

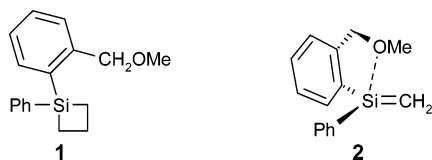
Intramolecular Nucleophile-Induced Photorearrangements and Silene Formation from an *o*-(Methoxymethyl)phenylsilacyclobutane

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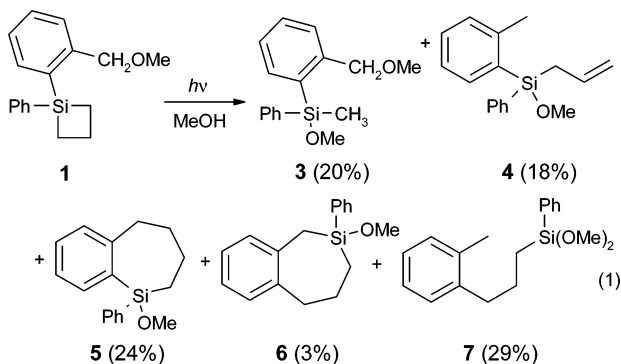
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Silenes are kinetically unstable species that react rapidly with nucleophiles or (in their absence) dimerize to yield the corresponding 1,3- or 1,2-disilacyclobutanes.¹ They can be stabilized by attaching substituents that reduce the natural polarity of the Si=C bond² or sterically protect it from reaction,^{2,3} or by complexation with Lewis bases such as ethers^{4,5} and amines.⁶ As would be expected, amines are more effective than ethers in this regard,⁶ and stable examples of both inter-⁶ and intramolecular⁷ silene-amine complexes have been reported. Following our recent studies of the kinetic effects of ether (solvent) complexation on the reactivity of transient silenes,⁸ we turned our attention to investigating intramolecular effects of this type. We have thus synthesized the 1,1-diarylsilacyclobutane **1** as a potential photochemical precursor to silene **2**, which bears a methoxy group in an appropriate location to interact with the reactive Si=C bond. We wish to report the rather unusual and unexpected photochemistry of **1**, and the results of a preliminary assessment of the effects of intramolecular ether complexation on the reactivity of the Si=C bond in **2**.



Direct photolysis (254 nm) of a deoxygenated 0.06 M solution of **1** in methanol led to the formation of ethylene, methoxysilane **3** from trapping of silene **2** by the solvent, and the four other silicon-containing products (**4–7**) shown in eq 1. Product yields were calculated from the slopes of concentration versus time plots and the material balance (95%), as determined by GC at low (5–30%) conversions of **1**. In contrast, photolysis of **1** as a 0.12 M solution in hexane afforded **4** (24%), **5** (28%), **6** (22%), and several other minor products whose yields were too low to enable isolation. The material balance in this experiment was ca. 83%.

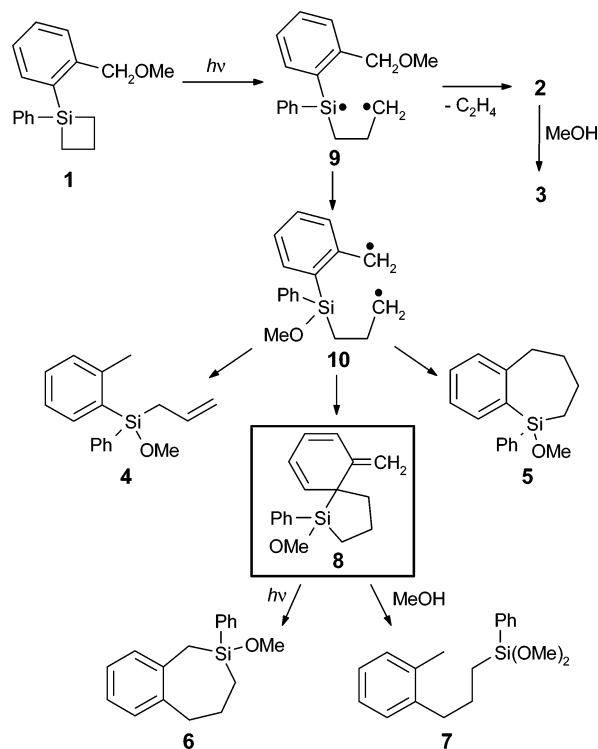


Photolysis of **1** in cyclohexane-*d*₁₂ solution, under conditions similar to those above, allowed **4–6** and ethylene to be detected in the crude photolysis mixture by ¹H NMR spectroscopy. The spectra

