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Communication

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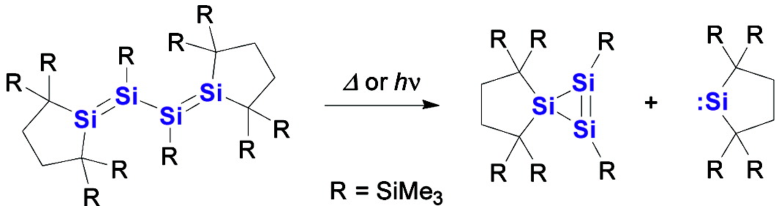

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Thermal and Photochemical Cleavage of Si═Si Double Bond in Tetrasila-1,3-diene

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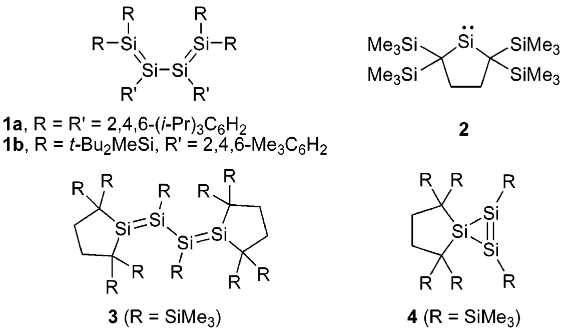
Although various types of stable disilenes (silicon−silicon doubly bonded compounds) have been synthesized and their structure and reactions have been investigated extensively,[1] very few studies have been devoted to the synthesis of stable conjugated disilenes, silicon congeners of polyenes; only two stable tetrasila-1,3-dienes, **1a**[2a−f] and **1b**,[2g] have been reported to date (Chart 1). Rather unexpectedly, these tetrasila-1,3-dienes adopt a synclinal conformation around the central Si−Si single bond in the solid states. During the course of our recent studies of unsaturated silicon compounds such as trisila-allene, silanechalcogenones, silaketenimines, etc.,[3] we have synthesized a novel tetrasila-1,3-diene **3** having an anticlinal conformation in the solid state by utilizing isolable dialkylsilylene **2**[4] as a building block. Thermolysis and photolysis of **3** showed highly selective cleavage of the Si═Si double bond giving cyclotrisilene **4**[5] and silylene **2**, in contrast to the unimolecular reactions of buta-1,3-dienes.[6]

Chart 1



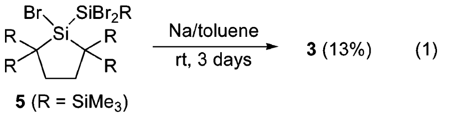
1a, R = R′ = 2,4,6-(i-Pr)$_3$C$_6$H$_2$
1b, R = t-Bu$_2$MeSi, R′ = 2,4,6-Me$_3$C$_6$H$_2$

2

3 (R = SiMe$_3$)

4 (R = SiMe$_3$)

Tetrasila-1,3-diene **3** was synthesized as air-sensitive red crystals in 13% yield by the reduction of tribromodisilane **5**, which was prepared by the reaction of silylene **2** with Me$_3$SiSiBr$_3$,[10] with sodium metal in toluene at room temperature (eq 1). Tetrasiladiene **3** was characterized by NMR spectroscopy, MS, elemental analysis, and X-ray crystallography.[11,12]



5 (R = SiMe$_3$)

The X-ray analysis of **3** has shown that the tetrasiladiene skeleton is not planar but highly twisted (Figure 1). However, in contrast to **1a** and **1b** having a synclinal conformation, **3** adopts an anticlinal conformation with the Si1−Si2−Si3−Si4 dihedral angle of 122.56(7)°. The Si═Si double bond distances of **3** are 2.1980(16) and 2.2168(16) Å and the central Si−Si single bond distance is 2.3400(15) Å.

