Photolysis of *anti*-Dodecaalkyltricyclo[4.2.0.0^{2,5}]octasilane: Generation and Reactions of Cyclotetrasilene

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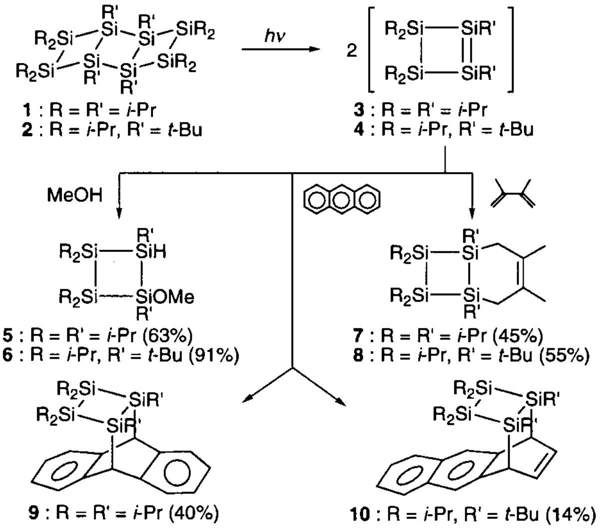
The photolysis of tricyclic ladder oligosilanes gave a cyclotetrasilene intermediate, which was trapped by methanol, 2,3-dimethyl-1,3-butadiene, and anthracene. Anthracene underwent a cycloaddition with the cyclotetrasilenes at the 9,10- and 1,4-positions depending on the substituents on the cyclotetrasilene rings.

The photochemical cleavage of Si–Si bonds of cyclotetrasilanes has been reported to generate several reactive intermediates.[1] For example, Nagai and co-workers reported that silylene and cyclotrisilane are generated during the photolysis of a cyclotetrasilane with a folded structure.[2] Shizuka, Nagai, West, and co-workers reported that the photolysis of planar cyclotetrasilanes gives two molecules of disilene.[3] The photolysis of ladder oligosilanes[4] seems to be an interesting subject since many Si–Si bond cleavage paths are possible. We report the generation of a cyclotetrasilene[5] by the photolysis of the tricyclic ladder oligosilanes and its reactions with methanol, 2,3-dimethyl-1,3-butadiene, and anthracene. Also, the structural features of products are noted.

Upon irradiation of hexane solutions of **1** and **2** in the presence of methanol, 2,3-dimethyl-1,3-butadiene, and anthracene with a high-pressure mercury lamp through a filter, the cyclotetrasilane derivatives **5**–**10** were formed.[6–9] In these reactions, the trap products of the dialkylsilylene and tetraalkyldisilene intermediates were not detected. These results indicate that two peripheral Si–Si bonds in the central cyclotetrasilane ring are selectively cleaved to afford two molecules of the cyclotetrasilene intermediates **3** and **4**. It seems interesting that silylene is not formed but cyclotetrasilene is formed from **1** and **2**, in which each cyclotetrasilane ring has a folded structure.[4e]



The site selectivity in the Diels-Alder reactions of **3** and **4** with anthracene is especially noted. The cycloaddition of **3** takes place at the 9,10-positions of anthracene according to the frontier orbital theory.[10] However, in the case of **4**, the cycloaddition at the 9,10-positions is unfavorable because of the steric hindrance between the *t*-butyl groups and a benzene ring. Avoiding such steric hindrance, the cycloaddition of **4** took place at the 1,4-positions to give **10**. To our knowledge, this is the first example of the Diels-Alder reaction of anthracene at the 1,4-positions.

The structures of **8**–**10** were determined by X-ray crystallography (Figures 1–3).[11–13] Compound **8** has a *cis*-fused bicyclic structure. The cyclotetrasilane ring has a moderately folded structure with fold angles of 14.0 and 14.3°. It is remarkable that the disilacyclohexene ring has a half-boat structure which is a transition state between the two stable half-chair structures of cyclohexene.[14] Compound **8** cannot adopt the half-chair structure which makes the Si(1)–Si(4) and Si(2)–Si(3) bonds axial and equatorial, causing a highly folded structure of cyclotetrasilane with an excessive steric hindrance between the isopropyl and *t*-butyl groups. Another feature of **8** is the significantly short length of the Si(1)–Si(2) bond (2.349(1) Å) compared with the other Si–Si bonds. The 2-butene-1,4-diyl group does not seem long enough to connect the Si(1) and Si(2) atoms without distortion.

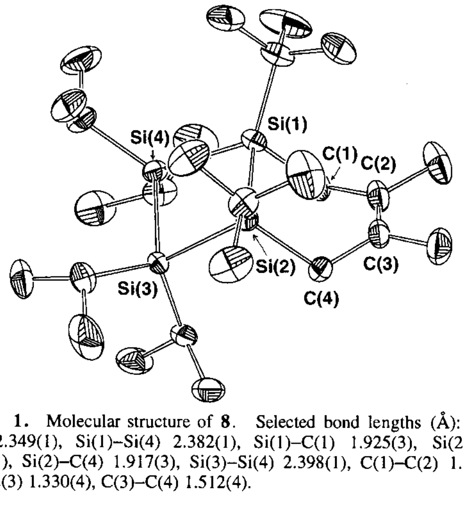


Figure 1. Molecular structure of **8**. Selected bond lengths (Å): Si(1)–Si(2) 2.349(1), Si(1)–Si(4) 2.382(1), Si(1)–C(1) 1.925(3), Si(2)–Si(3) 2.398(1), Si(2)–C(4) 1.917(3), Si(3)–Si(4) 2.398(1), C(1)–C(2) 1.514(4), C(2)–C(3) 1.330(4), C(3)–C(4) 1.512(4).

