

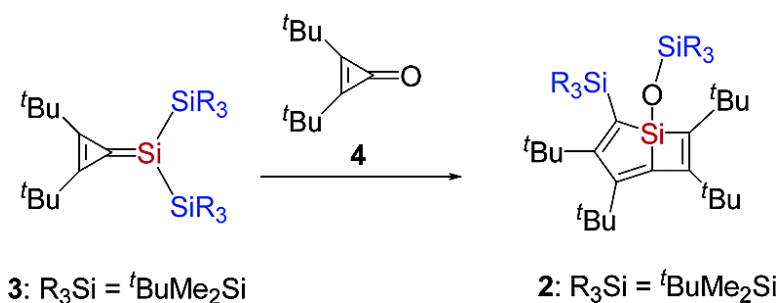
Communication

A Stable Silicon Congener of Highly Strained Bicyclo[3.2.0]hepta-1,3,6-triene

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J. Am. Chem. Soc., **2003**, 125 (31), 9310-9311 • DOI: 10.1021/ja0359097 • Publication Date (Web): 15 July 2003

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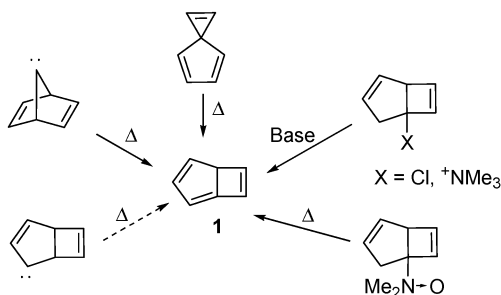
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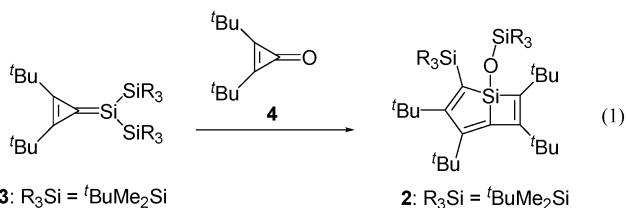
Received May 2, 2003; E-mail: mkira@si.chem.tohoku.ac.jp

Bicyclo[3.2.0]hepta-1,3,6-triene (**1**) and its derivatives with highly strained bridgehead double bonds have been neither isolated nor detected spectroscopically so far, although the intermediary formation of these compounds has attracted much attention both experimentally¹ and theoretically.² Bicyclo[3.2.0]heptatriene **1** was generated by the HX-eliminations of various precursors,^{1a,b} thermal rearrangements of spiro[2,4]hepta-1,4,6-trienes,^{1c} and a rearrangement of 7-norbornadienelidene,^{1d} but the generation was proved only by the detection of the corresponding dimer; interestingly, no evidence was obtained for the isomerization of bicyclo[3.2.0]hepta-3,6-diene-2-ylidene to **1**^{1e} (Scheme 1). During the course of our study of the reactions of 4-silatriafulvenes,³ we have succeeded in the synthesis of 5-silabicyclo[3.2.0]hepta-1,3,6-triene **2** as a stable silicon congener of **1**. Despite the highly strained ring structure revealed by X-ray crystallography, **2** was thermally very stable even in the air.

Scheme 1



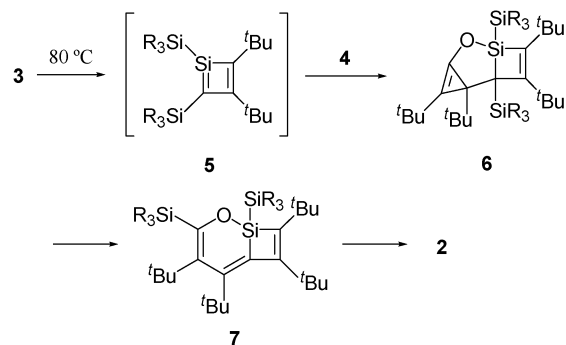
The reaction of 4-silatriafulvene **3** with di-*tert*-butylcyclopropenone (**4**) in benzene at 80 °C for 2 days gave 5-silabicyclo[3.2.0]heptatriene **2** in quantitative yield as pale yellow crystals (eq 1). The structure was characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopies and X-ray crystallography.⁴



While the detailed reaction mechanism remains open, the formation of **2** would involve the [4+2] addition of silacyclobutadiene **5** formed by the thermal isomerization of **3**⁵ to ketone **4** giving **6**,⁶ the ring expansion of **6** to **7** followed by a formal dyotropic rearrangement⁷ will give **2** (Scheme 2).

