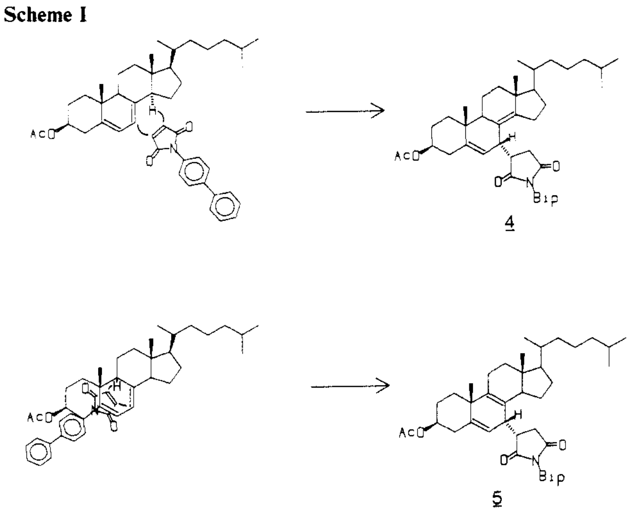
Scheme I



the two reactants are aligned with their long axes perpendicular to one another,[19] while formation of **5** requires a parallel relative orientation. Given the known ability of liquid crystals to orient dissolved solutes in a manner and to an extent that depends primarily on the structural similarities between the solute and the mesogen,[13b,20] it is expected that **1** and **2** will have preferred parallel relative orientations in the mesophase. The observed enhancement in the relative yield of **5** is proposed to result from a relative destabilization of those transition states that require considerable deviation of the reactants from their favored relative orientations in the ordered solvent. The extent to which such alterations in relative product yields will occur should depend on a number of factors, such as the extent to which the reactants themselves disrupt local solvent order, the lengths and flexibilities of the reactants, and the interplay between the ordered solvent's effects on the activation enthalpy (which should favor "parallel transition states") and entropy (which should favor "perpendicular" ones).[3d,10,11]

Given the much greater degree of order and rigidity associated with smectic B phases compared to cholesterics and nematics,[13,20] the similarity in the effects of the cholesteric and smectic (S1544) solvents on the product distribution may be surprising. This is apparently not due to poor solubility of the reactants in the smectic phase (leading to solubilization and subsequent reaction primarily in a solute-rich nematic phase),[11d] since thermal microscopic inspection of variously proportioned mixtures of **1** and S1544 (1-5 wt%) indicates uniform solubility over the entire Sm B temperature range, even at the 5 wt% level. The relatively small effect of the smectic phase on the reaction may be the result of the reactive solutes' immediate environment being somewhat disordered, which is reasonable considering the substantial differences in the structures of **1** and the smectogen.[21a] Microscopic solvation effects of this type have been proposed previously in other related studies[2,4,10,11] and are substantiated by thermodynamic data.[20e] By the same token, local solvent order in the cholesteric phases should be only slightly disrupted by the presence of **1**, so that the potential effect of this phase type on the reactivity of **1** is maximized. These factors are reflected macroscopically in the effects of solute incorporation on the transition temperatures of the pure mesogens (see Table I).

We are continuing our investigations of this system to examine the extent to which the ability of various liquid crystalline phases to control reactivity in this fashion depends on mesophase type and reactant length and flexibility.

Acknowledgment. We thank E. Merck (Darmstadt) for generous supplies of S1544 and S1409 and Dr. D. Hughes (McMaster University) for acquiring the high field NMR spectra. Financial support for this work was provided by the Research Corporation and the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for **3**, **4a**, **4b**, and **5** (9 pages). Ordering information is given on any current masthead page.

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(18) Adduct **5** has been isolated from runs in several of the cholesteric and isotropic solvents employed and has been shown to consist of only a single component by HPLC analyses under several different sets of conditions.

(19) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references cited therein. (b) Stephenson, L. M.; Mattern, D. L. *J. Org. Chem.* **1976**, *41*, 3614 and references cited therein.