Compounds **9** and **10** have several structural features. The Si(1)–Si(4) bond lengths (**9**: 2.343(1) Å, **10**: 2.367(2) Å) are shorter than the other Si–Si bonds (**9**: 2.370(1)–2.396(1) Å, **10**: 2.399(1)–2.440(1) Å). The cyclotetrasilane rings have slightly folded structures with fold angles of 4.2° in **9** and 7.7° in **10**. The fold angles produce strain by making the two Si–C(benzyl) bonds unparallel and orienting the two C(ipso)–C(benzyl) bonds above and below the benzene ring. As a result, the naphthalene ring of **10** cannot adopt a planar structure but only a partially twisted structure, the dihedral angle between the terminal rungs (C(5)–C(14) and C(9)–C(10)) being 6.3°. Another deformation is caused by the steric repulsion between the benzene ring and the isopropyl groups. In the case of **9**, for example, the Si(2)–Si(1)–C(1) (116.4(1)°) and Si(3)–Si(4)–C(8) (116.7(1)°) bond angles are larger than the C(1)–Si(1)–C(15) (109.7(1)°) and C(8)–Si(4)–C(16) (107.2(2)°) bond angles, and the Si(1)–C(1)–C(14) (112.3(2)°) and Si(4)–C(8)–C(9) (111.5(2)°) bond angles are larger than the Si(1)–C(1)–C(2) (104.6(2)°) and Si(4)–C(8)–C(7) (105.3(2)°) bond angles. In spite of this deformation, the methine protons of the two isopropyl groups are located above the benzene ring with the short distances of 2.81 and 2.86 Å in **9** and 2.49 and 2.61 Å in **10**, causing an upfield shift in the ^{1}H NMR spectra (**9**: δ 0.18 ppm, **10**: δ –0.17 ppm).

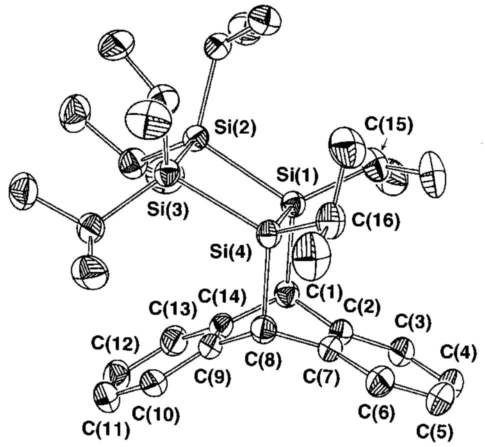


Figure 2. Molecular structure of **9**. Selected bond lengths (Å): Si(1)–Si(2) 2.370(1), Si(1)–Si(4) 2.343(1), Si(1)–C(1) 1.948(3), Si(2)–Si(3) 2.396(1), Si(3)–Si(4) 2.391(1), Si(4)–C(8) 1.948(3), C(1)–C(2) 1.502(4), C(1)–C(14) 1.502(4), C(2)–C(7) 1.391(4), C(7)–C(8) 1.511(4), C(8)–C(9) 1.506 (4), C(9)–C(14) 1.393(4).

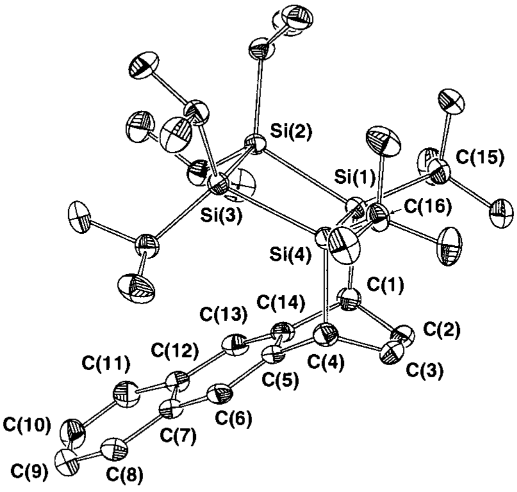


Figure 3. Molecular structure of **10**. Selected bond lengths (Å) and angles (°): Si(1)–Si(2) 2.399(1), Si(1)–Si(4) 2.367(2), Si(1)–C(1) 1.968(3), Si(2)–Si(3) 2.407(2), Si(3)–Si(4) 2.440(1), Si(4)–C(4) 1.967(4); Si(2)–Si(1)–C(1) 113.6(1), C(1)–Si(1)–C(15) 106.4(2), Si(3)–Si(4)–C(4) 115.2(1), C(4)–Si(4)–C(16) 108.8(2), Si(1)–C(1)–C(2) 104.3(2), Si(1)–C(1)–C(14) 113.6(3), Si(4)–C(4)–C(3) 106.9(2), Si(4)–C(4)–C(5) 110.4(2).

