

# The First Silatriafulvene Derivative: Generation, Unusually Low Reactivity toward Alcohols, and Isomerization to Silacyclobutadiene

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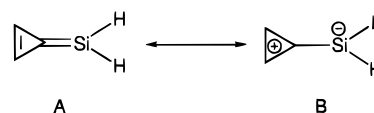
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Among the various 4-heterosubstituted methylenecyclopropenes having potential aromaticity,<sup>1</sup> 4-silatriafulvene is quite unique with an exo Si=C double bond that is intrinsically polarized as Si<sup>+</sup>–C<sup>–</sup> in contrast to a typical 4-heterosubstituted triafulvene such as cyclopropenone. The polarity of the Si=C double bond is reduced by resonance structure **B** as shown in Chart 1, indicating that unusual reactivity can be expected for 4-silatriafulvene in comparison with the well-studied silaethenes.<sup>2,3</sup> Although a number of theoretical studies on the geometry and aromaticity of silatriafulvene have been reported,<sup>4</sup> no experimental studies have been performed to date. Here, we report quantitative generation of the first silatriafulvene derivative, 1,2-di-*tert*-butyl-4,4-bis(trimethylsilyl)-4-silamethylenecyclopropene (**1**),<sup>5</sup> its unusually low reactivity toward alcohols, and the facile isomerization to the corresponding silacyclobutadiene.

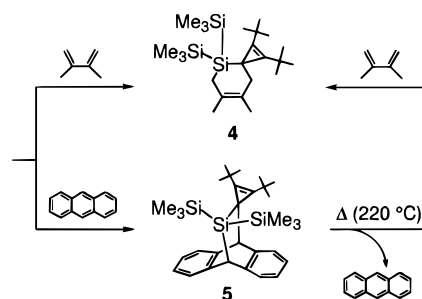
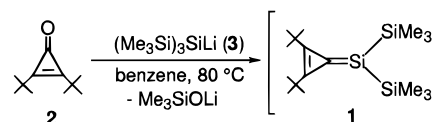
The silatriafulvene (**1**) was generated using a sila-Peterson type reaction reported by Apeloig *et al.*<sup>3b,6</sup> and Oehme *et al.*<sup>7</sup> as shown in Scheme 1. Thus, reactions of di-*tert*-butylcyclopropenone (**2**)<sup>8</sup> with tris(trimethylsilyl)silyllithium (**3**) in refluxing benzene in the presence of 2,3-dimethyl-1,3-butadiene and anthracene as trapping reagents gave **4** and **5** in the yields of 27 and 25%, respectively.<sup>9,10</sup> The production of **4** and **5** indicates intermediacy of the silatriafulvene (**1**) via nucleophilic addition of **3** to **2** followed by elimination of Me<sub>3</sub>SiOLi.

As expected,<sup>11</sup> the anthracene adduct **5** was found to be a good thermochemical precursor of **1**. Thus, thermolysis of a toluene solution of **5** in the presence of 2,3-dimethyl-1,3-butadiene at 220 °C in a sealed tube gave **4** quantitatively. Rather

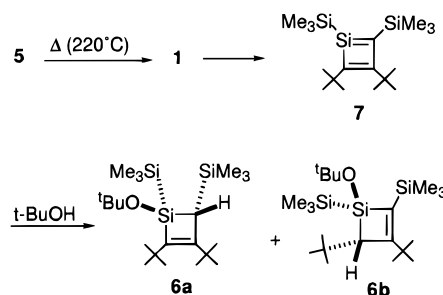
Chart 1



Scheme 1



Scheme 2



unexpectedly, thermolysis of a toluene solution of **5** in the presence of excess *tert*-butyl alcohol at 220 °C for 1 h in a sealed tube gave four-membered ring compounds **6a** and **6b** in 75 and 25% yields, respectively,<sup>12</sup> under 60% consumption of **5**; no direct alcohol adduct of **1** was produced. Apparently, **6a** and **6b** are produced via isomerization of **1** to a silacyclobutadiene **7** followed by addition of *tert*-butyl alcohol, as shown in Scheme 2. The results indicate that (1) 4-silatriafulvene (**1**)

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(1) For a review, see: Eicher, T.; Weber, I. L. *Top. Curr. Chem.* **1975**, *57*, 1.

(2) For recent reviews of unsaturated organosilicon compounds, see: (a) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 17.

(3) Electrophilic reactivity of silenes depending on the polarity of the Si=C double bonds is discussed in the following papers: (a) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676. (b) Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D. *J. Am. Chem. Soc.* **1996**, *118*, 12228. (c) Miracle, G. E.; Ball, J. L.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1993**, *115*, 11598.

