Synthesis and Structure of Strained, Cyclic Bisallenes

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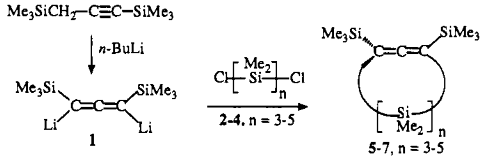
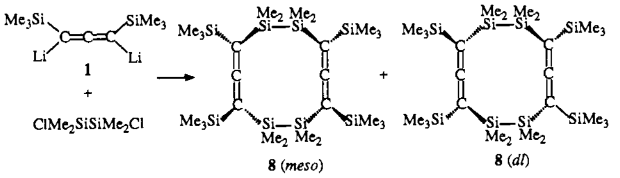
Although we recently reported the surprising observations that 1,3-dilithio-1,3-bis(trimethylsilyl)allene (**1**) cleanly condenses with α-, ω-dichlorosilanes **2–4** to produce the strained silacycloallenes **5–7**,[1] we assumed that polymerization, not cyclization, was the only reasonable option for the condensation of **1** and $ClMe_2SiSiMe_2Cl$ or Me_2SiCl_2.



In contrast to this assumption, reaction of **1** and $ClMe_2SiSiMe_2Cl$ in THF affords in combined 57% yield an ca. 1:1 mixture of diastereomers **8** (*meso*) and **8** (*dl*). One of these diastereomers could be purified by fractional crystallization, thus allowing subtraction for the spectral features of the other.[2]



Assignment of structure could not be accomplished by NMR as chiral shift reagents were ineffective, but the meso structure was established for the selectively crystallized isomer by X-ray diffraction[3] and the molecular structure is shown in Figure 1. The allene unit is bent only slightly from linearity to 178.6° but is twisted to produce a dihedral angle of 80.6° as defined as plane Si(1)C(1)C(2) vs Si(4)C(3)C(2). However, a dihedral angle of 86.1° is obtained from plane Si(1)C(1)Si(2) vs Si(3)C(3)Si(4), and comparison of plane Si(2)C(1)C(2) and Si(3)C(3)C(2) yields an apparently normal 89.4°—a result of both the bending and apparent rehybridization of the allene carbons as evidenced both by the bond angles and pyramidalization.

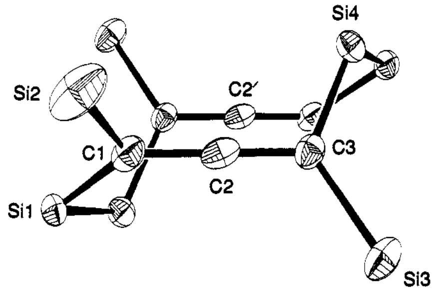
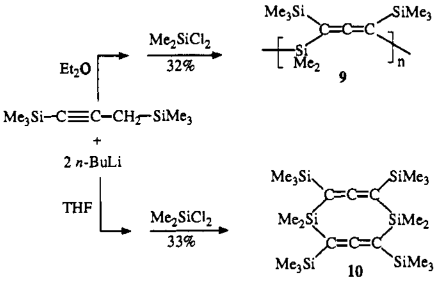


Figure 1. ORTEP drawing of **8** (*meso*). The methyl groups have been omitted for clarity. Selected bond distances (Å) and angles (deg) are Si(1)–C(1) = 1.866(4), C(1)–C(2) = 1.305(5), Si(2)–C(1) = 1.879(4), C(2)–C(2') = 4.162, Si(1)–C(1)–Si(2) = 124.5(2), Si(1)–C(1)–C(2) = 118.9(3), Si(2)–C(1)–C(2) = 116.6(3), C(1)–C(2)–C(3) = 178.6.

