Synthesis of Fullerene Derivatives with Novel Structures
— Liquid-Phase versus Solid-State Reactions —

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Received July 13, 2004

Abstract: Reactions of C60 with various carbon nucleophiles, particularly those with substituted acetylide and fluorenide ions in the liquid phase, give various C60 derivatives. While the reaction with cyanide salts only affords the cyanated C60 in liquid phase, the solid-state mechanochemical reaction selectively gives the dumbbell-shaped dimer. As typically shown by this example, the solid-state reaction was found to be quite advantageous for the formation of various types of fullerene dimers. The reaction of C60 with phthalazine also results in formation of entirely different products depending on the reaction phase. While the solid-state reaction gives a fullerene dimer incorporated in a bicyclic framework, the liquid-phase thermal reaction affords a derivative of an open-cage fullerene. Utilizing this reaction, an attempt has been made for organic synthesis of endohedral fullerene encapsulating molecular hydrogen through a series of procedures, i.e., opening a hole on the fullerene cage, insertion of molecular hydrogen, and reduction of the size of the opening.

1. Introduction

Since the achievement of macroscopic production of fullerenes, research on this entirely new type of carbon allotropes has been developed explosively in various fields of science covering chemistry, physics, biology, and interdisciplinary areas. Particularly, [60]fullerene (C60), which is produced in the largest quantity and is regarded as a representative of all the fullerenes, has attracted researchers not only because of the beauty of the molecular shape with high Ih symmetry but also owing to its great potential as functional materials and from curiosity regarding its fundamental physical and chemical properties.

Today, it is widely accepted that C60 is not a super-aromatic compound but should be regarded as a polynyl molecule with 30 double bonds on its surface. With its low-lying triply degenerate LUMO levels, C60 behaves as an electron-deficient olefin. Among numerous organic reactions reported so far, representative and frequently used reactions are summarized in Scheme 1. Among these, the most versatile and widely applied reactions are the “Prato reaction” and the “Bingel reaction”, which can afford C60 derivatives fused with variously substituted pyrrolidine and cyclopropane ring, respectively. These reactions are typical examples of the 1,3-dipolar cycloadditiion and the nucleophilic addition reactions to C60.

Since fullerenes are clusters of a large number of carbon atoms, their solubility in common organic solvents is generally quite low, and the requirement of the use of a large amount of solvent sometimes becomes problematic. In order to overcome this inconvenience, reactions without the use of any solvent, or solid-state reactions, have been used in our group. It has been found that these solvent-free reactions can sometimes afford products which have not been produced in liquid-phase reactions and are uniquely obtained under solid-state reaction conditions. In the present article, our approach to create fullerene derivatives with novel structures by the selective use of liquid-phase and solid-state reactions will be presented.

2. Addition of Carbon Nucleophiles to C60

In the early stage of fullerene research in the 1990s,
Hirsch and coworkers showed that, under carefully controlled conditions, typical carbon nucleophiles such as organolithiums (RLi) and Grignard reagents (RMgX) react with C60 to give R-C60H in 47 to 80% yield after acidification. However, curiously there had been no report on the addition of alkynyllithium to C60. We were able to add various alkynyl reagents, R-C≡C-Li (R = Si(CH3)3, C6H5, C6H13, den-drimer unit, and, terthiophenyl), to C60 to give the corresponding 1,2- or 1,4-fullerene adducts, R-C ≡C-C60-R' (1) after treating the reaction mixture with appropriate electrophiles (Scheme 2).

A characteristic feature of the alkynyllithium addition to C60 is that the product yield is fair to good and unfavorable formation of bisadduct is suppressed owing to delocalization of the negative charge in the first formed fullereny anion R-C≡C-C60-

The dumbbell-like C60 dimer with two fullerene cages connected by an acetylenic linkage 2 was synthesized in order to examine the possible electronic interaction between the two cages, but such interaction was not detected at the ground state upon electrochemical reduction.

On the other hand, in the case of a dendrimer having a fullerene core, weak interaction between the C60 core and the dendron units was observed upon laser flash photolysis.