An X-ray analysis of a single crystal of **2** obtained by the crystallization from *tert*-butyl methyl ether showed the highly strained structure with a silacyclopentadiene (silole) ring fused with a silacyclobutene ring (Figure 1).⁸

Scheme 2



The skeletal structure of **2** was in good accord with those of parent 5-silabicyclo[3.2.0]hepta-1,3,6-triene **8** and its carbon analogue **1** calculated at the B3LYP/6-31+G(d,p) level.⁹ The following are the structural characteristics of **2** as compared to those of models **8** and **1** (Chart 1): (1) The sum of the three bond angles around the unsaturated bridgehead carbon C⁵ ($\Sigma@C^5$) was 333.4°, indicating remarkable pyramidalization at the C⁵ atom. The degree of pyramidalization was well reproduced in the theoretical models **8** and **1**; the $\Sigma@C^5$ values were 337° and 338° for **8** and **1**, respectively. The $\Sigma@C^5$ value for **2** was even smaller than that for one of the most highly strained anti-Bredt olefins, **9**¹⁰ (Chart 2); $\Sigma@(\text{the bridgehead unsaturated carbon}) = 349.4^\circ$. The deformation at C⁵ in **2** was mostly observed in the pyramidalization but not in

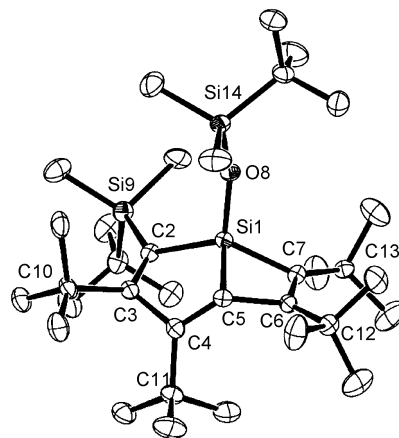


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å): Si(1)–C(2) 1.894(7), C(2)–C(3) 1.379(10), C(3)–C(4) 1.541(10), C(4)–C(5) 1.350(10), C(5)–C(6) 1.538(10), C(6)–C(7) 1.368(9), Si(1)–C(7) 1.891(7), Si(1)–O(8) 1.630(5), Si(1)–C(5) 1.826(7), Si(9)–C(2) 1.872(7). Selected bond angles (deg): O(8)–Si(1)–C(2) 108.3(3), O(8)–Si(1)–C(5) 125.2(2), O(8)–Si(1)–C(7) 110.4(3), C(2)–Si(1)–C(7) 138.4(3), Si(1)–C(2)–C(3) 99.8(5), C(2)–C(3)–C(4) 114.9(6), C(3)–C(4)–C(5) 110.5(6), C(4)–C(5)–C(6) 138.7(6), C(5)–C(6)–C(7) 100.8(6), C(6)–C(7)–Si(1) 91.9(5), C(2)–Si(1)–C(5) 95.7(3), Si(1)–C(5)–C(4) 105.5(5), Si(1)–C(5)–C(6) 89.2(4), C(5)–Si(1)–C(7) 74.2(3).

Chart 1

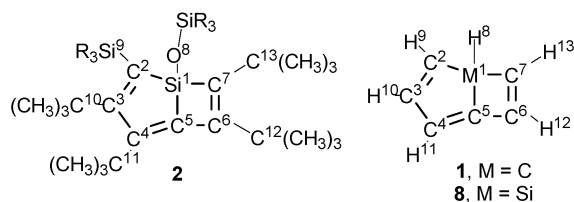
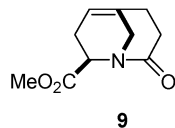


