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Reaction of a C_{60}-Substituted Benzotetrasilacyclohexene with Bromine

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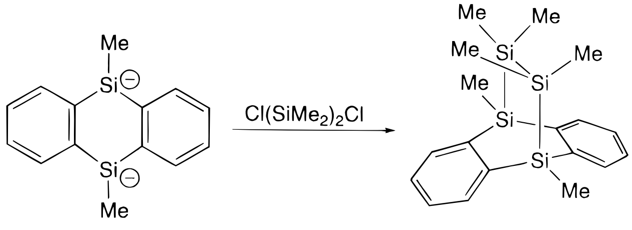
*Summary: Reaction of C_{60}-substituted benzotetrasilacyclohexene (**3**) and bromine gives rise to the 6,7:8,9-dibenzo-3-oxo-1,2,2,4,4,5-hexaphenyl-1,2,4,5-tetrasilabicyclo[3.2.2]nonadiene (**5**) and C_{60}. Intramolecular cyclization of a silyl radical intermediate is proposed to account for the obtained products.*

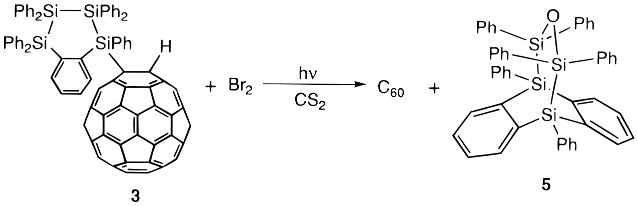
The chemistry of the 9,10-disilaanthracene derivative has been developed considerably for sometime by Jutzi[1] and Bickelhaupt[2] and modified by Corey,[3] Nishiyama,[4] and Chatgilialoglu.[5] Previously, we reported the reaction of the 9,10-disilaanthracene dianion (**1**) with 1,2-dichloro-1,1,2,2-tetramethyldisilane to give 5,6:7,8-dibenzo-1,2,2,3,3,4-hexamethyl-1,2,3,4-tetrasilabicyclo[2.2.0]octadiene (**2**) in moderate yield, Scheme 1.[6] Meanwhile, we have shown that the photolysis of cyclotetrasilanes in a solution containing C_{60} afforded the C_{60} adduct of benzotetrasilacyclohexadiene (**3**).[7] In a continuation of our studies of the reactions of fullerene−silicon derivatives, we have prepared 6,7:8,9-dibenzo-3-oxo-1,2,2,4,4,5-hexaphenyl-1,2,4,5-tetrasilabicyclo[3.2.2]-nonadiene (**5**) by the reaction of **3** with bromine. The cleavage of the Si−fullerene bond depends on the substituent on silicon, and the Si−Si bond of compound **3** is quite stable toward ionic and radical reagents. For example, di-*tert*-butyl peroxide, benzoyl peroxide, chlorine, and MeLi did not react with the silicon unit of **3** but gave complex product mixtures due to the reactions with the fullerene unit. On the other hand, compound **3** undergoes clevage of the silicon−fullerene bond on reaction with bromine.

Addition of bromine to a solution of **3** in carbon disulfide with exposure to daylight followed by purification of the products by gel-permeation chromatography afforded C_{60} and 6,7:8,9-dibenzo-3-oxo-1,2,2,4,4,5-hexaphenyl-1,2,4,5-tetrasilabicyclo[3.2.2]nonadiene (**5**) in yields of 93% and 45%,[8] respectively (Scheme 2).

Scheme 1



Scheme 2



The reaction rate was promoted by external irradiation (>400 nm) but the yield of **5** became too low.[9] However, the reaction did not occur in the dark. The EI-mass spectrum of **5** exhibits one peak at *m/z* 742 ($C_{48}H_{38}Si_4O$, M^+). For the two *o*-phenylene groups, two doublets at δ 127.9 and 129.55 appear in the ^{13}C NMR spectrum. As evidenced by homonuclear ($^1H-^1H$) and heteronuclear ($^1H-^{13}C$) shift correlation (COSY) experiments, the corresponding methine protons resonate at δ 7.21 (dd, J = 5.5,3.1 Hz), 7.33 (dd, J = 5.5,3.1 Hz) in the ^1H NMR spectrum. The other six phenyl groups give rise to six doublets in the ^{13}C NMR spectrum and two doublet and four triplet signals in the ^1H NMR spectrum. The ^{29}Si NMR spectrum of **5** shows two peaks at −33.6 and −11.2 ppm, which are assigned to the silicon atoms of **5**. The solid state structure of **5** was determined by X-ray crystallography. The ORTEP drawing is shown in Figure 1. Crystallographic data, positional parameters, and selected bond lengths and angles are given in Tables 1−2. Compound **5** crystallized in the $P2_1$ space group with two molecules of **5** and two benzene molecules per unit cell.