The terthiophene-fullerene dyad 4 was found to be redox active as shown by the typical repetitive cyclic voltammogram given in Figure 1. After the cyclic voltammetry (CV) in o-dichlorobenzene (ODCB), a brown-colored polymer film of 4 was found to be deposited on the electrode. When the same procedure was conducted on an indium tin oxide (ITO) electrode, the polymer film exhibited electrochromism; the color of the originally brown film changed to green upon application of cathodic voltage while the color faded upon anodic sweep. When ethylenedioxy units were attached to the terthiophene moiety to enhance the electron-donating ability, similarly produced polymer film 5 was found to be applicable as a key component in a device of a photovoltaic cell.

Among stable carbanions, a fluorenide anion (lithium salt) can also add to C60 in THF to give the monoadduct only under severely de-aerated conditions, i.e., under high vacuum (<10^-4 mmHg). When a trace of air is present, the first formed 2-(9-fluorenyl)-1-[60]fullereny anion 6 is oxidized to the corresponding radical, and is subjected to the addition of the fluorenide anion at the 4-position to give 1,4-di(9-fluorenyl) derivative of C60 (7) (Scheme 3).

This reaction is highly dependent on the counter cation. Thus, when potassium salt is used for the reaction, nucleophilicity of the fluorenide anion is enhanced so that the reaction gives tetrakisadduct 8 in 40% yield (Scheme 3). The structure of adduct 8 was determined by X-ray crystallography, which indicated that 8 is the first fullerene derivative having a fulvene-type π-conjugated system on the surface of the cage. Adduct 8 readily reacts with various carbon nucleophiles at the position which corresponds to the exocyclic methylene carbon of the fulvene moiety to give the corresponding pentakisadducts. Particularly by further addition of the fluorenide anion, the cyclopentadienyl-type stable anion 9 with Cs symmetry was formed. Theoretical calculations indicate that 9 has a propeller-like structure (Figure 2). Actually, the hydrocarbon obtained by protonation of 9 was shown to have molecular chirality by HPLC using a chiral column, and is composed of an isomer with the shape of...
3. Solid-State Reactions of C₆₀

As described above, nucleophilic additions to C₆₀ can give various derivatives of structural interest and possessing potential functionalities. One major disadvantage in carrying out these reactions is the low solubility of C₆₀ (and some of the products) so that a large amount of the solvents is required for the reaction and for the work-up process. It would be not only convenient but desirable from the viewpoint of environmental protection if we can conduct these reactions without the use of any solvent. This consideration has led us to attempt the solid-state reaction of C₆₀.

For the solid-state reaction to take place, the reactants have to be vigorously mixed by applying external mechanical energy. Thus, the solid-state reaction may be called mechanochemistry. The application of this method to purely inorganic reactions had not been well developed before the pioneering and systematic work by Toda and coworkers.

As the procedures for mechanochemical solid-state reactions, the simplest is grinding using a mortar and pestle. When a longer reaction time is required, ball-milling is used. In order to apply much higher mechanical energy for the reaction, we decided to use what we call a “high-speed vibration mill” (HSVM). This is a rapidly vibrating mill, frequently used in a laboratory for the purpose of forming a pellet for IR spectral measurement of organic compounds. The main part of this type of mill is essentially a stainless-steel capsule and a milling ball, which are rapidly vibrated at the speed of 3500 rpm. Based on the observation of phase transformation of inorganic materials such as BeF₂ and B₂O₃, pressure as high as 10⁻²⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻{-} 

