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Thermolyses of Hexakis(trimethylsilyl)benzene and Pentakis(trimethylsilyl)toluene. The First Unique Trimethylsilyl-Triggered Rupture of Benzene Rings[1)]

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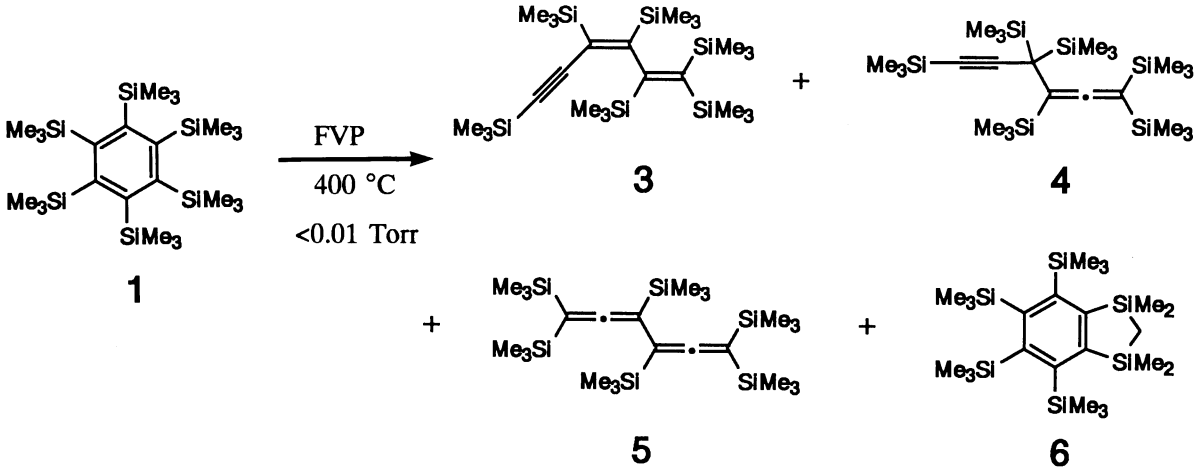
Thermolysis of highly distorted hexakis(trimethylsilyl)benzene and pentakis-(trimethylsilyl)toluene resulted in the formation of products arising from the ruptures of the aromatic rings.

The benzene ring, one of the most important ring systems in organic chemistry, is thermally quite stable. No cleavage of the benzene ring has been reported so far in thermolysis even for highly hindered benzenes.[2)] Recently, we have reported synthesis and unusual chemical and physical properties of hexakis(trimethylsilyl)-benzene (**1**). The benzene ring of **1** was highly distorted into a chair form and strong σ(C–Si)–π mixing was observed.[3)] We report herein quite unusual thermal reactions of **1** and pentakis(trimethylsilyl)toluene (**2**) to result in the rupture of the aromatic rings under rather mild conditions.

Hexakis(trimethylsilyl)benzene (**1**, 500 mg, 0.98 mmol) was sublimed into a pyrex tube under reduced pressure (<0.01 Torr). The flash vacuum pyrolysis (FVP) of **1** at 400 °C gave a mixture of 1,3,4,5,6,6-hexakis(trimethylsilyl)hexa-3,5-diene-1-yne **3** (75 mg, 15%), 1,3,3,4,6,6-hexakis(trimethylsilyl)hexa-4,5-diene-1-yne **4** (150 mg, 30%), 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene **5** (50 mg, 10%), 1,1,3,3-tetramethyl-4,5,6,7-tetrakis(trimethylsilyl)-1,3-disilaindane **6** (25 mg, 5%), and unreacted **1** (200 mg, 40%).[4)] The pyrolysates were collected in a receiver cooled by liquid nitrogen and the products were separated by preparative gel permeation chromatography equipped with a recycling system. The FVP at 480 °C led to the complete isomerization of **1** to **5**. It should be pointed out that none of the desilylated products could be found in the pyrolysis of **1**.

Heating the isolated pure acetylene-diene **3** at 110 °C for 10 h in toluene resulted in the formation of the acetylene-allene **4** in quantitative yield. Furthermore, the acetylene-allene **4** cleanly isomerized to the biallene **5** by heating at 200 °C in octane. Therefore, **3** and **4** are precursors to the acetylene-allene **4** and biallene **5**, respectively.

