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A Facile Synthesis of Tetrakis(trimethylsilyl)butatriene Properties and Cycloadditions[1)]

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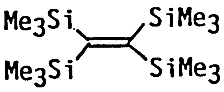
Tetrakis(trimethylsilyl)butatriene was readily prepared by flash vacuum pyrolysis of hexakis(trimethylsilyl)-2-butyne. The physical and chemical properties of the butatriene are described.

Recently we have reported unusual chemical and physical properties of tetrakis(trimethylsilyl)ethylene (**1**) due to sigma(Si-C)-pi mixing resulting from the distorted nonplanar structure in the ground state.[2)] In connection with our continuous studies on silyl substituted alkenes, it is interesting to us to investigate the physical and chemical properties of 1,1,4,4-tetrakis(trimethylsilyl)-1,2,3-butatriene (**2**) because of its unique structure.



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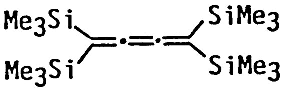

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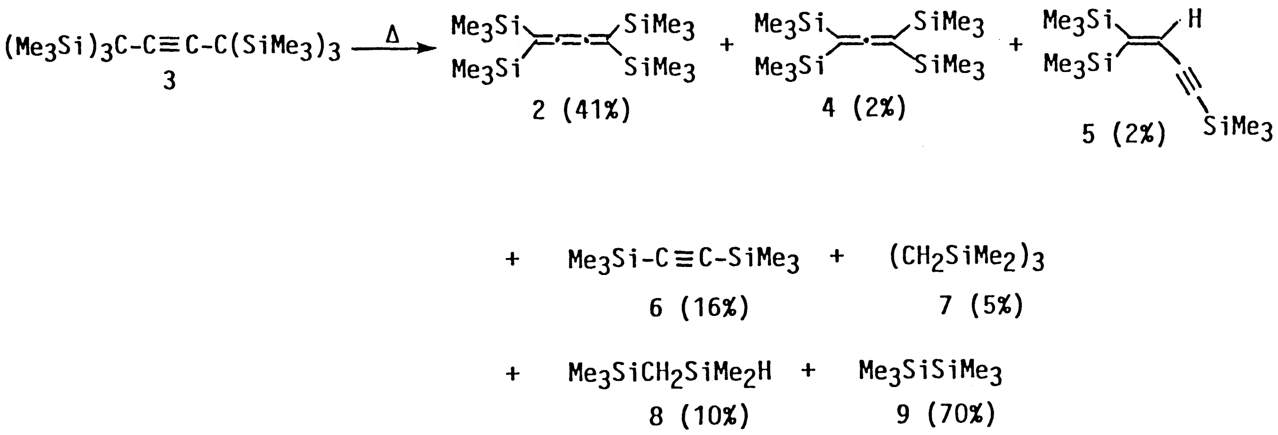
The butatriene has two sp-hybridized central and two sp^2-hybridized terminal carbon atoms and it is expected that the central pi-bond strongly interact with the sigma(Si-C) bonds, giving unique properties similar to **1**. Although the butatriene has been briefly mentioned in literatures,[3)] the chemical and physical properties remained unexplored as well as the effective method of the synthesis. During the course of our investigation, Kusumoto and Hiyama have reported the synthesis of **2** via palladium catalyzed double silylation of bis(trimethylsilyl)-butadiyne followed by methylation.[4)] Being prompted by the report, we wish to communicate herein an entirely different facile synthesis of **2** together with some physical and chemical properties including cycloaddition reactions with hexafluoro-2-butyne, disilene, silene, and butadiene.

Hexakis(trimethylsilyl)-2-butyne (**3**, 1.38 mmol) was pyrolyzed by passing through a quartz tube heated at 650 °C under reduced pressure (ca. 10^{-3} mmHg), and the pyrolysates were collected in a receiver cooled by liquid nitrogen.

To the pyrolysates, hexane was added and unreacted **3** was filtered off, and then the solution was concentrated. The residue was crystallized from ethanol to give pure **2** as pale orange crystals (41%).[5] Since the acetylene **3** is readily available from hexachloro-1,3-butadiene and trimethylchlorosilane by the reaction with magnesium,[6] the present pyrolysis provides a very simple and facile method of preparing the butatriene.



The pyrolysis reaction may proceed via homolytic bond cleavage of the Si-C bond of **3**, to give the trimethylsilyl radical and the butatriene. Indeed, GLC analysis of the pyrolysates revealed the formation of a variety of products (**4** - **9**) along with **2**. Products **7**, **8**, and **9** are evidently derived from the trimethylsilyl radical.[7] Compounds **5** and **6** are the thermal reaction products of the butatriene.