Although similar HSVM treatment of C₆₀ with organic bromides (R-Br; R = alkyl, aryl) and magnesium gave a complex mixture, the use of alkali metals afforded the expected C₆₀ derivatives R-C₆₀-H albeit in modest yields from 11 to 24%. The versatile cyclopropanation of C₆₀ known as the “Bingel reaction” (shown in Scheme 1) is a nucleophilic addition of a carbon nucleophile, generated by deprotonation of α-halogenated malonic acid esters or α-halogenated β-diketones, to C₆₀ followed by intramolecular nucleophilic substitution. In typical liquid-phase reactions, the most frequently used base for the deprotonation is DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Although an inorganic base such as NaH was used in early reports, there has been no report as to the use of weaker inorganic bases. However, for the Bingel reaction to proceed in the solid state under the solvent-free HSVM conditions, the organic base (DBU) was found to be not effective, but weak inorganic bases such as Na₂CO₃, NaHCO₃, NaOAc, Ca(OH)₂, and Na₂B₄O₇ were to be used. Thus, when a mixture of C₆₀, diethyl bromomalonate, and Na₂CO₃ in a 1:1:1 molar ratio was vigorously milled under the HSVM conditions for 30 min, cyclopropanated fullerene 10 was obtained in 51% yield (86% based on consumed C₆₀) along with 7% (12% based on consumed C₆₀) of bis-cyclopropanated product 11 (Scheme 5).

3.2 Solid-State Dimerization of Fullerenes

It has been known that NaCN can add to C₆₀ in solution to give cyano C₆₀ (12) (Scheme 6a). Unexpectedly, however, when C₆₀ was treated with KCN or NaCN under solid-state reaction conditions, no cyanoated product was formed but an entirely different product, that is, a dumbbell-shaped dimer C₉₀ (13) was selectively obtained (Scheme 6b). The structure of 13 was unambiguously determined by X-ray crystallography. It turned out later that it is not necessary to use such a poisonous compound like KCN as a catalyst but potassium salts such as CH₃CO₂K, KOH, and K₂CO₃, metals with high reducing power such as Li, Na, K, Mg, and Al, and also some solid amines such as 4-aminopyridine, 4-(dimethylamino)pyridine, and 3,4-diaminopyridine are as effective as KCN. It is to be noted that the yield of the...
produced dimer is nearly 30% and unreacted C_{60} is recovered in almost 70% yield regardless of the catalyst or reaction time employed.\textsuperscript{24a} Based on the effectiveness of the reducing metals, the mechanism of this reaction is assumed to involve one-electron transfer as a key step as shown in Scheme 6c. Thus, the formation of C_{60} radical anion, which is stable in solution but should be highly reactive in the solid without any solvation, must play an important role in its reaction with abundant C_{60} molecules surrounding it. The reverse reaction starting from dimer C_{120}(13) under the same solid-state reaction conditions was also found to give a reaction mixture of C_{60} and C_{120} in a ratio of nearly 7:3, which can thus be regarded as an equilibrium mixture.\textsuperscript{24a}

When C_{60} was allowed to react with 4-aminopyridine under solid-state HSVM conditions, not only the fullerene dimer C_{120}(13) but trimer C_{180}(14) was also produced albeit in a low yield (4%).\textsuperscript{25} For trimer 14, theoretically there are eight possible isomers with the linearly connected structures and one isomer with a cyclic structure. The experimentally obtained trimeric product actually consisted of two groups of isomers A and B, which must have structures substantially different from each other as judged from their behaviors on HPLC analysis. Because of the poor solubility, no spectroscopic identification was possible, but by direct observation with a scanning tunneling microscope (STM), the isomers included in A were found to be those with folded structures while the isomer in B was shown to have a cyclic structure.\textsuperscript{26} This assignment is in agreement with the results of theoretical calculations on the correlation between structures and energies of each isomer.

It was also possible to prepare a fullerene cross-dimer. Thus, when an equimolar mixture of C_{60} and C_{70} was allowed to react in the presence of 4-aminopyridine under the solid-state HSVM conditions for 30 min, the cross-dimer C_{130}(15) was obtained in 3% yield in addition to homodimer C_{120}(10%) and unreacted C_{60} (80%) and C_{70} (97%).\textsuperscript{27} The \textsuperscript{13}C NMR and electronic spectroscopy of produced C_{130} indicated that C_{60} reacted selectively at the 1,2-bond of C_{70}, which is known to be the most reactive due to the highest curvature present in this molecule and the resulting largest pyramidalization in the carbons at the 1,2-positions.\textsuperscript{3}