Condensation of Cl_2Me_2Si and dianion **1** in Et_2O produced in 32% yield the polysilaallene **9** (M_w = 6900, M_n = 6500) along with a trace of 1,3,5,7-tetrakis(trimethylsilyl)-4,8-disilacycloocta-1,2,5,6-tetraene (**10**).[4] The same condensation conducted in THF afforded **10** in 33% yield as crystalline needles, mp 115–17 °C. The ^1H NMR spectrum of **10** (Table I) revealed a symmetrical structure which could be rationalized as a rapidly equilibrating chair form which, however, was not supported by NMR studies down to −42 °C.



The molecular structure of **10** was solved by X-ray diffraction[5] and is shown in Figure 2. Of greatest interest is the allene bend of 175.2° and twist of 78.1°, as defined by the Si(2)–C(1)–C(2) and Si(4)–C(3)–C(2) planes. In addition, to accommodate two allenes in an 8-membered ring, the terminal carbons have undergone apparent rehybridization to decrease the internal bond angles with a concomitant increase in the external (Si–C–SiMe) angles (Figure 3).

All-carbon, cyclic bisallenes have been reported,[6] with the smallest isolated being the 10-membered ring **11**.[7–9] As the crystal structure of **11** has been determined,[8] the transannular distances between the central carbon atoms may be compared. As expected, the longer bonds associated with silicon produce a significantly longer C(2)–C(2') distance of 4.162 Å in **8** as opposed to 3.208 Å in **11**. However, this transannular distance in **10**, 2.859 Å, is notably shorter than in **11** but slightly longer (0.26 Å) than the transannular sp-carbon distances in the smallest cyclic diyne for which structural information is available, 1,5-cyclooctadiyne (**12**).[10] The sp-carbons of **12** (δ 95.8) are shifted considerably downfield from those of normal acetylenes, an effect which has been ascribed to the olefinic character of the bent acetylenes in

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(1) Pang, Y.; Petrich, S. A.; Young, V. G. Jr.; Gordon, M. S.; Barton, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 2534.

(2) **8** (*meso*): mp 215–216 °C; GCMS *m/z* 523 (57, $M^+ - {}^{28}SiMe_3$, M^+ not observed by GCMS), 341 (31), 283 (19), 225 (11), 185 (18), 171 (20), 155 (13), 73 (100); GC-FTIR (cm^{-1}) 2959 (m), 2904 (w), 1867 (vs), 1404 (w), 1254 (m), 881 (s), 844 (s); HRMS calcd for $C_{26}H_{60}Si_8$ *m/z* 596.284 93, measd (Kratos MS50) 596.284 55; UV (nm, hexane) λ_{max} = 202 (5.8×10^4), 258 (7.2×10^3). **8** (*dl*): GCMS (separated from **8** (*meso*) *m/z* 523 (57), 341 (34), 225 (10), 185 (16), 171 (18), 155 (13), 73 (100); GC-FTIR (cm^{-1}) 2960 (m), 1864 (vs), 1402 (w), 1255 (m) 874 (s), 846 (s), 790 (m); ^1H NMR (300 MHz, $DCCl_3$) δ 0.14 (s, 36 H), 0.17 (s, 12 H), 0.23 (s, 12 H); ^{13}C NMR ($DCCl_3$) δ −0.24 (4 C), 0.14 (4 C), 1.30 (12 C), 61.81 (4 C), 203.78 (2 C); ^{29}Si NMR (external TMS) δ −18.62 (4 Si), −2.33 (4 Si).

(3) Crystal data for **8** (*meso*) at −50 °C: $a = 8.768(2)$ Å, $b = 11.291(3)$ Å, $c = 11.726(3)$ Å, $\alpha = 104.74(2)°$, $\beta = 102.42(2)°$, $\gamma = 111.42(2)°$, $V = 982.1(4)$ Å^3, triclinic with space group $P1$, $Z = 1$, $\rho = 1.01$ g cm^{-3}. The structure was solved by direct methods, $R = 0.049$ and $R_w = 0.068$ for 2272 reflections with $F_o^2 > 3.0\sigma(F_o^2)$.

