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Decamethyl-1,4,5,8,11,12-hexasilabicyclo[6.6.0]tetradeca-2,6,9,13-tetrayne[1]

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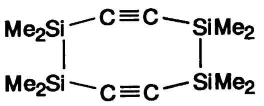
Decamethyl-1,4,5,8,11,12-hexasilabicyclo[6.6.0]tetradeca-2,6,9,13-tetrayne was prepared by the reaction of a di-Grignard reagent derived from 1,2-bis(ethynyl)-1,1,2,2-tetramethyldisilane and 1,2-dimethyltetrachlorodisilane. Some physical and chemical properties of the novel bicyclic compound are described.

After the discovery of the unique electronic absorption of aryl disilanes,[2] an intense interest has been accumulated on the electronic and chemical properties of σ-π conjugated systems.[3] The σ-π conjugation is exemplified most efficiently if the molecular framework is so fixed that interacting molecular orbitals can overlap in maximum. We have reported octamethyl-3,4,7,8-tetrasilacycloocta-1,5-diyne (**1**)[4] and octamethyltetrasila[2.2]paracyclophane (**2**)[5] as examples of such a system.



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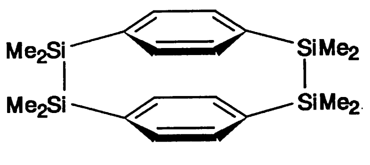

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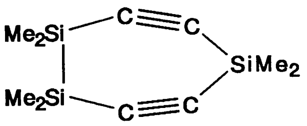
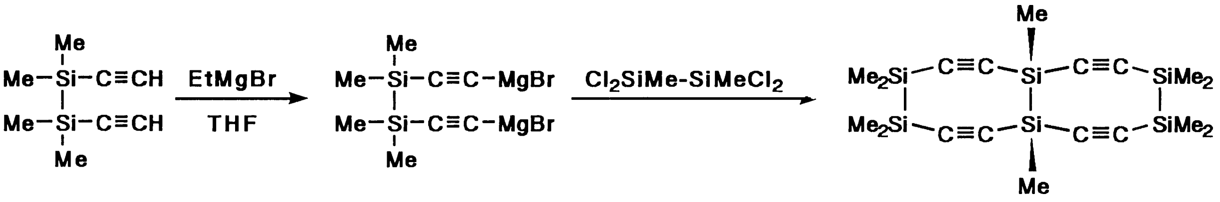


3

The compound **1** was first prepared by the ring contraction reaction of 3,3,4,4,7,7,8,8,9,9-decamethyl-3,4,7,8,9-pentasilacyclonona-1,5-diyne together with 3,3,6,6,7,7-hexamethyl-3,6,7-trisilacyclohepta-1,4-diyne (**3**)[4] but later the reaction of the di-Grignard reagent derived from 1,2-diethynyl-1,1,2,2-tetramethyldisilane with 1,2-dichlorotetramethyldisilane was applied to the preparation of **1**.[6] The reaction has been successfully extended to the preparation of the next higher member, dodecamethylhexasilacyclododeca-1,5,9-triyne[7] and the chemistry of the cyclic polysilapolynes has been further extended to cyclic polyacetylenes.[8]

As a logical extension of the work, we report herein the preparation and interesting properties of a bicyclic polydisilanylenepolyacetylene, decamethyl-1,4,5,8,11,12-hexasilabicyclo[6.6.0]tetradeca-2,6,9,13-tetrayne (**4**).[9] A typical procedure is shown as follows. 1,2-Dimethyl-1,1,2,2-tetrachlorodisilane (1.72 g, 7.54 mmol) in THF (50 ml) was added to a THF solution (80 ml) of di-Grignard reagent, derived from 1,2-diethynyl-1,1,2,2-tetramethyldisilane (2.47 g, 14.9 mmol). The reaction mixture was stirred for 5 h at room temperature, hydrolyzed, and then dried over sodium sulfate. The solution was concentrated in vacuo and the residue was subjected to chromatography on silica gel (benzene) to afford 673 mg (22%) of pure **4** as colorless crystals (mp 231 °C). The compound **4** is stable to air and water, and soluble in common organic solvents, such as benzene, hexane, ethers, and halocarbons.[10)]



4 (22%)

The structure of **4** was determined by the spectroscopic data.[11)] The ^1H, ^{13}C, and ^{29}Si NMR chemical shifts of **4** are similar to those of the monocyclic compound **1**, indicating that the framework of **4** is made up by the eight-membered ring system.[6,12)] Figure 1 shows UV spectra of **4** and the corresponding monocyclic compound **1** in hexane. The lowest energy absorption of **4** is observed at 260 nm, which is longer than **1** by 10 nm. The red shift of **4** is due to the expansion of the σ-π conjugation system which results in destabilization and stabilization of the HOMO and LUMO levels, respectively.

