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The Reaction of Fullerene C_{60} with 4,6-Dimethyl-1,2,3-triazine: Formation of an Open-Cage Fullerene Derivative

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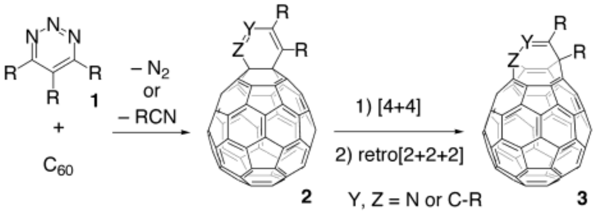
A thermal reaction of fullerene C_{60} with 4,6-dimethyl-1,2,3-triazine (**4**) in *o*-dichlorobenzene gave azacyclohexadiene-fused fullerene derivative **5**, by the reaction with intermediate azete **11**, and then, after flash chromatography over SiO_2, open-cage fullerene derivative **6** having an eight-membered ring orifice on the C_{60} cage. Compound **6** is assumed to be formed via addition of diradical intermediate **13** to C_{60}. Compound **6** underwent a further photochemical reaction with singlet oxygen with the cleavage of one of the double bonds at the rim of the orifice to afford triketone derivative **8** having a 12-membered ring orifice.

Introduction

1,2,3-Triazines (**1**) are known to behave as dienes in the Diels−Alder reaction with inverse-electron demand to afford pyridines or pyridazines after extrusion of nitrogen or alkanenitrile, respectively.[1] On the other hand, the 6−6 junction double bond of C_{60} acts as an electron-deficient dienophile in the Diels−Alder reaction.[2] Therefore, the direct Diels−Alder reaction of fullerene C_{60} with 1,2,3-triazines (**1**) should be a rather unfavorable one. However, if the reaction takes place, it is expected to give an aza- or diazacyclohexadiene-fused derivative such as **2** by extrusion of N_2 or RCN, as shown in Scheme 1. Derivative **2** is expected to afford aza-open-cage fullerene derivatives[3] such as **3** by the intramolecular [4 + 4] cycloaddition followed by the retro[2 + 2 + 2] reaction. Actually, the carbon analogue of **2** (Y = Z = CH, R = H) gave open-cage fullerene derivative **3** under the irradiation of UV light as reported by Rubin.[4,5] Introduction of a nitrogen atom into the fullerene cage would change physical and electrochemical properties as well as the chemical reactivity of the fullerene cage.[6] In an attempt to synthesize such an aza-open-cage fullerene as **3**, we carried out the reaction of C_{60} with 1,2,3-triazines, the results of which are reported herein.

Results and Discussion

Scheme 1



The reaction was carried out by heating a solution of fullerene C_{60} and 3 equiv of 4,6-dimethyl-1,2,3-triazine (**4**)[7] in *o*-dichlorobenzene (ODCB) at 180 °C for 24 h to give a dark brown solution with the formation of an insoluble dark brown material (ca. 40% of the total weight of the product). After filtration, the reaction mixture was subjected to flash chromatography over SiO_2 to give two products, **5** (10%) and **6** (7%), both as brown powders, along with unchanged C_{60} (30%) (Scheme 2). As described below, the products were characterized as an azacyclohexadiene-fused derivative **5** and an open-cage fullerene **6**.

The molecular formula of **5** was determined as $C_{65}H_7N$ by high-resolution FAB mass spectroscopy, indicating that the product was formed by the addition of a C_5H_7N moiety to C_{60}. The ^1H NMR exhibited a quartet at δ 6.52 corresponding to an olefinic proton and doublet and singlet methyl-proton signals at δ 2.64 and 2.52, respectively. The ^{13}C NMR showed 32 signals in the sp^2 carbon region (with one signal overlapped) and 4 signals in the sp^3 carbon region at δ 82.38, 60.19, 26.41, and 22.59 ppm. The UV−vis spectrum exhibited a typical absorption pattern of the 1,2-dihydro[60]fullerene derivative char-

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[2] Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: New York, 1994.