(20) (a) Sackmann, E.; Krebs, P.; Rega, H. U.; Voss, J.; Mohwald, H. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 283. (b) Saeva, F. D. *Pure Appl. Chem.* **1974**, *38*, 25. (c) Luz, Z. In *Nuclear Magnetic Resonance of Liquid Crystals*; NATO ASI Series, Ser. C, Emsley, J. W., Ed.; D. Reidel Publishing Co.: Dordrecht, 1985; Vol. 141, Chapter 13. (d) Meirovitch, E.; Freed, J. H. *J. Phys. Chem.* **1984**, *88*, 4995 and references cited therein. (e) Martire, D. E. In *The Molecular Physics of Liquid Crystals*; Gray, G. W., Luckhurst, G. R., Eds.; Academic Press: New York, 1979; Chapter 11, and references cited therein.

(21) (a) Alternatively, the result may indicate that reaction of **1** and **2** takes place primarily in the relatively fluid, interlayer region of the smectic phase, as has been suggested previously to explain the behavior of other probe molecules in Sm B phases,[3e,8,21b,c] although we have no real evidence to support this suggestion. (b) Lin, W.; Freed, J. H. *J. Phys. Chem.* **1979**, *83*, 379. (c) Meirovitch, E.; Ignere, D.; Ignere, E.; Moro, G.; Freed, J. H. *J. Chem. Phys.* **1982**, *77*, 3915.

Radical Intermediates in the Epoxidation of Alkenes by Cytochrome P-450 Model Systems. The Design of a Hypersensitive Radical Probe

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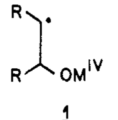
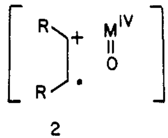
Received August 28, 1987

The cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) has been used as a trap for radical intermediates in enzymic[1] and nonenzymic[2] reactions. Radical and cationic intermediates proposed[3] for the epoxidation of alkenes by metalloporphyrin model and cytochrome P-450 systems are



1



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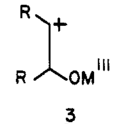

3

We report preliminary observations on the use of the *trans*-2,-*trans*-3-diphenylcyclopropyl substituent as a trap for intermediates **1** and **2**. The synthetic procedures for preparing compounds **4-Z**, **4-E**, **5-t**, **5-c**, **6**, **8**, and **9** required for this study, along with full structural characterizations (elemental analysis, mass spectroscopy, H^1 NMR and FT-IR) will be given in the full report.

Epoxidation of **4-Z** with $(\mathrm{F_{20}TPP})\mathrm{Fe^{III}(Cl)}$[4] and $\mathrm{C_6F_5IO}$ ($\mathrm{CH_2Cl_2}$ solvent, under $\mathrm{N_2}$) provided **5-c** in 92–95% yield based on reacted **4-Z**. Neither **4-E** nor **5-t** are present as $\geq$0.1% (detection limit) of the reaction products. These stereoisomerization products would result from carbon–carbon bond rotation in **1**, **2**,

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(1) For recent examples, see: (a) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 3415. (b) Silverman, R. B.; Zieske, P. A. *Biochemistry* **1985**, *24*, 2128. (c) Fitzpatrick, P. F.; Villafranca, J. J. *J. Am. Chem. Soc.* **1985**, *107*, 5022. (d) Guengerich, F. P.; Willard, R. J.; Shea, J. P.; Richards, L. E.; Macdonald, T. L. *Ibid.* **1984**, *106*, 6446. (e) Wollowitz, S.; Halpern, J. *Ibid.* **1984**, *106*, 8319. (f) van Niel, J. C. G.; Pandit, U. K. *J. Chem. Soc., Chem. Commun.* **1983**, 149.

(2) For examples, see: (a) McCormick, J. P.; Fitterman, A. S.; Barton, D. L. *J. Org. Chem.* **1981**, *46*, 4708. (b) House, H. O.; Week, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2778. (c) Dauben, W. G.; Wolf, R. E. *J. Org. Chem.* **1969**, *34*, 374. (d) Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 4892. (e) Daubin, W. G.; Deviny, E. J. *J. Am. Chem. Soc.* **1966**, *31*, 3794.

(3) (a) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770. (b) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9. (c) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375.

(4) The abbreviation $(\mathrm{F_{20}TPP})\mathrm{Fe^{III}(Cl)}$ is for 5,10,15,20-*meso*-tetrakis(pentafluorophenyl)porphinatoiron(III) chloride.