(4) (a) Schriver, G. W.; Fink, M. J.; Gordon, M. S. *Organometallics* **1987**, *6*, 1977. (b) Bachrach, S. M.; Liu, M. *J. Phys. Org. Chem.* **1991**, *4*, 242. (c) Burk, P.; Abboud, J.-L. M.; Koppel, I. A. *J. Phys. Chem.* **1996**, *100*, 6992.

(5) An interesting 4-heterosubstituted triafulvene, 4-phosphenecyclopropene, is reported by Regitz *et al.*: Fuchs, E. P. O.; Heydt, H.; Regitz, M.; Schoeller, W. W.; Busch, T. *Tetrahedron Lett.* **1989**, *30*, 5111.

(6) Bravo-Zhivotovskii, D.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326.

(7) (a) Krempner, C.; Reinke, H.; Oehme, H. *Chem. Ber.* **1995**, *128*, 1083. (b) Luderer, F.; Reinke, H.; Oehme, H. *J. Organomet. Chem.* **1996**, *510*, 181. (c) Wendler, C.; Oehme, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 801. (d) Luderer, F.; Reinke, H.; Oehme, H. *Chem. Ber.* **1996**, *129*, 15. (e) Hoffmann, D.; Reinke, H.; Oehme, H. *J. Organomet. Chem.* **1996**, *526*, 185.

(8) Ciabattini, J.; Nathan, E. C.; Feiring, A. E.; Kocienski, P. *J. Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 991.

(9) An attempted generation of **1** by a similar method has been reported to have failed.<sup>7c</sup> Actually, without any trapping reagents, the reaction of **2** with **3** by our hands gave a complex mixture of the products including several dimers of **1**, whose structures will be reported elsewhere.

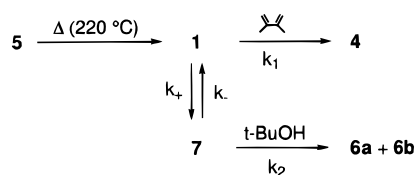
(10) For **4**: colorless oil; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.24 (18 H, s), 1.17 (18 H, s), 1.61 (3 H, s), 1.69 (2 H, s), 1.85 (3 H, s), 2.16 (2 H, s); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) 1.1, 16.9, 18.4, 21.9, 24.5, 30.2, 32.0, 51.7, 125.7, 125.8, 129.6; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –17.3, –45.9; HRMS calcd for C<sub>23</sub>H<sub>46</sub>Si<sub>3</sub> 406.2907, found 406.2906. For **5**: colorless crystals; mp 231 °C (dec); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.10 (18 H, s), 1.11 (18 H, s), 3.33 (1 H, s), 4.02 (1 H, s), 6.97–7.02 (4 H, m); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) 1.5, 27.8, 31.2, 31.9, 39.2, 65.8, 124.6, 124.9, 125.7, 126.2, 126.3, 143.7, 144.4; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –52.4, –15.2; HRMS calcd for C<sub>31</sub>H<sub>46</sub>Si<sub>3</sub> 502.2894, found 502.2905. In the mass spectra of **4** and **5**, a common characteristic ion with *m/z* 324 was observed as the base peak, which corresponds to the molecular ion of the silatriafulvene **1** formed by a retro-Diels–Alder reaction of **4** and **5**.

(11) Jones, P. R.; Bates, T. F. *J. Am. Chem. Soc.* **1987**, *109*, 913.

(12) For **6a**: colorless crystals; mp 146–147 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.23 (9 H, s), 0.36 (9 H, s), 1.12 (9 H, s), 1.27 (9 H, s), 1.29 (9 H, s), 1.63 (1 H, s); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.3, 1.9, 31.0, 30.9, 32.2, 33.6, 33.8, 37.9, 73.9, 157.3, 165.4; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –21.8, –12.4, –3.2. Anal. Calcd for C<sub>21</sub>H<sub>46</sub>OSi<sub>3</sub>: C, 63.239; H, 11.623. Found: C, 63.028; H, 11.622. For **6b**: colorless crystals; mp 140–142 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.33 (9 H, s), 0.37 (9 H, s), 1.15 (9 H, s), 1.22 (9 H, s), 1.24 (9 H, s), 2.51 (1 H, s); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, δ) 0.3, 3.3, 31.0, 32.2, 32.5, 33.2, 39.7, 58.3, 73.6, 153.5, 185.8; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, δ) –21.2, –16.1, –9.7. Anal. Calcd for C<sub>21</sub>H<sub>46</sub>OSi<sub>3</sub>: C, 63.239; H, 11.623. Found: C, 63.235; H, 11.690. Both products **6a** and **6b** were syn adducts of *tert*-butyl alcohol to **7** as determined by <sup>1</sup>H NMR NOE spectroscopy. The addition stereochemistry is in good accord with the mechanism proposed.<sup>13</sup>

(13) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986.