(4) **10**: mp 115–117 °C; GCMS *m/z* 480 (66, M^+), 465 (53), 155 (10), 73 (100); GCIR (cm^{-1}) 2961 (m), 2905 (w), 1871 (vs), 1406 (w), 1258 (m), 904 (s), 844 (s); UV (nm, hexane) λ_{max} = 204 (5.34×10^4), λ_{sh} = 252 (2.94×10^3); HRMS calcd for $C_{22}H_{48}Si_6$, *m/z* 480.237 18, measd 480.236 97.

(5) Crystal data for **10** at −60 °C: $a = 12.244(2)$ Å, $c = 10.523(2)$ Å, $V = 1577.5(7)$ Å^3, tetragonal with space group $P4_22_12$, $Z = 2$, $\rho = 1.013$ g cm^{-3}. The structure was solved by direct methods, $R = 0.031$ and $R_w = 0.046$ for 1063 reflections with $F_o^2 > 2.0\sigma(F_o^2)$.

(6) For an excellent review of cyclic allenes, see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(7) Skattebol, L. *Tetrahedron Lett.* **1961**, 167.

(8) Irngartinger, H.; Jager, H. U. *Tetrahedron Lett.* **1976**, 3595.

(9) The isomeric cyclodeca-1,2,5,6-tetraene is known, but structural details are not available: Baird, M. S.; Reese, C. B. *Tetrahedron* **1976**, *32*, 2153.

(10) Kloster-Jensen, E.; Wirz, J. *Helv. Chim. Acta* **1975**, *58*, 162.

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Table I. Selected Spectral Features of Tetrakis(trimethylsilyl)allene, **8** (meso), and **10**

compd	IR (cm^{-1})	^{1}H NMR (δ)	^{13}C NMR (δ)	^{29}Si NMR (δ)
$(Me_3Si)_4C_3$	1870		0.40 (12 C) 203.64 (1 C) 64.03 (2 C)	−3.93
8 (meso)	1867	0.12 (s, 36 H) 0.17 (s, 12 H) 0.22 (s, 12 H)	−0.56 (4 C) 0.05 (4 C) 0.97 (12 C) 62.21 (4 C) 203.72 (2 C)	−22.75 (4 Si) −3.24 (4 Si)
10	1871	0.09 (s, 36 H) 0.23 (s, 12 H)	0.55 (12 C) 2.24 (4 C) 66.0 (4 C) 205.38 (2 C)	−5.06 (4 Si) 0.20 (2 Si)

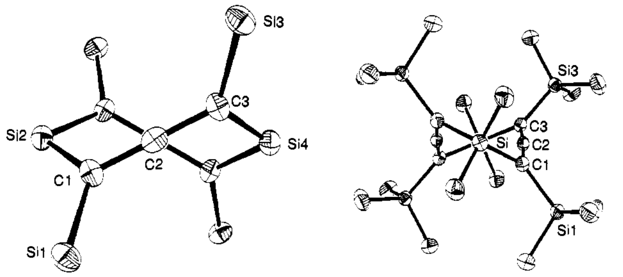


Figure 2. ORTEP drawings of **10**. Selected bond lengths (Å) and angles (deg) are Si(1)–C(1) = 1.861(2), Si(2)–C(1) = 1.881(2), C(1)–C(2) = 1.311(3), C(1)–C(2)–C(3) = 175.2(2).

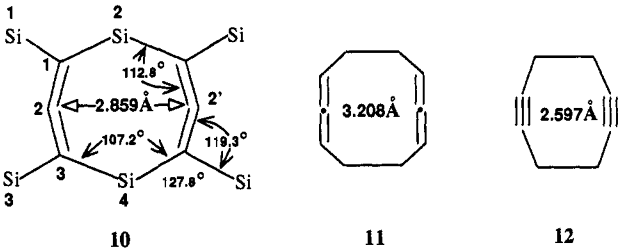
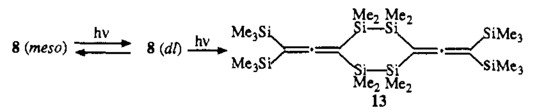


Figure 3. Comparison of transannular distances between sp-carbons in strained, cyclic bisallenes and 1,5-cyclooctadiyne.