The fullerene dimer connected by a single bond and a silicon or germanium bridge, 16 or 17, was also synthesized by the solid-state reaction. When a mixture of C_{60}, dichlorodiphenylsilane or -germane, and lithium metal was vigorously milled with HSVM for 30 min, 16 or 17 was obtained in 7.5%\textsuperscript{28} or 9%\textsuperscript{29} yield, respectively (Scheme 7). A similar dimer having a methylene bridge or an oxa-bridge has also been prepared by a solid-phase thermal reaction at 200°C.\textsuperscript{30}

Fullerenes are known to readily undergo cycloaddition reactions with dienes and 1,3-dipolar compounds.\textsuperscript{3} The most well-known example of the latter is the "Prato reaction",\textsuperscript{4} which takes place between fullerene and azomethine ylide formed in situ from derivatives of glycine and aldehydes. This reaction can also be conducted under the solid-state conditions. Thus, when the reaction of C_{60} with N-methyl- or N-ethyglycine in the presence of paraformaldehyde or various substituted benzaldehydes was conducted under the HSVM conditions (1 h), it gave a moderate yield (20 to 30%) of fulleroypyrrrolidine 18 together with about 50% recovery of C_{60} (Scheme 8).\textsuperscript{32} The optimum molar ratio of the reagents, C_{60}, glycine, and aldehyde, was found to be 1:1 to 1:2:2.

A reaction of C_{60} with anthracene can be taken as a typical example of the [4+2] cycloaddition. In a liquid-phase thermal reaction, the produced adduct also dissociates into the starting materials so that the reaction reaches an equilibrium state as shown in Scheme 9.\textsuperscript{33}
When this reaction was conducted under the solid-state reaction conditions using HSVM, the yields of both monoadduct 19 and bisadduct 20 increased to 55% and 19%, respectively, in spite of much shorter reaction time (1 h) as shown in Scheme 9. The time-dependence of the reaction is shown in Figure 3a. Apparently, the curve for the formation of 19 reaches a plateau with almost 60% yield at the reaction time of 30 min. The reverse reaction, i.e., the dissociation of 19, was also found to take place under the HSVM conditions, again leaving nearly 60% of 19 apparently unchanged as shown in Fig. 3b. Thus, a kind of equilibrium state appears to be attained even under the present heterogeneous solid-state reaction conditions.

In the case of the reaction of C₆₀ with pentacene, a liquid-phase reaction in refluxing toluene for 72 h gave only the monoadduct 21 and bispentacene adducts 22 in 59% and 13% yield, respectively, in accord with the generally known highest reactivity at 6,13-carbons of pentacene. In sharp contrast, the solid-state reaction of C₆₀ with an equimolar amount of pentacene using HSVM for 1 h afforded not only the adducts 21 and 22 in 19% and 15% yield, respectively, but the bisfullerene adduct 24 in 11% yield. The formation of 24 indicates that C₆₀ trapped the thermodynamically less favored monoadduct 23 formed by the cycloaddition of C₆₀ at 5,14-carbons (Scheme 10).

A quite similar type of solid-state [4+2] reaction was also observed between C₆₀ and an equimolar amount of di(2-pyridyl)-1,2,4,5-tetrazine under the HSVM conditions for 1 h (Scheme 11). The reaction was very clean and the ¹H and ¹³C NMR spectra of the resulting brown powder exhibited signals corresponding to 1:1 adduct 25 as a single product only contaminated by a small amount (5%) of unreacted C₆₀. The isolated yield of 25 was larger than 90%, and this is to be compared with 50-60% yield when the same reaction was conducted in refluxing toluene.

On the other hand, when the HSVM reaction was conducted between the same reactants in a 2:1 molar ratio and the resulting solid mixture was heated at 150°C for 2 h, further [4+2] addition of C₆₀ to 25 took place to give bisfullerene compound 26 with two C₆₀ cages incorporated in a 2,3-diazabicyclo[2.2.2]oct-2-ene framework in 27% yield along with C₆₀ recovered in 40%.

