

Photochemical isomerization of 1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene to 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene

Tadahiro Matsuno, Masaaki Ichinohe and Akira Sekiguchi*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan.

E-mail: sekiguch@staff.chem.tsukuba.ac.jp

Received (in Cambridge, UK) 7th February 2003, Accepted 2nd April 2003

First published as an Advance Article on the web 22nd April 2003

Upon irradiation of a benzene- d_6 solution of 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diaryl-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene [**1a**: aryl = phenyl, **1b**: aryl = 3,5-bis(trimethylsilyl)phenyl], 1,4,7,7-tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-diaryl-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (**2a,b**) was formed *via* skeletal rearrangement.

The photochemistry of organosilicon compounds is one of the most active areas for the creation of novel compounds and mechanistic studies.¹ Recently, we reported the reaction of tetrakis[di-*tert*-butyl(methyl)silyl]cyclotrisilene ($(^t\text{Bu}_2\text{MeSi})_4\text{Si}_3$)² with phenylacetylene to give the unusual product 1,2,2,5-tetrakis[di-*tert*-butyl(methyl)silyl]-4,7-diphenyl-1,2,5-trisilabicyclo[3.2.0]hepta-3,6-diene (**1a**), which has disilacyclobutene and trisilacyclopentene rings fused in a bicyclic manner.³ The reactivity of **1** promised to be quite interesting owing to its inherent ring strain and the presence of photo-sensitive Si–Si bonds. Thus, we have examined the photochemical reaction of **1** and have found an entirely unexpected photochemical isomerization of **1** to the 1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene derivative **2** containing several silicon atoms. This example of a 7-silabicyclo[2.2.1]hepta-2,5-diene derivative with several silicon atoms in the skeleton is very rare, because of the synthetic difficulty associated with their preparation.⁴ To the best of our knowledge, the sole example of this type of structure is a dibenzo annelated derivative, which was reported by the reaction of the 9,10-disilanthracene dianion with dichlorodimethylsilane.⁵ We report herein the isomerization of **1** to **2** and the crystal structure of **2**, along with a mechanistic discussion.

Upon irradiation of a benzene- d_6 solution of **1a** in a sealed NMR tube with a high-pressure Hg lamp (>300 nm),[†] **1a** completely disappeared within one hour. After removal of the solvent, the reaction mixture was separated by HPLC equipped with a reversed phase column to afford 1,4,7,7-tetrakis[di-*tert*-butyl(methyl)silyl]-2,5-diphenyl-1,4,7-trisilabicyclo[2.2.1]hepta-2,5-diene (**2a**) in 57% yield (Scheme 1). Compound **1b** also isomerized to **2b** in 73% yield.[‡]

The structure of **2a** was determined by mass spectrometry and by ^1H , ^{13}C , and ^{29}Si NMR[†] spectroscopy as well as by X-ray crystallography.[§] The NMR data on the structure of **2a** in C_6D_6 indicate a highly symmetrical structure. For example, the ^1H NMR spectrum showed only one set of peaks of olefinic protons at 8.03 ppm, as well as peaks indicating the presence of two different $^t\text{Bu}_2\text{MeSi}$ groups and one set of aromatic protons. The ^{29}Si NMR spectrum showed signals at -28.3 , 15.2 , 21.2 , and 62.6 ppm. The high field signal (-28.3 ppm) can be assigned to the silicon atoms at the bridgehead position, and the

low field signal (62.6 ppm) is assigned to the silicon atom at the 7-position of the 7-silabicyclo[2.2.1]hepta-2,5-diene skeleton. Such a characteristic deshielding of the 7-silicon atom is typical for the 7-silabicyclo[2.2.1]hepta-2,5-diene system.⁷ The mass spectrum of **2a** showed a very weak parent ion at m/z 916, with fragmentation peaks at m/z 859 ($\text{M}^+ - ^t\text{Bu}$) and 759 ($\text{M}^+ - \text{SiMe}^t\text{Bu}_2$). Fragmentations that are attributable to the expulsion of silylene [$(^t\text{Bu}_2\text{MeSi})_2\text{Si}$] and formation of a 1,4-disilabenzene were not observed.

The molecular structure of **2a** has been confirmed by X-ray analysis of a single crystal obtained by recrystallization from EtOH–hexane (Fig. 1). The Si–Si single bond lengths in the bicyclic skeleton are 2.4646(9) and 2.4811(8) Å, which are 5.6% longer than a normal Si–Si single bond (2.34 Å).

