Photochemical [2 + 3] Cycloaddition of C_{60} with Disiliranes[1]

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Organic chemical derivatization of buckminsterfullerene, C_{60}, continues to yield fascinating results.[2–4] C_{60} is a strong electron acceptor capable of taking on as many as six electrons, and photoexcited C_{60} is a stronger electron acceptor than C_{60} in the ground state.[5–7] Although photoinduced charge-transfer between C_{60} and various electron donors such as aromatic amines,[5,8] semiconductor colloids,[7] porphyrins,[9] and photoconducting polymers[10] can occur, there has so far been no example of formation of a photoadduct. Meanwhile, strained Si–Si σ bonds can act as electron donors.[11,12] We report here that the first photochemical reaction of C_{60} with a disilirane produces a [2 + 3] cycloadduct via a charge-transfer interaction.

Irradiation of a toluene solution of 1,1,2,2-tetramesityl-1,2-disilirane[11] (**1a**, 3.3×10^{-3} M) and C_{60} (3.3×10^{-3} M) with a high-pressure mercury-arc lamp (cutoff < 300 nm) resulted in formation of 1,1,3,3-tetramesityl-1,3-disilolane (**2a**) in 82% yield[13] with complete consumption of C_{60} (Scheme I). The adduct **2a** can be readily isolated by preparative HPLC. Very similar results were also obtained with 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilirane.[11] The disiliranes were thermally unreactive toward C_{60} at 90 °C.

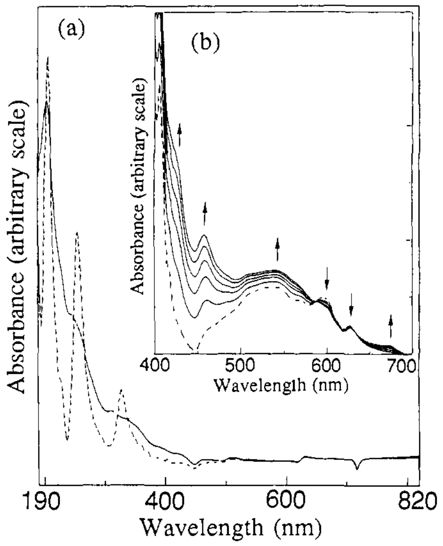
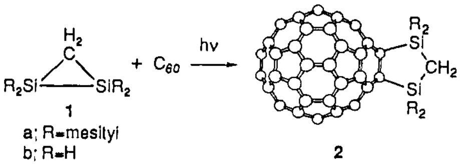


Figure 1. (a) UV–vis spectra of C_{60} (- - -) and**2a** (——) from 190 to 820 nm in hexane. (b) Time-dependent spectral changes of a toluene solution of C_{60} and **1a** upon irradiation.

Scheme I



FAB mass spectrometry of **2a** ($C_{97}H_{46}Si_2$) displays a peak for **2a** at *m/z* 1270–1266 as well as one for C_{60} at 723–720 which arises from the loss of **1a**.

The UV–vis absorption spectrum of **2a** is virtually identical to that of C_{60} except for subtle differences in the 400–500 nm region (Figure 1a). Photochemical changes in the absorption spectra are shown in Figure 1b and compared with those of C_{60}. Interestingly, the spectrum of **2a** has absorption features comparable with those of the carbon[3f] and oxygen[4b] analogues of **2a** and the related carbene,[3a-d] silylene,[1] and oxygen[4] adducts, as one would expect from the similarity of the chromophore in these compounds.

The ^{1}H NMR spectrum of **2a** displays six methyl signals at 3.16, 2.90, 2.41, 2.17, 2.13, and 2.10 ppm and four meta-proton signals of the mesityl groups at 6.68, 6.64, 6.50, and 6.46 ppm.[14] An AB quartet (J = 13.0 Hz) for the two methylene protons at 3.61 and 2.38, ppm supporting $C_s$symmetry of the molecule, is also observed. The ^{13}C NMR spectrum of **2a** shows 32 signals for the C_{60} skeleton.[14] Of the 32, 28 signals have a relative intensity of 2, and four signals have a relative intensity of 1: one at 73.36 ppm and the remainder between 130 and 150 ppm.[15] Twelve signals for four tertiary and eight quaternary aromatic carbon atoms and one signal for the methylene carbon atom of the disilirane component are also observed. These spectral data suggest C_s symmetry of **2a**. Analysis of the C–H three-bond coupling in the H–C COLOC NMR spectrum gave crucial

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[13] $(Mes_4Si_2CH_2)_2C_{60}$ (FAB MS, *m/z* 1816–1812) was also obtained in 8% yield.

[14] The NMR measurement was carried out in the binary solvent system (CS_2/CD_2Cl_2=3:1).

[15] ^{13}C NMR (125M Hz, CS_2/CH_2Cl_2=3:1): δ (number of carbon atoms on C60) 147.23 (2), 146.80 (2), 146.51 (2), 146.17 (12), 145.58 (2), 145.34 (2), 144.64 (2), 144.52 (2), 144.40 (2), 144.06 (2), 143.68 (1), 143.45 (1), 142.69 (2), 142.37, 142.17 (4), 142.57 (1), 141.69 (2), 141.57 (5), 141.37 (2), 140.95 (2), 139.10 (2), 138.57 (2), 135.38 (2), 130.58 (2), 73.36 (2).