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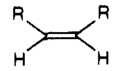
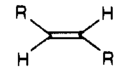
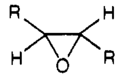


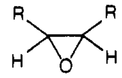
4-Z



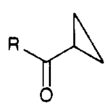
4-E



5-t



5-c



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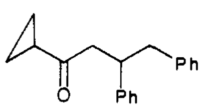

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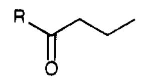

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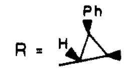
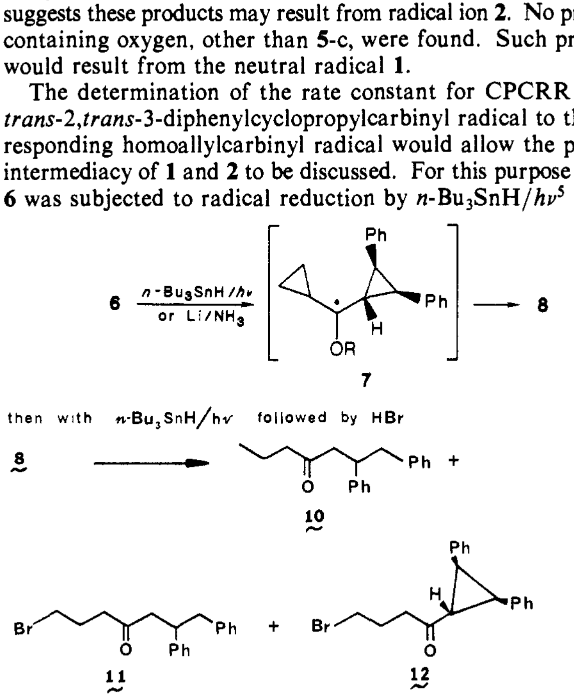


or 3. The remaining 5–8% of products were found as very nonpolar components. Preliminary evidence based on mass spectral data suggests these products may result from radical ion **2**. No products containing oxygen, other than **5-c**, were found. Such products would result from the neutral radical **1**.

The determination of the rate constant for CPCRR of the *trans*-2,*trans*-3-diphenylcyclopropylcarbinyl radical to the corresponding homoallylcarbinyl radical would allow the possible intermediacy of **1** and **2** to be discussed. For this purpose ketone **6** was subjected to radical reduction by n-Bu$_3$SnH/$h\nu$[5] (eq 1).



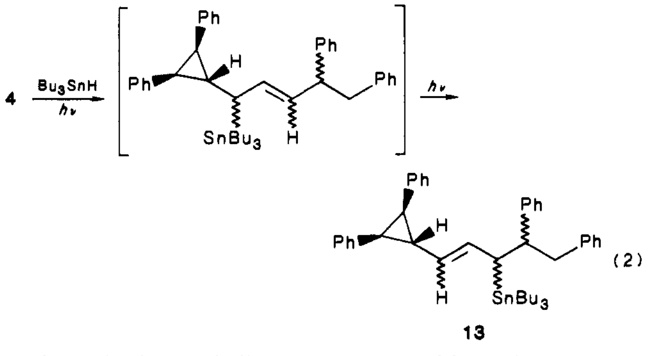
(1)

Radical **7** may either undergo a secondary to primary or a secondary to secondary benzylic CPCRR. The products after HBr(g) workup were identified by ^{1}H NMR, IR, and mass spectroscopy. Ketones **11** and **12** result from HBr cleavage[6] of **8** and **6**, respectively. Ketone **8** results from the secondary to secondary benzylic CPCRR in **7**, while ketone **10** results from further reduction of **8**. Evidence will be presented in the full manuscript showing that **10** does not arise from **9**. The possibility that **9** had also undergone HBr cleavage and was responsible for the 4% of reaction products which could not be identified was investigated by subjecting an authentic sample of **9** to the workup conditions. HPLC analysis showed no reaction products (0.1% detection limit) and complete recovery of **9**.

The inability to detect products (0.1% detection limit) resulting from the secondary to primary CPCRR of the unsubstituted cyclopropyl ring in **7** indicates the rate constant for the secondary to secondary benzylic radical rearrangement is at least 10^3 times greater than for the secondary to primary radical rearrangement. The rate constant for a secondary to primary CPCRR is $\sim 2 \times 10^7$ s^{-1} at 30°.[8] Since the rate constant for the secondary to secondary benzylic radical rearrangement of **7** is 10^3 times greater than for rearrangement of a secondary to primary radical, then the rate constant for trapping of a secondary radical by an adjacent *trans*-2,*trans*-3-diphenylcyclopropyl substituent is $\sim 2 \times 10^{10}$ s^{-1}.

