, 58.47; H, 11.22.

(Cyclopropylmethyl)methoxydimethylsilane (13a). A mixture of 5.62 g (0.0860 mol) of zinc dust (Aldrich), 0.43 g (4.34 m mmol) of cuprous chloride (Aldrich), and 40 mL of anhyd ether was refluxed under nitrogen for 30 min, and then 5.60 g (0.0430 mol) of methoxydimethyl(2-propenyl)silane[10d] in 15 mL of ether was added dropwise, followed by 11.5 g (0.043 mol) of diiodomethane (Aldrich) in 6 mL of ether while maintaining reflux. The mixture was refluxed for a total of 41 h, cooled, and decanted into 200 mL of pentane. After washing six times with 30 mL of water, the mixture was dried over anhyd Na_2SO_4 and concentrated by distillation. Fractionation of the residue through a 6-in. Vigreux column gave 3.50 g (56.4% yield) of silyl ether **13a**, bp 52–56 °C (27 mm), which was further purified by preparative GC on column A (90 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ −0.004 to −0.051 (m, 2 H, cyclopropyl), 0.12 (s, 6 H, methyl), 0.42–0.48 (m, 2 H, cyclopropyl), 0.56–0.64 (m, 3 H, methylene and methine), 3.42 (s, 3 H, methoxy); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −2.34, 5.31, 6.42, 21.29, 49.95; IR (CCl_4) 3.25, 3.33, 3.38, 3.45, 3.47, 3.53, 6.85, 7.11, 7.33, 7.98, 8.35, 9.15, 9.59, 9.86, 11.12, 11.84, 12.22 μm; GC–MS (70 ev) *m/z* (relative intensity) no parent, 129 (5), 97 (6), 91 (4), 90 (8), 89 (100), 75 (10), 60 (5), 59 (62), 58 (7), 55 (4), 45 (8), 43 (11). Anal. Calcd for $C_7H_{16}OSi$: C, 58.27; H, 11.18. Found: C, 58.07; H, 10.84.

(Cyclopropylmethyl)dimethyl(2,2,2-trifluoroethoxy)silane (13b). Trifluoroethoxysilane **13b**, bp 49–54 °C (10 mm), was prepared in 49.7% yield from 6.20 g (0.0313 mol) of dimethyl(2-propenyl)(2,2,2-trifluoroethoxy)silane (supplementary material), following the procedure described above for the synthesis of silyl ether **13a**, except that the reflux time was 45 h. The product was purified by preparative GC on column B (88 °C) and then on column A (110 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) −0.01 to 0.01 (m, 2 H, cyclopropyl), 0.20 (s, 6 H, methyl), 0.47–0.50 (m, 2 H, cyclopropyl), 0.59–0.63 (m, 3 H, methylene and methine), 3.92 (q, J = 8.0 Hz, 2 H, trifluoroethoxy); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −2.13, 4.98, 6.34, 21.40, 61.20 (q, J = 36 Hz), 123.92 (q, J = 278 Hz); IR (CCl_4) 3.25, 3.33, 3.38, 3.41, 3.46, 3.58, 6.85, 7.07, 7.32, 7.67, 7.77, 7.96, 8.59, 9.42, 9.56, 9.84, 10.34, 11.12, 11.77, 12.22 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 177 (0.4), 157 (11), 156 (4), 107 (5), 103 (1), 97 (2), 89 (7), 81 (6), 79 (6), 77 (100), 63 (6), 61 (13), 55 (10), 49 (8), 47 (9), 43 (7), 41 (4). Anal. Calcd for $C_8H_{15}OSiF_3$: C, 45.26; H, 7.12. Found: C, 45.12; H, 7.21.

***tert*-Butoxy(cyclopropylmethyl)dimethylsilane (13c).** The (cyclopropylmethyl)silane **13c** was prepared in 80% yield, bp 56–68 °C (10 mm), from 2.30 g (0.0134 mol) of (*tert*-butoxy)dimethyl(2-propenyl)silane,[10d] following the procedure described above for the synthesis of silyl ether **13a**, except that the reflux time was 23 h. The product was purified by preparative GC on column A (120 °C). The spectral data were as follows: ^{1}H NMR

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(300 MHz, $CDCl_3$ in CCl_4) δ −0.06 to −0.01 (m, 2 H, cyclopropyl), 0.34 (s, 6 H, methyl), 0.39–0.45 (m, 2 H, cyclopropyl), 0.53 (br d, *J* = 6.0 Hz, 2 H, methylene), 0.57–0.68 (br m, 1 H, methine), 1.24 (s, 9 H, *tert*-butoxy); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ 1.28, 5.66, 6.37, 24.08, 32.04, 71.69; IR (CCl_4) 3.25, 3.36, 3.41, 3.44, 3.48, 6.84, 7.19, 7.33, 8.10, 8.33, 9.02, 9.52, 9.76, 11.16, 11.88, 12.41 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 171 (3), 131 (11), 115 (3), 113 (5), 97 (3), 85 (5), 77 (4), 76 (7), 75 (100), 61 (8), 59 (9), 58 (3), 55 (4), 47 (7), 45 (10), 43 (6), 41 (4). Anal. Calcd for $C_{10}H_{22}SiO$: C, 64.45; H, 11.90. Found: C, 64.43; H, 11.67.

Methoxydimethyl(4-pentenyl)silane (17a). To 1.50 g (0.0468 mol) of methyl alcohol, 3.36 g (0.0260 mol) of quinoline, and 60 mL of pentane was added dropwise 3.80 g (0.0233 mol) of chlorodimethyl(4-pentenyl)silane (supplementary material) in 20 mL of pentane. After refluxing overnight the mixture was cooled and filtered, and the pentane was removed by distillation. Short-path distillation of the residue at 69–74 °C (20 mm) gave 2.30 g (62.2%) of silyl ether **17a**, which was purified by preparative GC on column A (115 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6 H, methyl), 0.57–0.64 (m, 2 H, methylene), 1.38–1.53 (m, 2 H, methylene), 2.03–2.11 (m, 2 H, methylene), 3.42 (s, 3 H, methoxy), 4.91–5.02 (m, 2 H, vinyl), 5.80 (ddt, *J* = 17.0 Hz, 10.2 Hz, 6.8 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.71, 15.43, 22.61, 37.34, 114.55, 138.76; IR (CCl_4) 3.23, 3.38, 3.42, 3.50, 3.53, 6.09, 6.87, 6.94, 7.07, 7.45, 7.98, 8.40, 9.15, 10.02, 10.15, 10.49, 10.96, 11.88 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 143 (2.1), 116 (2), 115 (17), 111 (2), 91 (4), 90 (8), 89 (100), 75 (10), 61 (3), 59 (45), 55 (2), 45 (8), 43 (8). Anal. Calcd for $C_8H_{18}OSi$: C, 60.70; H, 11.46. Found: C, 60.56; H, 11.27.

