chemistry problem in styrene–quinone additions directed at the oxygenated 1,4,10-phenanthrene system required for the polycyclic xanthones.

Naphthalenes of general structure **2**, in which the eventual "elbow bend" is implicit in the 1,2,5,8-substitution pattern, might be elaborated to phenanthrenes with the desired oxygenation pattern. Naphthalenes **2** are themselves, formally, the Diels–Alder products of styrenes **4** and diethyl acetylenedicarboxylate (**3a**) or diethyl allenedicarboxylate (**3b**). Not surprisingly,[9] attempts to effect these condensations led to complex mixtures.

2a R=CH$_2$CO$_2$Et, X=Br	
2b R=CH$_2$CO$_2$Et, X=H	**4a** X=H
2c R=CO$_2$Et, X=Br	**4b** X=Br
2d R=CO$_2$Et, X=H	
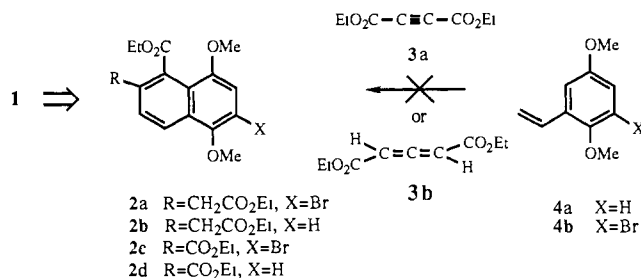
Consideration of the reactivity problems inherent in a styrene diene led us to attempt the preparation and Diels–Alder reactions of the synthetically equivalent but nonaromatic vinylquinone bis-ketals. The results of these studies and selected transformations of the adducts are summarized in Table I.

The facile electrochemical procedure developed by Swenton[10] was found to effect the oxidation of 2,5-dimethoxystyrene to diene substrate **5** in 91% yield. Likewise, the electrochemical oxidation of bromostyrene **4b** afforded the substituted vinylquinone bis-ketal **10** in 63% yield.

Heating a mixture of diene **5** and diethyl acetylenedicarboxylate (**3a**) in benzene in a sealed tube afforded a high yield of the remarkably stable adduct **6**.[11] Acid-catalyzed aromatization gave the substituted naphthalene dicarboxylic ester **2d** (54% from **5**).[12]

Under similar conditions, diene **5** added to diethyl allenedicarboxylate (**3b**) to give a mixture which contained partially aromatized material; treatment of this mixture with anhydrous toluenesulfonic acid completed the aromatization, affording diester **2b** (48% from **5**). The expected regiochemistry of the Diels–Alder reaction of **5** with **3b** was supported by nuclear Overhauser difference experiments on **2b**: irradiation of the C-3 proton (7.44 ppm) resulted in enhancement of the methylene signal (AB at 3.75 and 3.76 ppm); irradiation at 3.78 or at 3.71 ppm resulted in enhancement of the signal at 7.44 ppm. Additional confirmation of the substitution pattern in **2b** was obtained by a long-range heteronuclear cosy experiment[13] in which three-bond proton-carbon couplings between the C-3 aromatic proton and the benzylic methylene carbon and also between the benzylic protons and the C-3 aromatic carbon were observed.[14]

Condensation of vinylquinone acetal **5** with monounsaturated dienophiles gave adducts which could be isolated and characterized or converted to dihydronaphthalenes. For example, diene **5** added to *N*-methylphthalimide to give the stable Diels–Alder adduct in 76% yield (see Supplementary Material for details). Treatment of this adduct with toluenesulfonic acid effected its conversion to the 1,2-dihydronaphthalene-1,2-dicarboxylic acid derivative **7**.

Adducts derived from monounsaturated dienophiles could also be converted to naphthalenes. Thus, the crude reaction mixture

from diene **5** and fumaronitrile was subjected to oxidative aromatization (TsOH, PtO$_2$) to afford naphthalene 1,2-dicarbonitrile **8**. Similarly, the mixture obtained from the reaction of diene **5** and naphthoquinone was converted to benzanthracenedione **9**.

