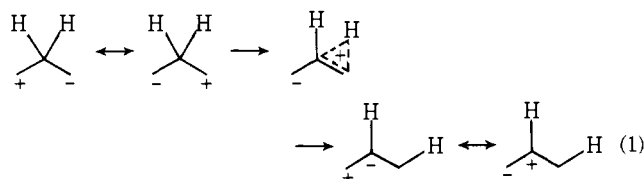


at the HMO level), but the exchange integral, which favors the T state energetically, should also be larger (cf. the larger value of  $D$ ). The hyperfine coupling constant for the methylene protons is isotropic as expected and of the right order of magnitude (using Hückel spin densities and standard relations,<sup>10</sup> one expects  $a \approx (1/2) (3/\sqrt{26} + 3/\sqrt{26})^2 \times 42.6 \times \cos^2 30^\circ = 22$  (G)).

The UV-vis absorption spectrum of III is one of the very few ever recorded for the singlet state of an even conjugated hydrocarbon without a classical valence structure.<sup>11</sup> It is strikingly different from the spectra of ordinary alternant hydrocarbons in that it contains a long succession of very weak absorption bands at long wavelengths. It is in fair agreement with our PPP calculation which suggests that there is an additional forbidden transition near  $9000 \text{ cm}^{-1}$  and that the observed fluorescence is of the  $S_2 \rightarrow S_0$  type. Our attempts to locate this predicted transition in the near-IR region failed.

2,3 shifts in 1,3 biradicals have been frequently discussed, e.g., in the thermal rearrangement of cyclopropanes to propenes,<sup>12</sup> and in their photochemical interconversion.<sup>13</sup> We believe that ours is the first direct observation of a 2,3-hydrogen shift in a 1,3 biradical, and indeed of the whole sequence commonly postulated<sup>13</sup> in the photochemical process arylcyclopropane  $\rightarrow (h\nu)$  1,3 biradical  $\rightarrow (\Delta)$  arylpropene (at  $20^\circ \text{C}$ , irradiation of I smoothly produces II).

The expected relative ease of 2,3 shifts in 1,3 biradicals is usually attributed to the partial development of the 1,2 double bond as the transition state is reached. This argument holds only for the  $S_0$  state; such assistance is missing in  $T_1$  state and in the lowest excited singlet state  $S_1$ , in which the reactions are more nearly thermoneutral. Naively, one could expect the reaction to be facile in the "zwitterionic"<sup>13,14</sup>  $S_1$  state, in which it can be approximately described as a 2,3 shift in a carbonium ion carrying a carbanion substituent (carbon 1) (eq 1). These



qualitative notions and the resulting expectation of an increase in the activation energy for the shift in the order  $S_1 < S_0 < T_1$  are supported qualitatively by approximate calculations for the 1,3-trimethylene biradical  $\rightarrow$  propene rearrangement which we have performed at the STO-3G SCF +  $3 \times 3$  CI level, with considerable but not exhaustive geometry optimization.

Accordingly, we would expect the thermal transformation III  $\rightarrow (\Delta)$  II to involve the  $S_0$  state of III and a nonvanishing activation energy, and the photochemical transformation III  $\rightarrow (h\nu)$  II to occur for that fraction of excited molecules which reaches the very low lying  $S_1$  state, with little or no activation energy.

The presently available photochemical results are compatible with these expectations if we postulate that the calculated very weak  $S_0 \rightarrow S_1$  transition in the infrared is too weak to be observed against the background of solvent overtones and that a radiationless  $S_2 \rightarrow S_1$  process competes with  $S_2 \rightarrow S_0$  emission (such emission is plausible in view of the large calculated  $S_2$ - $S_1$  gap). However, the frequency factor of the thermal reaction III  $\rightarrow$  II is abnormally low and suggests that the reaction involves either tunneling or a spin-forbidden process such as might result from the presence of a large barrier in the  $S_0$  and a small one in the  $T_1$  surface. We wonder, however, whether the temperature dependence of the reaction rate does not reflect as much the properties of the glass as those of the isolated molecule even for a possibly simple monomolecular

process such as III  $\rightarrow$  II. E.g., over the temperature range used (119–133 K), the viscosity of 1-pentanol changes by a factor of  $3 \times 10^4$ . Similar huge changes also occur for other glasses over the temperature region in which they are transparent and stable. Some curious variations in the frequency factor for the rate of disappearance of trimethylenemethane in glasses were reported recently.<sup>15</sup> Clearly, now that the agreement of the optical and ESR kinetic data for III in 1-pentanol has been demonstrated, it will be necessary to perform ESR studies, which do not require good transparency, in a large number of glasses, and also to explore isotope and substituent effects.