Dimethyl(2,2,2-trifluoroethoxy)(4-pentenyl)silane (17b). The (2,2,2-trifluoroethoxy)silane **17b** was prepared in 74.3% yield, bp 69–76 °C (12 mm), from the reaction of 3.00 g (0.0184 mol) of chlorodimethyl(4-pentenyl)silane, 3.68 g (0.0368 mol) of 2,2,2-trifluoroethanol, and 2.58 g (0.020 mol) quinoline in 100 mL of pentane, following the procedure described above for the synthesis of silyl ether **17a**. The product was purified by preparative GC on column A at 120 °C. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.16 (s, 3 H, methyl), 0.61–0.67 (m, 2 H, methylene), 1.39–1.50 (m, 2 H, methylene), 2.04–2.12 (m, 2 H, methylene), 3.89 (q, *J* = 9.0 Hz, 2 H, trifluoroethoxy), 4.93–5.02 (m, 2 H, vinyl), 5.85 (ddt, *J* = 16.8, 10.4, 6.3 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −2.45, 15.42, 22.12, 37.15, 61.15 (q, *J* = 35 Hz), 114.92, 123.90 (d, *J* = 278 Hz), 138.04; IR (CCl_4) 3.25, 3.41, 3.46, 3.49, 6.09, 6.85, 6.94, 7.06, 7.67, 7.77, 7.96, 8.61, 10.02, 10.34, 10.93, 11.84, 12.33 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 185 (0.9), 158 (3), 157 (31), 131 (3), 127 (2), 111 (2), 107 (5), 103 (14), 99 (4), 84 (3), 81 (7), 79 (5), 78 (7), 77 (100), 69 (4), 63 (7), 61 (17), 59 (5), 55 (3), 49 (6), 47 (9), 43 (8), 42 (5), 41 (14). Anal. Calcd for $C_9H_{17}SiOF_3$: C, 47.77; H, 7.57. Found: C, 47.73; H, 7.66.

(*tert*-Butoxy)dimethyl(4-pentenyl)silane (17c). To 2.24 g (0.020 mol) of potassium *tert*-butoxide (Aldrich) and 50 mL THF was added dropwise 3.00 g (0.0184 mol) of chlorodimethyl(4-pentenyl)silane in 10 mL of THF. After 4 h reflux, 100 mL of pentane was added, followed by suction filtration and distillation of the solvent. Additional salt was removed by adding 50 mL of pentane and filtering. Distillation of the solvent and then short-path distillation of the residue at 78–83 °C (10 mm) gave 2.10 g (56.8%) of silyl ether **17c**, which was purified by preparative GC on column A (117 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.09 (s, 6 H, methyl), 0.50–0.58 (m, 2 H, methylene), 1.24 (s, 9 H, *tert*-butoxy), 1.37–1.47 (m, 2 H, methylene), 2.07 (q, *J* = 7.0 Hz, 2 H, methylene), 4.91–5.02 (m, 2 H, vinyl), 5.79 (ddt, *J* = 17.1 Hz, 10.3 Hz, 6.7 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ 0.93, 18.21, 22.86, 31.98, 37.37, 71.74, 114.35, 138.72; IR (CCl_4), 3.25, 3.36, 3.42, 3.51, 6.09, 6.94, 6.85, 7.07, 7.21, 7.33, 7.46, 8.00, 8.33, 9.56, 9.79, 9.99, 10.15, 10.48, 10.96, 11.42, 11.95 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 185 (2), 157 (1), 132 (2), 131 (18), 127 (8), 115 (2), 101 (18), 100 (2), 99 (14), 85 (7), 77 (4), 76 (7), 75 (100), 61 (10), 59 (12), 58 (5), 57 (5), 55 (3). Anal. Calcd for $C_{11}H_{24}SiO$: C, 65.93, H, 12.07. Found: C, 66.12; H, 11.89.

Synthesis of 3-Methoxy-1,1-dimethylsilacyclohexane (18a). The methoxysilacyclohexane **18a** was prepared in 76.6% yield, bp 87–92 °C (40 mm), from 2.00 g (0.0159 mol) of silacyclohex-2-ene **10** following the procedure described above for the synthesis of methoxysilacyclopentane **12a**. The product was purified by preparative GC on column A at 115 °C. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02, 0.07 (overlapping singlets, 6 H, methyl), 0.32–0.66 (complex m, 3 H, methylene), 1.07–1.42 (complex m, 3 H, methylene), 1.89–2.10 (m, 2 H, methylene), 3.26 (s, 4 H, methoxy plus methine); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −3.26, −1.65, 13.07, 20.44, 21.19, 35.05, 54.47, 79.06; IR (CCl_4) 3.42, 3.50, 3.55, 6.89, 7.08, 7.42, 8.00, 8.38, 8.57, 8.67, 9.15, 10.15, 10.46, 10.93, 11.42, 11.88 μm; GC–MS (70 eV) *m/z* (relative intensity) no parent, 157 (0.3), 145 (0.3), 144 (1.2), 143 (8), 127 (3), 117 (7), 116 (10), 115 (50), 111 (4), 101 (8), 100 (4), 99 (16), 97 (3), 91 (4), 90 (8), 89 (100), 87 (4), 85 (8), 83 (4), 75 (26), 73 (10), 72 (55), 71 (7), 61 (5), 60 (5), 59 (62), 58 (13), 57 (4), 55 (7), 53 (4), 45 (20), 43 (32). Anal. Calcd for $C_8H_{18}OSi$: C, 60.70; H, 11.46. Found: C, 60.69; H, 11.22.

Synthesis of 3-*tert*-Butoxy-1,1-dimethylsilacyclohexane (18c). To a stirred solution of 1.60 g (3.75 mmol) of mercuric trifluoroacetate and 10 mL of *tert*-butyl alcohol (distilled from CaH_2) was added 0.470 g (3.75 mmol) of silacyclohex-2-ene **10** immediately followed by ca. 0.1 g of potassium *tert*-butoxide. After 40 min of stirring, 4 mL of 3.0 M aqueous NaOH and 4 mL of 0.5 M sodium borohydride in 3.0 M aqueous NaOH were added. The mixture was stirred for 2 h until the mercury had coagulated. Extraction with pentane and standard workup gave NMR pure product, which was isolated by preparative GC on column A at 134 °C. Several attempts to obtain a satisfactory combustion analysis failed. *tert*-Butyl ether **18c** prepared by this procedure was not stable and decomposed to three minor products over several days from GC–MS, ^{1}H NMR, and ^{13}C NMR analyses. The spectra data of GC–MS and NMR pure samples were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.036, 0.058 (slightly overlapping singlets, 6 H methyl), 0.29–0.40 (m, 1 H, methylene), 0.58–0.76 (m, 2 H, methylene), 0.96–1.03 (m, 2 H, methylene), 1.189, 1.194 (overlapping singlets, ratio ca. 2:1, 9 H, *tert*-butoxy), 1.27–1.43 (complex m, 1 H, methylene), 1.73–1.80 (complex m, 1 H, methylene), 1.92–2.01 (complex m, 1 H, ethylene), 3.55 (tt, *J* = 11.0 Hz, 3.0 Hz, 1 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.54, −1.66, 12.83, 21.31, 26.03, 28.47, 38.86, 70.13, 73.06; IR (CCl_4) 3.36, 3.41, 6.89, 7.10, 7.21, 7.35, 7.46, 7.99, 8.33, 8.56, 8.67, 9.56, 9.81, 10.15, 10.90, 11.03, 11.45, 11.88 μm; GC–MS (70 eV) *m/z* (relative intensity) 200 (0.6), 185 (0.6), 158 (11), 157 (6), 144 (2), 129 (17), 127 (19), 116 (3), 103 (10), 102 (18), 101 (99), 100 (16), 99 (61), 97 (5), 87 (8), 85 (11), 83 (5), 77 (4), 75 (100), 72 (42), 71 (12), 69 (4), 61 (17), 59 (62), 58 (20), 57 (100), 53 (4). Anal. Calcd for $C_{11}H_{24}SiO$: C, 65.93; H, 12.07. Found: C, 65.09; H, 11.89.

