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PREPARATION AND REACTIONS OF DODECAMETHYL-3,4,7,8,11,12-HEXASILACYCLODODECA-1,5,9-TRIYNE[1)]

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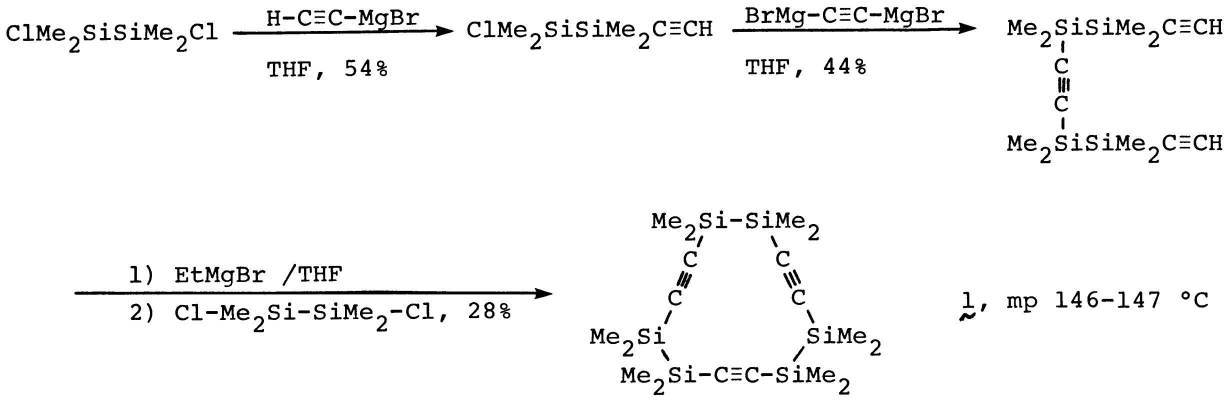
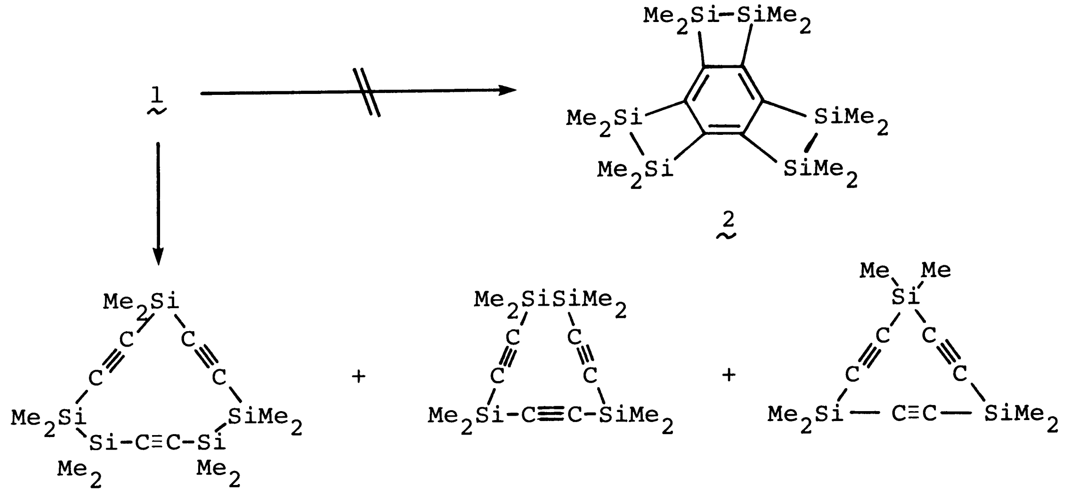
Pyrolysis of the title silicon-containing cyclic triyne gave, by stepwise extrusion of dimethylsilylene, hexamethyltrisilacyclonona-1,4,7-triyne, which was further converted to a novel tris-bridged cyclophane. Fifteen-membered trioxahexasilatriyne, prepared by the oxidation of the title triyne, isomerized to the corresponding benzene derivative thermally.