also showed a new singlet at δ 3.47 ppm and several additional, very weak signals in the δ 5.2–6.5 ppm range, which integrated to a total of twice the area of the 3.47 ppm singlet. The signals at 3.47 and 5.2–6.5 ppm built up during the initial stages of the photolysis, did not grow in further as it was continued, and disappeared if the solution was allowed to stand in the dark for 30–60 min or was irradiated briefly at 350 nm. Unfortunately, the changes in the NMR spectra resulting from these treatments were too subtle to identify the products of the thermal or photochemical decomposition of the species responsible for these signals. The species could also be detected by static UV spectroscopy of partially photolyzed mixtures in hexane solution as a strong absorption with $\lambda_{\text{max}} = 333$ nm that decayed with pseudo-first-order kinetics and a lifetime (τ) of ca. 29 min. The same species could be detected in neat methanol solution, where it exhibited a lifetime of $\tau = 3.2$ min.

We assign the structure of this long-lived transient product to the spirocyclic isotonene derivative **8**, and propose a mechanism to account for the formation of it and **3–7** in Scheme 1. The primary photochemical event is envisioned to be cleavage of one of the silacyclobutyl Si–C bonds in the excited singlet state of **1** to yield 1,4-biradical **9**. This species is proposed to undergo competing loss of ethylene to yield silene **2** and migration of the methoxy group from the benzylic carbon to silicon, the driving force for which is the formation of the relatively strong Si–O bond in the product

Scheme 1

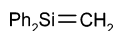


biradical, **10**. The latter intermediate can be expected to decay by competing intramolecular disproportionation (yielding **4**) and ring closure (yielding **5** and **8**). Compound **6** is the product of photochemically allowed [1,3]-silyl migration in **8** and is thus proposed to be a secondary photolysis product, while dialkoxysilane **7** is the product expected from (dark) reaction of **8** with methanol.⁹ The considerably lower yield of **6** in the photolysis of **1** in methanol (compared to that in hexane) is consistent with a lower pseudo-photostationary state concentration of **8** due to its reaction with the solvent to form **7**. Additional evidence that **6** is formed via secondary photolysis of **8** was obtained by photolyzing a hexane solution of **1** simultaneously with 254 and 350 nm light sources. The result was a higher material balance than in the photolysis with 254 nm light alone (ca. 90% vs. 83%) and an increase in the yield of **6** (27% vs 22%). The UV and NMR spectra of **8**, its lifetime, and photochemical and ground-state reactivities are analogous to those of other 1-methylene-6-silyl-2,4-cyclohexadiene derivatives that have been reported.⁹

The rearrangement of **9** to **10** can be viewed as an intramolecular homolytic substitution resulting from attack of the silicon radical center at oxygen. While we are unaware of any precedent for this process in silicon (mono)radical chemistry, preliminary DFT calculations indicate that the analogous rearrangement of a silyl radical closely related to **9** is exothermic by ca. 30 kcal/mol. However, at this stage we cannot rule out the possibilities that the process might be unique to biradicals such as **9**, which can be expected to possess some zwitterionic character owing to the electronegativity difference between the two radical centers,¹⁰ or that biradical **10** is formed via a direct excited state pathway, in which methoxy migration accompanies or slightly precedes ring opening in the excited singlet state of **1**.