We considered naphthalene **2a**, functionalized on both rings of the naphthalene, to be a particularly desirable intermediate for regiospecific elaboration to the cervinomycins and to other nonlinear polyketides. Condensation of diene **10** with allene dicarboxylate **3b** gave naphthalene **2a** directly in 37% yield.

Although these Diels–Alder/aromatization procedures proceed in modest overall yield, they are easily performed, and they provide valuable synthetic intermediates which are essentially inaccessible by other methods. The elaboration of these intermediates and the exploration of other strategies for the preparation of nonlinear polyketides are the subjects of further study.

Supplementary Material Available: Description of experimental procedures including spectroscopic data (^{1}H NMR, ^{13}C NMR, IR, and HRMS) and a heteronuclear COSY plot (8 pages). Ordering information is given on any current masthead page.

2,4,6-Tri-*tert*-butylselenobenzaldehyde, the First Stable Selenoaldehyde

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Received March 6, 1989

In recent years much attention has been paid to the chemistry of multiple bond compounds containing heavier typical elements.[1] Some years ago we reported the isolation of the first stable aromatic[2] and aliphatic[3] thioaldehydes.[4] Since selenocarbonyl compounds are much less stable than thiocarbonyl compounds,[1i–k] selenoaldehydes have eluded isolation so far, although some heterocyclic selenoaldehydes stabilized by mesomeric effect of heteroatoms such as nitrogen and sulfur have been synthesized.[5]

(9) Low yields of 1:1 adducts have been obtained for β-substituted styrenes with maleates and with diethyl acetylenedicarboxylate; however, attempts to effect similar addition reactions with β-unsubstituted styrenes afforded polymeric materials. (a) Diment, J. A.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1969**, *22*, 1721. (b) Hudson, B. J. F.; Robinson, R. *J. Chem. Soc.* **1941**, *143*, 715.

(10) (a) Henton, D. R.; McCreery, R. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 369. (b) Swenton, J. S.; Jackson, D. K.; Manning, M. J.; Raynolds, P. W. *J. Am. Chem. Soc.* **1978**, *100*, 6182.

(11) All new compounds were characterized by IR, NMR, and high resolution mass spectrometry or combustion analysis.

(12) Yields represent chromatographed, homogeneous materials.

(13) Sato, Y.; Geckle, M.; Gould, S. J. *Tetrahedron Lett.* **1985**, *26*, 4019.

(14) For full NMR data, see Supplementary Material.

(1) For reviews on multiple bond compounds containing group 14–16 elements, see the following. Group 14: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (c) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (d) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. Group 15: (e) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (f) Lochschmidt, S.; Schmidtpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73. (g) Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484. Group 16: (h) Duus, F. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, pp 373–487. (i) Magnus, P. D. *Ibid.* Vol. 3, Part 12. (j) Jensen, K. A.; Kjaer, A. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1986; Vol. 1, Chapter 1. (k) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986; Chapter 3. (l) Okazaki, R. *Yuki Gosei Kagaku Kyokai Shi* **1988**, *46*, 1149.

(2) (a) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187. (b) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 849. (c) Okazaki, R.; Fukuda, N.; Oyama, H.; Inamoto, N. *Chem. Lett.* **1984**, 101.

(3) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Am. Chem. Soc.* **1987**, *109*, 279.

(4) For an aliphatic thioaldehyde stable in solution, see: Vedejs, E.; Perry, D. A.; Wilde, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2985.

(5) Reid, D. H.; Webster, R. G.; McKenzie, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2334.