Barriers to ring closure in 1,3 biradicals are of considerable current interest.<sup>15</sup> The absence of competing thermal conversion III  $\rightarrow$  I shows that in rigid 1-pentanol the barrier is considerable in the case of III. Since the ring closure requires a larger geometry change than the hydrogen shift, extrapolation to gas phase is not straightforward. Also, the presence of the rigid and conjugating naphthalene unit is undoubtedly unfavorable for ring closure.

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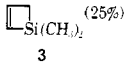
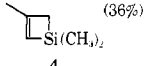
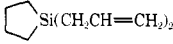
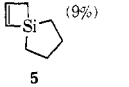
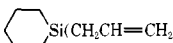
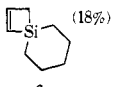
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## Silacyclobutenes: A Simple Synthesis<sup>1</sup>

Sir:

Silacyclobutenes have been largely ignored during the recent surge of interest in the preparation and reactions of strained-ring organosilicon compounds.<sup>2</sup> This neglect, which seems

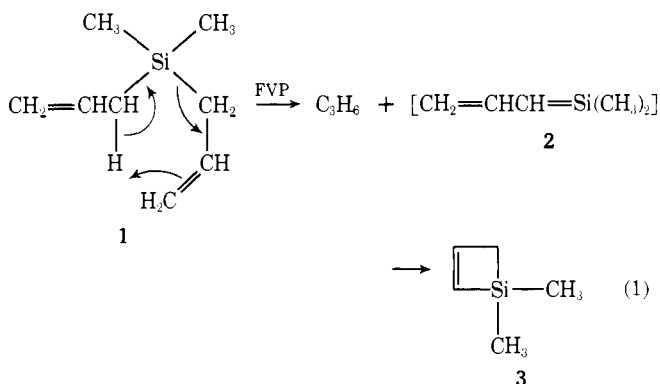
**Table I.** Silacyclobutenes Prepared by Flash Vacuum Pyrolysis of Diallylic Silanes

Entry	Reactant	Structure (yield) <sup>a</sup>	Silacyclobutene	
			IR: C=C (cm <sup>-1</sup> )	<sup>1</sup> H and <sup>13</sup> C NMR <sup>b</sup>
1	(CH <sub>2</sub> =CHCH <sub>2</sub> ) <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub>	 (25%) 3	1511 (m)	<sup>1</sup> H: δ 0.33 (s, 6 H, CH <sub>3</sub> ), 1.55 (d, 2 H, J = 1.8 Hz, CH <sub>2</sub> ), 6.27 (d, 1 H, J = 7.3 Hz, =CHSi), 7.16 (d of t, 1 H, J = 1.8, 7.3 Hz, =CH); <sup>13</sup> C: δ <sub>C</sub> 0.83 (CH <sub>3</sub> ), 22 (CH <sub>2</sub> ), 142 (=CHSi), 152 (=CH)
2	(CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>2</sub> Si(CH <sub>3</sub> ) <sub>2</sub>	 (36%) 4	1580 (m) <sup>c</sup>	<sup>1</sup> H: δ 0.27 (s, 6 H, Si-CH <sub>3</sub> ), 1.38 (m, 2 H, CH <sub>2</sub> ), 1.87 (m, 3 H, C-CH <sub>3</sub> ), 5.70 (m, 1 H, =CHSi); <sup>13</sup> C: δ <sub>C</sub> -1.46 (Si-CH <sub>3</sub> ), 23.1, 24.1 (CH <sub>2</sub> and CH <sub>3</sub> on C; assignment not made), 132.1 (=CHSi) <sup>d</sup>
3	 Si(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	 (9%) 5	1507 (m)	<sup>1</sup> H: δ 0.7-1.0 (m, 4 H, CH <sub>2</sub> CH <sub>2</sub> Si), 1.5-1.8 (m, 6 H, CH <sub>2</sub> CH <sub>2</sub> Si + SiCH <sub>2</sub> CH=), 6.09 (d of t, 1 H, J = 7.1, 0.7 Hz, =CHSi), 7.12 (d of t, 1 H, J = 7.1, 1.9 Hz, =CH); <sup>13</sup> C: δ <sub>C</sub> 11.9 (CH <sub>2</sub> CH <sub>2</sub> Si), 21.5, 26.5 (other CH <sub>2</sub> carbons; assignment not made), 139.3 (=CHSi), 152.9 (=CH)
4	 Si(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	 (18%) 6	1510 (m)	<sup>1</sup> H: δ 0.89 (t, 4 H, J = 6 Hz, CH <sub>2</sub> CH <sub>2</sub> Si), 1.3-1.9 (m with d of d at 1.53, J = 1.95, 0.49 Hz, 8 H; other CH <sub>2</sub> protons with CH <sub>2</sub> CH= at 1.53), 6.16 (d of t, 1 H, J = 0.7, 7.3 Hz, =CHSi), 7.12 (d of t, 1 H, J = 1.8, 7.1 Hz, =CH); <sup>13</sup> C: δ <sub>C</sub> 14.7, 20.9, 24.9, 29.7 (CH <sub>2</sub> carbons), 140.5 (=CHSi), 152.1 (=CH)

