Organic chemical derivatization of fullerene

T. Akasaka,[a] W. Ando,[a] K. Kobayashi,[b] and S. Nagase[b]

[a]Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
[b]Department of Chemistry, Faculty of Education, Yokohama National University
   Yokohama 240, Japan

In this paper the recent topics we obtained are discussed; i) reaction of silylene with Buckminsterfullerene (C_{60}) and ii) photochemical [2+3] cycloaddition of C_{60} with disilirane.

1. INTRODUCTION

Since the isolation of Buckminster-fullerene (C_{60})[1] in preparatively useful quantities,[2] much attention has been devoted to its chemical reactivities.[3-5] In spite of their potential usefulness as organomaterials, only a few discrete individual products such as the fulleroids and methanofullerene derivatives[4] and the fullerene epoxide,[5] have been prepared and completely characterized in several functionalizations attempted. Meanwhile, organosilicon compounds represent a unique feature of materials such as polysilanes, which may approaching commercialisation. We believe that combination of fullerene and organo-silicon compounds might form a new class of organic compounds and at the same time open a new field of material science. In this paper we would like to briefly summarize our results obtained on organic chemical derivatization of C60 with activated organosilicon compounds; i) addition of bis(2,6-diisopropyl-phenyl)-silylene as a reactive divalent species to C_{60} furnishes the isolable adduct [6] and ii) photochemical [2+3] cycloaddition of C_{60} with 1,1,2,2-tetramesityl-1,2-disilirane affords the cycloadduct as a doubly silylated product onto C_{60}.[7]

2. THE FIRST FULLERENE SILIRANE

When trisilane 1 (0.1 mmol) as a silylene precursor was photolyzed with a low-pressure mercury lamp in a toluene solution of C_{60} (0.1 mmol), the color of the solution changed from purple to dark brown. Flash chromatography on silica gel furnished thermally stable 2 and

Scheme I

3 (Scheme I). A small amount of 4 and 5 were also obtained. A product composition of a silylene-addition reaction varies with an amount of the trisilane used.

The following spectroscopic analyses were carried out. FAB mass spectrometry of 2 displays a peak for adduct 2 at 1074-1070 as well as for C_{60} at 723-720 which arises from loss of the silylene. The FAB mass spectra of 3, 4 and 5 adducts of C_{60} were reasonably analyzed. The UV-vis absorption spectra of 2 is virtually identical to that of C_{60} except for subtle differences in the 400-700 nm region. Several bands are observed with four bands which correspond to those in the C_{60} spectrum.

The FAB mass, UV-vis and FTIR spectra of 2 contain a number of unique features, but also suggest that this new fullerene retains the essential electronic and structural character of C_{60}. The silirane structure 2a, of C_{2V} symmetry,[3a,3e-g,4a] would derive from addition of 1 across the reactive 6-ring-6-ring

junction. Silamethano[10]annulene 2b could arise via isomerization of 2a.

The proton NMR was consistent with the Dip_2Si adduct of C_{60}. The ^{13}C NMR spectrum of 2 shows 17 signals for the C_{60} skeleton, of which four correspond to two carbon atoms and thirteen correspond to four carbon atoms; one at $\delta=71.12$ ppm and the remainder between $\delta=140$ and $\delta=150$. This is the appropriate number and ratio of peak intensities for a C_{60} adduct of C_{2V} symmetry . The ^{13}C NMR signal at $\delta=71.12$ strongly supports 2a rather than 2b; an sp^2 C-Si should give rise to a signal below $\delta=130$.[8] The ^{29}Si NMR spectrum of 2 shows a peak at $\delta=-72.74$ which is also assigned to the silicon atom of 2a. The chemical shift of the silicon atom on a silirane ring typically appears at high field ranging from $\delta=-50$ to $\delta=-85$.[8] The ^{29}Si chemical shift of diphenyldivinylsilane can be anticipated to appear at $\delta=-20$.[8] Thus, the chemical shifts of the two-carbon signal at $\delta=71.12$ and the silicon one at $\delta=-72.74$ are fully consistent with expectations for the silirane carbon atoms and silicon atom in 2a.