The butatriene exhibits absorption bands (log ϵ) in hexane at 507 (1.96), 463 (1.58), 298 (4.60), 283 (4.34), and 211 nm (4.59), whereas 1,1,4,4-tetra-t-butyl-1,2,3-butatriene (**10**) has absorptions at 268 (4.56), and 228 nm (4.02). The extremely large bathochromic shift of **2** compared with **10** is a result of the strong interaction of the central pi-bond with the sigma(Si-C) bonds.

CNDO/2 calculation also supports that the orbital interaction between the central pi and sigma-(Si-C) bonds causes the remarkable destabilization of the HOMO level and slight stabilization of the LUMO as shown in Fig. 1. Consequently, it is interesting to see whether the cycloaddition of **2** occurs at the central double bond or the terminal ones.

We studied the reactions of **2** with hexafluoro-2-butyne, disilene,

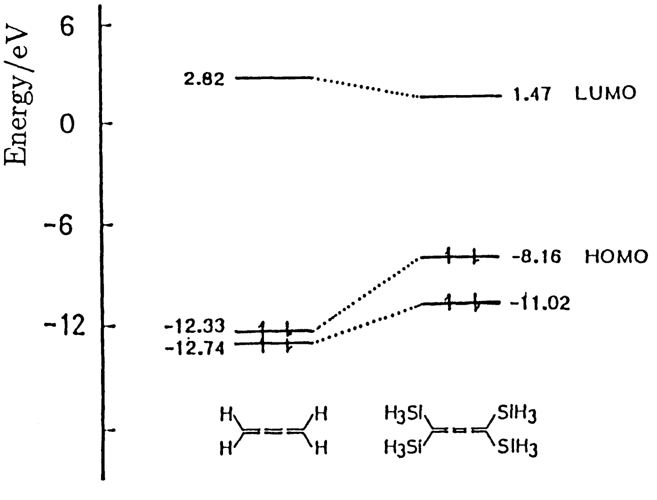
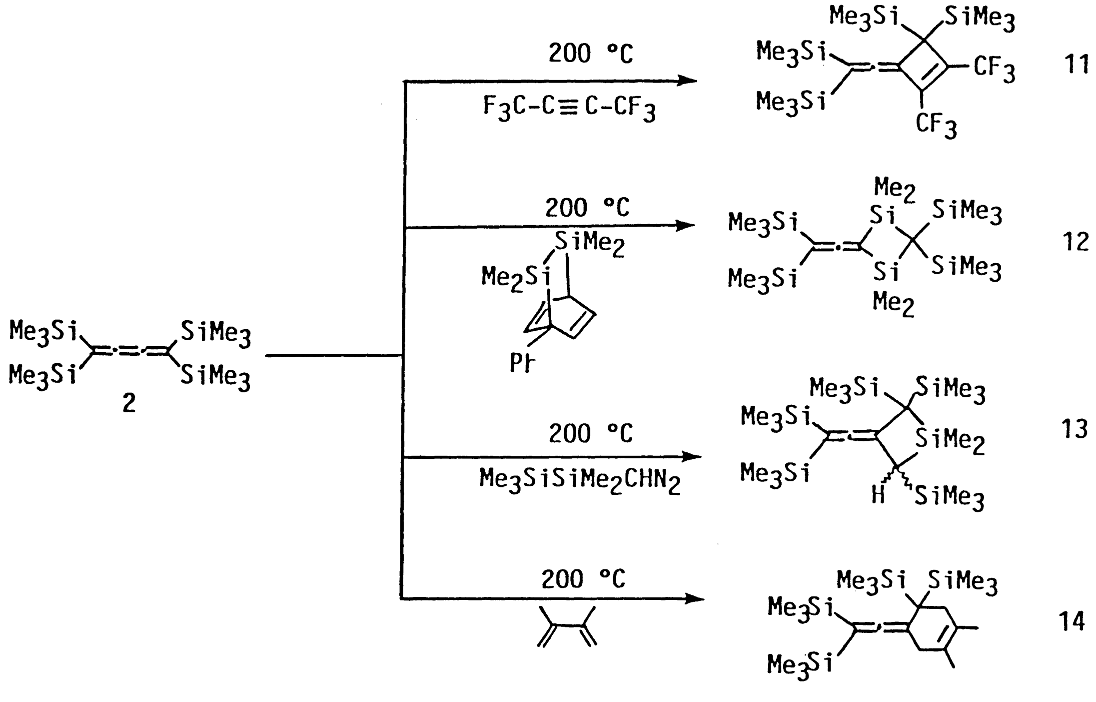