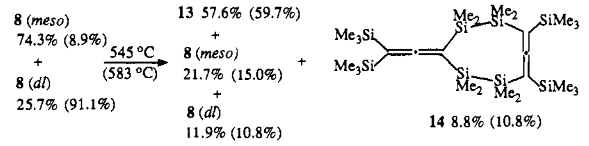
12 rather than to a "proximity effect".[11] Although no large shifts are observed in the ^{13}C NMR of **10** relative to **8**, future efforts at probing the chemistry of these cyclic bisallenes will seek evidence for proximity interaction.

Photolysis of **8** (*meso*) or **8** (*dl*) in hexane with a low-pressure Hg-arc lamp produced an approximately 1:1 mixture of the two diastereoisomers. After ca. 2 h of irradiation, a third isomer (**13**)[12] was observed in the reaction mixture (14% after 24 h). The



photoinduced racemization of allenes is well established,[13] but the photoisomerization of **8** to **13** is to our knowledge unprecedented and formally represents two dyatropic rearrangements. Under the same conditions of photolysis, **10** failed to react.

Gas-phase flow pyrolysis of two different mixtures of **8** (*meso*) and **8** (*dl*), one at 545 and one at 585 °C, also produced **13** as the major product along with a significant amount of isomer



14,[14] which is assumed to be an intermediate in the **8**-to-**13** conversion. Bisallene **10** was unchanged upon pyrolysis at 600 °C and at 650 °C began to decompose to a myriad of products.

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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(11) For a review of "proximity interaction of acetylenes", see: Misuni, S.; Kaneda, T. In *The Chemistry of the Carbon–Carbon Triple Bond*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1978; Chapter 16.

(12) **13**: colorless crystals, mp 190–191 °C; GCMS (M^+ not observed) *m/z* 523 (24, $M^+ - SiMe_3$), 411 (15), 185 (11), 155 (11), 73 (100); HRMS calcd for $C_{22}H_{48}Si_6$ *m/z* 596.284 93, measd (Kratos MS50) *m/z* 596.284 87, GC-FTIR (cm^{-1}) 2959 (m), 2903 (w), 1861 (vs), 1254 (m), 868 (s), 803 (s); ^{1}H NMR (300 MHz, $DCCl_3$) δ 0.096 (s, 36 H), 0.141 (s, 24 H); ^{13}C NMR ($DCCl_3$) δ −2.24 (8 C), 0.66 (12 C), 60.83 (2 C), 64.43 (2 C), 201.81 (2 C); ^{29}Si NMR ($DCCl_3$, external TMS) δ −24.51 (4 Si), −3.98 (4 Si); UV (nm, hexane) λ_{max} = 208 (5.9×10^4), λ_{sh} = 226 (4.5×10^4), 256 (1.8×10^4).

(13) Photoinduced racemization of allenes has been reported: Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 3971.

(14) **14**: GCMS *m/z* 523 (50, $M^+ - SiMe_3$), 341 (10), 283 (12), 185 (13), 73 (100); GC-FTIR (cm^{-1}) 2959 (m) 2902 (w), 1860 (vs), 1402 (w), 1254 (m), 891 (s), 844 (s); NMR spectra by subtraction of **8** and **13** from pyrolysate of **8**; ^{1}H NMR ($DCCl_3$) δ 0.104 and 0.107 (singlets, 1:1), 0.185 and 0.192 (singlets, 2:1), other absorptions overlapped; ^{13}C NMR ($CDCl_3$) δ −1.90 (2 C), −1.74 (2 C), −0.88 (2 C), 0.18 (2 C), 0.59 (6 C), 0.82 (6 C), 60.65 (1 C), 60.67 (1 C), 61.72 (2 C), 202.82 (1 C), 203.81 (1 C); ^{29}Si NMR ($CDCl_3$, external TMS) δ − 21.59 (2 Si), −14.89 (2 Si), −3.88 (2 Si), −3.98 (2 Si).