General Procedure for Preparative Direct Photolyses. Photolyses were performed with a quartz immersion well apparatus of either 40- or 70-mL volume. Runs with methanol or 2,2,2-trifluoroethanol as the solvents were conducted at 5 °C; the temperature was 27 °C with *tert*-butyl alcohol as the solvent. The 214-nm light source was a Philips Model 93106E zinc lamp (Ealing), which was cooled by a stream of air. All photolysates were purged with argon 1 h prior to and during photolyses. Photolyses were monitored by GC or GC–MS analyses of aliquots taken at time intervals. Each 0.25–0.5-mL aliquots was subjected to a standard workup involving addition of 0.5 mL of pentane, followed by washing one to five times with 1 mL of water and drying over anhyd Na_2SO_4.

Preparative Direct Photolyses of 1,1-Dimethylsilacyclopent-2-ene (9) in Methanol. A solution of 298 mg (2.66 mmol) of silacyclopentene **9** in 70 mL of methanol was irradiated at 214 nm for 23 h following the general procedure described above. GC–MS analyses of aliquots after workup showed only four peaks with retention times and mass spectra corresponding to authentic samples of **9**, **11a**, **13a**, and **12a**. After 40 mL of pentane was added the photolysate was washed twice with 40 mL of water and dried over anhyd. Na_2SO_4. The bulk of the pentane was distilled, and the reactant and photoproducts were isolated by preparative GC on column D at 83 °C. Each of the products was identified by ^{1}H and ^{13}C NMR, IR, and GC–MS analyses.

Preparative Direct Photolyses of 1,1-Dimethylsilacyclopent-2-ene (9) in 2,2,2-Trifluoroethanol. A solution of 180 mg (1.61 mmol) of silacyclopentene **9** in 40 mL of 2,2,2-trifluoroethanol was irradiated at 214 nm for 19 h following the general procedure described above. GC–MS analyses of aliquots after workup showed only four peaks with retention times and mass spectra corresponding to authentic samples **9**, **11b**, **13b**, and one unknown product. After 40 mL of pentane was added, the photolysate was washed with 40 mL of water and dried over anhyd Na_2SO_4. The bulk of pentane was distilled, and the reactant and products were isolated on column A at 95 °C. Products **11b** and **13b** were further identified by ^{1}H and ^{13}C NMR, IR, and GC–MS analyses. The unknown photoproduct was identified as 3-(2,2,2-trifluoroethoxy)-1,1-dimethylsilacyclopentane (**12b**). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.14 (s, 3 H, methyl), 0.19 (s, 3 H, methyl), 0.48–0.58 (m, 1 H, methylene), 0.70–0.80 (m, 2 H, methylene), 0.87–0.93 (m, 1 H, methylene), 1.98 (m, 2 H, methylene), 3.68–3.80 (m, 2 H, trifluoroethoxy), 3.94 (quintet, $J = 5.6$ Hz, methine); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −1.23 and −1.07 (overlapping), 8.84, 19.66, 31.63, 65.58 (q, $J = 34$ Hz), 83.09, 123.86 (q, $J = 278$ Hz); IR (CCl_4) 3.39, 0.85, 7.10, 7.43, 7.81, 8.00, 8.03, 8.90, 9.24, 9.42, 10.26, 11.84, 12.41 μm; GC–MS (70 eV) m/z (relative intensity) no parent, 157 (13), 156 (4), 119 (9), 113 (12), 107 (6), 105 (26), 101 (4), 97 (3), 84 (34), 86 (53), 85 (9), 81 (12), 79 (23), 78 (8), 77 (100), 71 (5), 69 (5), 64 (16), 63 (19), 61 (13), 59 (33), 58 (58), 55 (5), 53 (6), 49 (6), 47 (10), 45 (11), 43 (41), 41 (21). Anal. Calcd for $C_8H_{13}OSiF_3$: C, 45.20; H, 7.12. Found: 45.16; H, 7.20.

Preparative Direct Photolysis of 1,1-Dimethylsilacyclopent-2-ene (9) in *tert*-Butyl Alcohol. A solution of 500 mg (4.46 mmol) of silacyclopentene **9** in 250 mL of *tert*-butyl alcohol was purged with nitrogen for 1.5 h and then irradiated through quartz with a Hanovia 450-W medium-pressure mercury lamp for 5 h. GC–MS analyses of aliquots after workup showed four peaks with retention times and mass spectra corresponding to authentic samples of **9**, **11c**, **13c**, as well as one unknown product. After 120 mL of pentane was added the photolysate was washed 10 times with 100 mL of water and dried over anhyd Na_2SO_4. The bulk of pentane was distilled and the reactant and photoproducts were isolated by preparative GC on column A at 120 °C. Products **11c** and **13c** were further identified by ^{1}H and ^{13}C NMR, IR, and GC–MS analyses. The unknown product was identified as 3-*tert*-butoxy-1,1-dimethylsilacyclopentane (**12c**). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.10 and 0.14 (overlapping singlets, 6 H, methyl) 0.33–0.92 (complex multiplets, 4 H, methylene), 1.16 and 1.17 (overlapping singlets, 9 H, *tert*-butoxy), 1.42–1.80 (m, 2 H, methylene), 3.73–3.89 (m, 1 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −0.94 and −0.89 (overlapping peaks), 9.68, 23.43, 28.51, 34.83, 72.43, 73.64; IR (CCl_4) 3.36, 6.85, 7.10, 7.21, 7.33, 8.00, 8.33, 8.67, 8.81, 8.94, 9.31, 9.52, 9.86, 11.22, 11.49, 11.87, 12.37 μm; GC–MS (70 eV) m/z (relative intensity) 186 (1), 171 (1), 158 (1), 157 (5), 143 (5), 131 (2), 117 (2), 115 (23), 113 (11), 102 (9), 101 (48), 97 (12), 88 (5), 87 (47), 86 (33), 85 (17), 76 (7), 75 (100), 71 (7), 69 (4), 61 (10), 60 (7), 59 (63), 58 (29), 57 (76), 47 (9), 45 (21), 43 (55), 41 (39). Anal. Calcd for $C_{10}H_{22}SiO$: C, 64.45; H, 11.90. Found: C, 64.20; H, 12.04.

