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Photochemical Isomerization and X-ray Structure of Stable [Tris(trialkylsilyl)silyl]cyclotrisilene

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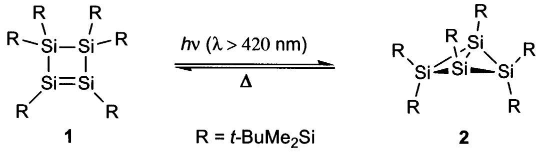
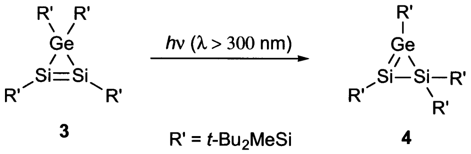
*Summary: Upon irradiation of a stable cyclotrisilene, 1,3,3-tris(tert-butyldimethylsilyl)-2-[tris(tert-butyldimethylsilyl)silyl]cyclotrisilene (**5**), in toluene with a low-pressure mercury-arc lamp, the isomerization of **5** to hexakis(tert-butyldimethylsilyl)bicyclo[1.1.0]tetrasilane (**2**) occurred in high yield; **2** isomerized further to the corresponding cyclotetrasilene **1** by a thermal process as previously reported. The distance of the silicon−silicon double bond in **5** determined by X-ray crystallography (2.132(2) Å) was similar to those of the known stable disilenes.*

Introduction

Since the first synthesis of a stable silicon−silicon doubly bonded compound (disilene) in 1981, a number of interesting thermal reactions of disilenes have been reported.[1] In contrast, very few photochemical reactions of disilenes have been known up to date. West and coworkers found the photochemical *E*,*Z*-isomerization of geometrical isomers of tetraaryldisilenes.[2] We have reported recently a unique photochemical isomerization of hexakis(*tert*-butyldimethylsilyl)cyclotetrasilene (**1**) to its valence isomer, hexakis(*tert*-butyldimethylsilyl)-bicyclo[1.1.0]tetrasilane (**2**), in addition to the reverse thermal isomerization of **2** to **1** (eq 1).[3] Using deuterium-labeled **1** and **2**, these two isomerizations were revealed to proceed via 1,2-silyl migration.[3b] Sekiguchi and coworkers have recently reported that a tetrakis(trialkylsilyl)disilagermacycloprop-1-ene (**3**) undergoes photochemical isomerization to the corresponding disilagermacycloprop-2-ene (**4**) also via the 1,2-silyl migration (eq 2).[4] Here, we report a novel photochemical isomerization of 1,3,3-tris(*tert*-butyldimethylsilyl)-2-[tris(*tert*-butyldimethylsilyl)silyl]cyclotrisilene (**5**), which was synthesized recently as the first stable cyclotrisilene,[5] to the corresponding bicyclo[1.1.0]tetrasilane **2**, together with the X-ray structural analysis of cyclotrisilene **5**.



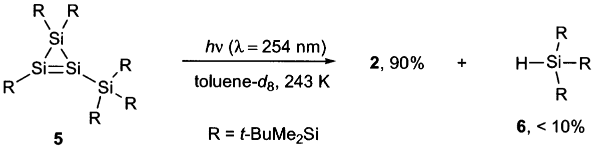
(1)



(2)

Results and Discussion

When a dark red toluene-d_8 solution of cyclotrisilene **5** (2.4×10^{-2} M) in a quartz NMR tube was irradiated using a low-pressure mercury-arc lamp ($\lambda = 254$ nm) at 243 K, the solution turned gradually dark brown. After 70 min irradiation, the ^{1}H NMR spectrum of the mixture showed the complete consumption of cyclotrisilene **5** together with the formation of the corresponding bicyclo[1.1.0]tetrasilane **2** (ca. 90% yield) and a small amount of tris(*tert*-butyldimethylsilyl)silane (**6**, ca. 10% yield) (eq 3, Figure 1). Expectedly, when the product mixture was allowed to warm to room temperature, the ^{1}H NMR signals due to bicyclotetrasilane **2** disappeared gradually and those due to cyclotetrasilene **1** appeared.[3] In contrast to the clean photolysis of **5**, thermolysis of **5** at 423 K gave a mixture of unidentified products.