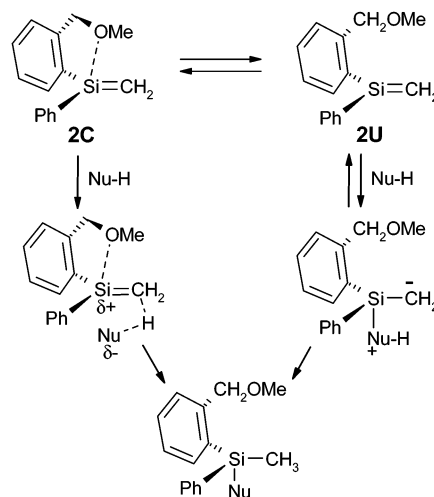
Laser flash photolysis of flowed, air-saturated acetonitrile solutions of **1** (0.003 M, 25 °C) with the pulses from a KrF excimer laser (248 nm, 25 ns) allowed the detection of a transient which decayed with first-order kinetics ($\tau \approx 10 \mu\text{s}$) and exhibited a broad absorption spectrum with $\lambda_{\text{max}} = 295 \text{ nm}$ and a shoulder at ca. 320 nm, superimposed on a nondecaying absorption ($\lambda_{\text{max}} = 335 \text{ nm}$) which matched that assigned above to isotoluene **8** in static UV experiments. Addition of nucleophilic reagents such as methanol (MeOH), acetone, and acetic acid (AcOH) shortened the lifetime of the transient species in direct proportion to the concentration of added reagent. Absolute second-order rate constants for reaction of the transient with the three reagents at 25 °C were obtained from the slopes of plots of $(1/\tau)$ vs reagent concentration: $k_{\text{MeOH}} = (1.9 \pm 0.1) \times 10^8$, $k_{\text{acetone}} = (8.6 \pm 0.3) \times 10^5$, and $k_{\text{AcOH}} = (2.14 \pm 0.05) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. On the basis of this behavior, we assign the species to silene **2**.

The Hammett σ_p -value for the $-\text{CH}_2\text{OMe}$ substituent is +0.01,¹¹ indicating it to be approximately electronically neutral. Thus, comparison of the rate constants for reaction of **2** with these reagents to the corresponding ones for 1,1-diphenylsilene (**11**) should give a reasonable estimate of the effects of intramolecular complexation of the benzylic methoxy group with the $\text{Si}=\text{C}$ bond in **2**, ignoring possible contributions from steric effects. The rate constants for reaction of **11** with these reagents under the same conditions as **2** are $k_{\text{MeOH}} = (1.5 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{acetone}} = (1.8 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{AcOH}} = (1.5 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹² Thus, **2** reacts ca. 200 and 8 times slower than **11** does with acetone and MeOH, respectively, but ca. 1.5 times faster than **11** with AcOH.

**11**

The UV spectrum of **2**, compared to the much sharper spectrum exhibited by **11** under the same conditions,¹³ is consistent with **2**

Scheme 2



existing as a mixture of both intramolecularly complexed (**2C**) and uncomplexed (**2U**) isomers, presumably in rapid equilibrium with one another (see Scheme 2).⁸ The kinetic data are consistent with competitive reaction from these two isomers, with the nature of the competition and the mode of reaction depending mainly on the Brønsted acidity of the nucleophilic reagent. Reaction with acetone, an extremely weak acid, is proposed to proceed mainly via the more electrophilic, uncomplexed form of **2** (**2U**) by initial nucleophilic attack of the carbonyl oxygen at silicon. Reaction with acetic acid, on the other hand, is proposed to proceed via the more nucleophilic, complexed form (**2C**), either concertedly or by initial protonation at carbon. The intermediate effects observed for methanol may be consistent with reaction via both isomers.

A more extensive analysis of the effects of intramolecular ether complexation on the reactivity of **2** is in progress.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and F. Lollmahomed and Dr. P. Ayers for theoretical calculations.

Supporting Information Available: Spectral and analytical data for all new compounds, and time-resolved UV spectra and decay traces for isotoluene **8** and silene **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA035283K