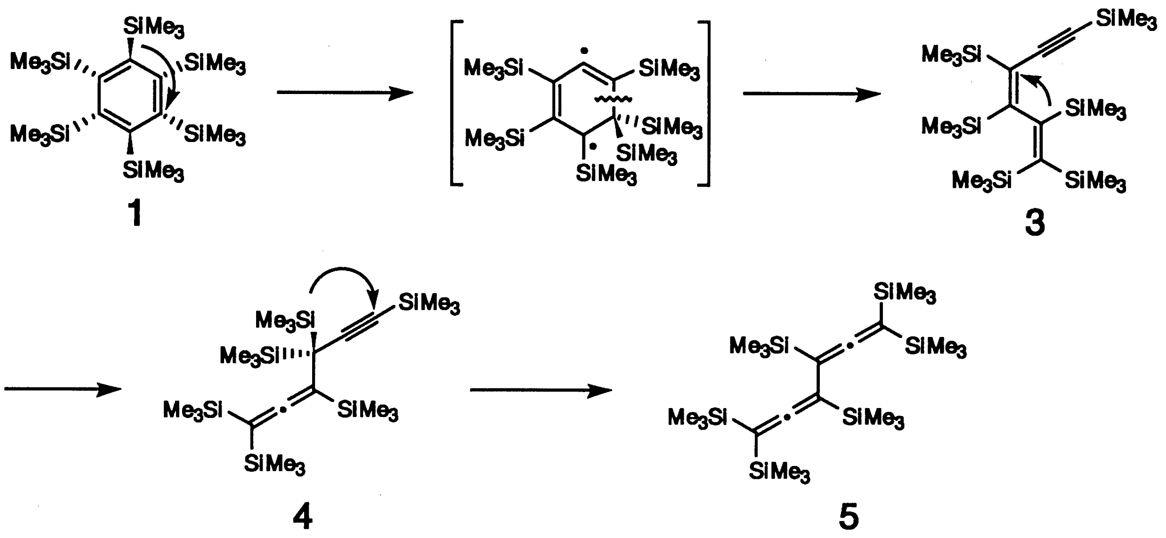
Next, we have examined the static thermolysis of **1**. Heating a solution of **1** (200 mg, 0.39 mmol) and octane (1.5 ml) in a sealed tube at 200 °C for 5 h resulted in the formation of acetylene-allene **4** (40%), biallene **5** (50%), and unreacted **1** (10%). Thermolysis of **1** at 200 °C for 10 h gave the biallene **5** (100%) as a sole product.



In solution, hexakis(trimethylsilyl)benzene **1** exists as an equilibrium mixture consisting of chair and boat forms.3a) The chair form is the most stable and abundant conformer at room temperature (89/11 at 293 K). However, the relative amount of the boat form increases by raising temperature. At 200 °C, the proportion of the boat form is estimated to be 70%. In the boat conformer, the two trimethylsilyl groups at the stem position receive out-of-plane deformation appreciably from the benzene ring. Thus, it is reasonable to assume that the trimethylsilyl groups located at this position easily undergo 1,3-shift followed by cleavage of the benzene ring to afford the acetylene-diene **3** (Scheme 1). The subsequent 1,3-shift of a trimethylsilyl group leads to the acetylene-allene **4**, which ultimately produces the biallene **5** by further 1,3-shift of a trimethylsilyl group. The steric hindrance appreciably lowers the temperature for the 1,3-silyl shift.

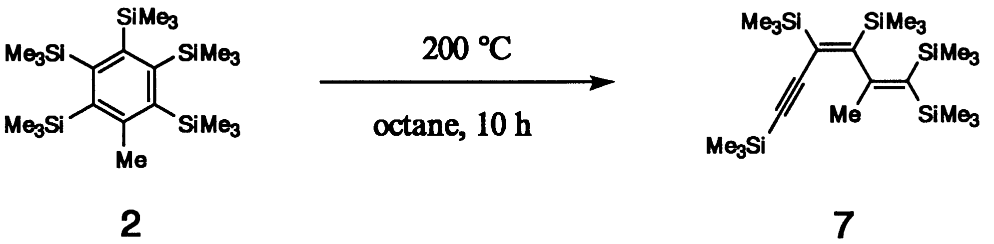
Thermolysis of **2**5) in octane at 200 °C for 10 h in a sealed tube resulted in the formation of 1,3,4,6,6-pentakis(trimethylsilyl)-5-methyl-hexa-3,5-diene-1-yne (**7**, 100%).6) The methyl group was regiospecifically located on the vinyl carbon as determined by long-range H/C COSY (COLOC) spectra. Since the acetylene-diene **7** is an analogous compound to **3**, a similar 1,3-silyl shift followed by the rupture of the benzene ring is involved as found in **1**.

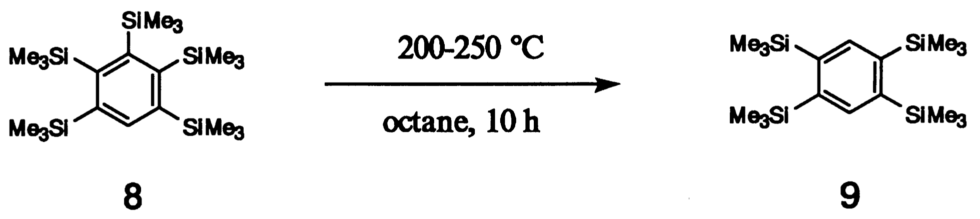
In contrast to **1** and **2**, thermolysis of pentakis(trimethylsilyl)benzene **8**5) in octane at 200 - 250 °C for 10 h gave no ring-ruptured product but a small amount of 1,2,4,5-tetrakis(trimethylsilyl)benzene **9** (10 - 15%) arising from desilylation. Most of **8** (90 - 85%) was recovered unreacted. The fact that no rupture of the benzene ring in **8** occurred may be ascribed to the smaller steric hindrance of **8** than **1** and **2**.