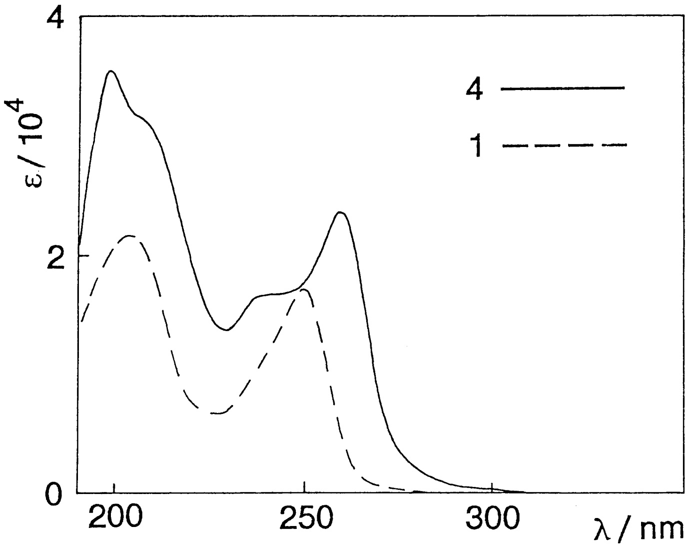
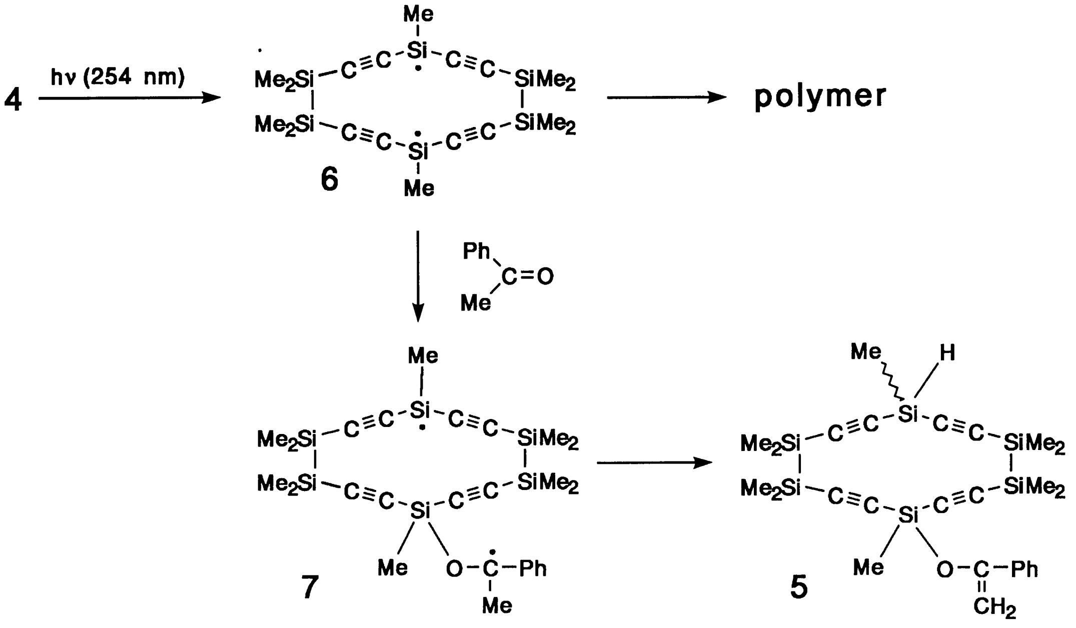


Fig. 1. UV spectra of **1** and **4**.

The central Si-Si bond of **4** is reactive and we have found an efficient photochemical cleavage of the bond. Thus irradiation of **4** in benzene with a low pressure mercury arc lamp afforded pale yellow polymeric materials. The molecular weight distribution of the polymer was determined by gel permeation chromatography, calibrated by polystyrene standards, with chloroform as eluent; $\overline{Mw}$ = 5700, $\overline{Mn}/\overline{Mw}$ = 1.35. The resulting polymer is, however, photosensitive because of the ethynyldisilane units and the secondary photodecomposition of the polymer made the structure of the polymer rather complicated. The rate of disappearance of **4** in the photolysis in the presence of acetophenone or carbon tetrachloride decreased, suggesting that the polymerization may proceed by a radical chain mechanism.[13,14]

Irradiation of a benzene solution of **4** in the presence of acetophenone afforded decamethyl-1-(1-phenylvinyloxy)-1,4,5,8,11,12-hexasilacyclotetradeca-2,6,9,13-tetrayne (**5**) in 4% yield as a single product except for polymeric materials. The ^{1}H NMR spectrum of **5** was complicated, but can be analyzed as a mixture of syn and anti stereoisomers. A pair of Si–Me doublet signals can be assigned to methylsilylene groups of the two isomers. Furthermore, two vinylidene signals standing very close can be assigned to 1-phenylvinyloxy groups.[15] The equal intensity of these isomer signals indicates the ratio of the isomers to be 1:1.