(3)

As illustrated in Scheme 1, the photochemical isomerization of cyclotrisilene **5** is rationalized by a mechanism

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[1] For reviews on R$_2$M=MR$_2$ (M = Si, Ge, Sn), see: (a) West, R. *Pure Appl. Chem*. **1984**, *56*, 163. (b) Raabe G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 17, p 1015. (e) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (f) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (g) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125. (h) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (i) Kira, M.; Iwamoto, T. *J. Organomet. Chem.* **2000**, *611*, 236. (j) Weidenbruch, M. In *The Chemistry of Organic Silicon Compounds Volume 3*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 2001; Chapter 5, p 391. (k) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39.

[2] (a) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826. (b) Shephered, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664.

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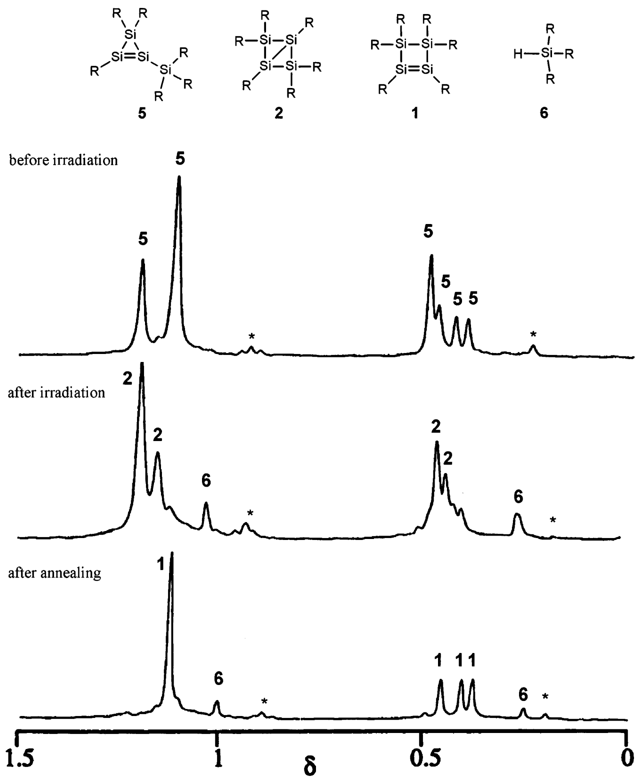


Figure 1. Photochemical isomerization of cyclotrisilene **5** to bicyclotetrasilane **2** and thermal isomerzation of **2** to cyclotetrasilene **1** monitored by ^{1}H NMR spectroscopy at 243 K. Top: before irradiation. Middle: after irradiation for 70 min at 243 K. Bottom: after annealing at ambient temperature in the dark for 1 day. Signals marked as "*" are due to impurity.

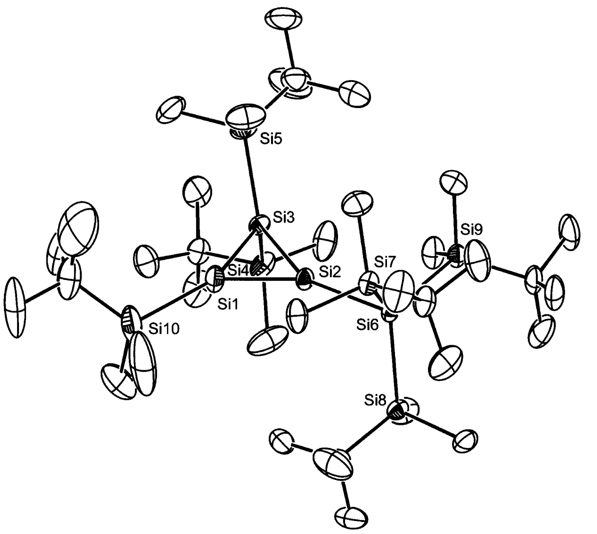
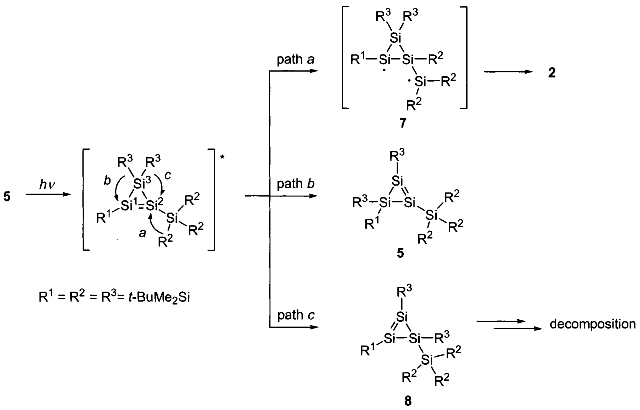