Computer graphics construction[9] of the diphenylcyclopropyl moiety in **4-Z** using X-ray coordinants for the cyclopropyl ring[10] shows that the two phenyl rings are parallel to each other and bisect the plane defined by the carbon atoms of the cyclopropyl ring. Thus, the phenyl substituents are not in resonance with the cyclopropyl ring bonds and will only be acting as electron withdrawing groups. Therefore, the dominant effect of the phenyl substituents in the reactant ground state may result from van der Waals repulsion between the phenyl rings at the C-1′ atoms. Another important effect upon the rate constants of CPCRR is the thermodynamic stability of the product ground state. Thus, the rate constant for CPCRR of primary to secondary radicals is nearly 10-fold less than the CPCRR for secondary to secondary radicals.[7] Consideration of the bond strength energies for homolytic formation of primary alkyl and secondary benzyl radicals shows a 15 kcal mol^{-1} difference.[11] This will be reflected in the transition state energies for CPCRR. A value of 4.2 kcal mol^{-1} for $\Delta\Delta G^{\ddagger}$ is required for the observed 10^3-fold increase in the rate constant for the CPCRR brought about by *trans*-2,*trans*-3-diphenyl substitution.

Radical reduction of **4** (eq 2) with n-Bu$_3$SnH/$h\nu$ provides two tin adducts (4:1 ratio). ^{1}H homonuclear decoupling experiments on the major isomer indicate a structure with one intact *trans*-2,*trans*-3-diphenylcyclopropyl ring attached to a vinyl system. The other cyclopropyl ring had rearranged to give a 1,2-diphenylethyl group which is now isolated from the cyclopropylvinyl system. On the basis of these observations, the product from radical reduction of **4** is **13**.[12] This experiment establishes that a cyclopropylcarbinyl radical generated from **4** readily undergoes the CPCRR.



13

(2)

Oxidation of **4-Z** by the metalloporphyrin model system does not result in the formation of products attributable to **1** (detection limit 0.1%). Consequently, if **1** were formed its rate of conversion to epoxide is required to be $>10^{12}$ s^{-1}. Such a rate constant would exclude **1** as a discreet intermediate. If one assumes that the 5–8% of the nonpolar products arise exclusively from **2** and that **2** is an intermediate to epoxidation which is trapped with a rate constant of 2×10^{10} s^{-1}, then the rate constant for collapse of the intimate pair [**2** + (F$_{20}$TPP)Fe$^{\mathrm{IV}}$(O)] to epoxide (**5-c**) + (F$_{20}$TPP)Fe$^{\mathrm{III}}$(X) would equal $\sim 2 \times 10^{11}$ s^{-1}. However, the 2×10^{10} s^{-1} rate constant for trapping of **2** would only apply if resonance interaction between the ($\bullet$) and (+) centers is unimportant. Conjugation of the ($\bullet$) and (+) centers with the diphenylcyclo-

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[5] (a) Mariano, P. S.; Bay, E. *J. Org. Chem.* **1980**, *45*, 1763. (b) Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc, Perkin Trans. 2* **1979**, 589. (c) Davies, A. G.; Muggleton, B.; Godet, J.-Y.; Pereyre, M.; Pommier, J.-C. *Ibid.* **1976**, 1719. (d) Ratier, M.; Pereyre, M.; Davies, A. G.; Sutcliff, R. *Ibid.* **1984**, 1907.

[6] For a review of electrophillic addition to cyclopropanes, see: De Puy, C. H. *Top. Curr. Chem.* **1973**, *40*, 73.

[7] (a) Matthew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981. (b) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc, Perkin Trans. 2* **1980**, 1473. (c) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (d) Carlsson, D. J.; Ingold, K. U. *Ibid.* **1968**, *90*, 7047.

[8] Ref. 7b reports the rate constant for a secondary to primary radical rearrangement to be 7×10^6 s^{-1} at 0 °C. From the temperature dependence found in ref 7a we may expect this rate to be 2×10^7 s^{-1} at 30 °C.

[9] Computer graphics and calculations carried out with the Tripose Co. software package SYBIL.

[10] Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta. Crystallogr.* **1964**, *17*, 538.