[3] Other types of the aza-open-cage fullerene derivatives have been reported; see: (a) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003−7004. (b) Schick, G.; Jarrosson, T.; Rubin, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2360−2363.

[4] Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775−3776.

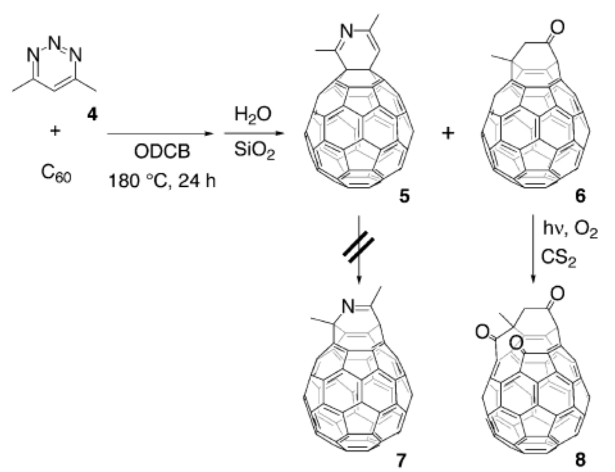
[5] The related reactions were reported; see: (a) Hsiao, T.-Y.; Santhosh. K. C.; Liou, K.-F.; Cheng, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 12232−12236. (b) Qian, W.; Bartberger, M. D.; Pastor, S. J.; Houk, K. N.; Wilkins, C. L.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 8333−8334. (c) Inoue, H.; Yamaguchi, H.; Suzuki, T.; Akasaka, T.; Murata, S. *Synlett* **2000**, 1178−1180. (d) Murata, Y.; Kato, N.; Komatsu, K. *J. Org. Chem.* **2001**, *66*, in press.

[6] For examples of derivatives of $C_{59}N$, see: (a) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554−1556. (b) Keshavarz-K., M.; González, R.; Hicks, R. G.; Srdanov, G.; Srdanov, V. I.; Collins, T. G.; Hummelen, J. C.; Bellavia-Lund, C.; Pavlovich, J.; Wudl, F.; Holczer, K. *Nature* **1996**, *383*, 147−150. (c) Bellavia-Lund, C.; González, R.; Hummelen, J. C.; Hicks, R. G.; Sastre, A.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 2946−2947. (d) Nuber, B.; Hirsch, A. *Chem. Commun.* **1998**, 405−406. (e) Reuther, U.; Hirsch, A. *Chem. Commun.* **1998**, 1401−0402. (f) Hirsch, A.; Nuber, B. *Acc. Chem. Res.* **1999**, *32*, 795−804. (g) Hauke, F.; Hirsch, A. *Tetrahedron* **2001**, *57*, 3697−3708 and references therein. For examples of derivatives of $C_{69}N$, see: Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421−1422.

[7] Ohsawa, A.; Arai, H.; Ohnishi, H.; Itoh, T.; Kaihoh, T.; Okada, M.; Igeta, H. *J. Org. Chem.* **1985**, *50*, 5520−5523.

10.1021/jo010798k CCC: $20.00

Scheme 2



acterized by λ_{max} at 433 nm.[8] These data strongly support the structure of **5**.