Fig. 1. Energy diagram of butatriene.

silene, and butadiene. The reaction of **2** with hexafluoro-2-butyne did not take place at room temperature probably due to the steric bulkiness around the double bonds. However, when a mixture of **2** with an excess amount of hexafluoro-2-butyne was heated at 200 °C for 24 h in a sealed tube, an adduct (**11**)[8] was obtained in 45% yield along with recovered **2**. A regioisomer of **11**, the adduct at the central double bond, was not found in the reaction mixture. Adducts **12**, (13%) and **13**, (11%)[8] of tetramethyldisilene or 1,1-dimethyl-2-trimethylsilyl-1-silaethylene at the terminal double bonds were also produced in thermolysis with 7,7,8,8-tetramethyl-1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene or pentamethyldisilanyldiazomethane.

2,3-Dimethyl-1,3-butadiene also reacted with **2** at the terminal position to afford the product **14** in 52% yield.[8] Product **12** may be formed from the [2 + 2] adduct of $Me_2Si{=}SiMe_2$ at the terminal double bond of **2** followed by rearrangement similar to that reported by Ishikawa et al.[9]

The regiochemistry of these cycloadditions, which may be rationalized on both electronic and steric grounds, is summarized below.



Further works are in progress. The work is supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 62115003).

References

1) Chemistry of Organosilicon Compounds 253.

2) H. Sakurai, Y. Nakadaira, M. Kira, and H. Tobita, Tetrahedron Lett., 21, 3077 (1980); H. Sakurai, Y. Nakadaira, H. Tobita, T. Ito, K. Toriumi, and H. Ito, J. Am. Chem. Soc., 104, 300 (1982).

3) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, J. Am. Chem. Soc., 101, 2768 (1979); W. Kaim and H. Bock, J. Organomet. Chem., 164, 281 (1979); G. Maier, H. W. Lage, and H.-P. Reisenauer, Angew. Chem., Int. Ed. Engl., 20, 976 (1981).

4) T. Kusumoto and T. Hiyama, Tetrahedron Lett., 28, 1807, 1811 (1987).

5) Compound **2**: mp 100-101 °C; ^{1}H NMR ($CDCl_3$) δ 0.24 (s); ^{13}C NMR ($CDCl_3$) δ 0.39, 156.9, 205.4; ^{29}Si NMR ($CDCl_3$) δ -6.78; High resolution mass: Calcd for $C_{16}H_{36}Si_4$: 340.1894. Found: 340.1873.

6) J. Dunogues, E. Jousseaume, and R. Calas, J. Organomet. Chem., 71, 377 (1974).

7) G. Fritz, J. Grobe, and D. Kummer, Adv. Inorg. Chem. Radiochem., 7, 349 (1965); H. Sakurai, A. Hosomi, and M. Kumada, Chem. Commun., 1968, 930; R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, J. Organomet. Chem., 34, 53 (1972); I. M. T. Davidson and A. B. Howard, Chem. Commun., 1973, 323.

8) All the new compounds **11** - **14** showed NMR and IR as well as high resolution mass spectra consistent with the structures assigned. Some representative data are as follows. Compound **12**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18H), 0.18 (s, 18H), 0.42 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 0.91, 5.16, 5.61, 6.59, 60.2, 64.0, 193.9; ^{29}Si NMR ($CDCl_3$) δ -2.81, -1.65, 0.25; IR (CCl_4) 1894 cm^{-1} (C=C=C); High resolution mass: Calcd for $C_{20}H_{48}Si_6$: 456.2372. Found: 456.2368. Compound **14**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H), 0.16 (s, 18H), 1.67 (m, 6H), 2.12 (br.s, 2H), 2.60 (br.s, 2H); ^{13}C NMR ($CDCl_3$) δ 0.71, 0.91, 17.8, 18.7, 19.1, 35.1, 38.4, 87.1, 90.0, 126.2, 211.3; IR (CCl_4) 1896 cm^{-1} (C=C=C); High resolution mass: Calcd for $C_{22}H_{46}Si_4$: 422.2677. Found: 422.2663.

9) M. Ishikawa, T. Fuchikami, M. Kumada, T. Higuchi, and S. Miyamoto, J. Am. Chem. Soc., 101, 1348 (1979).

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