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

$$\underset{\mathbf{1}}{\mathrm{ArCHSe}} \xrightarrow{\mathrm{RLi}} \underset{\mathbf{10}}{\mathrm{ArCH_2SeR}} + \underset{\mathbf{11}}{\mathrm{ArCHR(SeH)}} + \underset{\mathbf{12}}{\mathrm{ArCH{=}CHAr}}$$

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 $(\mathrm{ArCH_2Se})_2$ (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.

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

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

Dhananjay B. Puranik and Mark J. Fink*

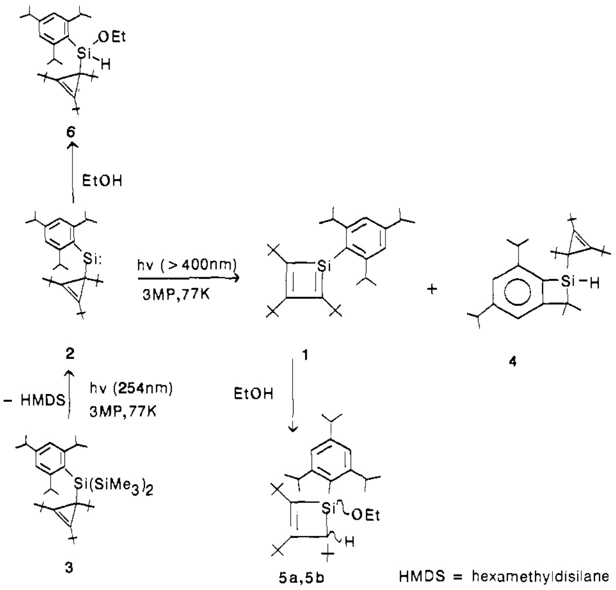
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received December 22, 1988

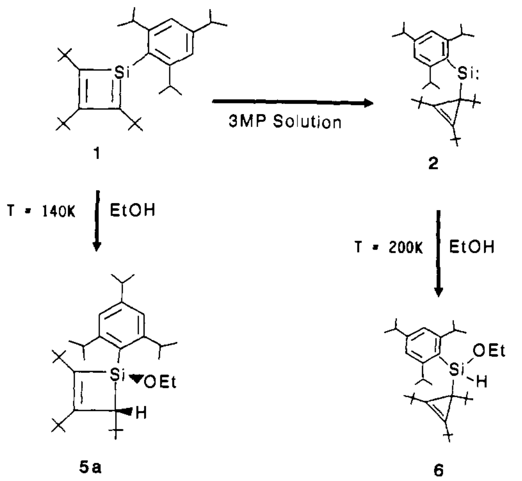
The $\mathrm{SiC_3H_4}$ isomer surface,[1] which includes silacyclobutadiene,[2] silatetrahedrane, and cyclopropenylsilylene,[3] offers a unique comparison of highly ring strained, low valent, and multiply bonded organosilicon species. Of particular interest are the relative energetics and transformations of these isomers. In contrast to the analogous $\mathrm{C_4H_4}$ 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** ($\lambda_{\max}$ = 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 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]

Scheme I



Scheme II



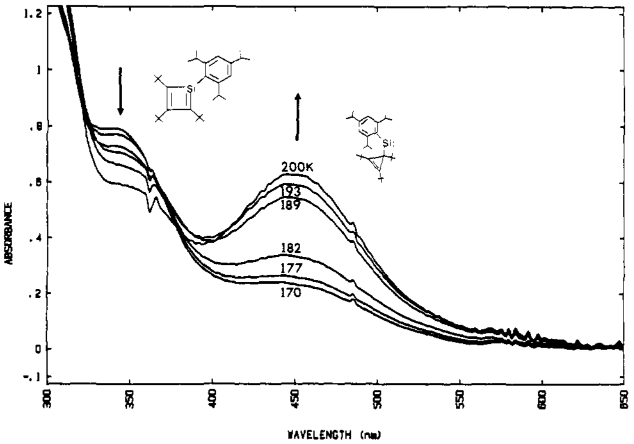


Figure 1. Electronic absorption spectral changes observed during the warmup of a 3-MP solution containing **1**. The absorption band at 340 nm is due to **1**; the band at 448 nm is due to **2**.

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[7] All new compounds are totally consistent with spectroscopic data.

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Also observed are the stable benzosilacyclobutene **4** (14%), formed from the photochemical insertion of the silylene into the benzylic C–H bond of an ortho isopropyl group,[5] and a small amount of trapping product from the silylene **6** (13%).[10]

In the absence of a trapping agent, thawing[11] of an initially colorless 3-MP glass containing **1** results in the onset of a yellow color at 160 K, which reaches a maximum intensity at 200 K, and then disappears near 250 K. Figure 1 shows the spectroscopic changes during the warmup of the glass when monitored with a 0.1-s acquisition time. The 340-nm band due to **1** decreases with increasing temperature, while a new band due to cyclopropenylsilylene **2** (λ_{max} = 448 nm) grows in.[12] The changes in the absorption spectra follow isosbestic behavior from 170 to 190 K, indicating a clean conversion of **1** to **2**.