<sup>a</sup> Yields determined by NMR or GC analysis. <sup>b</sup> All <sup>13</sup>C spectra determined in CDCl<sub>3</sub> solution except for that of **3** which was used neat; the <sup>1</sup>H spectra were determined in CCl<sub>4</sub> (silacyclobutenes **3** and **4**) or CDCl<sub>3</sub> (silacyclobutenes **5** and **6**). <sup>c</sup> Note that 3-methyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene also has a C=C band at 1580 cm<sup>-1</sup>: C. S. Liu, J. L. Margrave, and J. C. Thompson, *Can. J. Chem.*, **50**, 465 (1972). <sup>d</sup> Under the FT NMR conditions employed, the quaternary olefinic carbon was not seen.

surprising in view of the rich chemistry associated with cyclobutenes,<sup>3</sup> may be due to the general rarity of silacyclobutenes. To date only silacyclobutenes ring-substituted with aryl groups have been synthesized and these by multistep procedures.<sup>2d</sup> We now wish to report a simple one-step synthesis of silacyclobutenes which makes available for study a wide range of these compounds including those unsubstituted on the ring.

This synthesis was discovered during an attempt to examine by flash vacuum pyrolysis (FVP) spectroscopic techniques<sup>1a</sup> silabutadienes (e.g., **2**) which we hoped to generate through retro-ene reaction<sup>4</sup> of diallylsilanes such as **1** (eq 1). In the



event, initial study of the FVP of **1** (utilizing a pyrolysis system connected directly to the source of a mass spectrometer<sup>1a</sup>) suggested the clean decomposition of **1** to species of formulas C<sub>5</sub>H<sub>10</sub>Si (*m/e* 98) and C<sub>3</sub>H<sub>6</sub> (*m/e* 42) in the gas phase beginning at temperatures of ca. 600 °C. Repetition of the pyrolysis on a preparative scale using a 2 × 68 cm quartz tube filled with

porcelain Berl saddles<sup>5</sup> and heated in a tube furnace at 710 °C with a sample flow rate of 3 ml/h at ca. 0.01 mm<sup>6</sup> gave 1,1-dimethylsilacyclobutene (**3**) (25% yield; 41% yield based on unrecovered **1**), propylene (22% yield based on isolation of 1,2-dibromopropane), diallyldimethylsilane (**1**) (55% recovery), and a number of minor products as indicated by GC analysis. Starting material **1** could be recovered by distillation and pyrolyzed again to give additional **3**. Silacyclobutene **3**, showing a GC retention time nearly identical with that of authentic 1,1-dimethylsilacyclobutane,<sup>7</sup> had bp 70-71 °C.<sup>8</sup> High resolution mass spectrometry indicated a parent ion at *m/e* 98.05510 (base peak; calcd for C<sub>5</sub>H<sub>10</sub>Si 98.05510) with prominent peaks corresponding by exact mass to P - CH<sub>3</sub> (93%), C<sub>3</sub>H<sub>5</sub>Si (47%), and C<sub>3</sub>H<sub>8</sub>Si (28%). Gas-phase IR showed bands at 3065 (m), 3019 (w), and 1511 cm<sup>-1</sup> (m) among others (all bands absent from the IR spectrum of 1,1-dimethylsilacyclobutane); <sup>1</sup>H NMR (CCl<sub>4</sub>) showed δ 0.33 (s, 6 H), 1.55 (d, 2 H, J = 1.8 Hz), 6.27 (d, 1 H, J = 7.3 Hz), and 7.16 (d of t, 1 H, J = 1.8, 7.3 Hz); <sup>13</sup>C FT NMR showed δ<sub>C</sub> 0.83 (q, J = 120 Hz), 22 (t, J = 131), 142 (d, J = 170 Hz), and 152 (d, J = 168 Hz); <sup>29</sup>Si NMR showed δ<sub>Si</sub> -9.6 ppm (proton decoupled; upfield from tetramethylsilane). The IR band at 1511 cm<sup>-1</sup> may be identified as the C=C stretch; the long wavelength position is fully consistent with the data for cyclobutane (C=C at 1566 cm<sup>-1</sup>)<sup>10</sup> and the "conjugative" effect of silicon. The <sup>1</sup>H NMR spectrum of **3** is in excellent agreement with the data reported for aryl-substituted silacyclobutenes.<sup>2d,11</sup> The <sup>1</sup>H and <sup>13</sup>C NMR results are also consistent with literature values for related systems<sup>2b,3</sup> including 1-silacyclopent-2-enes.<sup>12</sup> The <sup>29</sup>Si NMR peak position shows none of the dramatic shielding associated with silacyclopropanes and silacycloprenes.<sup>2b</sup>

Additional examples of the synthesis of silacyclobutenes by