Table I. Spectral Data of **1**[a]

| ^{1}H NMR, δ CDCl$_3$	^{13}C NMR, δ CDCl$_3$	^{77}Se NMR, δ CDCl$_3$	UV–vis/λ_{max}/nm(ϵ)	
			hexane	ethanol
1.35 (s, 27 H)	31.1, 32.4, 34.8	2397.7	250 (6700)	718 (28)
7.36 (s, 2 H)	37.1, 122.0, 141.6		263 sh (6400)	738 (27)
17.38 (s, 1 H, C*H*Se)	149.4, 153.0		362 (1200)	
	258.2 (CHSe)		722 (42), 758 (39)	

[a] All the spectra were measured at –20 °C under an argon atmosphere.

Scheme I[a]
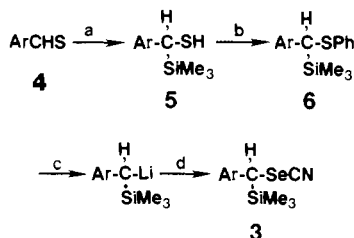
[a] (a) Me$_3$SiLi, THF–HMPA, –78 °C, 85%; (b) (i) *n*-BuLi, THF, –78 °C; (ii) PhI catalyst Pd(Ph$_3$P)$_4$, PhH reflux, 3 h, 98%; (c) lithium naphthalenide, –78 °C, 3.5 h; (d) (i) CuCN, 0 °C 80 min; (ii) (SeCN)$_2$, –78 to 0 °C, 20 h, 57%.

In contrast to the successful isolation of several selenoketones,[6] simple, electronically unperturbed selenoaldehydes have been known only as transient species[7] or complexes with transition metals.[8] We wish to delineate here the first stable selenoaldehyde, 2,4,6-tri-*tert*-butylselenobenzaldehyde (**1**), isolated by kinetic stabilization due to a bulky substituent.

We previously reported that the reaction of selenoformates with 2,4,6-tri-*tert*-butylphenyllithium, a reaction similar to that employed in the synthesis of stable thioaldehydes,[2,3] resulted in the possible formation of **1**, but it underwent rapid isomerization into
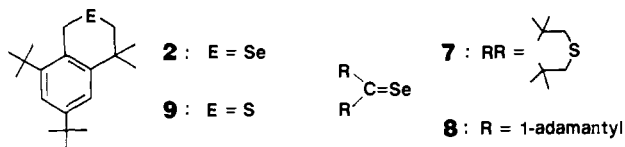
benzoselenane **2** under the reaction conditions (20–60 °C).[9] After some other disappointing experiments, we found that fluoride-induced elimination of cyanotrimethylsilane from α-silyl selenocyanates reported by Krafft and Meinke[10] was successfully applied to the synthesis of **1**.

When α-silyl selenocyanate **3**, prepared from 2,4,6-tri-*tert*-butylthiobenzaldehyde (**4**)[2] by the route depicted in Scheme I[11]
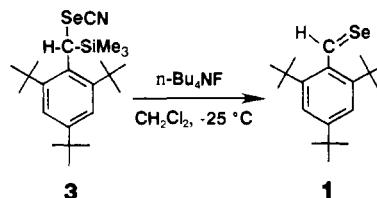
(Ar denotes 2,4,6-tri-*tert*-butylphenyl hereafter in this paper) was treated with tetrabutylammonium fluoride in dichloromethane at –25 °C, selenoaldehyde **1** was isolated in 44% yield after flash chromatography at –50 °C.[12]

The selenoaldehyde **1** is a blue crystalline compound and can be stored in a refrigerator (–15 °C) for a long time. In the solid state, it is stable in the air at room temperature at least for 7 days without any appreciable change. In solution, however, **1** is highly sensitive to oxygen even at low temperatures (–40 ~ –50 °C), leading to the rapid formation of the corresponding aldehyde. In Table I are listed the spectral data of **1** which have some interesting features. The selenoformyl proton is highly deshielded (δ 17.38) indicating a strong anisotropic effect of the C=Se bond. This is, to our knowledge, the most deshielding signal so far observed for a proton bound to neutral carbon although there have been reported some more deshielding protons for annulenyl anions.[13] This signal occurs at considerably lower field than those (δ 12–13) of electronically stabilized heterocyclic selenoaldehydes,[6] suggesting that **1** has "the purest selenocarbonyl nature" among selenoformyl compounds isolated so far. The ^{77}Se NMR shift of **1** (δ 2398) is also unique in that it is more deshielding than those for **7** (δ 2135)[14] and **8** (δ 2134)[15] which exhibit the most deshielding ^{77}Se signals so far known.