The formation of **2** is quite interesting, which prompted us to investigate the mechanism of isomerization. First, we have examined the photolysis of **1a** in the presence of MeOH, an effective trapping reagent for unsaturated silicon compounds; however, no MeOH trapped products were detected, indicating the absence of low-coordinated silicon compounds such as the trisilacycloheptatriene derivative with $>\text{Si}=\text{C}<$ bonds, which can be formed by the cleavage of the bridging Si–Si bond. It is likely that the reaction proceeds *via* concerted pathway a or pathway b (Scheme 2): a skeletal rearrangement with the breaking of two σ -bonds (Si–C and Si–Si) and formation of two new σ -bonds (Si–C and Si–Si) (path a); or an isomerization involving 1,2-silyl migration with cleavage of a Si–C bond in the four-membered ring (path b). The photochemically induced 1,2-silyl migration is already well established.⁸ To differentiate between these two possibilities, we have performed the photoreaction of the deuterium-labeled 1,2,5-trisilabicyclo-

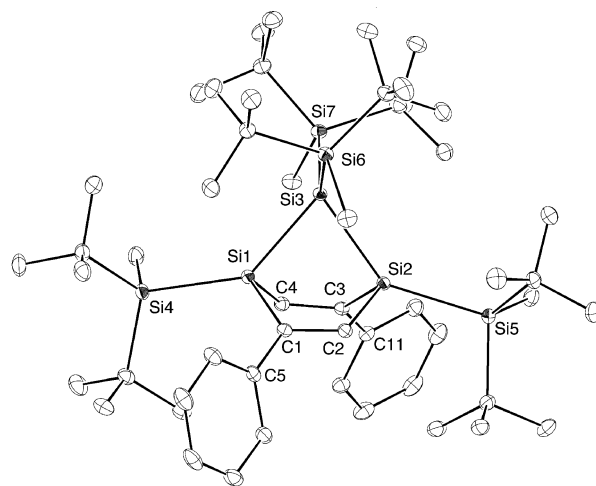
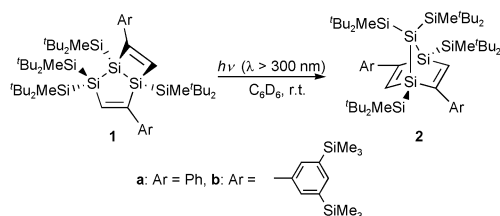
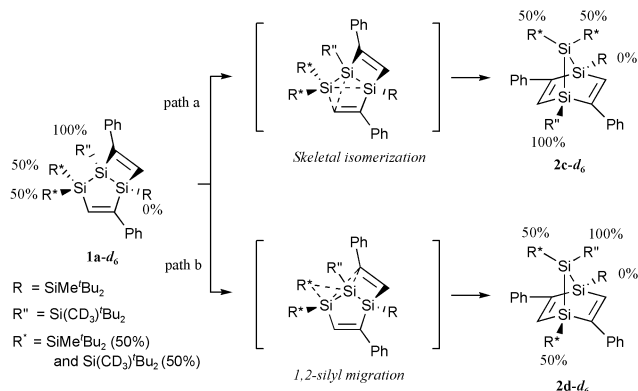


Fig. 1 Structure of **2a** (hydrogen atoms and hexane molecule are omitted for the clarity). Selected bond lengths (Å) and angles ($^\circ$): Si1–C4 1.892(2), Si1–C1 1.920(2), Si1–Si3 2.4646(9), Si2–C2 1.898(2), Si2–C3 1.933(2), Si2–Si3 2.4811(8), C1–C2 1.355(3), C3–C4 1.351(3); C4–Si1–C1 101.33(9), C4–Si1–Si3 93.10(7), C1–Si1–Si3 97.49(7), C2–Si2–C3 101.50(10), C2–Si2–Si3 94.88(7), C3–Si2–Si3 94.77(7), Si1–Si3–Si2 75.73(3), C2–C1–Si1 112.43(16), C1–C2–Si2 119.85(16), C4–C3–Si2 111.86(16), C3–C4–Si1 120.48(17).



Scheme 1



Scheme 2

[3.2.0]hepta-3,6-diene derivative **1a-d₆**, which was prepared by the reaction of deuterium-labeled cyclotrisilene with phenylacetylene.³ If the isomerization occurs *via* path a, the relative intensities of the two signals assigned to the methyl groups on silyl substituents at the 7- and 1,4-positions in the ¹H NMR spectrum should be the same. On the other hand, in the case of isomerization *via* 1,2-silyl migration, path b, the ratio of the intensities of the methyl group on the 7-position to those on the 1,4-positions would be 3 : 1. In fact, the photoreaction of **1a-d₆** under the same conditions as shown in Scheme 2 produced **2c-d₆**,⁹ indicating that the isomerization of **1** to **2** occurs *via* a skeletal isomerization, rather than through a 1,2-silyl migration.

This work was supported by a Grant-in-Aid for Scientific Research (Nos. 13440185, 14044015 and 14078204) from the Ministry of Education, Science and Culture of Japan, JSPS Research Fellowships for Young Scientists (T. M.), TARA (Tsukuba Advanced Research Alliance), and the COE (Center of Excellence) program.