Preparative Direct Photolyses of 1,1-Dimethylsilacyclohex-2-ene (10) in Methanol. A solution of 223 mg (1.77 mmol) of silacyclohexene **10** in 70 mL of methanol was irradiated at 214 nm for 6 h following the general procedure described above. GC–MS analyses of aliquots after workup showed only three peaks with retention times and mass spectra corresponding to authentic samples **10**, **17a**, and **18a**. The photolysate was diluted with 35 mL of pentane, washed twice with 40 mL of water, and then dried over anhyd Na_2SO_4. The bulk of the pentane was distilled, and the reactant and products were isolated by preparative GC on column D at 130 °C. Each of the products was identified by ^{1}H and ^{13}C NMR, IR, and GC–MS analyses.

Preparative Direct Photolyses of 1,1-Dimethylsilacyclohex-2-ene (10) in 2,2,2-Trifluoroethanol. A solution of 155 mg (1.23 m mol) of silacyclohexene **10** in 40 mL of 2,2,2-trifluoroethanol was irradiated at 214 nm for 5.5 h following the general procedure. GC–MS analyses of aliquots after workup showed only three peaks with retention times and mass spectra corresponding to authentic samples of **10** and **17b**, as well as an unknown product. After 75 mL of pentane was added, the photolysate was washed once with 40 mL of water and dried over anhyd Na_2SO_4. The bulk of the pentane was distilled, and the products were isolated by preparative GC on column A at 130 °C. Product **17b** was further identified by ^{1}H and ^{13}C NMR, IR, and GC–MS analysis. The unknown photoproduct was identified as 3-(2,2,2-trifluoroethoxy)-1,1-dimethylsilacyclohexane (**18b**). The spectral data were as the follows: ^{1}H NMR (300 MHz, $CDCl_3$ in CCl_4) δ 0.04 and 0.08 (overlapping singlets, 6 H, methyl), 0.36–0.47 (m, 1 H, methylene), 0.61–0.71 (m, 2 H, methylene), 1.17–1.50 (m, 3 H, methylene), 1.90–2.03 (m, 2 H, methylene), 3.51–3.61 (m, 1 H, methine), 3.71–3.82 (m, 2 H, trifluoroethoxy); ^{13}C NMR (75 MHz, $CDCl_3$ in CCl_4) δ −3.52, −1.87, 12.70, 20.31, 21.15, 35.16, 64.75 (q, $J = 34$ Hz), 80.01, 124.10 (q, $J = 279$ Hz); IR (CCl_4) 3.42, 3.50, 3.56, 6.89, 7.07, 7.39, 7.81, 7.98, 8.33, 8.59, 8.94, 9.45, 9.68, 10.10, 10.90, 11.32, 11.88, 12.30 μm; GC–MS (70 eV) m/z (relative intensity) no parent, 183 (2.2), 157 (23), 132 (3), 131 (25), 127 (10), 126 (3), 111 (6), 107 (7), 104 (5), 103 (53), 100 (9), 99 (17), 93 (6), 89 (7), 87 (4), 85 (8), 83 (10), 81 (13), 79 (7), 78 (7), 77 (100), 75 (7), 73 (10), 72 (63), 71 (7), 69 (11), 67 (10), 63 (17), 61 (17), 59 (42), 58 (11), 55 (18), 43 (59), 41 (34). Anal. Calcd for $C_9H_{17}OSiF_3$: C, 47.79; H, 7.52. Found: C, 47.77; H, 7.57.

Preparative Direct Photolyses of 1,1-Dimethylsilacyclohex-2-ene (10) in *tert*-Butyl Alcohol. A solution of 206 mg (1.63 mmol) of silacyclohexene **10** in 40 mL of *tert*-butyl alcohol was irradiated at 214 nm for 5.5 h following the general procedure described above. GC–MS analyses of aliquots after workup showed only six peaks with retention times and mass spectra corresponding to authentic samples of **10**, **17c**, **18c**, and three unidentified dimers of **10**. After 50 mL of pentane was added the photolysate was washed eight times with 60 mL of water. The bulk of the pentane was distilled, and the reactant and products of **17c** and **18c** were isolated by preparative GC on column A at 130 °C. Products **17c** and **18c** were further identified by ^{1}H NMR, ^{13}C NMR, IR, and GC–MS analyses.

Determination of Product Yields and Rates from Photolyses of 1,1-Dimethylsilacyclopent-2-ene (9) and 1,1-Dimethylsilacyclohex-2-ene (10). Solutions of 0.01–0.02 M silacyclopentene **9** or silacyclohexene **10** plus internal standard in various alcohols were irradiated following the general procedure for direct photolyses. Aliquots taken at time intervals for GC analyses were subjected to the standard workup described above. Product yields are given in the Results and rates in M min^{-1} are collected in Table I. Data for $\%P_i/\Sigma\%P_i$ are provided in the supplementary material.

Silacyclopentene 9. The internal standard was *n*-octane. GC analyses (column G at 60 °C) of runs with methanol as solvent showed products **11a**, **13a**, and **12a** at retention times of 30, 38, and 51 min, respectively. Under the same GC conditions, but with 2,2,2-trifluoroethanol as the solvent, products **11b**, **13b**, and **12b** were observed at retention times of 32, 39, and 53 min, respectively. With *tert*-butyl alcohol as the solvent products **11c**, **13c**, and **12c** were observed at retention of 45, 54, and 63 min, respectively (column temperature of 60 °C for 30 min and then 90 °C).

Silacyclohexene 10. GC analyses used column G. In runs with methanol as solvent and *n*-undecane as internal standard the retention times of products **17a** and **18a** were 23 and 39 min (column 100 °C). With 2,2,2-trifluoroethanol as solvent and *n*-nonane as internal standard adducts **17b** and **18b** had retention times of 34 and 42 min (column programmed at 72 °C for 16 min and then 2 °C min^{-1} to 140 °C). With *tert*-butyl alcohol as solvent and *n*-nonane as internal standard products **17c** and **18c** were observed at 53 and 72 min (column programmed for 70 °C for 30 min and then 90 °C). During photolyses in *tert*-butyl alcohol, photodimers of silacyclohexene were observed at 56 min for dimer A, 60 min for dimer B plus dimer C (column programmed for 90 °C for 32 min and then 8 °C min^{-1} to 200 °C). Dimer B plus dimer C were only separable during capillary GC–MS analysis.