Scheme 1.

Examples of thermal 1,3-shift of the trimethylsilyl group at 500 °C have been reported for allylsilanes.[7] The trimethylsilyl groups of **1** and **2** are lifted from the benzene and as a result, the σ(C–Si)–π conjugation becomes important. Certainly, thus enhanced σ(C–Si)–π conjugation should play an important role in facile ring rupture triggered by 1,3-silyl shift in addition to steric hindrance.





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References

1) Chemistry of Organosilicon Compound. 289.

2) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964); A. van Bruijnsvoort, L. Eilermann, H. van der Meer, and C. H. Stam, *Tetrahedron Lett.*, **1968**, 2527; T. T. Tidwell, *Tetrahedron*, **34**, 1855 (1978); A. Greenberg and J. F. Liebman, "Strained Organic Molecules," Academic Press, New York, N. Y., U. S. A. (1978).

3) a) H. Sakurai, K. Ebata, C. Kabuto, and A. Sekiguchi, *J. Am. Chem. Soc.*, **112**, 1799 (1990); b) A. Sekiguchi, K. Ebata, C. Kabuto, and H. Sakurai, *ibid.*, **113**, 1464 (1991).

4) Compound **3**: colorless crystals, mp 151 – 152 °C; ^{1}H NMR (C_6D_6) δ 0.21 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 0.38 (s, 9H, $SiMe_3$), 0.39 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 0.38, 1.38, 2.92, 5.25, 5.34, 5.49, 106.8, 110.5, 132.4, 151.2, 177.4, 183.5; ^{29}Si NMR (C_6D_6) δ –19.4, –9.87, –9.36, –8.94, –7.01, –6.95; IR (KBr, cm^{-1}) 2112 ($C\equiv C$); High resolution mass: Calcd for $C_{24}H_{54}Si_6$: 510.2841. Found: 510.2837. Compound **4**: colorless crystals; mp 103 °C; ^{1}H NMR (C_6D_6) δ 0.20 (s, 9H, $SiMe_3$), 0.23 (s, 18H, $SiMe_3$), 0.34 (s, 18H, $SiMe_3$), 0.41 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 0.20, 0.71, 1.70, 2.80, 20.1, 76.8, 80.1, 87.2, 111.8, 204.4; ^{29}Si NMR (C_6D_6) δ –20.4, –2.41, –1.87, 6.53; IR (KBr, cm^{-1}) 2158 ($C\equiv C$), 2102 ($C\equiv C$), 1851 (C=C=C); High resolution mass: Calcd for $C_{24}H_{54}Si_6$: 510.2841. Found: 510.2843. Compound **5**: mp 109 – 110 °C; ^{1}H NMR (C_6D_6) δ 0.23 (s, 36H, $SiMe_3$), 0.28 (s, 18H, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 0.76, 0.80, 75.1, 80.1, 206.9; ^{29}Si NMR (C_6D_6) δ –3.72, –2.26; IR (KBr, cm$^{-1)}$ 1884 (C=C=C). Compound **6**: pale yellow crystals; ^{1}H NMR (C_6D_6) δ –0.10 (s, 2H, $SiCH_2Si$), 0.34 (s, 18H, $SiMe_3$), 0.44 (s, 18H, $SiMe_3$), 0.49 (s, 12H, $SiMe_2$); ^{13}C NMR (C_6D_6) δ 2.01 ($SiCH_2Si$), 5.00 ($4SiMe_3$), 5.26 ($SiMe_2$), 151.5, 152.4, 160.6; ^{29}Si NMR (C_6D_6) δ –7.28, –5.34, 4.42; High resolution mass: Calcd for $C_{23}H_{50}Si_6$: 494.2528. Found: 494.2493.

5) Syntheses and molecular structures of **2** and **8** will be reported elsewhere.

6) Compound **7**: colorless crystals; mp 48 °C; ^{1}H NMR (C_6D_6) δ 0.20 (s, 9H, $SiMe_3$), 0.25 (s, 9H, $SiMe_3$), 0.28 (s, 9H, $SiMe_3$), 0.33 (s, 9H, $SiMe_3$), 0.41 (s, 9H, $SiMe_3$), 1.90 (CH_3); ^{13}C NMR (C_6D_6) δ –0.13, 0.26 ($2SiMe_3$), 3.01, 4.01, 30.4 (CH_3), 104.3, 108.9, 131.4, 133.0, 165.2, 177.7; ^{29}Si NMR (C_6D_6) δ –19.0, –8.87, –7.62, –6.96, –3.90; IR (KBr, cm^{-1}) 2118 ($C\equiv C$); High resolution mass: Calcd for $C_{22}H_{48}Si_5$: 452.2603. Found: 452.2597.

7) J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95**, 8678 (1973).

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