Figure 2. Molecular structure of cyclotrisilene **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−Si2 2.132(2), Si1−Si3 2.327(2), Si2−Si3 2.339(2), Si1−Si10 2.321(3), Si2−Si6 2.365(2), Si3−Si1−Si10 146.59(10), Si3−Si1−Si2 63.09(6), Si2−Si1−Si10 147.04(8), Si3−Si2−Si1 62.52(6), Si3−Si2−Si6 150.13(7), Si1−Si2−Si6 147.34(6), Si1−Si3− Si2 54.39(6), Si6−Si2−Si1−Si10 21.4(2).

including 1,2-silyl migration as proposed for the isomerization of cyclotetrasilene **1**[3] and disilagermacycloprop-1-ene **3**.[4] Whereas there are three possible 1,2-silyl migration pathways (paths **a**−**c**) for **5**, only path **a** leads to the observed product **2**; the formation of an intermediate 1,3-silyl biradical **7** via 1,2-migration of a trialkylsilyl group (R^2) followed by intramolecular radical recombination affords **2**. Path **b**, involving the 1,2-silyl migration of an R^3 group to an unsaturated silicon atom (Si^1), results in the identity reaction. Although another 1,2-silyl migration of an R^3 group (path **c**) should lead to the formation of cyclotrisilene **8**, the pathway would be prohibited sterically; the minor product **6** may be obtained by this pathway.

Scheme 1



Combining with our previous findings,[3] we have realized transformation among the three Si_4R_6 isomers **1**, **2**, and **5** using thermal and photochemical reactions as shown in eqs 1 and 3. Cyclotrisilene **5** isomerizes photochemically to bicyclo[1.1.0]tetrasilane **2**, which converts thermally to cyclotetrasilene **1**; **1** isomerizes photochemically to **2**. However, no evidence was found for the intervention of the corresponding tetrasila-1,3-diene and tetrasila-1,2-diene in the Si_4R_6 interconversion. It is interesting to note that the fashion of interconversion among Si_4R_6 isomers is quite different from that among C_4R_6 isomers. Thus, alkylcyclopropenes are known to give ring-opening products such as allenes and/or butadienes during photolysis[6] and thermolysis of bicyclo[1.1.0]butane gives unsually 1,3-butadiene rather than cyclobutene.[7] The absence of the 1,3- and 1,2-dienes in the Si_4R_6 interconversion would be ascribed to their high thermal instability; *transoid*- and *cisoid*-tetrasila-1,3-dienes and tetrasila-1,2-diene were calculated to be 33.3, 34.2, and 21.7 kcal/mol higher in energy, respectively, than the parent bicyclo[1.1.0]-tetrasilane at the B3LYP/6-311+G(d,p) level with ZPE correction.[8] Interestingly, the relative energy for 1-silylcyclotrisilene (21.6 kcal/mol) is rather high and comparable to that for tetrasila-1,2-diene at the same theoretical level. In contrast, among C_4H_6 isomers, buta-1,3-diene is the most stable isomer, which is 9.4, 23.0, and 21.7 kcal/mol lower in energy than 1-methylpropa-1,2-diene, 1-methylcyclopropene, and bicyclo[1.1.0]-