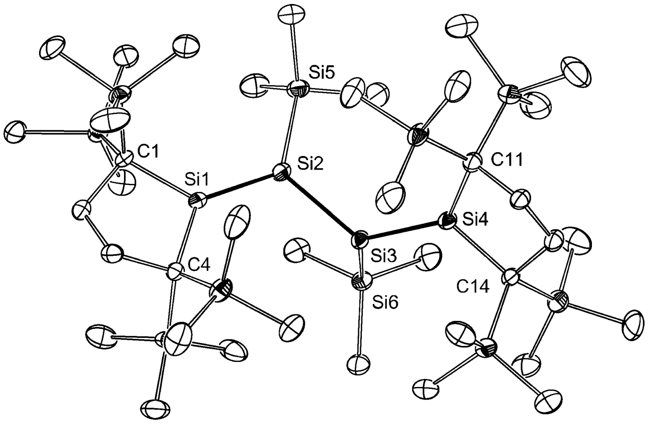


Figure 1. Molecular structure of **3**. In an asymmetric unit, two crystallographically independent molecules were observed. Since they have almost the same structural characteristics, only the structure of one molecule is shown. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and a dihedral angle (deg): Si1−Si2, 2.1980(16); Si2−Si3, 2.3400(15); Si3−Si4, 2.2168(16); Si1−Si2−Si3−Si4, −122.56(7).

The UV−vis spectrum of tetrasila-1,3-diene **3** shows the longest-wavelength absorption maximum at 510 nm (ϵ 1200) at 77 K in a 3-methylpentane glass matrix assignable to a $\pi \rightarrow \pi^*$ transition band. The maxima is comparable to those of **1a** (518 nm)[2a] and **1b** (531 nm)[2g] even though there are no aromatic substituents in **3**, suggesting significant conjugation between the two π(Si═Si) systems.[13]

The ^{29}Si resonances of central and terminal unsaturated Si nuclei of **3** were observed at 9.3 and 210.2 ppm.[15] The ^{1}H NMR spectrum showing four singlet signals due to trimethylsilyl groups on one silacyclopentane ring at room-temperature suggests that the anticlinal geometry of Si═Si−Si═Si framework in **3** is maintained in solution.

Thermolysis of **3** at 80 °C in benzene for 3 h afforded **4** and cyclic silene **6** in high yields, together with complete consumption of **3** as determined by ^{1}H NMR spectroscopy (Scheme 1). Irradiation of **3** in benzene with a filtered high-pressure mercury arc lamp (λ > 390 nm) for 2 h afforded **4** and silepin **7** in 51 and 43% yields, respectively, after 89% consumption of **3** (Scheme 1). The structure of **4** was identified by NMR spectroscopy, MS, elemental analysis, and X-ray structural analysis.[16] Compounds **6** and **7** are known to form quantitatively during the thermolysis[3a] and photolysis[17] of silylene **2** in benzene, respectively. As shown in eq 2, the formation of cyclotrisilene **4** would be explained by the facile intramolecular silylene insertion into the Si═Si bond of disilenylsilylene **8** formed via a Si═Si double bond dissociation.

Because a number of thermal and photochemical dissociation reactions of disilenes giving the corresponding two silylenes have been reported,[14,18] the present reactions of **3** giving **8** and **2** are not unexpected. However, theoretical calculations of the Si$_4$R$_6$ systems (R = H, Me)[19] have revealed that the tetrasila-1,3-dienes are much

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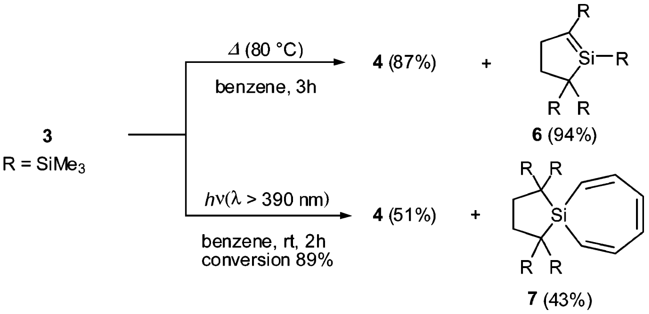
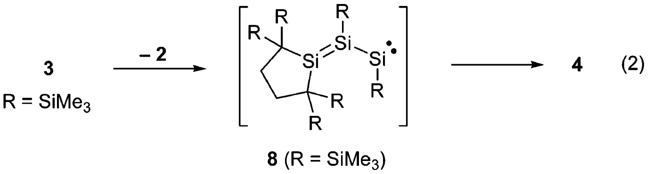
Scheme 1