Photolysis of 1,1-Dimethylsilacyclopent-2-ene (9) in the Presence of Trimethylmethoxysilane. A solution of 326 mg (2.92 mmol) of silacyclopent-2-ene **9** and 3.01 g (0.0289 mol) of trimethylmethoxysilane (Aldrich) in 40 mL of pentane at 10 °C was irradiated at 214 nm for 7 h following the general procedure for preparative direct photolyses described above. GC–MS analysis of aliquots showed the presence of three trimethylmethoxysilane adducts. After concentrating the photolysate to ca. 1 mL, the products were isolated by preparative GC on column E (126 °C). Two of the isomeric products could not be separated from each other preparatively. A third isomer was obtained NMR pure and spectroscopically identified as (1-cyclopropyl-1-(trimethylsilyl)methyl)dimethylmethoxysilane (**23**). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.64 (d, J = 10.7 Hz, 1 H, methine), 0.0–0.06 (m, 2 H, methylene), 0.08 (s, 9 H, methyl), 0.16 (s, 6 H, methyl), 0.50–0.60 (m, 3 H, methylene and methine), 3.40 (s, 3 H, methoxy); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.27, −0.64, −0.10, 7.14, 7.74, 8.10, 20.88, 50.12; IR (CCl_4) 3.25, 3.38, 3.45, 3.53, 6.85, 7.35, 7.98, 8.42, 9.26, 9.52, 9.74, 10.81, 11.84, 12.33, 12.66 μm; GC–MS (70 eV) m/z (relative intensity) 216 (0.7), 201 (6), 187 (4), 160 (1), 147 (4), 113 (16), 112 (32), 97 (68), 89 (100), 73 (53), 59 (76), 58 (11), 45 (32), 43 (23).

Direct 214-nm Photolysis of 1,1-Dimethylsilacyclopent-2-ene (9) in the Presence of Acetone. A solution of 135 mg (1.20 mmol) of silacyclopent-2-ene **9** and 33.5 mg (0.58 mmol) of acetone (Aldrich) in 35 mL of pentane at 5 °C was irradiated at 214 nm for 7 h following the general procedure for preparative direct photolyses described above. Aliquots were taken and analyzed by GC–MS, which showed one product. The photolysate was concentrated to ca. 1 mL, and the product was isolated by preparative GC on column F at 85 °C and identified spectroscopically as (cyclopropylmethyl)dimethyl (1-methylethenyl)oxy)silane (**24**). The spectral data were as follows: ^{1}H NMR (300 MHz, C_6D_6) δ −0.04 to −0.02 (m, 2 H, methylene), 0.22 (s, 6 H, methyl), 0.38–0.41 (m, 2 H, methylene), 0.59–0.62 (m, 3 H, methylene and methine), 1.74–1.75 (m, 3 H, methyl), 4.11 (m, 1 H, vinyl), 4.19 (m, 1 H, vinyl); ^{13}C NMR (75 MHz, C_6D_6) δ −1.08, 5.64, 6.67, 22.10, 22.93, 91.02, 156.30; GC–MS (70 eV) m/z (relative intensity) no parent, 156 (0.4), 155 (3.2), 141 (24), 115 (62), 97 (17), 85 (5), 76 (7), 75 (100), 73 (7), 61 (10), 59 (12), 55 (5), 47 (18), 45 (28), 43 (13).

Quantum Yields for Direct Photolyses. A jacketed aluminum cell holder and lamp enclosure was used[1,10d] with a 15-W Philips Model 93106E zinc lamp (Ealing) and a 25-mm-diameter Acton 214-B-ID interference filter (42.5% transmittance at 214 nm, 410-Å handwidth). 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 quartz cylindrical cell containing 3.0 mL of photolysate was maintained at 27 °C for *tert*-butyl alcohol as solvent and at 5 °C for the other alcohols by circulating methanol–water from a constant temperature bath. Solutions of 0.02 M silacyclopent-2-ene **9** and silacyclohex-2-ene **10** in 3.0 mL of alcohol were purged with nitrogen 45 min prior to and during the photolyses. The photolysates were diluted by an equal volume of pentane, washed once or six times with water, and dried over anhyd Na_2SO_4 prior to GC analyses. The general procedure for product analyses (vide supra) was used.

Procedure B as described by Pitts, Margerum, Taylor, and Brim[11c] was used for uranyl oxalate actinometry.[11] The only modification was a dilution prior to UV analysis of the final actinometer solution. Actinometry was performed before and after each photolysis. Average deviation of light output for the entire set of quantum yield runs was 4.8%. The quantum yields of all photoproducts are the average of pairwise runs and are collected in Table I. Details are given below.

When the quartz cylindrical cell was treated by soaking in concentrated ammonium hydroxide for 15 min, followed by washing with distilled water and methanol, and then dried, relative quantum yields for methanol adduct formation from silacyclopent-2-ene **9** were within 7.2% of the values reported under entry 1 in Table I.

Silacyclopentene 9 in Methanol as Solvent. Run 1: reactant, 0.0212 M, 0.0243 mEinsteins, product **11a**, 1.64×10^{-3} mmol, $\Phi = 0.0675$; product **13a**, 3.28×10^{-4} mmol, $\Phi = 0.0135$; product **12a**, 1.23×10^{-4} mmol, $\Phi = 0.0051$; percent conversion, 3.3%. **Run 2:** reactant, 0.0212 M, 0.0209 mEinsteins, product **11a**, 1.38×10^{-3} mmol, $\Phi = 0.0661$; product **13a**, 2.76×10^{-4} mmol, $\Phi = 0.0132$; product **12a**, 1.16×10^{-4} mmol, $\Phi = 0.0055$, percent conversion, 2.9%.

Silacyclopentene 9 in 2,2,2-Trifluoroethanol as Solvent. Run 1: reactant, 0.0197 M; 1.35×10^{-2} mEinsteins, product **11b**, 9.47×10^{-4} mmol, $\Phi = 0.0702$; product **13b**, 2.47×10^{-4} mmol, $\Phi = 0.0183$; product **12b**, 1.59×10^{-4} mmol, $\Phi = 0.0118$, percent conversion, 2.3%. **Run 2:** reactant, 0.0197 M, 0.0190 mEinsteins, product **11b**, 1.49×10^{-3} mmol, $\Phi = 0.0783$; product **13b**, 3.81×10^{-4} mmol, $\Phi = 0.0201$; product **12b**, 2.21×10^{-4} mmol, $\Phi = 0.0117$, percent conversion, 3.5%.

Silacyclopentene 9 in *tert*-Butyl Alcohol as Solvent. Run 1: reactant, 0.0229 M, 2.67×10^{-2} mEinsteins, product **11c**, 5.57×10^{-4} mmol, $\Phi = 0.0221$; product **13c**, 2.47×10^{-4} mmol, $\Phi = 0.0097$; product **12c**, 2.03×10^{-4} mmol, $\Phi = 0.0080$, percent conversion, 1.5%. **Run 2:** reactant, 0.0229 M, 2.67×10^{-2} mEinsteins, product **11c**, 5.88×10^{-4} mmol, $\Phi = 0.0220$; product **13c**, 2.55×10^{-4} mmol, $\Phi = 0.0096$; product **12c**, 2.27×10^{-4} mmol, $\Phi = 0.0085$, 1.6% conversion.

Silacyclohexene 10 in Methanol as Solvent. Run 1: reactant, 0.0187 M, 1.41×10^{-2} mEinsteins, product **17a**, 2.58×10^{-3} mmol, $\Phi = 0.1832$; product **18a**, 4.42×10^{-4} mmol, $\Phi = 0.0313$, percent conversion, 5.4%. **Run 2:** reactant, 0.0187 M, 1.41×10^{-2} mEinsteins, product **17a**, 2.39×10^{-3} mmol, $\Phi = 0.1697$; product **18a**, 4.05×10^{-4} mmol, $\Phi = 0.0287$, 5.0% conversion.