Although a degassed benzene solution of **1** is quite stable at room temperature, the blue color of the solution gradually fades away upon heating at 70 °C, resulting in the quantitative formation of benzoselenane **2** after 50 h. This suggests that **1** is thermally far more labile than thiobenzaldehyde **4**, since **4** can be recovered unchanged after 2 weeks of refluxing in degassed benzene[2a] and a similar isomerization into benzothiane **9** needs heating around 200 °C (14 h).[2b] Photolysis of **1** (THF, 100 W high pressure Hg lamp, –30 °C, 2 h) also affords **9** (52%).

Reaction of **1** with organolithiums (RLi) gave three types of products **10–12** depending on R (R = Me, **10** 52%, **12** 12%; R

(6) (a) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079. (b) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104. (c) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1429. (d) Guziec, F. S., Jr.; Moustakis, C. A. *J. Org. Chem.* **1984**, *49*, 189. (e) Guziec, F. S., Jr.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843. (f) Ishii, A.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 861.

(7) Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8671. Segi, M.; Nakajima, S.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976. Erker, G.; Hock, R.; Notle, R. *J. Am. Chem. Soc.* **1988**, *110*, 624. Nakayama, J.; Akimoto, K.; Hoshino, M. *J. Phys. Org. Chem.* **1988**, *1*, 53. Nakayama, J.; Sugihara, Y. *J. Phys. Org. Chem.* **1988**, *1*, 59. Nakayama, J.; Akimoto, K.; Niijima, J.; Hoshino, M. *Tetrahedron Lett.* **1987**, *28*, 4423. Meinke, P. T.; Krafft, G. A. *Tetrahedron Lett.* **1987**, *28*, 5121. Okuma, K.; Sakata, Y.; Tachibana, Y.; Honda, T.; Ohta, H. *Tetrahedron Lett.* **1987**, *28*, 6649. Kirby, G. W.; Tretheway, A. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1152. Krafft, G. A.; Meinke, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 1314.

(8) Fischer, H.; Gerbing, U.; Riede, J.; Benn, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 78. Fischer, H.; Triliomis, A.; Gerbing, U.; Huber, B.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1987**, 559. Fischer, H.; Gerbing, U.; Müller, G.; Alt, H. G. *Chem. Ber.* **1987**, *120*, 1905 and references cited therein.

(9) (a) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1986**, 71. (b) Ishii, A.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2529.

(10) Krafft, G. A.; Meinke, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 1314.

(11) The final step of Scheme I was carried out by the reported method: Meinke, P. T.; Krafft, G. A.; Guram, A. *J. Org. Chem.* **1988**, *53*, 3632.
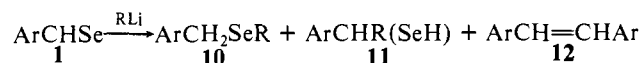
(12) A typical procedure of the synthesis of **1** follows. To a degassed dichloromethane solution (5 mL) of **3** (421 mg, 0.963 mmol) was added a cold THF solution of *n*-Bu$_4$NF (1 M THF solution, 1.16 mL) at –78 °C under an argon atmosphere. As soon as dropping was started, the color of the solution became bright blue. The reaction mixture was warmed to –25 °C and stirred for 7 min. The solvent was removed at this temperature in vacuo. The green residue was subjected to low-temperature flash chromatography (–50 °C, silica gel, pentane–dichloromethane 10:1). A blue fraction was collected, and the solvent was removed at –30 °C in vacuo to give **1** (144 mg, 44%). **1** melted at 164 °C forming a green liquid, which was gradually isomerized into colorless **2** and melted again at 181 °C, the melting point of **2**.[9a] Exact mass for C$_{19}$H$_{30}$^{80}Se: 338.1539, found 338.1542. For spectral data, see Table I.

