A Novel Ring Expansion of the Holey Ketolactam Derivative of C60

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The migrative addition reaction of phenylhydrazine to the ketolactam derivative of C60 occurred with a regioselective cage scission to give a 15-membered ring-opened fullerene bearing a methylene carbon and an acenaphthenequinone monophenylhydrazone unit along the orifice.

Among the numerous entries of surface modifications of fullerenes,[1] opening a hole on the fullerene surface by a controlled carbon–carbon bond cleavage has received much attention, because the resulting holey derivatives allow atoms and small molecules to access into their inner sphere.[2] This methodology has been expected as an innovative route for the endohedral fullerenes; preparation from the existing framework of empty fullerenes by a general organic synthesis.[2,3] In addition, the holey fullerene itself also has the potential for molecular recognition or storage.[3b] Recently, the first successful result of the insertion of helium and molecular hydrogen was reported by Rubin et al.[3a] However, low yields and drastic reaction conditions due to the narrow orifice are hardly sufficient for practical applications. It has been required that new methodologies for expanding the size of the orifice and modifying the circumferential properties.

We have recently described that the oxidative C=C bond cleavage of the bis(fulleroid)[4] afforded a diketone derivative bearing a 12–membered opening.[5,6] Since the related bond cleavage of the fulleroid derivatives is the first step in opening a hole on the fullerene surface,[7] we have been exploring further transformations of the diketone derivative under various conditions. Very recently, we found that the addition reaction of phenylhydrazine to the diketone occurred with the unexpected cage scission to yield the product having a 16–membered ring.[6c,8] In order to clarify the scope and limitation of this controlled cage scission, we focused on the ketolactam 1 which is well known as the first example of the holey fullerene obtained by the similar oxidative ring opening of azafulleroid.[7a] Although 1 has an α,β-unsaturated carbonyl structure as well as the diketone, further derivatization on the ring system has not been investigated.[7b] In this paper, we would like to describe the reaction of a phenylhydrazine to 1.

The reaction of 1 with phenylhydrazine proceeded at room temperature in chlorobenzene. Even in the presence of an excess amount of hydrazine, only a single product was recognized in the crude ^{1}H NMR spectrum. After purification by silica-gel chromatography, product 2a was obtained in 84% yield as a reddish brown solid. The same reaction of 1,1-diphenylhydrazine was rather slow and sluggish, and 2b was obtained in 35% yield (58% yield based on consumed 1) at 100 °C (Scheme 1).

The product data depicted below suggest that the migration of two hydrogen atoms from the hydrazine to fullerene with a
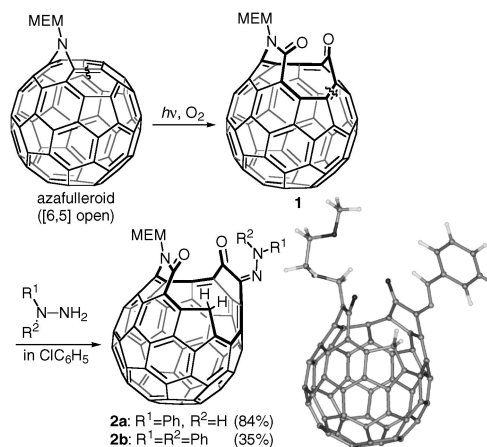

Scheme 1. Reactions of 1 with aromatic hydrazines. The structure of 2a is shown as the ball and stick model (AM1).