Recently we have reported synthesis of octamethyl-3,4,7,8-tetrasilacyclo-1,5-octadiyne,[2,3)] interesting chemistry of which has been extended successfully to the next higher member, dodecamethylhexasilacyclododeca-1,5,9-triyne (1), prepared by the scheme shown below.



1, mp 146-147 °C

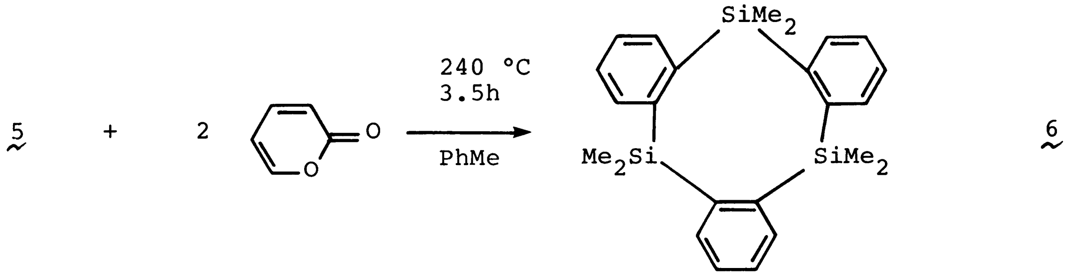
The corresponding carbon analogue, 1,5,9-cyclododecatriyne, isomerized thermally to the corresponding tris-cyclobutenabenzene or hexaradialene as a reactive intermediate.[4)] However, when 1 was heated at 200-300 °C in the presence of excess diethyl maleate, diphenylacetylene, or acetylene dimethyl dicarboxyate, no product of cycloaddition of the presumed silicon analogue of tris-cyclobutenabenzene (2) with these unsaturated compounds was obtained. Instead, three cyclic triynes, 3, 4, and 5 were obtained by stepwise extrusion of dimethylsilylene.[5)] Hexamethyl-3,6,9-trisilacyclonona-1,4,7-triyne (5) is the smallest known cyclic triyne so far isolated. Whereas the pyrolysis of 1 gave three products (3, 4, and 5) in respective moderate yields (8%, 27%, and 11%) at 540 °C, 5 is the single product under more forced conditions of 690 °C in 68% yield. 5 was stable not only thermally but also oxidatively.



3, mp 89-90 °C 4, mp 106-108 °C 5, mp 145-146 °C

The photoelectron spectra of 1 and 5 show first ionization bands at 8.45 and 9.70 eV, respectively. Theoretical studies on the unique electronic structures of these compounds will be reported in detail later.[6)]

Cycloaddition of 5 with α-pyrone led to a novel tris-bridged cyclophane (6) as a white solid (mp 199-189 °C) in 55% yield. The chemistry of the corresponding carbon analogue, cyclotriveratrylene (CTV),[7,8)] is of current interest.[9)]



^{13}C-NMR spectrum of 6 at room temperature showed three signals due to aromatic carbons at 127.94, 135.78, and 146.28 ppm and one signal due to methyl carbons at 2.81 ppm. The ^{1}H-NMR spectrum of aromatic protons exhibited an AA'BB' pattern in accordance with an ortho-disubstituted benzene derivative. Very broad and temperature-dependent signals of methyl protons, observed in the ^{1}H-NMR spectrum at room temperature at 0.10 ppm, changed to three signals with equal integrated areas at -0.85, 0.41, and 0.53 ppm in CD_2Cl_2 at -70 °C. The characteristically shielded signal at -0.85 ppm suggests that the corresponding two methyl groups are located upward to the benzene ring in a fixed conformation at low temperature.

