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A Novel Photorearrangement of a Cyclohexadiene Derivative of C_{60}

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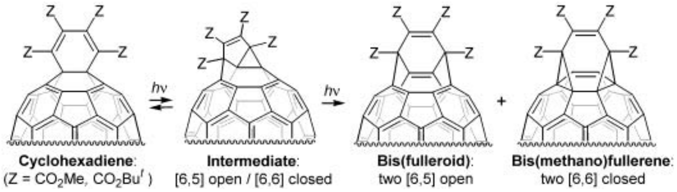
ABSTRACT



Photorearrangement of tetraalkoxycarbonyl-substituted cyclohexadiene derivatives of C_{60} yields not only well-known bis(fulleroid) but also bis(methano)fullerene. Existence of a labile and structurally new intermediate is observed in the reaction mixture. The discovery of the compound suggests the existence of another possible pathway giving those two products other than the widely accepted [4 + 4]/[2 + 2 + 2] mechanism.

Among various exohedral fullerene derivatives, fulleroid (a C_1 homologue with the [6,5] open structure on C_{60}) has been collecting much attention since publishment of Wudl's pioneer work because of the ability to recover the original 60π-electron system and of its mechanistically unique rearrangement to the methanofullerene ([6,6] closed structure) through the [6,5] closed intermediate.[1−4] The unique structural and physical features of the related fulleroid derivative, bis(fulleroid) (**3**), containing two neighboring [6,5] open units connected by an ethylene linker has been reported by Rubin.[5−7] Compound **3** has been thought to be produced exclusively by the photochemical reaction of the cyclohexa-

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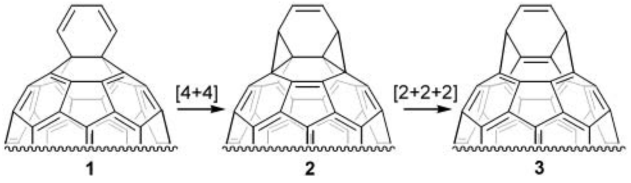
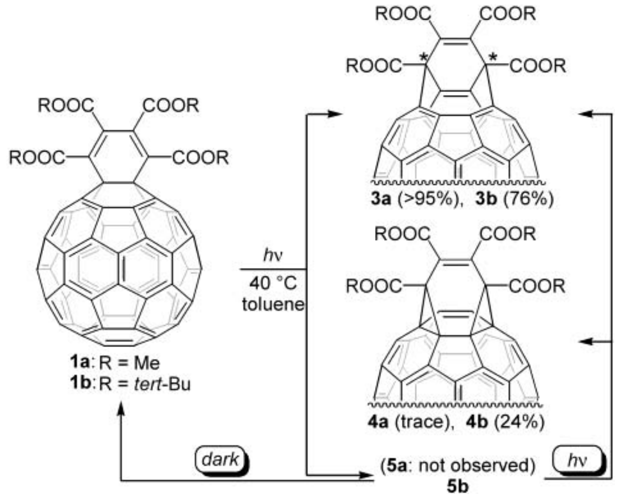
diene derivative (**1**) via the [6,5] closed intermediate (**2**) (Scheme 1). If two fulleroid units in **3** can behave individually, the rearrangement of each unit to the [6,6] closed methanofullerene unit might be possible to afford bis(methano)fullerene. Although the existence and stability of bis(methano)fullerene was confirmed by synthesis using phosphine-mediated addition of two propiolate units on C_{60},[6b] experimental evidence that confirms the chemical relationship between bis(fulleroid) and bis(methano)fullerene was not clarified.

Scheme 1. Proposed Mechanism for the Rearrangement of **1**



Recently, we have reported that the reactions of C_{60} with alkoxycarbonyl-substituted palladacyclopentadiene derivatives gave the cyclohexadiene derivatives (**1a** and **1b**), which afforded bis(fulleroid) (**3a** and **3b**) by irradiation with visible light.[8a] Since this is the first example for the bis(fulleroid) bearing substituents at the fulleroid bridgehead positions (shown by * on the structure **3a** and **3b** in Scheme 2), we are interested in substituent effects on the rearrangement. Herein we would like to describe the mechanistic aspects of the rearrangement of cyclohexadiene derivatives **1a** and **1b** and structures and behaviors of bis(methano)fullerene and the novel intermediate, both of which are isolated for the first time in the rearrangement of bis(fulleroid) (**3**).