The experimental finding for 2a was confirmed by AM1 molecular orbital calculation[9,10] on the reaction of C_{60} and silylenes, Ph_2Si: and H_2Si:. Ph_2Si: and H_2Si: add across the junction of two six-membered rings in C_{60} to give siliranes (a 6-6 adduct), 6a and 6a', with an exothermicity of

2a   **2b**
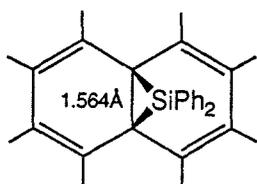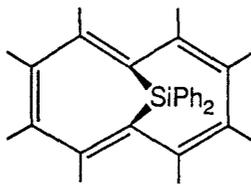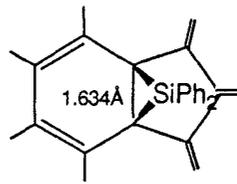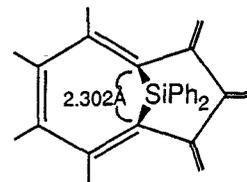
6a   **6b**   **7a**   **7b**

61.3 and 78.0 kcal/mol, respectively. The isomeric 6b and 6b' were not located on the potential energy surface. The optimized structure of 6a is shown in Figure 1. The 6-6 adduct 6a was 19.4 and 10.7 kcal/mol more stable than the 5-6 adducts 7a' and 7b', respectively. 6a' was 19.0 and 6.2 kcal/mol more stable than the 5-6 adducts 7a and 7b, respectively. The less stable 7a and 7a' isomerize to 7b and 7b'with a small barriers of

2.0 and 1.0 kcal/mol, respectively. Interestingly this is in contrast with the addition of diphenylmethylene for which the 6-6 adduct was calculated to be only 1.2 kcal/mol more stable than the 5-6 adduct.

Based on these observations, it might be realized that addition of silylene 1 onto C_{60} actually forms the silirane 2a, similar to the case of a carbene-addition.[3c]

Fig. 1 The optimized structure of 6a.

- ● Si
- ○ C
- ○ H
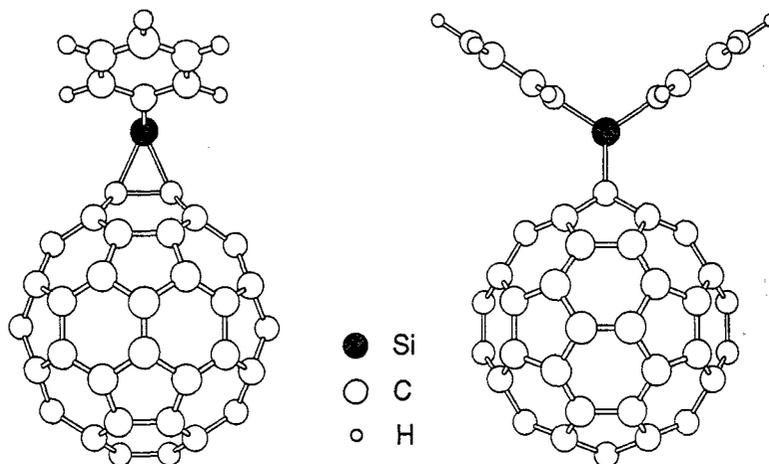
3. PHOTOCHEMICAL [2+3] CYCLO-ADDITION OFC60 WITH DISILIRANE

C_{60} is a strong electron acceptor capable of taking on as many as six electrons, and photo-excited C_{60} is a stronger electron acceptor than C_{60} in the ground state.[5,11,12] Although photo-induced charge-transfer between C_{60} and various electron donors such as aromatic amines,[5,13] semiconductor colloid,[12] porphyrins,[14] and photoconducting polymers[15] can occur, there has so far been no example of

formation of a photoadduct. Meanwhile, strained Si-Si σ bonds can act as an electron donor.[16,17] We report here that the first photochemical reaction of C_{60} with a disilirane produces a [2 + 3] cycloadduct.

Irradiation of a toluene solution of 1,1,2,2-tetramesityl-1,2-disilirane (8a, 0.1 mmol) and C_{60} (0.1 mmol) with a high-pressure mercury-arc lamp resulted in formation of 9a and 10a with complete consumption of C_{60}. (Scheme II) The adducts can be readily isolated by preparative HPLC.

