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.

(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

Mark J. Fink,* Dhananjay B. Puranik, and M. Pontier Johnson

Department of Chemistry, Tulane University New Orleans, Louisiana 70118

Received August 26, 1987

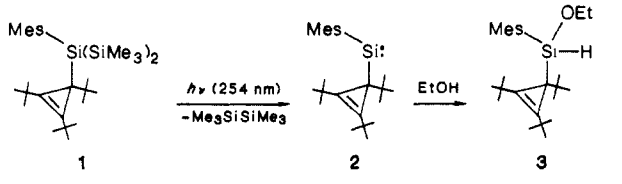
Silacyclobutadiene (I) bears close formal resemblance to the well-studied antiaromatic molecule cyclobutadiene (II). Mo-

I II

lecular 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]

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



1 2 3

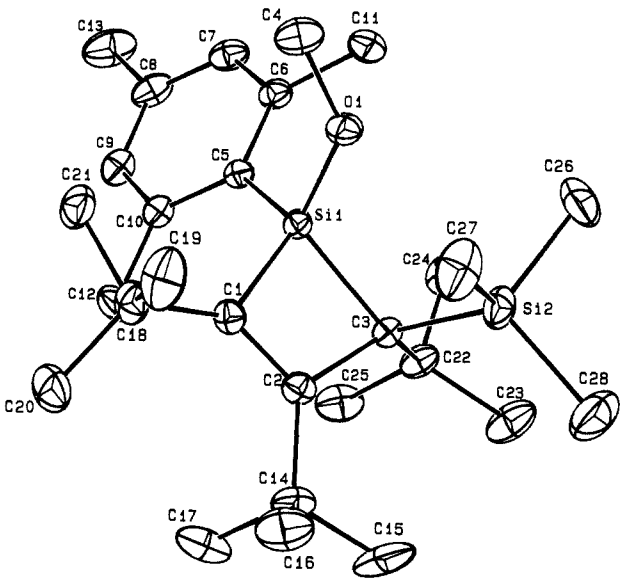


Figure 1. ORTEP diagram of **5** showing all non-hydrogen atoms (25% thermal ellipsoids). Selected bond lengths (angstroms) and angles (deg), errors in last digit shown in parentheses. Lengths: Si1–O1, 1.638 (2); Si1–C1, 1.837 (3); Si1–C3, 1.928 (3); C1–C2, 1.367 (4); C2–C3, 1.599 (4); Si2–C3, 1.933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

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]

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

(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.

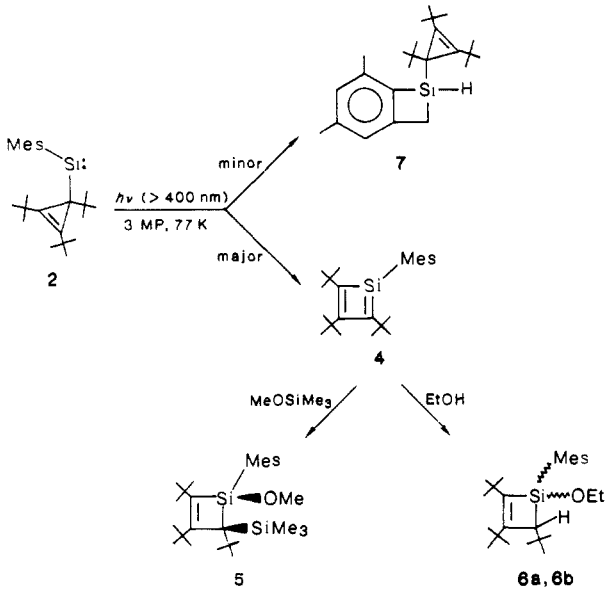
(6) The silylene absorption band at 450 nm is presumably a silicon centered n → p transition: Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Comm.* **1985**, 1048.

(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.

0002-7863/88/1510-1315$01.50/0

Scheme I. Generation and Trapping of Silacyclobutadiene 4



Mes = mesityl; 2,4,6-trimethylphenyl

the silacyclobutadiene. The trapping experiments are summarized in Scheme I.

Also formed in each of the photolyses are smaller amounts (9%) of the benzosilacyclobutene **7**.[9] This compound likely arises from the photochemical insertion of the silylene **2** into a carbon–hydrogen bond of an ortho mesityl methyl group. An additional product from the ethanol trapping experiment is compound **3** (19%), the trapping product of the silylene **2** with ethanol.

The addition of methoxytrimethylsilane across the silicon–carbon double bond of the silacyclobutadiene is a completely stereospecific syn addition. This result is in good accord with reports by Jones on syn additions of this reagent (as well as methanol) to simpler acyclic silenes.[10] The formation of two diastereomers in our ethanol trapping experiments is explainable by photoisomerization of an initially formed diastereomer. Trapping of the silacyclobutadiene after only *one* cycle of photolysis gives only one diastereomer, **6a**, which is probably the syn addition product.

Further evidence for the photoisomerization of **6a** is found in the independent photolysis of either **6a** or **6b** in 3-MP glass at 77 K, followed by warming to room temperature. Photolysis of either pure diastereomer gives a photostationary mixture of **6a** and **6b** in approximately 1.2:1 ratio. The mechanism of photoisomerization is likely a concerted photochemical disrotatory ring opening to give a silabutadiene intermediate. A subsequent thermal conrotatory ring closure would be expected to produce the alternate stereoisomer. Interconversions of silacyclobutenes to silabutadienes have been suggested for several other systems.[11]

Finally, the silacyclobutadiene is not stable in solution despite the presence of sterically protecting groups. Annealing of a 3-MP glass containing **4** results in the loss of the silacyclobutadiene absorption bands and the generation of a stable dimeric product. The identity of this dimer is currently being investigated.