The structural determination of **6** was not simple and was achieved by comparison with the open-cage fullerene derivative **9** reported by Rubin and co-workers.[5b] The molecular formula of **6** was determined as $C_{65}H_6O$ by high-resolution FAB mass spectroscopy, indicating that the product has one oxygen atom instead of a nitrogen atom. The IR spectrum showed a strong band at 1723 cm^{-1} corresponding to a carbonyl group. The ^1H NMR exhibited a doublet at δ 6.50 (J = 1.1 Hz) and a singlet at δ 2.64, corresponding to a methine proton and methyl protons, respectively. In addition, a doublet at δ 3.29 (J = 20.6 Hz) and a doublet of doublets at δ 2.79 (J = 20.6 and 1.1 Hz) were visible, both corresponding to geminal methylene protons coupled with each other. The ^{13}C NMR showed a signal at δ 200.75 corresponding to a carbonyl carbon, 56 signals in the sp^2 carbon region (with 4 signals overlapped), and 4 signals in the sp^3 carbon region at δ 55.24, 46.60, 43.72, and 34.07 ppm. The close resemblance of the chemical shifts of the ^1H and ^{13}C NMR as well as the coupling constants of ^1H NMR to the reported values for **9** as shown in Figure 1 strongly support the structure of **6** as the methyl derivative of **9**. The color of the solution of this compound in $CHCl_3$ is purple, and the UV−vis spectrum has a maximum absorption at 533 nm, closely resembling the spectrum of C_{60} and thus indicating that the 60 original fullerene carbons retain their sp^2 hybridization in a π-conjugated system.[4,5]

Plausible mechanisms for the formation of **5** and **6** are shown in Scheme 3. Azete **11** is reported to be generated by thermal extrusion of N_2 from **4**[9] and would react with C_{60} in a [4 + 2] manner to afford intermediate **12**, which gives **5** by ring enlargement. In the case of the formation of **6**, before the generation of azete **11**, diradical **10** is assumed to undergo a 1,3-hydrogen shift to give diradical **13**. The reaction of this diradical with C_{60} is supposed to give imine **14**, which would isomerize to 2-aminodiene **15**. Diene **15** would then undergo intramolecular [4 + 4] cycloaddition to give **16**, followed by the retro[2 + 2 + 2] reaction to produce open-cage enamine **17**, which would be transformed to open-cage imine **18**. Imine **18** is thought to be susceptible to hydrolysis upon contact with SiO_2 and readily furnishes open-cage ketone **6** after chromatography. The relative heats of formation calculated at the PM3 level are shown in Scheme 3. The gradual increase in stability observed in accord with the progress of the reaction (except for the formation of **16**) is considered to be consistent with the proposed mechanism.

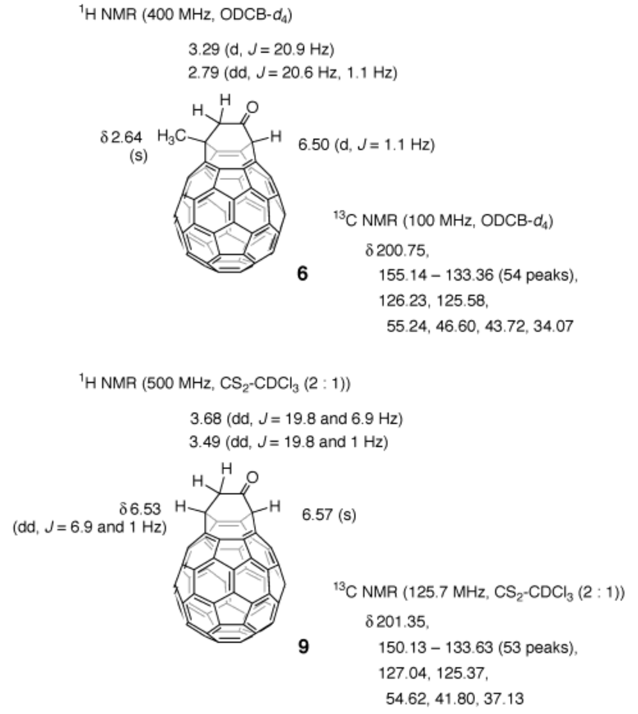


Figure 1. Selected NMR data of **6** and **9**.[5b]

Although it was expected that **5** might rearrange into an aza-open-cage fullerene derivative such as **7** under photochemical conditions, as has been reported for the carbon analogue,[4,5] the irradiation of **5** by a high-pressure mercury lamp with or without heating only gave an insoluble and intractable material. No transformation of **5** into open-cage fullerene **7** was observed (Scheme 2).