The most likely course of this conversion of **3** to **5** involves bromine atom abstraction of a fullerene-bonded hydrogen of **3**. The resulting radical then may undergo homolysis of the fullerene−silicon bond as shown in Scheme 3. The silyl radical thus formed then undergoes intermolecular cyclization to give **4**. While this type of intramolecular reaction occurs readily with radical species, it is not a common one in silicon ring systems. The Si−Si bond of **4** then must react with bromine, and hydrolysis to give siloxane **5** follows.

Experimental Section

General Procedure. Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected.

[⊗] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

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(3) (a) McCarthy, W. Z.; Corey, J. Y.; Corey, E. R. *Organometallics* **1984**, *3*, 255. (b) Corey, J. Y.; McCarthy, W. Z. *J. Organomet. Chem.* **1984**, *271*, 319. (c) Welsh, K. M.; Corey, J. Y. *Organometallics* **1987**, *6*, 1393.

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(7) Kusukawa, T.; Kabe, Y.; Ando, W. *Organometallics* **1995**, *14*, 2142.

(8) Formation of $C_{48}H_{38}Si_4O_2$ was determined by mass spectroscopy as a byproduct with an unknown structure.

(9) Probably because of the rapid bromo radical fromation to cause complexed reactions.

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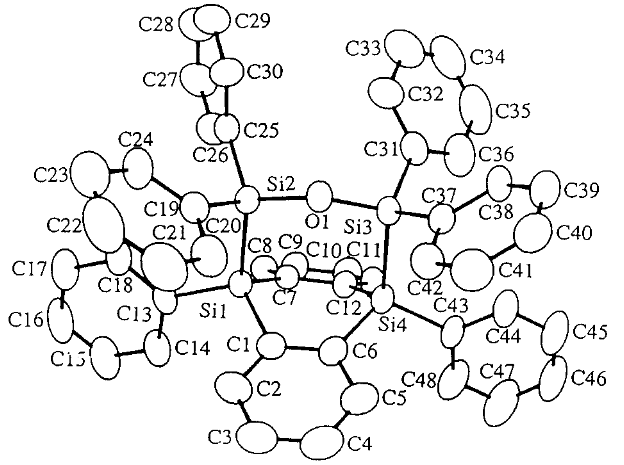


Figure 1. X-ray-determined structure of **5**. The ellipsoids represent 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg)

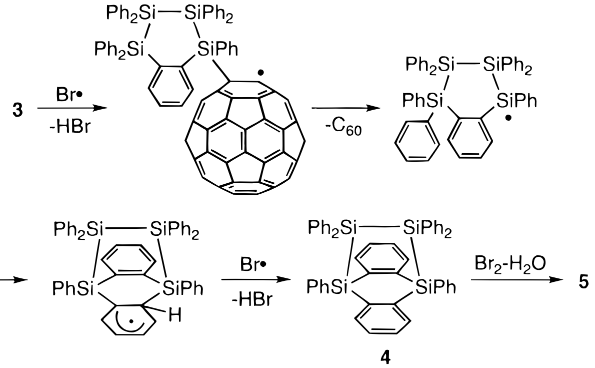
Si(1)−Si(2)	2.365(1)	Si(3)−Si(4)	2.360(1)
Si(1)−C(1)	1.888(4)	Si(4)−C(6)	1.888(4)
Si(1)−C(7)	1.876(4)	Si(4)−C(12)	1.888(4)
Si(2)−O(1)	1.649(2)	C(1)−C(6)	1.417(5)
Si(3)−O(1)	1.641(3)	C(7)−C(12)	1.413(5)
Si(2)−Si(1)−C(1)	103.3(1)	Si(3)−Si(4)−C(12)	109.5(1)
Si(2)−Si(1)−C(7)	112.4(1)	Si(2)−O(1)−Si(3)	144.4(2)
C(1)−Si(1)−C(7)	106.0(2)	Si(1)−C(1)−C(6)	119.2(3)
Si(1)−Si(2)−O(1)	106.8(1)	Si(4)−C(6)−C(1)	121.2(3)
Si(4)−Si(3)−O(1)	105.6(1)	Si(1)−C(7)−C(12)	121.3(3)
Si(3)−Si(4)−C(6)	106.3(1)	Si(4)−C(12)−C(7)	119.5(3)