The parent CTV has been shown to possess a rigid crown conformation,[7)] but a saddle conformation also has been suggested for several substituted CTV derivatives.[8)] The NMR spectra of 6 observed at low temperature indicates the twisted saddle conformation possessing C_2 symmetry, and indeed as shown in Figure 1, the

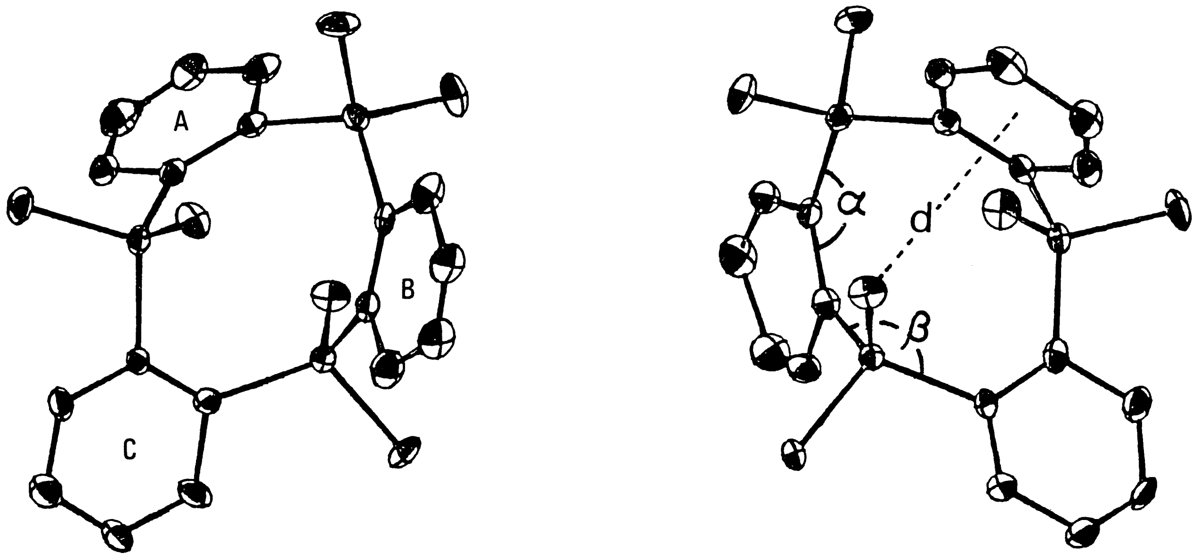
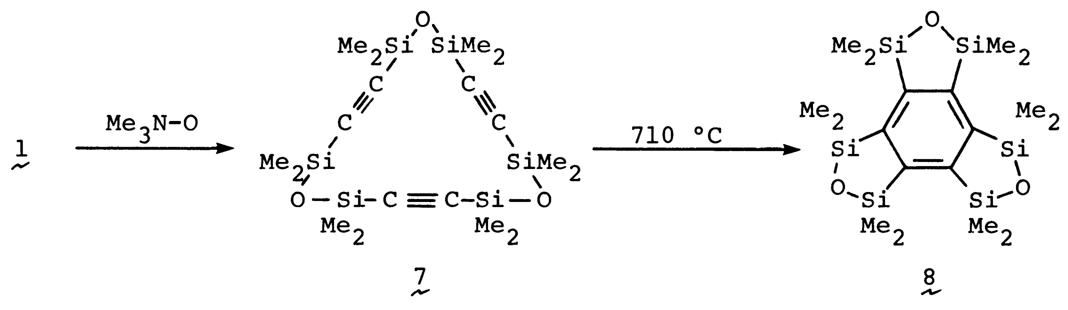


Fig. 1. The ORTEP drawing of two independent molecules of **6** viewed along a axis. Thermal ellipsoids are drawn at the 30% probability level. Some meaningful dimensions of the structure are as follows: the dihedral angles are av. 142° for A∧B and av. 90° for A∧C and B∧C planes; the internal angles fused by benzene rings are all expanded to 125-130°; the distance of a methyl carbon and the center of benzene rings (d) is av. 3.35 Å.

molecular structure of **6** determined by X-ray crystallographic analysis of the single crystal10) indicates a twisted saddle conformation.