Scheme 2. Photochemical Rearrangement of **1a** and **1b**



When a deoxygenated toluene solution of **1a** was irradiated by 100W incandescent lamp at 40 °C for 1 h, **3a** was obtained quantitatively with >95% purity, together with a trace amount of **4a** (<5%).[8a,9] On the contrary, the similar reaction of **1b** bearing *tert*-butyl ester afforded a 76:24 mixture of **3b** and **4b**, which can be separated by using silica gel column chromatography and yields were 73% and 22%, respectively.

The structure of **4b** was characterized as bis(methano)fullerene by ^{1}H NMR, ^{13}C NMR, IR, UV/vis spectra, electrospray mass spectrometry, and elemental analysis. ^{13}C NMR spectrum of **4b** showed 29 C_s symmetric signals in the sp^2 carbon region, and three kinds of sp^3 carbons characteristic to the cyclopropane structure were detected at 44.92, 53.46, and 66.86 ppm in $CDCl_3$ (cf. one sp^3 carbon at 57.71 ppm was observed for C_s symmetric **3b**). Chemical shifts of these sp^3 carbons were comparable to those of the previously reported bis(methano)fullerene.[6b] UV/vis spectra of these compounds were in agreement with typical features of each structure. The visible region of the absorption spectrum of **3b** resembles that of C_{60}; on the other hand, the spectrum of 56π-electronic **4b** exhibits a hypsochromic shift and a diagnostic peak at 436 nm.

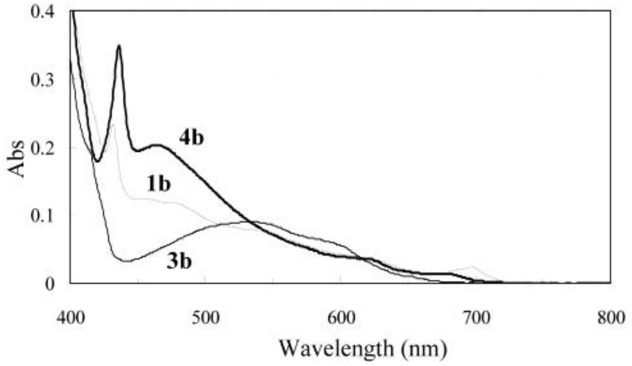


Figure 1. Visible region of UV/vis spectra of **1b**, **3b**, and **4b** (8.1−8.2 × 10^{-5} M $CHCl_3$ solution).

When the rearrangement of **1b** was monitored by ^{1}H NMR in C_6D_6 at 40 °C using a 20 W fluorescent lamp, another set of four singlet signals indicating an unsymmetrical structure (**5b**) was observed together with **3b** and **4b**, and the ratio of **5b**: **3b**: **4b** was 29:56:15 (87% conversion), see Figure 2.

Compound **5b** was isolated in 90% purity by silica gel column chromatography and subsequently HPLC purification. Interestingly, isolated **5b** was smoothly converted into

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(9) Pure **4a** was isolated in 1% yield after complete oxidation of **3a** (ref 8b), and fully characterized by NMR, IR, UV/vis, MS, and elemental analysis (see Supporting Information).