regioselective carbon–carbon bond cleavage took place, and the most considerable structure of the product is the 1:1 adduct bearing a 15-membered opening as shown in Scheme 1.[9] The ES-mass spectra (negative) of 2a and 2b showed a molecular ion peak at m/z 963 and 1039, respectively, indicating that the products were 1:1 adducts without any elimination such as water. In the ^{1}H NMR spectrum of 2a (in C6D6), a pair of doublets was observed at δ 6.15 and 4.67 ppm (each 1H, $J = 18$ Hz) in addition to the signals assignable to the methoxyethoxymethyl (MEM) group. Furthermore, a labile proton, which disappeared by treatment on D2O, was observed at δ 13.90 ppm. The downfield chemical shift of the latter indicates the existence of hydrogen bonding with the Z configuration of the hydrazone, and is in good agreement with that of the acenaphthenequinone monophenylhydrazone which is a model compound for the modified ketone moiety.[10] In accordance with a couple of geminal protons observed in the ^{1}H NMR, one methylene carbon was observed at δ 42.32 ppm in the ^{13}C NMR and DEPT135 spectra. This is similar to that of the adduct derived from the diketone (43.97 ppm in C6D6).[8] Two carbonyl signals assignable to the ketone and the lactam were still observed at δ 187.62 and 164.39 ppm, respectively. The upfield chemical shift of the former (ca. 10 ppm relative to 1)[7a] suggests the hydrazone–azo tautomeric equilibrium structure. In the IR spectrum, whereas compound 1 showed two carbonyl absorptions at 1727 (ketone) and 1693 (lactam) cm⁻¹,[7a] 2a showed one overlapped absorption at 1672 cm⁻¹. These data are reasonably compared to both the lactam absorption in 1 which remained intact and the model acenaphthenequinone monohydrazone (1670 cm⁻¹).[10] The UV–vis spectra of 2a and 2b were distinctly different from that of 1 reflecting the change in the π-conjugation system by the cage breaking, and showed strong absorp-
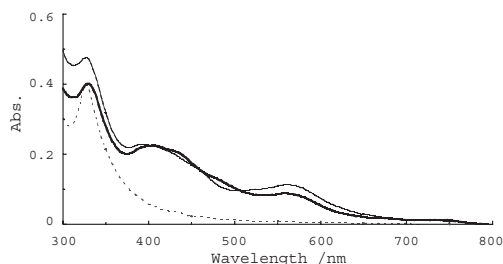
Figure 1. UV–vis spectrum of **1** (dot), **2a** (bold) and **2b** (plane) in CH_2Cl_2.
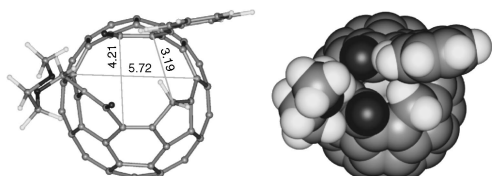
Figure 2. Top view of the AM1 calculated structure of **2a**. Bottom atoms are omitted for clarity: (left) Ball and stick molecular model. Selected atom distances are shown in Å. (right) Space-filling representation.

tions in the visible region (Figure 1). Compound **2a** showed diagnostic absorptions at λ 406, 435, 559, and 741 nm. In contrast to the product derived from the diketone, which showed a significant fluorescence at 720 nm,[8] the fluorescent intensities of **2a** and **2b** were quite low and were same level as that of **1**.

The AM1 structure of **2a** shows that the 15-membered ring orifice has an elliptical shape, and the size is approximately 3.2×5.7 Å (Figure 2). It is larger than that of **1** (ca. 2.9×4.6 Å), however, the CPK model suggests that the opening is not still wide enough to allow any molecules to enter the cage. As pointed out by Wudl et al.,[7a] flexibility in the methylene moiety at elevated temperatures or removal of the MEM protecting group might be required for access into the cavity.

In summary, the addition reaction of the ketolactam derivative of C_{60} with aromatic hydrazine proceeds with a regioselective carbon–carbon bond cleavage to give a ring expanded product having a methylene carbon and an acenaphthenquinone monohydrazone unit along the orifice. The reaction is characteristic and general to the α,β-unsaturated carbonyl structure on the C_{60} surface. Compound **1** has been well known as a precursor of $(C_{59}N)_2$ and $RC_{59}N$.[7b] The similar transformations of **2a** and **2b** would be expected to provide new azafullerene derivatives. Further investigations of the crystallographic analysis, reaction mechanism, and physical properties of holey fullerenes are now in progress.