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butane, respectively, at the B3LYP/6-311+G(d,p) level with ZPE correction.[8] The relative stabilities among Si_4H_6 isomers are remarkably different from those among C_4H_6 isomers, which should be responsible at least in part for the apparent differences in the interconversion mode between two sets of M_4R_6 isomers (M = C and Si).[9]

Recrystallization of **5** from hexane at room temperature afforded orange prisms suitable for a single-crystal X-ray diffraction study. Data collection was carried out at 230 K because the single crylstal of **5** cracked below 230 K. The skeletal structure of **5** is similar to that of tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene (**9**) reported by Sekiguchi et al.,[10] while the geometries around two unsaturated silicon atoms in **5** are different because of the two different substituents on the endocyclic Si−Si double bond. The unsaturated silicon atom Si^1 is slightly pyramidalized, while the geometry around Si^2 is planar; the sums of three bent angles around the unsaturated silicon atoms are 356.7° for Si^1 and 360.0° for Si^2, and the dihedral angle $Si^6-Si^2-Si^1-Si^{10}$ was 21.4(2)°. Since the optimized structure of a model tetrakis(trihydrosilyl)cyclotrisilene calculated at the B3LYP/6-31G(d) level has C_{2v} symmetry with a planar Si═Si double bond,[11] pyramidalization at Si^1 atoms in **5** would be mainly due to steric repulsion among substituents as observed in cyclotrisilene **9** (the corresponding dihedral angle Si−Si═Si−Si is 31.9(2)°).[10] The Si═Si double-bond distance in **5** is 2.132(2) Å, which is similar to those of the known three-membered disilenes, cyclotrisilene **9** (2.138(4) Å),[10] disilagermacycloprop-1-ene **3** (2.146(1) Å),[4] and tetrakis(tris(*tert*-butyldimethylsilyl)silyl)spiropentasiladiene (2.186(3) Å).[11] In accord with heavier steric hindrance between substituents on Si^2 and Si^3 than that between substituents on Si^1 and Si^3, the Si^2-Si^3 bond (2.339(2) Å) is a little longer than the Si^1-Si^3 bond (2.327(2) Å).

Experimental Section

All operations were performed in oven-dried or flame-dried glassware under a dry argon atmosphere. Toluene-d_8 was dried over potassium mirror and distilled through a vacuum line before use. ^1H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (59 MHz) NMR spectra were recorded on a Bruker AC300P NMR spectrometer.

Photolysis of Cyclotrisilene 5. A toluene-d_8 (0.5 mL) solution of **5** (0.010 g, 2.4×10^{-2} M) in a sealed quartz NMR tube was irradiated using a low-pressure mercury-arc lamp (λ = 254 nm) at 243 K for 70 min. The photoreaction was followed by ^1H NMR spectroscopy at the same temperature.

X-ray Crystallography of Cyclotrisilene 5. Single crystals of **5** suitable for X-ray diffraction study were obtained by recrystallization from dry hexane. X-ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.71073 Å) at 230 K. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997). Crystallographic data of **5** are summarized in Table 1.

Table 1. Crystallographic Data for Cyclotrisilene 5

formula	$C_{36}H_{90}Si_{10}$
molecular weight	803.96
cryst syst	triclinic
space group	$P\bar{1}$(#2)
a/Å	10.780(1)
b/Å	14.290(2)
c/Å	19.782(3)
α/deg	70.660(6)
β/deg	76.304(5)
γ/deg	71.434(3)
V/Å^3	2696.1(5)
Z	2
D_{calcd}/(g cm^{-3})	1.006
F(000)	892.00
μ, cm^{-1}	2.69
temperature/K	230.0
no. of measd reflns	22 744
no. of ind reflns	10 606 (R_{int} = 0.039)
goodness of fit on F^2	1.02
final R indices	$R1 = 0.064$ ($I > 2\sigma(I)$), $wR2 = 0.178$ (all data)

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Supporting Information Available: Tables giving the details of the X-ray structure determination, bond lengths, and bond angles of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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