However, in an attempt to enlarge the orifice of the open-cage fullerene **6**, it was found that when an air-saturated solution of open-cage ketone **6** in CS_2 was irradiated by room light for 1 h, the color of the solution gradually changed from purple to brown, and a new compound with a larger orifice **8** was obtained in 60% yield as a single product after the separation by preparative HPLC (a Cosmosil "5PBB" column eluted with ODCB) (Scheme 2).

The structure of the product **8** was determined by the following spectral data and the accompanying discussion. The molecular formula of **8** was determined as $C_{65}H_6O_3$ by high-resolution FAB mass spectroscopy, indicating that this compound is a product of the addition of two oxygen atoms to **6**. The IR spectrum showed three strong bands at 1741, 1718, and 1697 cm^{-1} corresponding to three carbonyl groups. In the ^1H NMR, a large downfield shift of one of the methylene proton's signal was observed (δ 3.29 for **6** to δ 4.79 for **8**) due to the deshielding by newly formed carbonyl groups located in close proximity. The ^{13}C NMR showed three signals corresponding to

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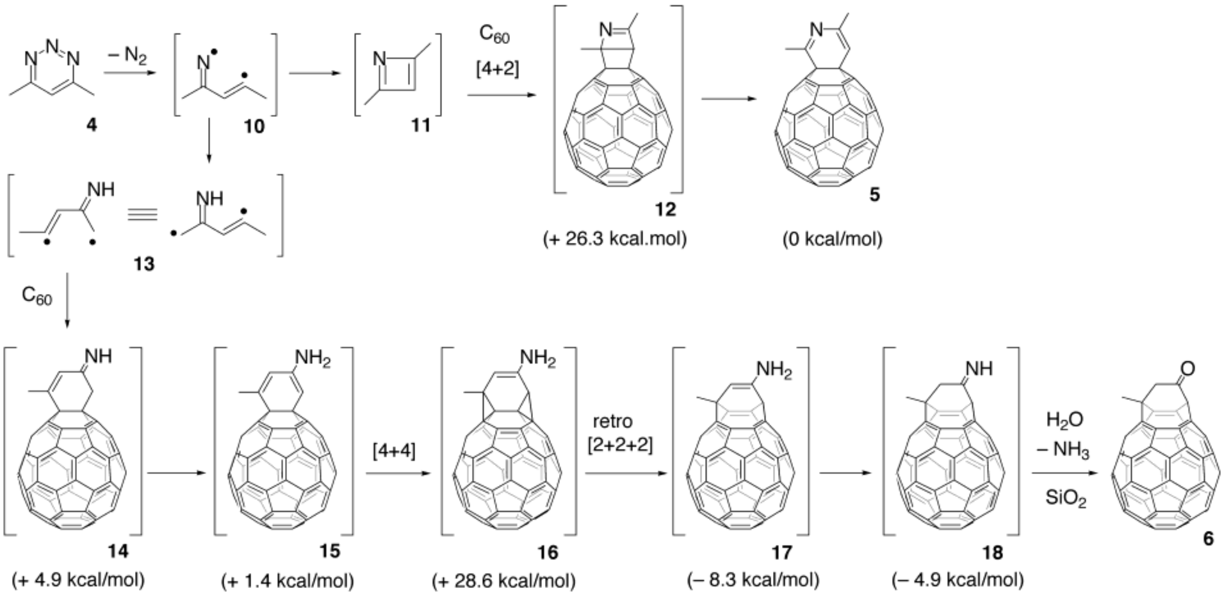
[8] For example, see: (a) Murata, Y.; Kato, N.; Fujiwara, K.; Komatsu, K. *J. Org. Chem.* **1999**, *64*, 3483−3488 and references therein. (b) Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061−7064. (c) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061−1067.