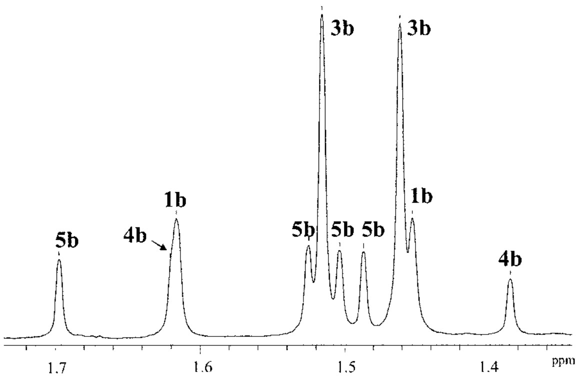


Figure 2. *tert*-Butyl region of ^{1}H NMR spectrum after 12 h of irradiation of **1b** in C_6D_6.

a 1:1 mixture of **3b** and **4b** under bright condition and gradually went back to **1b** in the dark (Figure 3). ^{13}C NMR revealed that **5b** has the C_1 symmetric structure along with four sp^3 signals at 71.30, 66.10, 57.72, and 49.53 ppm.[10] The ^{13}C NMR study on **5b** prepared from ^{13}C (10−15%)-enriched C_{60} indicates that two carbons at 71.30 and 49.53 ppm are assigned to the carbons on the C_{60} surface.[11] Although there still remained three possible structures as shown **5b-I**−**III** in Figure 4, **5b-I** is less stable than **1b** by 9.2, 12.6, and 22.3 kcal/mol at the B3LYP/6-31G(d), RHF/6-31G(d),[12] and AM1 levels,[13] respectively. In contrast, neither **5b-II** nor **5b-III** could be located as a local minimum. Furthermore B3LYP chemical shifts of **5b-I** are in good agreement with the experimental values supporting this structure (Figure 5).

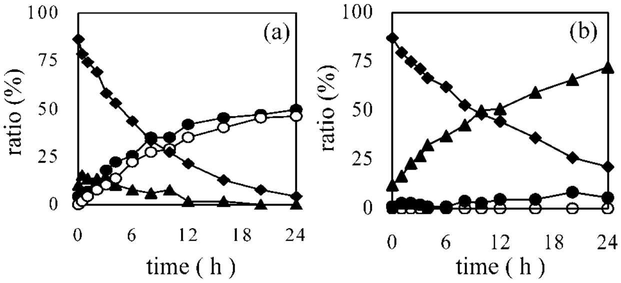
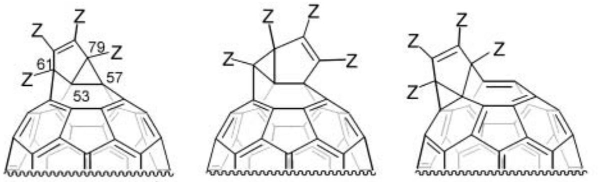


Figure 3. Time conversion plot of compound **5b** in C_6D_6 at 40 °C: (◆) **5b**, (▲) **1b**, (●) **3b**, (○) **4b**. (a) Irradiation with 20 W fluorescence lamp and (b) dark.

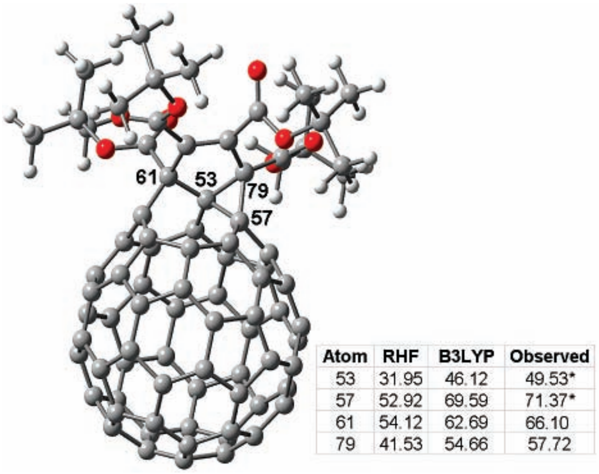


5b-I (Z = CO_2Bu^t)
[6,5] open / [6,6] closed
on six membered ring

5b-II

5b-III
[6,5] open / [6,5] closed
on five membered ring

Figure 4. Possible structures for **5b**.