Selective oxidation of three tetramethyldisilanylene units of **1** with trimethylamine N-oxide11) gave a 15-membered macrocyclic trioxahexasilatriyne (**7**) in almost quantitative yield. **7** is thermally stable under usual conditions but isomerizes slowly to the corresponding benzene derivative (**8**)12) under rather drastic conditions of 710 °C in 4.9% yield. This is the first definitive example of intramolecular cyclization of acetylene to benzene in a manner of the [2+2+2] reaction.



The transition metal complexes-catalyzed intramolecular trimerization of three acetylene units of 7 will be reported in a forthcoming paper.

We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

References

1) Chemistry of Organosilicon Compounds 192.
2) H. Sakurai, Y. Nakadaira, A. Hosomi, and Y. Eriyama, J. Am. Chem. Soc., 105, 3359 (1983).
3) H. Sakurai, Y. Nakadaira, A. Hosomi, and Y. Eriyama, Chem. Lett., 1982, 1971.
4) A. J. Barkovich, K. P. C. Vollhardt, J. Am. Chem. Soc., 98, 2667 (1976); K. P. C. Vollhardt, Acc. Chem. Res., 10, 1 (1977); A. J. Barkovich, E. S. Strauss and K. P. C. Vollhardt, J. Am. Chem. Soc., 99, 8321 (1977); W. V. Dower and K. P. C. Vollhardt, Angew. Chem., 94, 712 (1982); W. V. Dower and K. P. C. Vollhardt, J. Am. Chem. Soc., 104, 6878 (1982).
5) Satisfactory spectral data and correct elemental analysis were obtained for all new compounds.
6) The photoelectron spectra were taken by Prof. R. Gleiter, Heidelberg. Details of spectra and theoretical studies on the electronic structure of 1, 5 and related compounds will be published in a forthcoming paper.
7) H. Erdtmann, F. Haglid, and R. Ryhage, Acta Chem. Scand., 18, 1249 (1964); A. Collet and J. Gabard, J. Org. Chem., 45, 5400 (1980); A. Collet and J. Gabard, J. Am. Chem. Soc., 103, 204, 5912 (1981).
8) T. Sato, T. Akima, and K. Uno, J. Chem. Soc., Perkin Trans. 1, 1973, 891; J. F. Manville and G. E. Troughton, J. Org. Chem., 38, 4278 (1973); N. K. Anand, R. C. Cookson, B. Halton, and I. D. R. Stevens, J. Am. Chem. Soc., 88, 370 (1966); R. C. Cookson, B. Halton, and I. D. R. Stevens, J. Chem. Soc., B, 1968, 767.
9) F. Vögtle and E. Weber, Angew. Chem., Int. Ed. Engl., 13, 814 (1974).
10) Crystal data for 6. $C_{24}H_{30}Si_3$, Fw 402.77; the cell dimensions; a = 30.134(1) Å, b = 9.806(1) Å, c = 17.340(1) Å, β = 114.39(2)°, V = 4666.59(4) $Å^3$; the space group: Cc (Z = 8); ρ_{calcd} = 1.146 g/cm^3; number of reflections; 3465 within 2θ = 120° (CuK_α radiation); the final R value; 0.09. The refinement decided the space group to be Cc, but the two independent molecules were found to locate approximately on the positions related by the space group C2/c. Therefore, these two molecules assume essentially the same structure. The observed conformation of nine-membered ring is not a rigid saddle but twisted one so as to separate equally contacts of two benzene rings and the methyl groups located upward, and thus the molecule has C_2 symmetry through one unique benzene ring plane.
11) H. Sakurai, M. Kira, M. Kumada, Bull. Chem. Soc. Jpn., 44, 1161 (1971).
12) 8 has been prepared by an entirely different method. W. Fink, Helv. Chim. Acta, 57, 1010 (1974); A. Frensch and F. Vögtle, Liebigs Ann. Chem., 1979, 2121; F. M. Menger, M. Takesita, and J. F. Chow, J. Am. Chem. Soc., 103, 5938 (1981).

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