[11] Calculated from thermochemical data given in the following: (a) Benson, S. W.; et al. *Chem. Rev.* **1969**, *69*, 279. (b) O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: NY, 1973; Vol. II, pp 338–340.

[12] For examples of allylic rearrangements of allyltins, see: (a) Gambaro, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1981**, *210*, 57. (b) Matarasso-Tchiroukhine, E.; Cadiot, P. *Ibid.* **1976**, *121*, 169.

propyl substituents would ensure this by disrupting the resonance stabilization between these centers. This effect should be similar for *cis*-stilbene, wherein epoxidation by the same system studied here provides products (*trans*-stilbene and *trans*-stilbene oxide[13]) which can be attributed to the formation of a radical cation. One e$^-$ oxidation of alkene to provide a radical ion may, of course, be independent of the mechanism of epoxidation.

Acknowledgment. A.J.C. expresses gratitude to the National Institutes of Health for a National Research Service Award (GM 11623-01), and T.C.B. gratefully acknowledges the support of this work by the National Institutes of Health.

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(13) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.

Silacyclobutadienes: The Generation of 1-Mesityl-2,3,4-tri-*tert*-butyl-1-silacyclobutadiene

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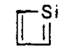
Received August 26, 1987

Silacyclobutadiene (I) bears close formal resemblance to the well-studied antiaromatic molecule cyclobutadiene (II). Molecular orbital calculations[1] indicate that the singlet ground state of silacyclobutadiene is planar with alternate Si=C and C=C bonds. A large antiaromatic destabilization energy, presumably due to the combined effects of cyclic π delocalization and angle strain, is calculated for this molecule. An excited triplet state is also predicted to be only 5 kcal/mol above the singlet ground state.[1b]



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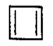
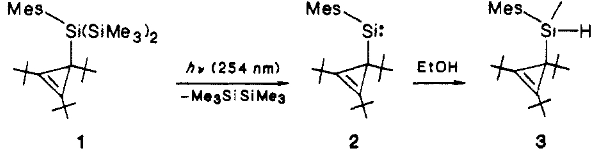


II

In spite of theoretical interest in silacyclobutadiene, there is little experimental data for its generation.[2] Attempts to observe the formation of silacyclobutadienes through the thermal rearrangements of cyclopropenylsilylenes in solution have been shown to be unsuccessful[3] despite similar known rearrangements of cyclopropenyl carbenes[4] and nitrenes.[5] However, we have recently observed a *photochemical* rearrangement of a cyclopropenylsilylene to give a silacyclobutadiene in hydrocarbon glass at 77 K. We report herein the generation of a silacyclobutadiene and reaction with two chemical trapping reagents.

The 254-nm photolysis of 2-mesityl-2-(1,2,3-tri-*tert*-butylcyclopropenyl)hexamethyltrisilane (**1**) in a 3-MP glass gives mesityl(1,2,3-tri-*tert*-butylcyclopropenyl)silylene (**2**) which is a yellow species with λ_{max} = 450 nm.[6] If the glass contains ethanol, annealing results in the loss of the yellow color and the formation of the silylene trapped product, mesityl(1,2,3-tri-*tert*-butylcyclopropenyl)ethoxysilane (**3**). Compound **3** is also observed in the solution photolysis of **1** in ethanolic hexane.[3]