[9] (a) Itoh, T.; Ohsawa, A.; Okada, M.; Kaihoh, T.; Igeta, H. *Chem. Pharm. Bull.* **1985**, *33*, 3050−3052. (b) Itoh, T.; Okada, M.; Nagata, K.; Yamaguchi, K.; Ohsawa, A. *Chem. Pharm. Bull.* **1990**, *38*, 2108−2111.

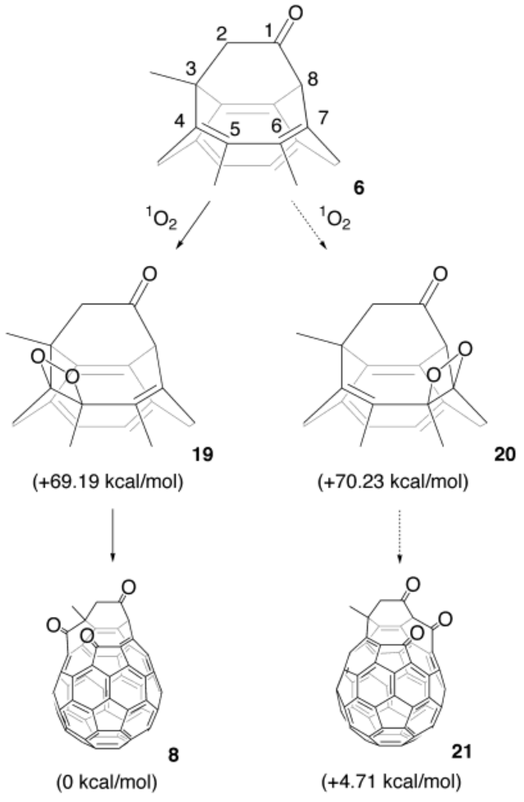
Scheme 3



(The relative heat of formation with reference to **5** calculated by PM3 are shown in parentheses.)

carbonyl carbons at δ 200.42, 198.17, and 193.49 ppm, 52 signals in the sp^2 carbon region (with six signals overlapped), and four signals in the sp^3 carbon region at δ 51.77, 48.61, 47.51, and 37.64 ppm. These data support that the structure of **8** is formed by oxidative cleavage of one of the double bonds at the rim of the eight-membered-ring orifice on the C_{60} cage by the reaction with singlet oxygen. It is now well recognized that the singlet oxygen is readily generated by the action of the fullerene cage excited by visible light.[10]

Scheme 4



(The relative energy with reference to **8** calculated by B3LYP/6-31G(d) are shown in parentheses.)

In the literature, there are two reports dealing with similar oxidative cleavage of the double bond of C_s symmetrical open-cage fullerene derivatives.[11] In the case of the C_1 symmetrical molecule **6**, there are two different double bonds at “C4−C5” and “C6−C7” positions to be cleaved. To further confirm the structure of **8**, the DFT calculations were carried out for **6**, **8**, and the positional isomer **21**, as well as the dioxetane intermediates **19** and **20** at the B3LYP/6-31G(d) level, as shown in Scheme 4.[12] The HOMO of **6** was found to be localized primarily at the two double bonds, as shown in Figure 2. Absolute values of the coefficients of C4 and C5 (−0.32 and −0.27) are slightly larger than those of C7 and C6 (+0.32 and +0.24), and singlet oxygen should preferentially attack the C4−C5 double bond. The obtained optimized structures of **8** and **21** are shown in Figure 3. The relative energy of the thus-formed **8** was calculated to be lower than that of **21** by 4.71 kcal/mol. Dioxetane **19** was also shown to be more stable than dioxetane **20** by 1.04 kcal/mol. Finally, the GIAO (SCF/6-31G(d)//B3LYP/6-31G(d)) calculations were performed for both **8** and **21** in order to compare the results with the ^{13}C NMR spectrum

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(10) (a) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11−12. (b) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886−8889. (c) Foote, C. S. *Top. Curr. Chem.* **1994**, *169*, 347−363.