As has been described in section 3.2, the mechanochemical solid-state reaction using HSVM sometimes gives a product totally different from that obtained from a liquid-phase reaction. Another example is the reaction of C₆₀ with phthalazine, i.e., 2,3-diazaphthalene. This reaction afforded bis-
fullerene compound 28 with two C\textsubscript{60} cages incorporated in a benzobicyclo[2.2.2]octene framework under the solid-state HSVM conditions followed by heating at 200°C while the reaction gave an open-cage benzofullerene derivative 30 when the starting materials were heated at 255°C in a solution in 1-chloronaphthalene.\textsuperscript{39} These reactions are considered to proceed by the mechanism via a common intermediate 27 as shown in Scheme 12. Thus, the intermediate 27, formed by the first \([4+2]\) reaction between the starting materials and the following nitrogen extrusion, is subjected to the second \([4+2]\) cycloaddition with one of the C\textsubscript{60} molecules surrounding 27 to give bisfullerene compound 28 in the solid-state reaction (route a). In contrast, when 27 is formed in solution the highly reactive butadiene unit of orthoquinodimethane structure in 27 undergoes the intramolecular formal \([4+4]\) reaction with the fullerene diene system to give 30 via the retro \([2+2+2]\) reaction of the second intermediate 29 (route b) in the liquid phase reaction.\textsuperscript{39}

Since the two C\textsubscript{60} cages are rigidly fixed in close proximity in bisfullerenyl compounds 26 and 28, a facile \([2+2]\) reaction takes place between the two cages upon irradiation of visible light to their solutions to give the more rigidly connected dimers 31\textsuperscript{38} and 32\textsuperscript{39} quantitatively. The electrochemical measurements indicated that the electronic interaction between two fullerene cages is stronger in 31 and 32 than in 26 and 28.

**4. Synthesis of Open–Cage Fullerenes**

The liquid–phase thermal reaction of C\textsubscript{60} with phthalexazine, which afforded a derivative of open–cage fullerene (Scheme 12b), prompted us to initiate the synthesis of open–cage fullerenes using the reaction with polyazaaromatic compounds.

We considered that this might lead to a “molecular surgery” approach\textsuperscript{40} to the organic synthesis of endohedral fullerenes. Although the endohedral fullerenes are expected to have great potential to be used as functional materials in molecular electronics and also in the medical field, their production still relies on the physical method, which has not made much progress since the early days of fullerene research. Thus, the preparation and isolation of the endohedral fullerenes require special techniques and tremendously laborious work. It is a truly challenging task for organic chemists to try for the organic synthesis of endohedral fullerenes in macroscopic amounts. Conceptually, this will be attained by the following steps, i.e., opening a large enough hole on the fullerene cage, inserting a small molecule or atom through this hole into the cage, and closing the hole, all using organic reactions.

**4.1 Opening a Hole on C\textsubscript{60}**

The typical examples of open–cage fullerenes having a hole larger than an 11–membered ring are shown in Figure 4. The first example of an open–cage fullerene having an 11–membered–ring hole (33) was synthesized by Wudl.\textsuperscript{41} This compound containing the smallest stable atom, helium, in a ratio of about 1/1000 was once prepared, and an attempt was made to discharge the helium atom by heating. However, it was found that a helium-3 atom could not pass through the opening upon heating at the temperature higher than 100°C.\textsuperscript{42} On the other hand, Rubin reported a derivative having a cobalt metal coordinated just above an 11–membered–ring opening of his open–cage compound, but it was not possible to push the metal atom inside the fullerene cage.\textsuperscript{43} However, he later synthesized an open–cage fullerene with a 14–membered–ring hole 34.\textsuperscript{44} He succeeded in incorporation of a helium atom or a hydrogen molecule in this compound under the high temperature and high pressure conditions (288–305°C/475 atm or 400°C/100 atm, respectively), but the incorporation rate was only 1.5\% and 5\%, respectively.\textsuperscript{40} Quite recently, Iwamatsu and Murata reported a reaction of