Silacyclohexene 10 in 2,2,2-Trifluoroethanol as Solvent. Run 1: reactant, 0.0144 M, 1.17×10^{-2} mEinsteins, product **17b**, 3.29×10^{-3} mmol, $\Phi = 0.2825$; product **18b**, 7.75×10^{-4} mmol, $\Phi = 0.0665$, percent conversion, 9.4%. **Run 2:** reactant, 0.0144 M, 8.91×10^{-3} mEinsteins, product **17b**, 2.31×10^{-3} mmol, $\Phi = 0.2593$; product **18b**, 5.68×10^{-4} mmol, $\Phi = 0.0637$, 6.7% conversion.

Silacyclohexene 10 in *tert*-Butyl Alcohol as Solvent. Run 1: reactant, 0.0157 M, 1.20×10^{-2} mEinsteins, product **17c**, 5.09×10^{-4} mmol, $\Phi = 0.0424$; product **18c**, 2.30×10^{-4} mmol, $\Phi = 0.0192$, percent conversions, 1.6%. **Run 2:** reactant, 0.0157 M, 1.20×10^{-2} mEinsteins, product **17c**, 5.22×10^{-4} mmol, $\Phi = 0.0426$; product **18c**, 2.79×10^{-4} mmol, $\Phi = 0.0232$, 1.7% conversion.

Preparative Toluene-Sensitized Photolysis of 1,1-Dimethylsilacyclopentene (9) and 1,1-Dimethylsilacyclohex-2-ene (10) in Methanol. Mounted in the center of a Rayonet reactor containing 16 RPR 2537 Å lamps was a Vycor filter into which a Vycor tube containing 29 mL of photolysate could be inserted. Methanol solutions of 143 mg (1.27 mmol) of silacyclopentene **9** or 150 mg (1.19 mmol) of silacyclohexene **10** which contained 0.10 mol of toluene were purged with nitrogen for 45 min and then irradiated for 7 and 3.5 h, respectively, while monitoring by GC–MS. After irradiation an equal volume of pentane was added, followed by washing three times with water and drying over anhyd Na_2SO_4. Concentration to ca. 2 mL at reduced pressure was followed by isolation of the photoproducts by preparative GC using column A (83 °C) for photolysates of **9** and column E (83 °C) for photolysates of **10**. Products **11a** and **12a** of **9** and products **17a** and **18a** of **10** were initially identified by comparison of GC–MS retention times and mass spectra, and the identities of **11a**, **17a**, and **18a** were confirmed by ^{1}H NMR spectroscopy. In the case of **9**, silyl ether **13a** was not detected as a photoproduct, as confirmed by coinjection of an authentic sample.

Quantum Yields for Toluene-Sensitized Photolyses of 1,1-Dimethylsilacyclopentene (9) and 1,1-Dimethylsilacyclohex-2-ene (10) in Methanol. Mounted in the center of a Rayonet reactor, containing eight RPR 2537 Å lamps, was a Vycor filter into which a Vycor tube containing 5.0 mL of photolysate could be inserted. Photolysates were purged with nitrogen for 30 min and then irradiated. An equal volume of pentane was added, and the photolysates were washed three times with water and dried over Na_2SO_4. Samples were analyzed by GC on column G at 55 °C for silacyclopentene **9** and at 80 °C for silacyclohexene **10**. Light output was determined by uranyl oxalate actinometry.

Silacyclopentene 9. Solutions of 0.0102 M silacyclopentene **9**, 0.851 M toluene (Aldrich), and decane internal standard in methanol (distilled from magnesium methoxide) were irradiated for 20–25 min. Only 3-butenylmethoxysilane **11a** could be quantified due to overlapping of byproducts of reaction of toluene with methanol with product **12a**. The ratio of **11a**:**12a** was thus determined by GC–MS of a separate run using selected ion monitoring and calibration of the mass spectrometer response with a known mixture. The ratio was 4.44:1 at <3% conversion. **Run 1:** 0.165 mEinsteins, product **11a**, 6.6×10^{-4} mmol, $\Phi = 0.0040$, percent conversion, 1.3%. **Run 2:** 0.132 mEinsteins, product **11a**, 6.40×10^{-4} mmol, $\Phi = 0.0045$, 1.2% conversion.

Silacyclohexene 10. Solutions of 0.0101 M silacyclohexene **10**, 0.850 M toluene (Aldrich), and undecane internal standard in methanol (distilled from Mg) were irradiated for 7–9 min. The retention times of methoxy(4-pentenyl)silane **17a** and methoxysilacyclohexane **18a** were 20 and 35 min. **Run 1:** 5.93×10^{-2} mEinsteins, product **17a**, 6.75×10^{-3} mmol, $\Phi = 0.1141$; product

18a, 1.52×10^{-3} mmol, $\Phi = 0.0257$, percent conversion, 16.4%. **Run 2**: 4.61×10^{-2} mEinsteins, product **17a**, 5.79×10^{-3} mmol, $\Phi = 0.1255$; product **18a**, 1.24×10^{-3} mmol, $\Phi = 0.0269$, 13.9% conversion. **Run 3**: 4.61×10^{-2} mEinsteins, product **17a**, 5.87×10^{-3} mmol, $\Phi = 0.1273$; product **18a**, 1.26×10^{-3} mmol, $\Phi = 0.0273$, percent conversion, 14.1%.

Direct Photolyses of 1,1-Dimethylsilacyclopent-2-ene (9) and 1,1-Dimethylsilacyclohex-2-ene (10) in Deuterated Alcohols. The direct photolyses in pure methanol-*O-d* (99.5+ atom % D) were performed as described for preparative 214-nm direct photolyses in the undeuterated solvent. The workup and product isolation were also the same as reported above. All ^{1}H and ^{2}H NMR spectra of products **11a**-*d*–**13a**-*d* of silacyclopentene **9** and products **17a**-*d* and **18a**-*d* of silacyclohexene **10** were determined with $CDCl_3$ as the solvent. Each product was found to be monodeuterated upon integration of the corresponding ^{1}H NMR spectrum. Photolyses with solutions of methanol-*O-d* in pentane were performed utilizing the same procedures, except that conversions were varied in order to assess the extent that secondary photolysis caused *E*, *Z* isomerization of silanes **11a**-*d* and **17a**-*d*.

Photolyses in 2,2,2-trifluoroethanol-d_3 (CF_3CD_2OD, Cambridge, 99 atom % D) as the solvent were performed with the sample contained in a quartz cuvette of 3-mL volume, utilizing the unfiltered output of a Hanovia 450-W medium-pressure mercury lamp. Three separate photolyses of 42.6, 41.2, and 41.1 mg of argon purged samples of silacyclopentene **9** were each taken to 20% conversion (3-h irradiation), as determined by GC analysis. Each sample was extracted with pentane, and the pentane extracts of the three runs were combined for subsequent product isolation. Photolyses performed with 2,2,2-trifluoroethanol-d_3 in pentane as the solvent utilized the same procedure as employed in preparative 214-nm direct photolyses in pure 2,2,2-trifluoroethanol (vide supra).