In summary, the photolysis of **1** and **2** results in the generation of peralkylcyclotetrasilenes, which provides the opportunity for assessing the reactivity of the unsaturated Si_4 framework.

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References and Notes

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6 **6**: ^{1}H NMR (C_6D_6) δ 1.26–1.51 (m, 45H), 1.58 (sept, 1H, J = 7.5 Hz), 3.56 (s, 3H), 4.06 (s, 1H); ^{13}C NMR (C_6D_6) δ 14.0, 14.9, 15.0, 15.2, 20.7, 22.2, 22.66, 22.70, 23.0, 23.1, 23.2, 23.6, 24.8, 29.1, 32.2, 55.2; ^{29}Si NMR (C_6D_6) δ –35.8, –9.4, –7.2, 41.4; IR (NaCl, cm^{-1}) 2940, 2860, 2830, 2030, 1460, 1380, 1360, 1090; MS *m/z* (%) 430 (M$^+$, 65), 415 (36), 373 (100), 331 (40), 317 (55), 275 (35), 89 (42), 73 (49), 58 (82).

7 The stereochemistries of **5** and **6** have not yet been determined because they do not easily crystallize. However, the ^{1}H NMR spectra show that **5** and **6** are single stereoisomers.

8 **8**: mp 156–158 °C; ^{1}H NMR (C_6D_6) δ 1.24–1.26 (m, 32H), 1.34 (d, 12H, J = 7.4 Hz), 1.44 (d, 2H, J = 14.4 Hz), 1.72 (sept, 2H, J = 7.4 Hz), 1.72 (d, 2H, J = 14.4 Hz), 1.87 (s, 6H); ^{13}C NMR (C_6D_6) δ 14.8, 14.9, 20.9, 21.0, 21.7, 22.3, 23.1, 23.2, 23.3, 31.1, 126.1; ^{29}Si NMR (C_6D_6) δ –1.7, –0.1; IR (NaCl, cm^{-1}) 2940, 2860, 1460, 1390, 1360; MS *m/z* (%) 480 (M$^+$, 83), 437 (51), 423 (53), 398 (44), 381 (26), 367 (32), 355 (71), 341 (35), 84 (94), 73 (100), 58 (90).

9 **10**: ^{1}H NMR (CD_2Cl_2) δ –0.17 (sept, 2H, J = 7.5 Hz), 0.70 (d, 6H, J = 7.5 Hz), 1.23 (d, 6H, J = 7.5 Hz), 1.26–1.27 (m, 24H), 1.31 (d, 6H, J = 7.5 Hz), 1.70 (sept, 2H, J = 7.5 Hz), 4.27 (dd, 2H, J = 5.2, 3.0 Hz), 6.42 (dd, 2H, J = 5.2, 3.0 Hz), 7.31 (dd, 2H, J = 6.3, 3.3 Hz), 7.52 (s, 2H), 7.64 (dd, 2H, J = 6.3, 3.3 Hz); ^{13}C NMR (CD_2Cl_2) δ 11.1, 14.3, 20.0, 21.3, 21.7, 22.5, 23.8, 31.3, 38.5, 121.7, 124.1, 126.3, 130.8, 131.0, 140.8; ^{29}Si NMR (CD_2Cl_2) δ –6.3, 9.5; IR (NaCl, cm^{-1}) 3050, 2940, 2860, 1460, 1380, 1360; MS *m/z* (%) 576 (M$^+$, 5), 398 (100), 355 (64), 342 (29), 341 (26), 178 (22).

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11 Crystal data for **8**: $C_{26}H_{56}Si_4$, F_w = 481.06, monoclinic, space group $P2_1/n$, a = 8.1616(3), b = 22.3982(9), c = 17.8184(4) Å, β = 103.199(3)°, V = 3171.2(2) Å^3, Z = 4, D_c = 1.008 g cm^{-3}, R = 0.046, R_w = 0.044 (w = $1/\sigma^2(F_o)$) for 4593 observed reflections.

12 Crystal data for **9**: $C_{32}H_{52}Si_4$, F_w = 549.10, monoclinic, space group $P2_1/c$, a = 9.8585(7), b = 19.7326(6), c = 17.3710(8) Å, β = 98.112(5)°, V = 3345.4(3) Å^3, Z = 4, D_c = 1.090 g cm^{-3}, R = 0.046, R_w = 0.043 (w = $1/\sigma^2(F_o)$) for 4340 observed reflections.

13 Crystal data for **10**: $C_{34}H_{56}Si_4$, F_w = 577.15, monoclinic, space group $P2_1/c$, a = 10.563(4), b = 20.029(7), c = 16.737(2) Å, β = 91.24(2)°, V = 3539(1) Å^3, Z = 4, D_c = 1.083 g cm^{-3}, R = 0.050, R_w = 0.042 (w = $1/\sigma^2(F_o)$) for 3976 observed reflections.

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