(13) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

(14) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055.

(15) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1429.

= *t*-Bu, **10** 26%, **11** 26%; R = Ph, **10** 24%, **12** 38%).

$$\text{ArCHSe} \xrightarrow{\text{RLi}} \text{ArCH}_2\text{SeR} + \text{ArCHR(SeH)} + \text{ArCH=CHAr}$$
$$\quad\;\; \mathbf{1} \qquad\qquad\;\; \mathbf{10} \qquad\quad\;\; \mathbf{11} \qquad\qquad\;\; \mathbf{12}$$

We previously observed that the reactivity of thioaldehyde **4** toward nucleophiles such as amines was much higher than that of the corresponding aldehyde, 2,4,6-tri-*tert*-butylbenzaldehyde (**13**). Thus, the reaction of hydrazine with **4** was complete within a few minutes at 0 °C while that with **13** needed heating at 180 °C for 4 days (in diethylene glycol) in the presence of acid catalysts.[15] Selenoaldehyde **1** is even more reactive than **3**. The reaction of **1** with butylamine in toluene proceeded at 0 °C within 45 min to give ArCH=N(*n*-Bu) (43%) and (ArCH₂Se)₂ (42%), whereas, in the case of **4**, the reaction required heating at 70 °C for 1 h to afford ArCH=N(*n*-Bu) (96%).[16] Further studies on the physical and chemical properties of **1** are in progress.

Acknowledgment. The generous supply of the silyl halides from Shin-etsu Chemical Co., Ltd., is gratefully acknowledged. We also thank the Ministry of Education, Science and Culture of Japan for the financial support.

Supplementary Material Available: Spectral data and exact mass analyses of new compounds (2 pages). Ordering information is given on any current masthead page.

(16) Okazaki, R. *Nippon Kagaku Kaishi* **1987,** 1142.

The Thermal Isomerization of a Silacyclobutadiene to a Cyclopropenylsilylene: Evidence for a Stable Silylene in Fluid Solution

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The SiC₃H₄ isomer surface,[1] which includes silacyclobutadiene,[2] silatetrahedrane, and cyclopropenylsilylene,[3] offers a unique comparison of highly ring strained, low valent, and multiply bonded organosilicon species. Of particular interest are the relative energetics and transformations of these isomers. In contrast to the analogous C₄H₄ isomer surface,[4] divalent silicon species (silylenes) are shown by ab initio calculations to be either equal in energy or more stable than many of their closed shell valence partners.[1c] We now report that the photogenerated 1-(2,4,6-triisopropylphenyl)-2,3,4-tri-*tert*-butyl-1-silacyclobutadiene, **1**, undergoes a clean isomerization to the thermodynamically more stable (2,4,6-triisopropylphenyl)(1,2,3-tri-*tert*-butylcyclopropenyl)silylene (**2**) in 3-methylpentane solution. Remarkably, the silylene **2** is stable to 200 K and may be directly observed by UV spectroscopy.