The ^{1,2}H NMR data are summarized in the Results, and the stereochemical outcomes are compiled in Table II. Spectral data of products are given in the supplementary material.

Synthesis of 6-Oxa-2,2-dimethyl-2-silabicyclo[3.1.0]hexane (25). A mixture of 0.70 g (6.24 mmol) of silacyclopent-2-ene **9** and 3.20 g (9.30–11.1 mmol) of 3-chloroperoxybenzoic acid (Aldrich, 50–60%) in 25 mL of dichloromethane was stirred at room temperature under nitrogen for 5 h. After filtration the filtrate was washed with 10% aqueous sodium sulfite, water, saturated aqueous $NaHCO_3$, and saturated NaCl. The solution was dried over anhyd Na_2SO_4 and concentrated by distillation. Molecular distillation of the residue gave 0.37 g (46%) of epoxide **25**, which was further purified by preparative GC on column E (112 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 3 H, methyl), 0.25 (s, 3 H, methyl), 0.28–0.52 (m, 2 H, methylene), 1.72–1.83 (m, 1 H, methylene), 2.21 (ddt, $J = 14.9, 9.1, 1.3$ Hz, 1 H, methylene), 2.45 (d, $J = 4.0$ Hz, 1 H, methine), 3.52 (dt, $J = 4.0, 1.3$ Hz, 1 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.83, −4.46, 4.80, 25.46, 47.71, 57.63; IR ($CDCl_3$) 3.34, 3.38, 3.43, 3.50, 3.51, 6.94, 7.08, 7.99, 8.20, 8.71, 8.88, 9.71, 10.35, 11.44, 11.81, 11.95 μm; GC–MS (70 eV) *m/z* (relative intensity) 128 (0.6), 127 (5), 113 (93), 111 (45), 99 (12), 87 (14), 85 (58), 75 (43), 73 (9), 72 (21), 71 (20), 69 (11), 61 (23), 59 (75), 58 (16), 55 (19), 54 (11), 53 (23), 45 (57), 44 (32), 43 (100), 42 (26), 41 (20). Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.11; H, 9.39.

Synthesis of *trans*-1,1-Dimethyl-2-deuteriosilacyclopentan-3-ol (26). The undeuterated compound was synthesized previously by a different method.[38] To 0.10 g (2.38 mmol) of lithium aluminum deuteride in 18 mL of anhyd ether was added 0.28 g (2.18 mmol) of epoxide **25** (vide supra). After stirring at room temperature under nitrogen for 3.5 h, water was slowly added and the aqueous phase was separated and extracted four times with 20 mL of ether. The combined organics were dried over anhyd Na_2SO_4 and concentrated by distillation. Molecular distillation of the residue gave 0.20 g (70% yield) of trans-deuterated silacyclopentanol **26**-*d*, which was purified by preparative GC on column E (125 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 3 H, methyl), 0.17 (s, 3 H, methyl), 0.48–0.58 (m, 1 H, methylene), 0.61 (br d, $J = 7.6$ Hz, 1 H, methylene), 0.73–0.82 (m, 1 H, methylene), 1.54–1.66 (m, 1 H, methylene), 1.78 (s, 1 H, hydroxy), 1.82–1.92 (m, 1 H, methylene), 4.16 (ddd, $J = 7.6$ Hz, 7.6 Hz, 4.2 Hz, 1 H, methine); ^{2}H NMR (46 MHz, $CDCl_3$) δ 0.65, 1.02, 4.18, ratio 1:13:2.6; GC–MS (70 eV) *m/z* (relative intensity) no parent, 132 (0.9), 131 (4.3), 130 (10), 117 (10), 103 (21), 102 (63), 98 (12), 89 (100), 86 (20), 75 (28), 60 (10), 59 (62), 58 (49), 45 (19), 43 (34).

Synthesis of *trans*-1,1-Dimethyl-2-deuterio-3-methoxysilacyclopentane (12a-*d*). A mixture of 0.08 g (3.33 mmol) of sodium hydride and 0.20 g (1.52 mmol) of trans-deuterated silacyclopentanol **26** (vide supra) and 20 mL of DME was reflux under nitrogen for 3 h, and then 0.43 g (3.03 mmol) of iodomethane was added. After 1 h of refluxing, followed by cooling, 40 mL of ether and water were added. The ether layer was separated and washed five times with 20 mL of water, dried over anhyd Na_2SO_4, and concentrated by distillation. Molecular distillation gave 0.10 g (45%) of trans-deuterated methoxysilacyclopentane **12a**-*d*, which was further purified by preparative GC on column E (109 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.11 (s, 3 H, methyl), 0.15 (s, 3 H, methyl), 0.42–0.53 (m, 1 H, methylene), 0.61 (br d, $J = 7.7$ Hz, 1 H methylene), 0.66–0.76 (m, 1 H, methylene), 1.56–1.69 (m, 1 H, methylene), 1.81–1.91 (m, 1 H, methylene), 3.29 (s, 3 H, methoxy), 3.64 (ddd, $J = 7.7, 7.7, 4.3$ Hz, 1 H, methine); ^{2}H NMR (46 MHz, $CDCl_3$) δ 0.66, 0.99, 3.66, ratio: 1:13:2.6; GC–MS (70 eV) *m/z* (relative intensity) no parent, 132 (0.8), 131 (4), 130 (10), 117 (10), 103 (21), 102 (63), 98 (11), 89 (100), 86 (21), 75 (30), 60 (13), 59 (77), 58 (56), 45 (24), 44 (13), 43 (47), 42 (11).

Synthesis of 7-Oxa-2,2-dimethyl-2-silabicyclo[4.1.0]heptane (27). The epoxide was prepared in 89% yield, bp 80–83 °C (13 mm), from 2.00 g (0.0159 mol) of silacyclohex-2-ene **10** and 8.20 g (0.0238–0.0285 mol) of 3-chloroperoxybenzoic acid (Aldrich, 50–60%) by the procedure used to prepare epoxide **25** (vide supra). Purification of epoxide **27** by preparative GC on column E (112 °C) or column F (100 °C) led to formation of a minor isomeric impurity (<2–3%) according to GC–MS analyses, although the product appeared to be NMR pure. Thus, the elemental analysis was not obtained in this case. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 3 H, methyl), 0.17 (s, 3 H, methyl), 0.21–0.32 (m, 1 H, methylene), 0.55–0.63 (m, 1 H, methylene), 1.44–1.55 (m, 1 H, methylene), 1.65–1.76 (m, 1 H, methylene), 2.04–2.11 (m, 1 H, methylene), 2.19 (d, $J = 5.1$ Hz, 1 H, methine), 3.34–3.38 (m, 1 H, methine); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.50, −3.12, 10.81, 15.09, 27.89, 46.24, 53.75; GC–MS (70 eV) *m/z* (relative intensity) no parent, 141 (0.4), 127 (6), 114 (7), 101 (6), 100 (10), 99 (100), 97 (12), 85 (7), 75 (18), 71 (11), 61 (17), 59 (31), 58 (13), 55 (15), 45 (28), 43 (44), 42 (10).