Scheme II

$$R_2Si \underset{\underset{SiR_2}{\diagdown}}{\overset{\overset{H_2}{C}}{\diagup}} + C_{60} \xrightarrow{h\nu} C_{60}(R_2SiCH_2SiR_2) + C_{60}(R_2SiCH_2SiR_2)_2$$

8 **9** **10**

a; R=mesityl 82% 8%
b; R=H
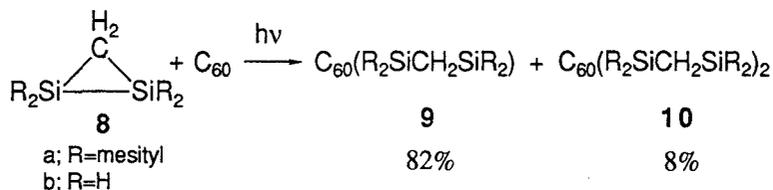
FAB mass spectrometry of **9a** displays a peak for **9a** at 1270-1266 as well as one of C_{60} at 723-720 which arises from loss of **8a**.

The UV-vis absorption spectra of **9a** is virtually identical to that of C_{60} except for subtle differences in the 400-500 nm region. Interestingly, the spectrum of **9a** has absorption features comparable with those of the carbon[3f] and oxygen[4b] analogues of **9a**, and the related carbene,[3a-d] silylene[6] and oxygen[4] adduct, as one would expect from the similarity of the chromophore in these compounds.

The ^{1}H NMR spectrum of **9a** displays six methyl signals and four meta-proton signals on the mesityl groups. An AB quartet (J=13.0 Hz) for the two methylene protons supporting Cs symmetry of the molecule is also observed. The ^{13}C NMR spectrum of **9a** shows 32 signals for the C_{60} skeleton. Of the 32, 28 signals have a relative intensity of 2 and 4 signals have a relative intensity of 1: one at 73.36 ppm and the remainder between 130 and 150 ppm. Twelve signals for 4 tertiary and 8 quaternary aromatic carbon atoms, and 1 signal for methylene carbon atom of the disilirane component are also observed. These spectral data suggest Cs symmetry of **9a**. The ^{29}Si NMR spectrum of **9a** shows a peak at -9.81 ppm which is assigned to the silicon atom of **9a**.[8]

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).

In order to obtain further information on the structure of **9a**, the variable-temperature ^{1}H NMR measurement was carried out. Coalescence of two para-methyl signals at 44 °C reflecting conformational change of the molecule was observed, yielding an activation energy $\Delta G^{\neq}$=17.0 kcal/mol. The two pairs of four resonances of the meta-proton and ortho-methyl groups also coalesce at 60 and 80°C, respectively and their $\Delta G^{\neq}$ 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) above.

Hypothesis (iii) was also supported by AM1[9] and *ab initio* 3-21G[18] 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 **9a** (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 2 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 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 <u>1a</u> to C_{60} is 43.2 kcal/mol smaller than that (77.3 kcal/mol) of <u>9b</u> at the AM1 level.

Studies on the reaction mechanism are in progress.

Fig. 2 The optimized structure of **9a**.

● Si
○ C
o H
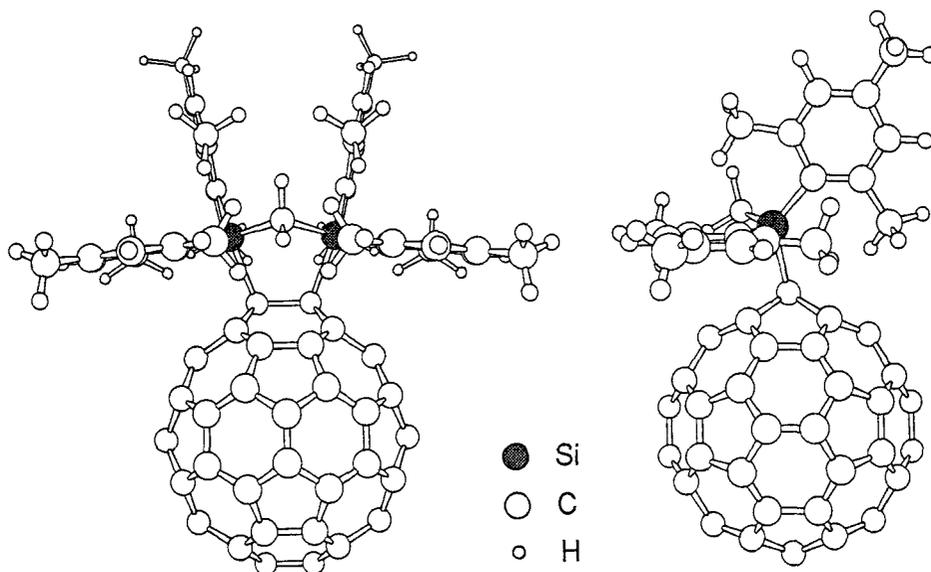
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