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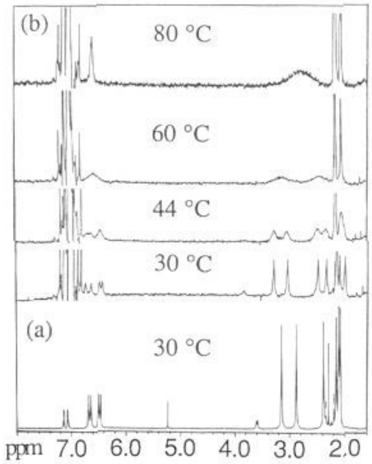

Figure 2. ^{1}H NMR spectra of **2a** (a) in CS_2/CD_2Cl_2 and (b) in $CD_3C_6D_5$ at different temperatures.

evidence for the identification of the 1,3-disilolane structure in **2a**. A cross-peak corresponding to a proton of the methylene group and two sp^3 carbon atoms of the fullerene skeleton at 73.36 ppm was observed. The ^{29}Si NMR spectrum of **2a** shows a peak at −9.81 ppm which is assigned to the silicon atom of **2a**.[14,16]

Symmetry arguments support the following possibilities: (i) a 5,6-ring junction on the fullerene without free rotation of mesityl groups at 30 °C and with a "frozen" (no ring inversion) single conformer in the envelope conformation; (ii) a 5,6-ring junction on the fullerene without free rotation of mesityl groups at 30 °C; and (iii) a 6,6-ring junction on the C_{60} without free rotation of mesityl groups at 30 °C and with a "frozen" conformer (no ring inversion).

To obtain further information on the structure of **2a**, the variable-temperature ^{1}H NMR measurement was carried out[17] (Figure 2). Coalescence of the para-methyl signals at 2.06 and 1.96 ppm at 44 °C reflecting conformational change of the molecule was observed, yielding an activation energy $\Delta G^{\neq} = 17.0$ kcal/mol.[18] The two pairs of four resonances between 6.7 and 6.3 ppm and between 3.3 and 2.3 ppm also coalesce at 60 °C and 80 °C, respectively. $\Delta G^{\neq}$ for both the meta-proton and ortho-methyl groups at coalescence temperatures is 16.2 kcal/mol. These results reveal equivalency of methylene, methyl, and aromatic protons over the coalescence temperature and supports hypothesis iii from above.

Hypothesis iii was also supported by AM1[19] and *ab initio* 3–21G[20] molecular orbital calculations on the reaction of C_{60} and disilirane **1b** which show that the 6,6-adduct is 16.9 (AM1) and 26.5 (3–21G//AM1) kcal/mol more stable than the 5,6-adduct. The experimental finding for the C_s structure of **2a** (6,6-adduct) was confirmed by the full geometry optimization at the AM1 level; its C_s structure corresponds to an energy minimum and is the most stable. As the optimized structure in Figure 3 shows, four bulky mesityl groups are beautifully spaced in C_s symmetry with the observed equivalency. The high barrier observed is ascribed to the fact that the space between C_{60} and the mesityl groups as well as between mesityl groups becomes filled upon transformation from one envelope-conformer to the other. Such a steric effect was also reflected in the fact that the exothermicity (34.1 kcal/mol) for the addition of **1a** to C_{60} is 43.2 kcal/mol smaller than that (77.3 kcal/mol) of **1b** at the AM1 level.

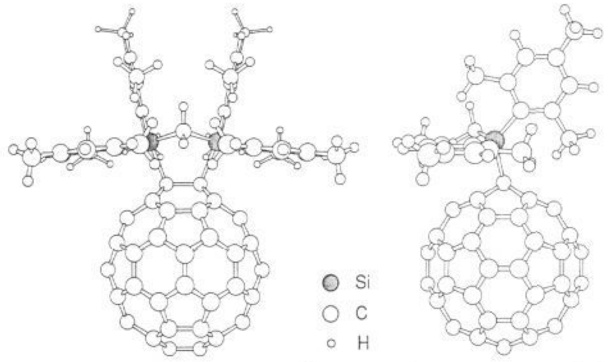

Figure 3. views of the C_s structure of **2a** calculated with the AM1 method.

The free energy change (ΔG) from **1a** to the triplet state of C_{60} is 8.1 kcal/mol.[5a,21] The rate of disappearance of C_{60} was suppressed by addition of 10 equiv of diazabicyclo[2.2.2]octane (E_p = 0.70V vs SCE)[22] and 100 equiv of 1,2,4,5-tetramethoxybenzene (E_p = 0.79V vs SCE), each of which has a lower oxidation potential and is unreactive to photoreaction of C_{60}. The reaction was completely inhibited by addition of 10 equiv of rubrene as triplet quencher.[5a] One plausible rationale for these observations is that an exciplex intermediate derived from **1a** and the triplet state of C_{60} may be responsible for formation of **2a**.[23] Further studies on the reaction mechanism are in progress.

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Supplementary Material Available: Detailed procedures for the preparation of **2a**, complete spectroscopic characterization of **2a**, and a computer-generated model of **2a** (13 pages). Ordering information is given on any current masthead page.

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