Notes and references

† A benzene-d₆ (0.5 mL) solution of **1a** (152 mg, 0.166 mmol) in a sealed NMR tube was irradiated with a high-pressure Hg lamp (> 300 nm) for 1 h. After removal of the solvent *in vacuo*, the reaction mixture was separated by HPLC equipped with a reversed phased ODS column (eluent: MeOH : ^tBuOMe = 1 : 1) to afford colourless crystals of **2a** (82 mg, 57%); mp 240

°C (dec.); MS (EI, 70 eV) *m/z* (%) 916 (*M*⁺, 10), 859 (*M*⁺ - ^tBu, 4.6), 759 (*M*⁺ - ^tBu₂MeSi, 32), 73 (100); δ_H (300 MHz, C₆D₆) 0.395 (s, 6H), 0.404 (s, 6H), 0.80 (s, 18H), 1.20 (s, 18H), 1.26 (s, 18H), 1.38 (s, 18H), 7.05 (t, *J* = 6.9 Hz, 2H), 7.22 (t, *J* = 6.9 Hz, 4H), 7.53 (d, *J* = 6.9 Hz, 4H), 8.03 (s, 2H); δ_C (75.5 MHz, C₆D₆) -2.9, 1.2, 22.3, 22.4, 22.5, 23.4, 30.6, 30.8, 31.9, 32.9, 126.8, 128.0, 128.4, 149.3, 165.5, 167.9; δ_{Si} (59.6 MHz, C₆D₆) -28.3, 15.2, 21.2, 62.6; UV-Vis (hexane) λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 264 (42700), 322 (6500); Anal. calc. for C₅₂H₉₆Si₇: C, 68.04; H, 10.54. Found: C, 68.05; H, 10.49%.

‡ **2b**: Mp > 300 °C; δ_H (300 MHz, C₆D₆) 0.27 (s, 6H), 0.40 (s, 36H), 0.49 (s, 6H), 0.79 (s, 18H), 1.15 (s, 18H), 1.28 (s, 18H), 1.45 (s, 18H), 7.62 (s, 4H), 7.75 (s, 2H), 7.97 (s, 2H); δ_C (75.5 MHz, C₆D₆) -3.4, -0.8, 1.8, 21.5, 22.1, 22.2, 23.4, 30.3, 30.8, 31.6, 32.7, 133.7, 136.0, 138.8, 149.0, 167.0, 169.2; δ_{Si} (59.6 MHz, C₆D₆) -29.8, -3.9, 17.1, 21.5, 56.0; UV-Vis (hexane) λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 265 (42200), 320 (6800).

§ *Crystal data* for **2a**(hexane): C₅₈H₁₁₀Si₇, *M* = 1004.09, monoclinic, *a* = 13.6260(3), *b* = 35.7560(12), *c* = 13.7020(5) Å, β = 110.604(2)°, *V* = 6248.8(3) Å³, *T* = 120 K, space group = *P*2₁/*c*, *Z* = 4, *D_c* = 1.067 g cm⁻³. Diffraction data were collected on a Mac Science DIP2030K image plate diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å). The final *R* factor was 0.0562 (*R_w* = 0.1568 for all data) for 14571 reflections with *I* > 2σ(*I*). GOF = 1.042. The structure was solved by direct methods and refined by full-matrix least-squares using the SHELXL-97 program. CCDC reference number 203803. See <http://www.rsc.org/suppdata/cc/b3/b301536j/> for crystallographic data in CIF or other electronic format.

- 1 A. G. Brook, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York, 1998, **vol. 2**, Part 2, ch. 21; M. G. Steinmetz, *Chem. Rev.*, 1995, **95**, 1527.
- 2 M. Ichinohe, T. Matsuno and A. Sekiguchi, *Angew. Chem., Int. Ed.*, 1999, **38**, 2194.
- 3 M. Ichinohe, T. Matsuno and A. Sekiguchi, *Chem. Commun.*, 2001, 183.
- 4 H. Gilman, S. G. Cottis and W. H. Atwell, *J. Am. Chem. Soc.*, 1964, **86**, 1596; Y. Nakadaira, T. Kobayashi, T. Otsuka and H. Sakurai, *J. Am. Chem. Soc.*, 1979, **101**, 486; H. Sakurai, H. Sakaba and Y. Nakadaira, *J. Am. Chem. Soc.*, 1982, **104**, 6156.
- 5 W. Ando, K. Hatano and R. Urisaka, *Organometallics*, 1995, **14**, 3625.
- 6 Compound **1b** was prepared by the reaction of cyclotrisilene (^tBu₂Me-Si)₄Si₃ with 3,5-bis(trimethylsilyl)phenylacetylene in 74% yield. See ref. 3.
- 7 H. Sakurai, Y. Nakadaira, T. Koyama and H. Sakaba, *Chem. Lett.*, 1983, 213.
- 8 M. Kira and T. Iwamoto, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, New York 2001, **vol. 3**, ch. 16.
- 9 The ratio of two signals at 0.395 and 0.404 ppm assigned to the methyl groups is 1 : 1, and these relative intensities were half the magnitude of those of **2a**.