(11) (a) Inoue, H.; Yamaguchi, H.; Iwamatsu, S.; Uozaki, T.; Suzuki, T.; Akasaka, T.; Nagase, S.; Murata, S. *Tetrahedron Lett.* **2001**, *42*, 895−897. (b) Murata, Y.; Komatsu, K. *Chem. Lett.* **2001**, 896−897.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, H. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, 1998.

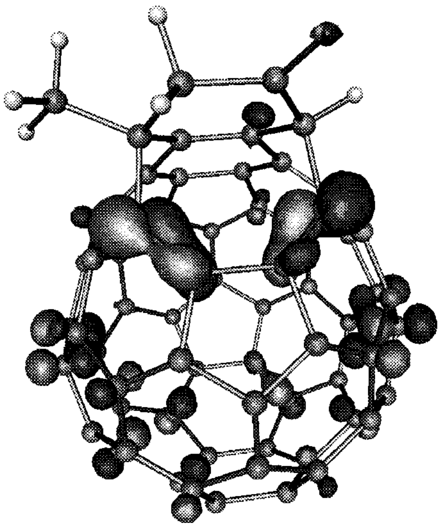

Figure 2. Optimized structure of **6** with HOMO calculated at the B3LYP/6-31G(d) level.

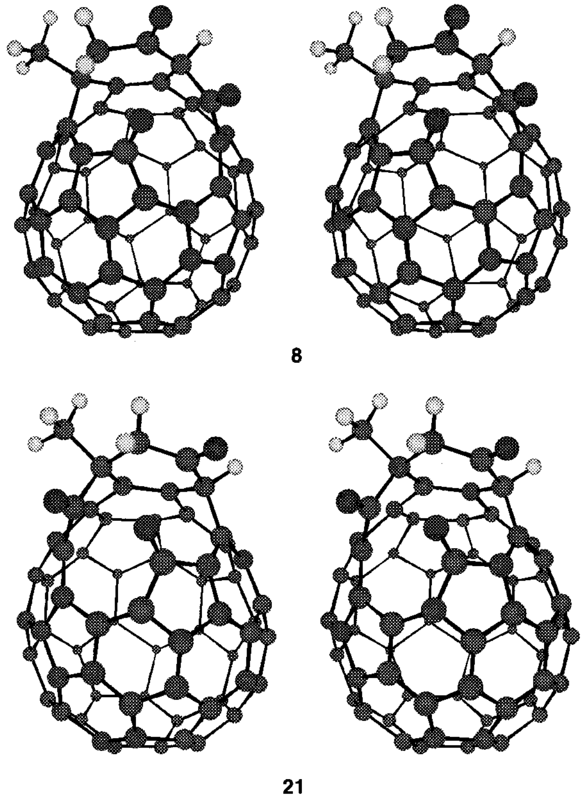

Figure 3. Optimized structures (stereoviews) of **8** and **21** calculated at the B3LYP/6-31G(d) level.

obtained experimentally. As shown in Figure 4, the calculated chemical shifts of **8** more closely resemble the experimental data than do those of **21**. These results of the theoretical calculations also support the structure of the oxidation product as **8** with a 12-membered ring orifice on the C_{60} cage.

Conclusion

It was demonstrated that a thermal reaction of fullerene C_{60} with 4,6-dimethyl-1,2,3-triazine caused a competition between the reactions of C_{60} with azete **11** and with rearranged 1,4-diradical intermediate **13**. The former reaction gave azacyclohexadiene-fused derivative **5** via [4 + 2] cycloaddition, while the latter reaction afforded an unexpected open-cage fullerene derivative **6** by multistep rearrangements and hydrolysis on silica gel. It is rather surprising that such multistep rearrangements could take place in a one-pot reaction and in a single chromatography column. Theoretical calculations were performed for some of the reaction intermediates and products, with these results supporting those obtained experimentally quite well. A facile oxidation of derivative **6** was found to take place to give the open-cage fullerene derivative **8** with a 12-membered ring orifice on the fullerene cage. Although aza-open-cage fullerene derivatives were not obtained in the present work, an investigation of the reaction of C_{60} with other 1,2,3-triazines or 1,2,4-triazines is now in progress in order to synthesize such derivatives, and the results will be reported in due course.