more unstable than the corresponding valence isomers such as bicyclo[1.1.0]tetrasilanes or cyclotetrasilenes; the calculated activation energies for the isomerization of tetrasila-1,3-diene to these valence isomers are known to be less than 10 kcal·mol^{-1}.[19a] On the other hand, the theoretical dissociation energy of the Si═Si double bond in 1,1,4,4-tetramethyl-2,3-bis(silyl)-tetrasila-1,3-diene (**3′**) is 48.5 kcal·mol^{-1} at the B3LYP/6-311++(d,p) level.[20] The isomerization to the valence isomers or dimerization via the [4+2] cycloaddition would be suppressed by severe steric repulsion between bulky substituents of **3** during the reactions.[21] The dissociation energy of the double bonds in **3** may be lowered by the steric strain than that for **3′** to make feasible the dissociation in benzene at reflux.[22] Preference of the Si═Si double bond cleavage to the central Si−Si single bond cleavage is a straightforward indication of the smaller bond dissociation energy of the double bond than that of the single bond in **3** as predicted by the CGMT model.[23]



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Supporting Information Available: Details for the syntheses of **3** and **5**, thermolysis and photolysis of **3**, X-ray crystallographic data for **4**, UV−vis spectra of **3**, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) **3**: air-sensitive red crystals; mp 100 °C (decomp). ^{1}H NMR (C_6D_6, δ) 0.354 (s, 18H, TMS), 0.364 (s, 18H, TMS), 0.38 (s, 18H, TMS), 0.46 (s, 18H, TMS), 0.71 (s, 18H, TMS), 1.99 (brs, 8H, CH_2). ^{13}C NMR (C_6D_6, δ) 3.7, 4.6, 4.9, 5.0, 7.3, 26.4, 27.1, 34.9, 35.8. ^{29}Si (C_6D_6, δ) −8.2, 0.7, 2.9, 3.1, 3.2 (Me_3Si), 9.3 (Si(central)═), 210.2 (Si(terminal)═). MS (EI, 70 eV) *m/z* (%) 946 (3, M$^+$), 931 (2, M$^+$-Me), 574 (25, M$^+$−:Si(CTMS$_2$-CH$_2$)$_2$), 501 (26), 73 (100). UV (hexane) λ_{max}/nm ($\epsilon \times 10^{-3}$) 439 (1.4), 362 (0.3), 298 (0.4), 255 (5.0). Anal. Calcd for $C_{38}H_{98}Si_{14}$: C, 48.12; H, 10.42. Found: C, 47.76; H, 10.27.

(12) Recrystallization from hexane gave single crystals of **3** suitable for data collection. Crystal data for **3**: $C_{38}H_{98}Si_{14}$; formula weight 948.42; triclinic, $a = 11.752(4)$ Å, $b = 20.105(7)$ Å, $c = 25.035(9)$ Å, $\alpha = 97.411(7)°$, $\beta = 94.372(6)°$, $\gamma = 97.689(7)°$, $V = 5787(4)$ Å^3, $T = -123$ °C, space group $P\bar{1}$; $Z = 4$; $D_{calcd} = 1.099$ g/cm^3; 84497 reflections measured, 26405 unique ($R_{int} = 0.0771$). The final $R1$ and $wR2$ values were 0.0905 [$I > 2\sigma(I)$] and 0.1814 (for all data), respectively.