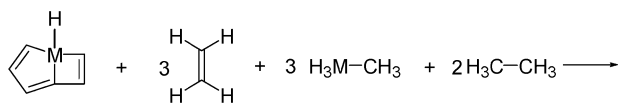
Chart 2



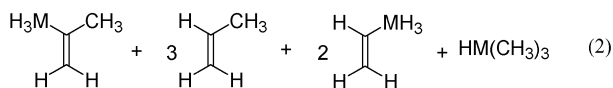
the twisting around the C⁴–C⁵ bond; the twist angle was defined as $(1/2)[\phi(C^3-C^4-C^5-Si^1) - \phi(C^{11}-C^4-C^5-C^6)] = 2.4^\circ$. (2) No significant pyramidalization was found at other unsaturated carbon atoms; the sum of the three bond angles around C², C³, C⁶ and C⁷ atoms for **2** was all in the range of 358.7–359.9°, while the sum around the C⁴ atom was 356.7°. The planar geometry around unsaturated ring carbons other than C⁵ was well reproduced in models **8** and **1**; the sum was within 358.2–359.9° for **8** and **1**. (3) Significant elongation of the C²=C³ bond distance (1.379(10) Å) observed for **2** may not be attributed to the steric repulsion between the substituents because a similar C²=C³ bond elongation was found for **8**. Shortening of the Si¹–C⁵ bond observed for **2** [1.826(7) Å] was not reproduced in model **8**. (4) The twisting of the substituents around the ring of **2** was quite large; the dihedral angles for Si⁹–C²–C³–C¹⁰, C¹²–C⁶–C⁷–C¹³, and C¹⁰–C³–C⁴–C¹¹ were –32°, 29°, and 73.5°, respectively; the corresponding dihedral angles were 4.8°, 4.6°, and 21.0° for **8**, and 6.9°, 3.0°, and 15.4° for **1**. The C³–C⁴ and C⁵–C⁶ bond distances for **2** [1.541(10) and 1.538(10) Å, respectively] were significantly longer than the corresponding distances for **8** and **1**; the distances were 1.480 and 1.477 Å for **8** and 1.462 and 1.477 Å for **1**. The lack of significant twisting of the substituents and the elongation of the C³–C⁴ and C⁵–C⁶ bonds in models **8** and **1** suggest that these deformations in **2** were due to the steric repulsion between the bulky substituents.

The theoretical calculations for models **8** and **1** at the MP2/6-31+G(d,p)//B3LYP/6-31+G(d) level revealed quite similar strain energies between **8** and **1**. Using the homodesmotic reactions shown in eq 2, the calculated strain energy was 30.15 and 30.69 kcal/mol for **8** and **1**, respectively.

Despite the highly distorted structure, **2** was quite thermally stable and could be kept in the air at room temperature for several months. Even at 150 °C, **2** was intact for 2 h in an argon atmosphere. The exceptional stability of **2** can be attributed to the effective steric protection provided by bulky substituents around the fused ring. The steric protection would be effective for the detection of the carbon analogue.



1, M = C; **8**, M = Si



Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan [Grants-in-Aid for Scientific Research (B) No. 11440185 (M.K.)].

Supporting Information Available: Details of the experiments and theoretical calculations, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and ORTEP drawings for **2** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) **2**: Pale yellow crystals; mp 122 °C; ¹H NMR (300 MHz, C₆D₆) δ 0.10 (s, 3H), 0.13 (s, 3H), 0.51 (s, 6H), 0.93 (s, 9H), 0.99 (s, 9H), 1.24 (s, 9H), 1.34 (s, 9H), 1.39 (s, 9H), 1.47 (s, 9H); ¹³C NMR (75 MHz, C₆D₆) δ –2.4, –2.1, –1.0, 0.5, 18.6, 19.0, 26.1, 28.4, 31.2, 32.8, 33.6, 33.9, 34.0, 37.0, 37.6, 41.3, 140.1 (C7), 143.9 (C2), 144.3 (C4), 148.5 (C5), 164.3 (C6), 198.4 (C3); ²⁹Si NMR (59 MHz, C₆D₆) δ –15.4, –5.7, 12.8, Anal. Calcd for C₃₄H₆₆O_{Si}: C, 71.00; H, 11.57. Found: C, 70.72; H, 11.44. The assignment of the unsaturated ¹³C resonances is based on the GIAO/B3LYP/6-311+G** for a model compound. For the details of the calculations, see the Supporting Information.
- (5) The thermal isomerization of **3** to **5** occurred at around 80 °C in solution.^{3b} See the Supporting Information for the experimental details.
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- (8) Crystal data for **2** at 150 K: C₃₄H₆₆O_{Si}, FW = 575.15, monoclinic, space group P2₁/n, a = 15.164(1), b = 11.6439(5), c = 42.775(4) Å, β = 98.969(1)°, V = 7460.2(9) Å³, Z = 8, d_{calc} = 1.024 g/cm³. The final R factor was 0.074 (R_w = 0.082) for 5734 reflections with I > 5σ(I). GOF = 2.07.
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JA0359097