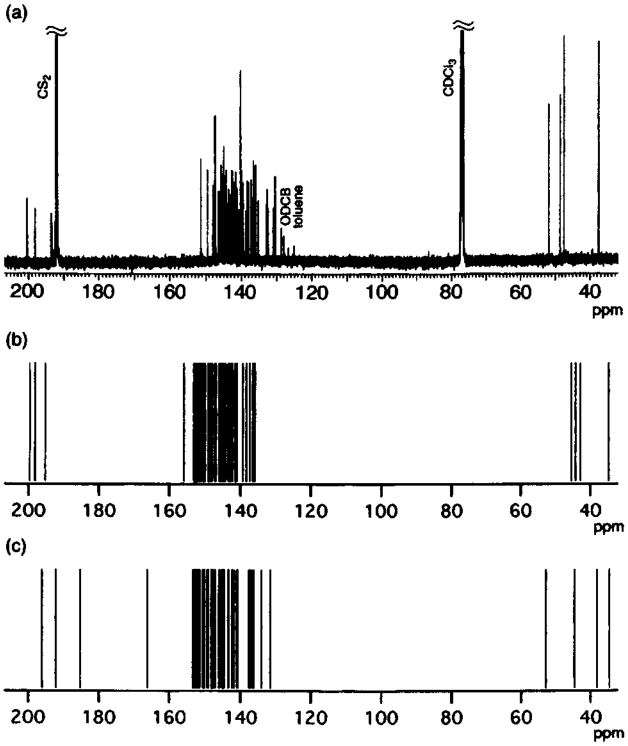

Figure 4. Observed (100 MHz, CS_2-CDCl_3 (1:1)) and calculated (GIAO (SCF/6-31G(d)//B3LYP/6-31G(d))) ^{13}C NMR spectra of (a) **8** (observed), (b) **8** (calculated), and (c) **21** (calculated).

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 300 or 400 MHz for ^1H NMR and 75 or 100 MHz for ^{13}C NMR, respectively. Preparative HPLC was conducted using a Cosmosil 5PBB column (10 mm × 250 mm) with 1,2-dichlorobenzene (ODCB) as an eluent, detected at 326 nm. The PM3 calculations were performed using the MOPAC 6.0 semiempirical molecular orbital package on a CRAY T94/4128 computer. All other calculations were performed with the Gaussian 98 program (rev.A.7)[12] on a HIT HPC-PA264U-8CPU model workstation. Fullerene C_{60} was the commercial material (>99.5%) purchased from Term Co. 4,6-Dimethyl-1,2,3-triazine (**4**) was synthesized by a reported procedure.[7]

Synthesis of 5 and 6. A solution of C_{60} (132.5 mg, 0.184 mmol) and 4,6-dimethyl-1,2,3-triazine (**4**) (60.0 mg, 0.550 mmol) in ODCB (9.0 mL) was heated at 180 °C for 24 h to give a dark brown solution and some insoluble material. The reaction mixture was subjected to a flash chromatography over silica gel eluted with CS_2 to give unchanged C_{60} (39.6 mg, 30%), **5** (14.2 mg, 10%), and **6** (10.4 mg, 7%) as brown powders.