## Scheme 3



reacts much faster with the diene than with the alcohol in contrast to usual silaethenes<sup>14</sup> and (2) facile isomerization occurs from a silatriafulvene to the corresponding silacyclobutadiene.

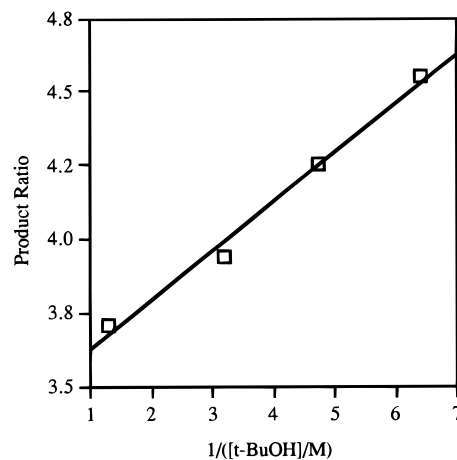
Isomerization of **1** to **7** complements the interconversion between a silacyclobutadiene and a cyclopropenylsilylene reported by Fink *et al.*<sup>15</sup> Since it is an interesting problem whether reversible interconversion between **1** and **7** is involved at 220 °C, we have investigated thermolysis of **5** at 220 °C in toluene in the presence of a mixture of *tert*-butyl alcohol and 2,3-dimethyl-1,3-butadiene by varying the concentration of *tert*-butyl alcohol from 0.15 to 0.80 M at constant concentrations of **5** (0.0159 M) and the diene (0.317 M). Under these conditions, generated **1** and **7** were trapped quantitatively by the diene and the alcohol, respectively. If we neglect the reactions of **1** with the alcohol and **7** with the diene, according to the experimental results, the whole diagram of thermolysis of **5** can be described as shown in Scheme 3. The product ratio of **4** and **6** (= **6a** + **6b**) is represented by eq 1 under the steady-state approximation for the concentration of **7**.

$$\frac{[4]}{[6]} = [\text{diene}] \left\{ \frac{k_1 k_-}{k_2 k_+} \left( \frac{1}{[t\text{-BuOH}]} \right) + \frac{k_1}{k_+} \right\} \quad (1)$$

In accordance with the equation, a good linear relationship was obtained between the product ratio,  $[4]/[6]$ , and  $1/[t\text{-BuOH}]$  (correlation coefficient = 0.994) as shown in Figure 1. From

(14) As a typical example, 1,1-dimethyl-2,2-bis(trimethylsilyl)silaethene has been reported to react with *tert*-butyl alcohol 960 times faster than with 2,3-dimethyl-1,3-butadiene: Wiberg, N. *J. Organomet. Chem.* **1984**, 273, 141.

(15) (a) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988**, 110, 1315. (b) Puranik, D. B.; Johnson, M. P.; Fink, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 706. (c) Puranik, D. B.; Fink, M. J. *J. Am. Chem. Soc.* **1989**, 111, 5951.



**Figure 1.** A plot of the product ratio,  $[4]/[6]$ , against  $([t\text{-BuOH}]/M)^{-1}$  for the reaction of **5** in the presence of a mixture of 2,3-dimethyl-1,3-butadiene and *tert*-butyl alcohol in toluene at 220 °C. The initial concentrations of **5** and 2,3-dimethyl-1,3-butadiene were 0.0159 and 0.317 M, respectively. The product ratio was determined by GLC.

the slope and the intercept, the values of  $k_1/k_+$  and  $k_-/k_2$  are evaluated to be 11 and 0.050, respectively. Significant dependence of the product ratio on the concentration of *tert*-butyl alcohol suggests the reversible interconversion between **1** and **7** at high temperatures.<sup>16</sup> The low reactivity of alcohol toward **1** would be explained by the reduced polarity of the Si=C double bond due to the contribution of the resonance structure **A**<sup>17</sup> in addition to the silyl substituent effects as recently discussed by Apeloig *et al.*<sup>3b</sup>

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(16) If the value of  $k_2/k_1$  is assumed as  $10^{3,14}$  the equilibrium constant,  $k_-/k_+$ , is estimated to be 500, suggesting that **1** is ca. 6 kcal/mol more stable than **7**; the energy difference may be unreliable because the  $k_1/k_2$  should depend significantly on the substituents on silaethene.

(17) A theoretical study at the MP2/6-311++G level has revealed that addition of water to the parent 4-silatriafulvene proceeds via a four-center cyclic transition state without formation of any intermediate complex with the activation energy of 19.4 kcal/mol, more than twice for the reaction of water with  $\text{H}_2\text{Si}=\text{CH}_2$ . Detailed theoretical analysis of the structure of 4-silatriafulvene, mechanisms for its addition to water, and isomerization to silacyclobutadiene will be reported elsewhere by T. Veszprémi, M. Takahashi, K. Sakamoto, J. Ogasawara, and M. Kira.