Acknowledgment. We thank the Tulane University Committee on Research and the Louisiana Board of Regents for support of this project.

(9) Also observed in each of the photolyses is another isomeric species with MW = 354, formed in approximately 5% yield. Attempts to purify this compound by preparative GC and HPLC have been currently unsuccessful.

(10) (a) Jones, P. R.; Bates, T. F.; Cowley, A. F.; Arif, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 3123–3124. (b) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913–914.

(11) (a) Valkovich, P. B.; Weber, W. P. *Tetrahedron. Lett.* **1975**, 2153–2154. (b) Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 1630–1632. (c) Tzeng, D.; Fong, R. H.; Soysa, H. S. D.; Weber, W. P. *J. Organomet. Chem.* **1981**, *219*, 153–161. (d) Conlin, R.; Namavari, M. 8th International Organosilicon Symposium, St. Louis, MO, June 1987.

Supplementary Material Available: Spectroscopic data for all new compounds, UV spectra, and tables of atomic coordinates with bond lengths and angles, positional parameters, anisotropic displacement parameters, and least-squares planes (16 pages); table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

A Heteroaromatic Trimethylenemethane

F. Wudl,* G. Srdanov, B. Rosenau, D. Wellman, K. Williams, and S. D. Cox

Institute for Polymers and Organic Solids
Department of Physics, University of California
Santa Barbara, California 93106

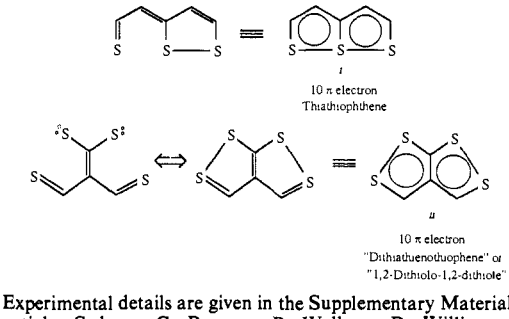
Received October 23, 1987

Trimethylenemethane and its two types of relatives, tetramethyleneethane and the non-Kekulé hydrocarbons, have been the subject of recent interest.[1-3] At the same time, the thiathiophthenes have also been of interest, particularly regarding unusual sulfur bonding.[4,5] In this communication we report on a novel sulfocarbon **1** which we found to be a trimethylenemethane embedded in a "pseudo-1,2-dithiolo-1,2-dithiole",[6] $(4n + 2)$ π-electron, milieu. A three-step synthesis of **1** is shown in Scheme I, below.[7]

Compound A was prepared as reported;[8] its conversion to B was possible only under basic conditions by suspension of A in aqueous base, followed by addition of a small amount of methanol to "wet" the solid.[6] The thionating reagent was prepared in situ from P_4S_{10} as described in the literature.[9] Thionation occurred cleanly only on the acid B and not the ester A.

The title compound forms small, air-stable orange (by transmission, purple by reflection) needles.[10] In solution the compound is orange [λ_{max}[CH_2Cl_2, nm (ϵ)] 251.5 (10280), 285.4 (18710), 305 sh (9890), 334.8 (13960), 351.1 (12990), 386.7 (7690), 415 sh (7950), 431.4 (9170) and 480 sh (2830)]. In the solid state, there are two bands at 350 and 440 as well as a shoulder at ca. 550 nm. The latter extends to the near-IR, indicative of solid-state intermolecular interactions. Since the usual spectroscopic structure determination techniques, particularly NMR,[11] were of little help, we resorted to X-ray crystallography. The structure presented some difficulty in its solution due to the relatively large unit cell[9] (16 molecules) with four distinct molecules per asymmetric unit

(1) Dowd, P. *J. Am. Chem. Soc.* **1987**, *109*, 5284 and references therein.
(2) Pranata, J.; Dogherty, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 1621.
(3) Berson, J. E. *Acc. Chem. Res.* **1978**, *11*, 446.
(4) Hansen, L. K.; Hordvik, A. *Acta Chem. Scand.* **1973**, *27*, 411.
(5) Hansen, L. K.; Hordvik, A. *J. Chem. Soc., Chem. Commun.* **1974**, 800. Brown, J. P.; Gay, T. B. *J. Chem. Soc., Perkin Trans. 1* **1974**, 866.
(6) A referee pointed this out as follows where our molecule is of type ii:



(7) Experimental details are given in the Supplementary Material, see end of this article: Srdanov, G.; Rosenau, B.; Wellman, D.; Williams, K.; Cox, S. D.; Wudl, F. Report in preliminary form at the first International Heteroatom Conference, Kobe, Japan, July, 1987.
(8) Jensen, K. A.; Henriksen, L. *Acta Chem. Scand.* **1968**, *22*, 1107.
(9) Davy, H. *J. Chem. Soc., Chem. Commun.* **1982**, 457.
(10) $C_6H_4S_6$: M = 268.48; monoclinic space group $P2_1/n$; a = 8.446 (1) Å, b = 26.530 (3) Å, c = 17.981 (2) Å, β = 101.24 (5)°, V = 3952 (5) Å^3, z = 16; μ = 12.72 cm^{-1}; D_c = 1.80 g cm^{-3}, D_o = 1.79 g cm^{-3}; T = 298 K; λ(Mo K_α) = 0.71069 Å; R_w = 6.4% for 2070 unique observed reflections.
(11) ^{1}H NMR ($CDCl_3$, δ rel to TMS) 3.5 s; ^{13}C NMR ($CDCl_3$, δ rel to TMS) 36.108, 140.129, 195.627, 211.489.

0002-7863/88/1510-1316$01.50/0