Atom	RHF	B3LYP	Observed
53	31.95	46.12	49.53*
57	52.92	69.59	71.37*
61	54.12	62.69	66.10
79	41.53	54.66	57.72

Figure 5. B3LYP/6-31G(d) optimized structure for **5b-I** and chemical shifts (ppm) for sp^3 carbons relative to TMS calculated at RHF/6-31G(d) and B3LYP/6-31G(d) levels and observed; (*) assigned to the carbons on the C_{60} surface).

It is possible to explain the formation of **5b-I** as follows: one carbon−carbon bond formation initially affords an allylic biradical species bearing one [6,5] closed structure as shown in Scheme 3. Then, isomerization from [6,5] close to the [6,5] open structure together with [6,6] closed ring formation affords **5b-I**. Rearrangement of either of methanofullerene or fulleroid unit in **5b-I** into the other gives **3b** or **4b**, respectively.

It is known that, in general, fulleroid is thermally less stable than methanofullerene and isomerizes to methanofullerene under various conditions.[3] However, the similar conversion of **3a** and **3b** to **4a** and **4b** did not proceed under

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(10) Chemical shifts of sp^3 carbons of **1b**, **3b**, and **4b** in C_6D_6 are follows: **1b**, 64.97; **3b**, 58.55; **4b**, 67.63, 54.08, and 45.72 ppm (Supporting Information).

(11) Further structural confirmation by INADEQUATE (Incredible Natural Abundance Double Quantum Experiment) NMR spectrum has not resulted in success at present because of their stability.

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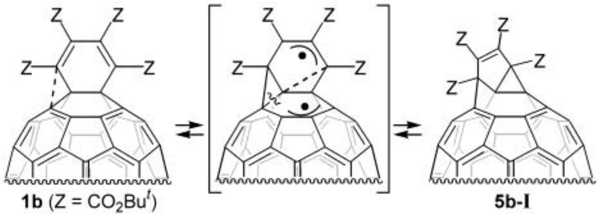
(13) AM1 calculations were performed by using a Hyperchem 6 molecular modeling system.

Scheme 3. Possible Mechanism for the Formation of **5b-I**



thermal (150 °C, 36 h, ODCB), photochemical (rt, 8 h, toluene), or acidic (excess CF_3CO_2H, rt, 12 h, toluene) conditions (**3a** was recovered as intact and *tert*-butyl ester groups of **3b** were cleaved). Therefore, the formation of **4a** and **4b** occurred not through bis(fulleroid) but directly from **5a-I** and **5b-I**, respectively (Figure 6). Although the 28 kcal/mol stability of **3b** to **4b** (AM1) suggests the possibility of the isomerization from **4b** to **3b**, **3a** and **3b** were not formed from **4a** and **4b**, respectively, under thermal, photochemical, or acidic conditions.

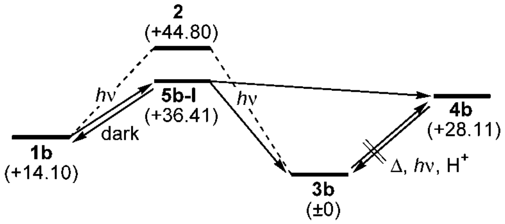


Figure 6. The proposed reaction coordinate for the isomerization of **1b** and their relative energies (kcal/mol) from AM1 calculations.

In summary, we demonstrate that photoinduced rearrangement of the cyclohexadiene derivative of C_{60} gives not only bis(fulleroid) but also bis(methano)fullerene. Unlike fulleroid-methanofullerene, the interconversion between bis(fulleroid) and bis(methano)fullerene does not occur. The existence of the versatile unsymmetrical intermediate in the photochemical rearrangement suggests that the rearrangement occurs via a different pathway than the previously described mechanism. The new mechanism is significant in substances with bulky substrates. Further investigation of the mechanism and transformation of ester groups are now in progress.

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Supporting Information Available: Experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra and UV/vis charts, and Cartesian coordinates optimized by using B3LYP/6-31G(d) (for **5b-I**) and AM1 methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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