Table 2. Crystallographic Data for 2

empirical formula	$C_{54}H_{46}Si_4O$
fw	823.31
cryst color, habit	colorless, needles
cryst dimens (mm)	0.20 × 0.40 × 0.40
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a (Å)	10.020(3)
b (Å)	14.580(4)
c (Å)	15.592(3)
α (deg)	99.81(2)
V (Å^3)	2244.7
Z	2
ρ_{calcd}	1.22
radiation	Mo Kα (λ = 0.710 74 Å)
temp (°C)	23
diffractometer	Enraf-Nonius CAD-4
scan type	$\omega-2\theta$
rate (deg min^{-1} in ω)	1−5
scan width (deg)	$(0.4 + 0.350 \tan \theta)$
$2\theta_{max}$	50.0
total reflns no. of	4276
no. of unique reflcns	4117
struct soln, refinement	direct methods, full-matrix least squares
no. of obs ($I > 3.00\sigma(I)$)	3748
no. of variables	531
R; R_w	0.0043; 0.0044

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker AM500 (500 and 125 MHz) and AC300 (300, 75, and 60 MHz) instruments. Infrared spectra were measured on a Jasco FT/IR-5000 spectrometer. Mass spectra were obtained on a JEOL JMS SX102A mass spectrometer. Elemental analyses were carried out by the Chemical Analytical Center of the University of Tsukuba. For the column chromatography, Kieselgel 60 (Merck) was used. Gel-permeation chromatography (GPC) was performed on a LC 908 instrument (Japan Analytical Industry, Co. Ltd) with a series of Jaigel 1H and 2H columns, using toluene as the eluent. All solvents and reagents were purified according to standard procedures.

Scheme 3



Reaction of C_{60}-Substituted Benzotetrasilacyclohexene (3) with Bromine. To a mixture of 52 mg of **3** (36 mmol) and 50 mL of CS_2 was added a solution of Br_2 (108 mmol) in CS_2 (0.36 mL) over a period of 5 min with exposure to daylight at room temperature. After the mixture was stirred for 21 h, the solvent was evaporated and the residue was separated by gel-permeation chromatography (GPC) to give C_{60} and **5** in 93% (24 mg) and 45% (12 mg) yields, respectively. Colorless needles; mp 252−253 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, 8H, J = 7.5 Hz), 7.21 (dd, 4H, J = 5.5, 3.1 Hz), 7.31 (t, 4H, J = 7.4 Hz), 7.33 (dd, 4H, J = 5.5, 3.1 Hz), 7.34 (d, 8H, J = 7.4 Hz), 7.40 (t, 4H, J = 7.6 Hz), 7.50 (t, 2H, J = 7.3 Hz), 7.68 (d, 4H, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 127.6 (d), 127.9 (d), 128.3 (d), 129.5 (d), 130.0 (d), 133.1 (d), 134.8 (d), 135.3 (d), 137.1 (s), 137.4 (d), 142.8 (s); ^{29}Si NMR (60 MHz, $CDCl_3$) δ −33.6, −11.2; MS m/e 742 (M$^+$). HRMS Calcd for $C_{48}H_{38}Si_4O$: 742.2000. Found: 742.2012.

Crystallographic Analysis. Crystals of suitable quality for X-ray analysis of the following dimensions were prepared by slowly cooling benzene solutions: 0.2 × 0.4 × 0.4 mm for **5**. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cells were determined and refined from 25 randomly-selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and the results of the analyses are listed in Table 2. All data processing was performed on a VAX 4000 computer by using the MOLEN structure solving program (Enraf-Nonius, Corp., Delft, The Netherlands). All intensities were corrected for Lorentz and polarization factors. Neutral atom scattering factors were calculated by the standard procedures.[10a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[10b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, $w = 1$.

Compound **5** crystallized in the monoclinic crystal system. The $\omega-2\theta$ scan technique was adopted varying ω scan width as function of θ (ω scan width = $0.6 + 1.260 \tan \theta$). Removal of the redundant data left 2700 unique data in the final data set. The structure was solved by direct methods (MULTAN) and refined via standard least-squares and difference Fourier techniques. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined.

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Supporting Information Available: Text giving the details of data collection, reduction, and structure solution and refinement, tables of experimental details, positional and thermal parameters, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, and bond distances and angles, and ORTEP diagram of **2** (27 pages). Ordering information is given on any current masthead page.

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(10) (a) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.3.1, pp 149−150.