Synthesis of *trans*-1,1-Dimethyl-2-deuterio-1-silacyclohexan-3-ol (28-*d*). The trans-deuterated alcohol was prepared in 45% yield from the reaction of 0.30 g (7.15 mmol) of lithium aluminum deuteride and 0.80 g (5.62 mmol) of epoxide **27** (vide supra) in 30 mL of anhyd ether, following the procedure described above for deuterated silacyclopentanol **26**. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3 H, methyl), 0.05 (s, 3 H, methyl), 0.34 (ddd, $J = 13.7, 13.7, 5.0$ Hz, 1 H, methylene), 0.59–0.67 (m, 2 H, methylene), 1.12–1.42 (complex m, 2 H, methylene), 1.50 (s, 1 H, hydroxy), 1.87–2.00 (complex m, 2 H, methylene), 3.78 (ddd, $J = 11.4, 11.4, 3.0$ Hz, 1 H, methine); ^{2}H NMR (46 MHz, $CDCl_3$) δ 0.66, 1.20, 3.79, ratio 1:5:2.4; GC–MS (70 eV) *m/z* (relative intensity) no parent, 132 (0.5), 131 (2.6), 130 (5.3), 112 (3), 104 (3), 103 (17), 102 (33), 101 (20), 88 (3), 85 (4), 76 (10), 75 (100), 72 (39), 61 (27), 59 (16), 47 (11), 45 (29), 44 (12), 43 (24).

Synthesis of *trans*-1,1-Dimethyl-2-deuterio-3-methoxysilacyclohexane (18a-*d*). The silacyclohexyl ether **18a**-*d* was prepared in 71% yield from reaction of 0.09 g (3.75 mmol) of sodium hydride, 0.27 g (1.86 mmol) of *trans*-1,1-dimethyl-2-deuteriosilacyclohexan-3-ol (**28**-*d*) (vide supra), and 0.45 g (3.18 mmol) of iodomethane in 20 mL of DME following the procedure described above for the synthesis of trans-deuterated silacyclopentyl ether **12a**-*d*. The product was further purified by preparative GC on column E (122 °C). The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3 H, methyl), 0.05 (s, 3 H, methyl), 0.38 (ddd, $J = 14.1, 14.1, 4.8$ Hz, 1 H, methylene), 0.49–0.54 (m, 1 H, methylene), 0.58–0.66 (m, 1 H, methylene),

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3.28 (br s, 4 H, methine and methoxy); ^{2}H NMR (46 MHz, $CDCl_3$) δ 0.56, 1.24, 3.28, ratio 1:5:2.2; GC–MS (70 eV) m/z (relative intensity) no parent, 146 (0.5), 145 (3), 144 (7), 128 (3), 117 (18), 116 (29), 115 (20), 100 (10), 99 (8), 90 (10), 89 (100), 75 (24), 73 (11), 72 (60), 59 (63), 58 (12), 45 (21), 44 (13), 43 (34).

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Supplementary Material Available: Syntheses of chlorosilane reactants, dimethyl(2,2,2-trifluoroethoxy)(2-propenyl)silane, and 1,1-dimethyl-1-silacyclohexan-3-ol (**28**), oxymercuration of silacyclopentene **9** and silacyclohexene **10** in 2,2,2-trifluoroethanol, details of photolyses and spectral data for deuterated solvents, sensitized photolyses in 2,2,2-trifluoroethanol, and tables of ratios of product yields, $\%P_i$, to total yields, $\Sigma\%P_i$, for 214-nm photolyses of 1,1-dimethylsilacyclopent-2-ene (**9**) and 1,1-dimethylsilacyclohex-2-ene (**10**) in methanol, 2,2,2-trifluoroethanol, and *tert*-butyl alcohol (17 pages). Ordering information is given on any current masthead page.

Electronic Control of Face Selection in the [3,3] Sigmatropic Rearrangement of Allyl Vinyl Sulfoxides

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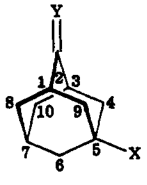
A study has been made of the thermal rearrangement of adamantylidenemethyl allyl sulfoxide **4** as well as of the racemic *RR,SS* and *RS,SR* 5-fluoro diastereomers **8** at 80 °C. The parent compound **4** initially gives a mixture of the (*E*)- and (*Z*)-sulfines **5**; the *E* product subsequently isomerizes, more slowly but completely, to the *Z* compound. Under the same conditions, mixtures of the diastereomers **8** produce mixtures of four mesoforms, two of which ((*EE*)- and (*ZE*)-**9**) subsequently rearrange further to the other two ((*EZ*)- and (*ZZ*)-**9**). The configurations of the starting materials and products were determined by NMR methods. A study of the rates of these various processes made it possible to define the compositions of the sulfine mixtures that form initially from sulfoxides **8**. The conclusion is that both a steric and an electronic effect are operating simultaneously to influence the stereochemistry. The steric effect is a response to the need to avoid axial oxygen in the pseudo-chair transition state; the electronic effect favors the formation of a CC bond antiperiplanar to the more electron-rich vicinal bonds. As was the case in the oxy-Cope reaction studied earlier, the steric effect is the larger of the two by a small margin.

Introduction

Recent studies of face selection in pericyclic reactions have strongly suggested that carbon–carbon bond formation in these processes is characterized by the same preference observed in nucleophilic addition to cations and carbonyl groups, in electrophilic attack on olefins, and in atom abstraction by radicals: approach antiperiplanar to the more electron-rich vicinal bond(s) is favored.[1] Our own contributions in this area have depended primarily on the use of 2,5-disubstituted adamantanes **1** as probes; steric equivalence of the two faces and conformational rigidity are among the advantages possessed by these molecules.



1

The oxy-Cope rearrangement was the first example of a sigmatropic shift to be examined in this fashion.[2] Both the (racemic) diastereomers (*RR*)- and (*RS*)-**2** were studied. Each gives a mixture of (*E*)- and (*Z*)-**3**, the former in the ratio of 36:64 and the latter in the ratio of 81:19, respectively. The reason for the difference in ratio is that in the former the electronically favored face (syn to the fluorine) can only be achieved in a chair transition state with a pseudoaxial phenyl group, whereas in the latter this state has the phenyl group in the pseudoequatorial position. Thus, the steric and electronic factors are opposed in the rearrangement of (*RR*)-**2**, while in (*RS*)-**2** they operate in unison. The steric factor is somewhat stronger than the electronic one in this instance.

Another sigmatropic rearrangement that drew our attention was Corey's thia-Claisen rearrangement, which appears to hold considerable promise as a way to replace a carbonyl oxygen by two carbon appendages.[3] Furthermore, a modification introduced by Block (use of sulfoxides) allows the rearrangement to be carried out under exceptionally mild conditions.[4] We therefore decided to extend our stereochemical investigations to include this reaction.

Results and Discussion

As in the oxy-Cope reactions, the racemic parent compound **4** has two pathways available for rearrangement:

[†] Stony Brook.

[‡] Buffalo.

[1] For references to our earlier work, see: Bodepudi, V. R.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2001.

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