The mechanism for the photoreaction of **4** is summarized in Scheme 1. The central Si–Si bond of **4** is cleaved efficiently under photochemical conditions to form a biradical **6**, which gives **7** by addition to acetophenone or undergoes polymerization. Intermolecular disproportionation of **7** gave **5** in 1:1 isomer ratio.[16] Further studies are in progress.



Scheme 1.

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2) H. Sakurai and M. Kumada, *Bull. Chem. Soc. Jpn.*, **37**, 1894 (1964).
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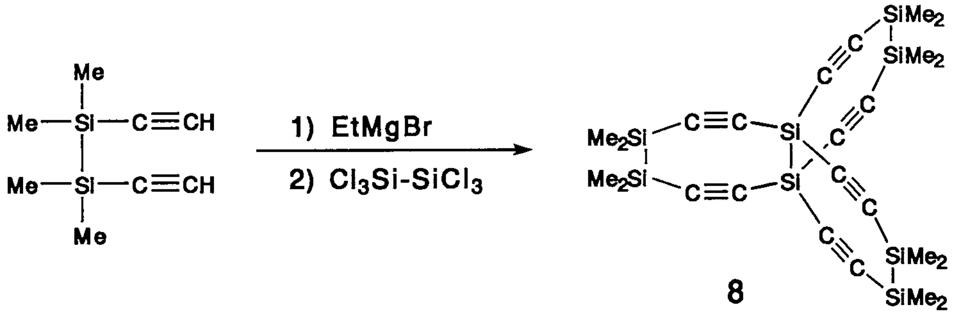
6) H. Sakurai, *Pure Appl. Chem.*, **59**, 1637 (1987); T. Iwahara and R. West, *J. Chem. Soc., Chem. Commun.*, **1988**, 954.

7) H. Sakurai, Y. Eriyama, A. Hosomi, and Y. Nakadaira, *Chem. Lett.*, **1984**, 1383.

8) H. Sakurai, "Recent Advances in Silicon-Containing Cyclic Polyacetylenes," in "Heteroatom Chemistry," ed by E. Block, VCH Publishers, Inc., New York, N. Y., U. S. A., Chapt 18 (1990).

9) A similar compound with isopropyl instead of methyl at the bridge-head silicon has been prepared recently. T. Iwahara and R. West, submitted for publication. We thank Professor West for sending us a preprint.

10) The reaction of the di-Grignard reagent has been further extended to the attempted preparation of a tricyclic compound **8** by the reaction with hexachlorodisilane. We could detect the parent mass peak (M^+) and a peak corresponding to M^+-15 at m/z 548 and 533, respectively, but the compound seems to be extremely unstable to decompose presumably by cleavage of the central Si-Si bond.



11) **4**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 12H), 0.28 (s, 12H), 0.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ -3.5, -3.2, -3.1, 113.4, 122.5; ^{29}Si NMR ($CDCl_3$) δ -33.6, -53.8; High Resolution Mass Found 414.0962, Calcd for $C_{18}H_{30}Si_6$ 414.0963; IR (KBr) 2089 cm^{-1}. The cis stereochemistry of **4** was assigned on the basis of the MM2 calculations. Calculations with parameters, modified to optimize the structure of **1**, indicate that the cis isomer is 17.8 kcal/mole more stable than the trans isomer. Details will be reported later.

12) **1**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s); ^{13}C NMR ($CDCl_3$) δ -3.07, 119.46; ^{29}Si NMR ($CDCl_3$) δ -33.62. The formation of a seven-membered system can be excluded because hexamethyl-3,6,7-trisilacyclohepta-1,4-diyne (**3**) is known to be extremely unstable due to the ring strain.[4)]

13) C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5119 (1982).

14) C. Chatgilialoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, **104**, 5123 (1982).

15) **5**: High Resolution Mass Found 534.1542, Calcd for $C_{26}H_{38}OSi_6$ 534.1538; ^{1}H NMR (mixture of syn and anti isomers, $CDCl_3$) δ 0.2-0.3 (m), 0.376 (d, J = 1.4 Hz), 0.379 (d, J = 1.4 Hz), 4.30 (m), 4.95 (d, J = 2 Hz), 4.97 (d, J = 2 Hz), 5.02 (d, J = 2 Hz), 5.04 (d, J = 2 Hz), 7.2-7.3 (m), 7.5-7.6 (m).

16) Photochemical addition of disilane with ketones accompanying intramolecular hydrogen abstraction was reported; H. Sakurai, K. Sakamoto, and K. Kira, *Chem. Lett.*, **1987**, 983.

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