The 254-nm photolysis of the trisilane **3**[5] in 3-methylpentane (3-MP) glass at 77 K gives the yellow cyclopropenylsilylene **2** (λ_{max} = 454 nm).[6] Subsequent irradiation of **2** with visible light ($\lambda \geq 400$ nm) results in loss of the 454-nm band due to **2** and the appearance of a new long wavelength absorption band at 340 nm

(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) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988,** *110,* 1315–1316.
(3) Fink, M. J.; Puranik, D. B. *Organometallics* **1987,** *6,* 1809–1811.
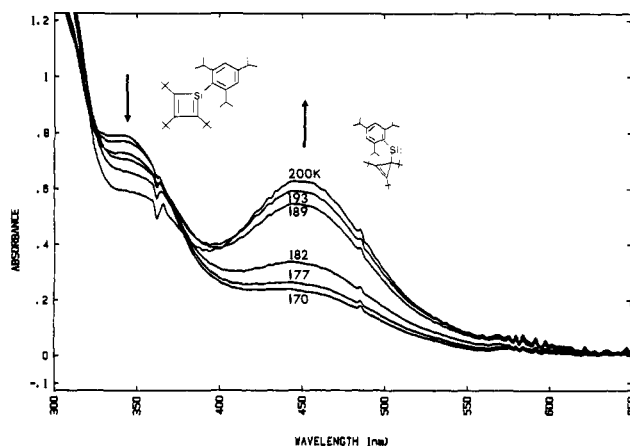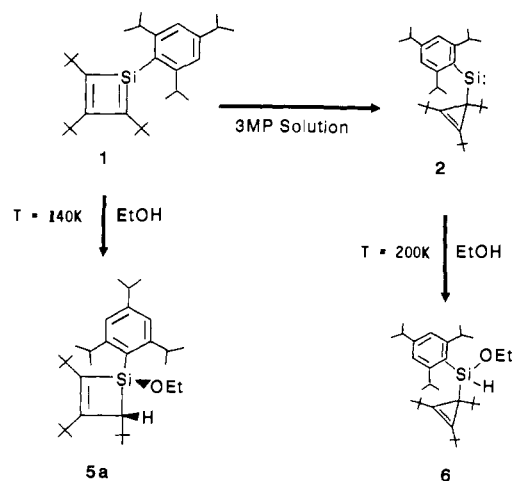(4) For an excellent review, see: Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 309–332.
(5) Puranik, D. B.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989,** *8,* 770–777.
(6) This absorption is typical of a silylene. See: Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Welsh, K.; West, R.; Michl, J. *Silicon, Germanium, Tin, Lead, Compds.* **1986,** *9,* 75–80.

Scheme I
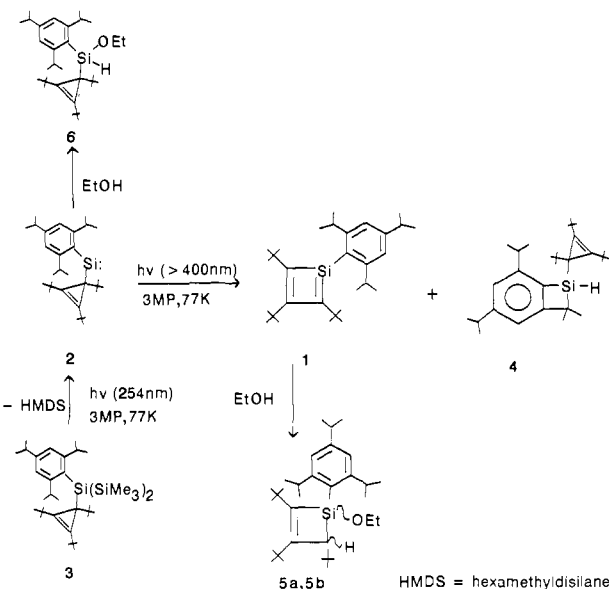
Scheme II

Figure 1. Electronic absorption spectral changes observed during the warmup of a 3-MP solution containing **1**. The absorption band at 340 nm is due to **1**; the band at 448 nm is due to **2**.

assigned to the silacyclobutadiene **1**. If ethanol is present in the glass as a trapping agent (Scheme I), repetitive photolysis and annealing gives two diastereomeric silacyclobutenes **5a** and **5b** in a combined yield of 68%.[7] The silacyclobutenes arise from the regiospecific addition of ethanol across the Si=C bond of **1**.[8,9]

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