![Figure 4. Examples of open–cage C\textsubscript{60} derivatives.](image-url)
diaminobenzene with an open-cage fullerene 35, which they prepared previously,\textsuperscript{45} to widely open the hole into a 20-membered ring (36).\textsuperscript{46} This compound with an amazingly large hole was found to readily incorporate a molecule of water into the opened cage in a ratio of about 75%.\textsuperscript{46}

Following the previous experience described above (Scheme 12b), we attempted a liquid-phase thermal reaction of C\textsubscript{60} with 4,6-dimethyl-1,2,3-triazine at 180°C, and obtained a C\textsubscript{60} derivative with an 8-membered-ring opening,\textsuperscript{47} which was further enlarged to a 12-membered-ring by photochemical oxidation. However, because of the low yield (7%) and extreme instability of the first obtained product, we decided to search for a better reaction.

We next examined a reaction of C\textsubscript{60} with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine in the hope of introducing a nitrogen atom at the rim of the hole, which was expected to be advantageous for further functionalization of the product. In addition, the aromatic substituents are favorable for enhancement of the solubility of the C\textsubscript{60} derivatives to be formed. When an equimolar mixture of C\textsubscript{60} and the 1,2,4-triazine was heated at 180°C in ODCB, there was obtained the expected open-cage C\textsubscript{60} derivative 37 in 50% yield (85% based on consumed C\textsubscript{60}) together with unchanged C\textsubscript{60} recovered in 41% (Scheme 13).\textsuperscript{48} The mechanism for this reaction is considered to be essentially the same as that for the formation of 30 in Scheme 12, that is, by (1) [4+2] cycloaddition of Co with the 3,6-positions of the triazine, (2) extrusion of nitrogen, (3) intramolecular formal [4+4] reaction, and (4) retro [2+2+2] reaction. In addition to the full spectroscopic data, the structure of 37 was unambiguously determined by X-ray crystallography as shown in Figure 5. Upon a close look at the structure, it is noticed that the double bond C\textsubscript{2}-C\textsubscript{3} on the rim of the orifice is considerably twisted with a dihedral angle for \( \angle \text{C1-C2-C3-C4} \) being 39°. The HOMO coefficients of the corresponding olefinic carbons are also relatively higher than those of other sp\textsuperscript{2}-carbons. These facts imply the high reactivity of these double bonds at the rim, which is advantageous for the further ring-enlargement reaction as will be described below.

4.2 Enlargement of a Hole on C\textsubscript{60}

In agreement with the previous reports,\textsuperscript{45,49} the enlargement of an eight-membered-ring hole on C\textsubscript{60} in 37 by air-oxidation under irradiation of visible light proceeded smoothly to give mainly two isomers of ring-opened diketones 38 and 39 (Scheme 14) in good total yield.\textsuperscript{48}

It is well known that C\textsubscript{60} itself is readily reduced to a tetraanion state upon cyclic voltammetry (CV) at room temperature and to a hexaanion state at low temperature, reflecting the presence of low-lying triply-degenerate LUMOs.\textsuperscript{3} Then it was of interest to examine the redox behaviors of the open-cage fullerenes 37, 38, and 39 with considerably ruptured \( \pi \)-conjugated systems. Surprisingly, when we conducted CV on these open-cage fullerenes they were found to exhibit four reversible one-electron reduction waves similarly to C\textsubscript{60} in spite of such structural deformation. Particularly, the first reduction potentials of compounds 38 and 39 (-0.97 and -0.98 V vs Fe/Fe\textsuperscript{3+}, respectively) are even lower than that of C\textsubscript{60} (-1.17 V). This is attributed to the presence of two carbonyl groups, which causes the lowering of their LUMOs, and, thus, 38 and 39 can be regarded as good electron acceptors.