The identity of the yellow species is clearly established as **2** by trapping experiments (Scheme II).[13] If a 3-MP glass containing **1** is thawed, allowed to warm to 140 K (solution is colorless), and then quenched with ethanol, only one diastereomeric silacyclobutene **5a** (36%) is obtained. This result shows that silacyclobutadiene **1** is present in solution at this temperature. However, if the thawed glass is allowed to warm to 200 K (maximum yellow coloration) before the ethanol is added, the silylene trapping product **6** (22%) is formed instead. In both cases, a small amount of the insertion compound **4** (~20%) is detected as the only other volatile product.[14]

The thermal transformation of **1** to **2** succinctly shows that **2** is the thermodynamically more stable of the two species. Ab initio calculations on the parent SiC_3H_4 system indicate that cyclopropenylsilylene and silacyclobutadiene are isoenergetic at the 631-G* level.[1c] The greater stability of **2** relative to **1** is therefore likely due to differences in steric interactions between the large peripheral substituents of these species.

The kinetic stability of the cyclopropenylsilylene **2** is remarkable. The silylene is stable in 3-MP solution to 200 K before significant decomposition begins. At 238 K, the "first-order" half-life of **2** is approximately 1 h.[15] Although an ether adduct of an organosilylene has been previously shown to exist in low-temperature solutions,[16] this is the first example of a *free* silylene stable under these conditions.[17] The extreme stability of **2** can be attributed to steric protection by its two bulky substituents. This is consistent with laser flash photolysis studies which show that steric hindrance is a primary factor governing organosilylene half-lives and bimolecular reactivity.[18]

Although the general pathway for the decomposition of organosilylenes in solution involves an initial dimerization to give disilenes ($R_2Si{=}SiR_2$),[6,19] the typical π–π^* absorption band[20] for these species is not observed as the silylene **2** disappears. This implies that either **2** does not decompose through a disilene intermediate or that the disilene, if formed, is extraordinarily reactive. Efforts are currently underway to elucidate the exact mode of decomposition for **2**.

Acknowledgment. We thank the Tulane Committee on Research for support of this work. High resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, an NSF Regional Instrumentation Facility (Grant CHE-8620177).

Supplementary Material Available: Complete characterization (^{1}H NMR, GC-MS, IR, and HRMS) of new compounds and electronic absorption spectra showing photochemical generation of **2** from **3** in 3-MP, 77 K; photoisomerization of **2** to **1** in 3-MP, 77 K; and warmup of **2** at $T > 200$ K in 3-MP solution (5 pages). Ordering information is given on any current masthead page.

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[8] Only one diastereomer, **5a**, is formed by the addition of ethanol to **1**. However, under conditions of repetitive photolysis and annealing, **5a** photolyzes to give a photostationary mixture of both **5a** and **5b**.

[9] The silacyclobutenes **5a** and **5b** do not arise from the reaction of EtOH with the silylene **2**. If only 254-nm photolysis is employed, the ratio **6**/**5a**+**5b** is 1.6 as compared to 0.2 if the visible photolysis is also included. Furthermore, photolysis of **3** in 3-MP solution at 253 K gives exclusively the silylene trapped product **6**.

[10] The silylene insertion product likely arises from reaction of the silylene with neighboring ethanol molecules in the matrix, since photobleaching of the silylene is complete before thawing of the matrix.

[11] The softening point of a 3-MP glass is approximately 100 K.

[12] There is a 6-nm shift in the absorption maximum of the silylene in solution versus that of the frozen matrix. This small change may be attributed to either a nonspecific matrix effect or to a slight thermochromism of the silylene.

[13] In a typical trapping experiment, a glass consisting of 6 mg of the trisilane **3** in 9 mL of 3-MP is photolyzed at 254 nm for 45 min, followed by photolysis with visible light (>400 nm) for 60 min. The glass is slowly thawed over liquid nitrogen vapors, and 1.2 mL of anhydrous, degassed, and prechilled ethanol is added via syringe. Temperature measurements are made by a small Pt RTD affixed to the photolysis tube. Photoconversions are approximately 90% based on **3**; absolute yields of products are based on GC-MS and ^{1}H NMR with $(Me_3Si)_4Si$ as an internal standard. Yields are highly reproducible; the average of triplicate experiments are reported.

[14] The slightly lower yield of **4** in those experiments where EtOH is copresent in the glass is attributed to scavanging of the silylene **2** by neighboring EtOH molecules. This depletes the amount of **2** which may undergo further photoreaction to give **4**.

[15] Due to experimental difficulties, we are unable to clearly distinguish between first- and second-order decomposition kinetics at this time. The half-life stated is based on the assumption of first-order decomposition. The concentration of **2** for the kinetics is 9×10^{-3} M.

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Stereomutation of Optically Active Poly(diphenyl-2-pyridylmethyl methacrylate)

Yoshio Okamoto,* Haruhiko Mohri, Tamaki Nakano, and Koichi Hatada

Department of Chemistry
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

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Polymers which manifest optical activity arising only from helicity have been of particular recent interest.[1] The existence of this phenomenon has recently been reported on several different types of synthetic polymers such as polyisocyanides,[2] polymethacrylates,[3-5] and polychloral.[6]

Optically active poly(triphenylmethyl methacrylate) (PTrMA) and poly(diphenyl-2-pyridylmethyl methacrylate) (PD2PyMA) have the unusual characteristic for vinyl polymers of the ability to maintain extended helical structures in solution.[3,4] These

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