1 **2** **3**

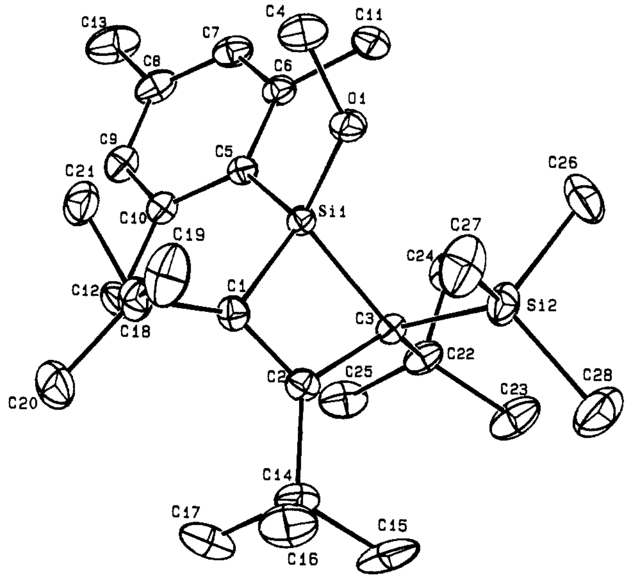


Figure 1. ORTEP diagram of **5** showing all non-hydrogen atoms (25% thermal ellipsoids). Selected bond lengths (angstroms) and angles (deg), errors in last digit shown in parentheses. Lengths: Si1-O1, 1.638 (2); Si1-C1, 1.837 (3); Si1-C3, 1.928 (3); C1-C2, 1.367 (4); C2-C3, 1.599 (4); Si2-C3, 1.933 (3). Angles: C1-Si1-C3, 78.6 (3); C1-C2-C3, 106.9 (2); Si1-C1-C2, 91.7 (2); Si1-C3-C2, 81.8 (2).

Irradiation of **2** in 3-MP at 77 K with visible light results in the loss of the silylene absorption bands and the formation of a new species with absorption bands at 278 nm, 328 nm (unresolved), and 400 nm (weak). Subsequent warming of the glass to room temperature results in the loss of these bands.

Trapping of the "278-nm" intermediate was accomplished by using either methoxytrimethylsilane or ethanol as trapping reagents. A typical trapping experiment was performed by using a 3-MP glass containing approximately 30 mg of the starting trisilane, a 20-fold excess of trapping reagent, and 10 mL of 3-MP. The glass was irradiated at 254 nm until a distinct yellow color appeared. The yellow glass was further irradiated with a visible source ($\lambda > 400$ nm) until most of the yellow color disappeared. The glass was subsequently allowed to warm to room temperature. This process was repeated for 20-25 cycles in order to achieve >95% conversion of the trisilane precursor. If methoxytrimethylsilane is used as a trapping reagent, only one diastereomer of 1-mesityl-1-methoxy-2,3,4-tri-*tert*-butylsilacyclobutene (**5**) is obtained in 72% yield.[7] An X-ray crystal structure of the adduct[8] is consistent with a syn addition of the methoxysilane across the carbon-silicon double bond of 1-mesityl-2,3,4-tri-*tert*-butyl-1-silacyclobutadiene (**4**). An ORTEP diagram of the adduct **5** with relevant bond lengths and angles is shown in Figure 1.

If the photolysis is carried out with ethanol copresent in the glass, two stable diastereomers of 1-ethoxy-1-mesityl-2,3,4-tri-*tert*-butyl-1-silacyclobutene, **6a** and **6b**, are formed in 35% and 30% yields, respectively. These products most likely arise from the addition of ethanol across the silicon-carbon double bond of

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(1) (a) Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1980**, 1131-1132. (b) Colvin, M. E.; Schaefer, H., III. *Faraday Sym. Chem. Soc.* **1984**, *19*, 39-48. (c) Schriver, G. W.; Fink, M. J.; Gordon, M. S. *Organometallics* **1987**, *6*, 1977-1984.

(2) (a) Gentle, T. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 304-305. (b) First proposal for the possibility of a cyclopropenylsilylene to silacyclobutadiene rearrangement. Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. Am. Chem. Soc.* **1982**, *104*, 1149-1150.

(3) Fink, M. J.; Puranik, D. *Organometallics* **1987**, *6*, 1809-1811.

(4) For a summary of routes to cyclobutadienes, see: (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 425-490. (b) Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343-370. (c) Maier, G. *Pure Appl. Chem.* **1986**, *58*, 95-104.

(5) Vogelbacher, U.-J.; Regitz, M.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842-843.

(6) The silylene absorption band at 450 nm is presumably a silicon centered n → p transition: Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Comm.* **1985**, 1048.

(7) All new compounds are consistent with spectroscopic data.

(8) Crystal data: dimensions, 0.20 × 0.13 × 0.46 mm; crystal system, monoclinic; space group, $P2_1/c$; a = 10.843 (1) Å, b = 16.334 (7) Å, c = 16.113 (6) Å, β = 98.19 (6); z = 4; absorption coefficient = 1.40 cm^{-1}; Mo Kα radiation with graphite monochromator; scan range 2θ = 0-52°; 5474 unique reflections with 3676 $\geq 3\sigma(I)$. Structure solution was obtained by direct methods and refined to convergence with full-matrix least-squares; R = 5.2, R_w = 5.4.