So, for the purpose of further enlargement of the 12-membered-ring hole on these compounds, insertion of a sulfur atom to the rim of the opening was attempted in the presence of tetrakis(dimethylamino)ethylene (TDAE) as a typical \( \pi \)-electron donor. As shown in Scheme 15, this reaction on 38 proceeded smoothly by heating in ODCB to give a C\textsubscript{60} derivative with a 13-membered-ring hole 40 as a single product in 77% yield.\textsuperscript{48}

Again, the structure of 40 was determined by X-ray crystallography as shown in Figure 6. The size of the opening measures 3.8 \( \times \) 5.6 Å by the distance between carbon atoms although the actual hole should be much smaller when real atomic sizes are taken into consideration. On the other hand, the shape of the opening in 40 is rather circular compared with that of 34 having a 14-membered-ring hole,
which is somewhat more elliptic. Thus, the energy for insertion of hydrogen as a representative of a small molecule into 40 was estimated to be 30.1 kcal mol⁻¹,⁵⁰ which is 11.3 kcal mol⁻¹ lower than that for 34.⁴⁰

Figure 6. X-ray structure of open-cage fullerene derivative 40.

4.3 Hydrogen Insertion through a 13–Membered-ring Hole on 40

Insertion of a hydrogen molecule into 40 was conducted simply by applying high pressure of hydrogen gas (800 atm) to the powdery sample of 40 heated at 200°C in an autoclave for 8 hours. There is no change or decomposition observed in the recovered sample, and it exhibited H and C NMR spectra which are the same as those of 40 itself except a sharp singlet signal appearing at −7.25 ppm in 1H NMR. This signal is assigned to the hydrogen molecule encapsulated in the fullerene cage, which is known to exert a strong shielding effect.³¹ The integrated intensity of this signal corresponded to 2.00 H, thus indicating that 100% encapsulation was attained to give the endohedral open-cage fullerene derivative, H₂@40.⁴⁰

Although H₂@40 was quite stable at room temperature under air or vacuum, it slowly released hydrogen when heated in an ODCB solution at 160 to 190°C. The rate of release followed the first-order kinetics. The activation energy for release of the encapsulated hydrogen was found to be 34.3 kcal mol⁻¹, which is in fairly good agreement with the calculated value, 28.7 kcal mol⁻¹.

The identity of H₂@40 was confirmed also by MALDI TOF MS spectrometry, which exhibited a clear molecular-ion peak for H₂@40 as shown in Figure 7(a). When the spectrum was taken under the irradiation of higher laser power, the peak intensity for H₂@40 decreased, but instead peaks at m/z 720 and 722 appeared as shown in Figure 7(b).³⁰ These peaks apparently correspond to C₆₀ and hydrogen containing fullerene, i.e., H₂@C₆₀, indicating that the structure of C₆₀ is energetically so favorable that it can be reconstructed even from such a complicated structure as 40 by a series of rearrangements involving removal of the benzene and pyridine rings and extra carbon, oxygen, and nitrogen atoms. It is to be noted that about 1/3 of the produced C₆₀ still retains hydrogen inside, based on the comparison of the peak intensities.

5. Conclusion

Among numerous organic reactions reported for fullerene C₆₀, nucleophilic reactions and cycloadditions, those which give rise to fullerene derivatives with structures of particular interest were selected in the present article. The advantage in the use of the solid–state, solvent–free reactions under the mechanochemical conditions has clearly been shown in the selective synthesis of the [2+2] type fullerene dimers, C₁₂₆ and C₁₃₈, in addition to other dimers of various structures. On the other hand, the liquid–phase thermal reaction of C₆₀ with a 1,2,4-triazine derivative was found to be a versatile method for the synthesis of an open–cage fullerene. A series of transformations including opening a cage on the fullerene surface, enlargement of the opening, and insertion of hydrogen gas into the cage through the opening have afforded a fullerene derivative containing molecular hydrogen in 100% for the first time. Gradual reduction of the size of the opening and final removal of the extra organic addends are expected to lead us to reach the first organic synthesis of endohedral fullerene in the near future.

Acknowledgments The present research was supported by a Grant-in-Aid for COE Research on Elements Science (No. 12CE2005) and by a Grant-in-Aid for Creative Scientific Research Collaboratory on Electron Correlation Toward a New Research Network between Physics and Chemistry (No. 13NPQ0201) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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