(13) At least three band maxima were observed at [λ_{max}/nm (ϵ); 510 (1200), 430 (4400), 355 (1600)) assignable to $\pi \rightarrow \pi^*$ transition bands for **3** at 77 K. The UV-vis spectrum of **3** in 3-methylpentane depends on temperature remarkably, suggesting the structural fluctuation of tetrasiladiene skeleton. See Supporting Information for the details. The maximum at 510 nm is much red-shifted to that of a tetraalkyldisilene $R_2Si{=}SiR_2$ [R = CH(SiMe$_3$)$_2$, λ_{max}/nm (ϵ) = 393 (12600)].[14]

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(15) Resonances due to unsaturated silicon atoms of **3** are comparable to those for $(H_3Si)_2Si{=}SiMe_2$ that are calculated to be 233.0 and −15.8 ppm for *Si*Me$_2$ and *Si*(SiH$_3$)$_2$, respectively, at the BP86-GIAO/IGLO-III//B3LYP/6-31+G(d) level: Auer, D.; Strohmann, C.; Arbuznikov, A. V.; Kaupp, M. *Organometallics*, **2003**, *22*, 2442.

(16) **4**: air-sensitive yellow crystals; mp 156−158 °C. ^{1}H NMR (C_6D_6, δ) 0.35 (s, 36H, TMS), 0.42 (s, 18H, TMS), 1.99 (s, 4H, CH_2). ^{13}C NMR (C_6D_6, δ) 1.9, 3.8, 12.0, 33.4. ^{29}Si (C_6D_6, δ) −18.2, −5.3, 3.5, 142.9 (Si═Si). MS (EI, 70 eV) *m/z* (%) 574 (20, M$^+$), 501 (6, M$^+$-TMS), 501 (16, M$^+$-2TMS), 372 (14, (CH$_2$TMS$_2$C)$_2$Si:), 73 (100). UV (hexane) λ_{max}/nm ($\epsilon \times 10^{-3}$) 391 (4.4), 277 (10.8). Anal. Calcd for $C_{22}H_{58}Si_9$: C, 45.92; H, 10.16. Found: C, 45.61; H, 9.81. See Supporting Information for the X-ray analysis of **4**.

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(19) Parent and methylated *s-cis-* and *s-trans*-tetrasila-1,3-dienes are more than 30 kcal·mol^{-1} higher in energy than the corresponding cyclotetrasilenes and bicyclo[1.1.0]butanes, while buta-1,3-diene is much more stable than cyclobutane and bicyclo[1.1.0]butane. (a) Müller, T. *Organosilicon Chemistry IV*; Auner, N., Weis, J., Eds.; Wiley-VDH: Weinheim, Germany, 2000; p 110. (b) Koch, R.; Bruhn, T.; Weidenbruch, M. *J. Mol. Struct. THEOCHEM* **2004**, *680*, 91.

(20) For the calculation details, see Supporting Information.

(21) As pointed out by a reviewer, the possibility of the formation of **2** and **4** via isomerization of **3** to the corresponding bicyclo[1.1.0]tetrasilane is difficult to be ruled out experimentally or theoretically. The alternative mechanism may be unlikely because the sterically unfavorable formation of bicyclo[1.1.0]tetrasilane. Incidentally, there are no reports on silylene elimination reactions of bicyclo[1.1.0]tetrasilanes.

(22) The activation enthalpy for the bond dissociation of the Si═Si bond in Tbt(Mes)Si═Si(Mes)Tbt (Tbt = 2,4,6-{(Me$_3$Si)$_2$CH}$_3$C$_6$H$_2$; Mes = 2,4,6-Me$_3$C$_6$H$_2$) is reported to be ca. 26 kcal·mol^{-1}.[18a,b]

(23) While dissociation energy of the C═C double bond is well known to be almost twice as large as that of the C−C single bond, the dissociation energy of an Si═Si double bond is even smaller than that of the corresponding Si−Si single bond. The fact is rationalized by the CGMT model,[24] which ascribes the relatively lower Si═Si bond dissociation energy to the relatively large singlet-to-triplet excitation energies (ΔE_{ST}) of the component silylenes.

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