5: mp > 300 °C; IR (KBr) ν 1678 (C=N), 1429, 851, 752, 527 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 258 nm (5.05), 313 (4.57), 433 (3.50), 698 (2.53); ^1H NMR (300 MHz, CS_2−acetone-d_6 (7:1)) δ 6.52 (q, $J = 1.5$ Hz, 1H), 2.64 (d, $J = 1.5$ Hz, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, CS_2−acetone-d_6 (7:1)) δ 159.35, 153.03, 148.80, 147.86, 147.72, 146.44, 146.35, 146.27, 146.01, 145.97, 145.85, 145.27, 145.25, 145.20, 145.12, 144.65, 144.06, 142.89, 142.52, 142.36, 142.25, 142.03, 141.99, 141.70, 141.47, 140.68, 140.31, 139.46, 138.91, 134.70, 133.02, 119.12, 82.38, 60.19, 26.41, 22.59; HR MS (+FAB) calcd for $C_{65}H_8N$ (M + 1), 802.0657, found 802.0648.

6: mp > 300 °C; IR (KBr) ν 1723 (C=O), 1509, 544, 537 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 261 nm (5.02), 329 (4.54), 533 (3.02); ^1H NMR (400 MHz, *o*-dichrolobenzene-d_4) δ 6.50 (d, $J = 1.1$ Hz, 1H), 3.29 (d, $J = 20.6$ Hz, 1H), 2.79 (dd, $J =$ 20.6 and 1.1 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, *o*-dichrolobenzene-d_4) δ 200.75, 155.14, 149.29, 145.53, 145.44, 145.36, 145.23, 145.21, 144.65, 144.56, 144.55, 144.51, 144.32, 144.26, 144.20, 144.13, 144.11, 144.03, 144.00, 143.79, 143.76, 143.70, 143.66, 143.57, 143.52, 143.48, 143.44, 143.32, 143.30, 143.15, 143.13, 142.92, 141.70, 141.08, 140.74, 140.59, 140.49, 140.39, 140.19, 140.10, 139.94, 139.77, 138.90, 138.46, 137.97, 137.92, 137.04, 136.99, 136.86, 136.28, 135.09, 134.40, 134.12, 133.75, 133.36, 126.23, 125.58, 55.24, 46.60, 43.72, 34.07; HR MS (+FAB) calcd for $C_{65}H_6O$ (M^+), 802.0418, found 802.0414.

Synthesis of 8. An air-saturated solution of **6** (10.4 mg, 0.013 mmol) in CS_2 (30 mL) was stirred at room temperature under the irradiation of room light for 1 h. The color of the solution changed gradually from purple to brown. After removal of the solvent, the residue was purified by HPLC (a "5PBB" column eluted with CS_2) to afford **8** (6.5 mg, 60%) as a brown powder.

8: mp > 300 °C; IR (KBr) ν 1741 (C=O), 1718 (C=O), 1697 (C=O), 553, 528 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 257 nm (5.04), 325 (4.62), 424 (3.63); ^1H NMR (400 MHz, CS_2−$CDCl_3$ (1:1)) δ 5.93 (s, 1H), 4.79 (d, $J = 18.5$ Hz, 1H), 3.02 (d, $J = 18.5$ Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$ (1:1)) δ 200.42, 198.17, 193.49, 151.39, 149.54, 148.06, 147.62, 147.42, 146.41, 146.38, 145.92, 145.88, 145.85, 145.57, 145.49, 145.43, 146.37, 145.29, 145.15, 145.13, 145.10, 145.01, 144.50, 144.27, 144.18, 143.78, 143.64, 142.97, 142.67, 142.20, 142.12, 142.08, 141.59, 141.55, 141.32, 140.84, 140.26, 140.23, 139.95, 139.90, 139.70, 139.55, 138.81, 138.34, 138.00, 137.28, 136.66, 136.60, 135.98, 135.22, 132.85, 132.71, 132.42, 131.02, 130.50, 51.77, 48.61, 47.51, 37.64; HR MS (+FAB) calcd for $C_{65}H_7O_3$ (M + 1) 835.0395, found 835.0403.

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Supporting Information Available: ^1H and ^{13}C NMR, UV−vis, and IR spectral data of **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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