References and Notes
1   a) A. Hirsch, *Top. Curr. Chem.*, **199**, 1 (1999). b) "Fullerenes: Chemistry, Physics, and Technology," ed. by K. M. Kadish and R. S. Ruoff, John Wiley & Sons, Inc., New York (2000), p 91.
2   a) Y. Rubin, *Top. Curr. Chem.*, **99**, 67 (1999). b) Y. Rubin and F. Diederich, in "Stimulaing Concepts in Chemistry," ed. by F. Vögtle, J. F. Stoddart, and M. Shibasaki, Wiley–VCH, Weinheim (2000), p 163.
3   a) Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, and R. J. Cross, *Angew. Chem., Int. Ed.*, **40**, 1543 (2001). b) J.-F. Nierengarten, *Angew. Chem., Int. Ed.*, **40**, 2973 (2001). c) S. Irle, Y. Rubin, and K. Morokuma, *J. Phys. Chem. A*, **106**, 680 (2002).
4   a) M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan, and Y. Rubin, *J. Am. Chem. Soc.*, **118**, 3775 (1996). b) C. H. Suresh, P. S. Vijayalakshmi, S.-I. Iwamatsu, S. Murata, and N. Koga, *J. Org. Chem.*, **68**, 3522 (2003) and references cited therein.
5   H. Inoue, H. Yamaguchi, S.-I. Iwamatsu, T. Uozaki, T. Suzuki, T. Akasaka, S. Nagase, and S. Murata, *Tetrahedron Lett.*, **42**, 895 (2001).
6   a) Y. Murata and K. Komatsu, *Chem. Lett.*, **2001**, 896. b) Y. Murata, M. Murata, and K. Komatsu, *J. Org. Chem.*, **66**, 8187 (2001). c) Y. Murata, M. Murata, and K. Komatsu, *Chem.—Eur. J.*, **9**, 1600 (2003).
7   a) J. C. Hummelen, M. Prato, and F. Wudl, *J. Am. Chem. Soc.*, **117**, 7003 (1995). b) J. C. Hummelen, B. Knight, J. Pavlovich, R. González, and F. Wudl, *Science*, **269**, 1554 (1995).
8   S.-I. Iwamatsu, F. Ono, and S. Murata, *Chem. Commun.*, **2003**, 1268.
9   Data for **2a**: mp 220 °C (dec.); ^1H NMR (C_6D_6) δ 13.90 (s, 1H), 7.65 (dd, $J = 8$, 1 Hz, 2H), 7.27 (dd, $J = 8$, 7 Hz, 2H), 7.02 (tt, $J = 7$, 1 Hz, 1H), 6.94 (d, $J = 11$ Hz, 1H), 6.15 (d, $J = 18$ Hz, 1H), 5.95 (d, $J = 11$ Hz, 1H), 4.67 (d, $J = 18$ Hz, 1H), 3.78 (ddd, $J = 11$, 6, 4 Hz, 1H), 3.75 (ddd, $J = 11$, 6, 4 Hz, 1H), 3.22 (ddd, $J = 11$, 6, 4 Hz, 1H), 3.17 (ddd, $J = 11$, 6, 4 Hz, 1H), 2.97 (s, 3H); ^{13}C NMR/DEPT135 (C_6D_6) δ 187.62, 164.39, 156.55, 154.79, 152.83, 150.49, 149.56, 149.54, 149.32, 149.16, 149.11, 149.11, 148.12, 147.35, 146.91, 146.63, 146.61, 146.56, 146.49, 146.47, 146.47, 146.32, 146.29, 146.20, 146.08, 145.73, 145.60, 145.34, 144.95, 144.91, 144.50, 144.41, 144.12, 143.77, 143.51, 143.31, 142.83, 142.67, 141.91, 141.73, 140.13, 139.88, 139.69, 139.46, 139.43, 139.37, 139.06, 138.32, 138.14, 137.91, 137.76, 137.38, 135.60, 133.45, 132.64, 131.71, 131.31, 130.65, 130.16 (CH), 126.72, 125.21 (CH), 115.84 (CH), 83.07 (CH_2), 71.78 (CH_2), 69.94 (CH_2), 58.58 (CH_3), 42.32 (CH_2); IR (KBr) 2915, 1672, 1593, 1537, 1480, 1400, 1256, 1089 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (ε) 258 (110,000), 330 (43,000), 406 (24,000), 435 (22,000), 559 (10,000), 741 (2,000) nm; ES–MS (neg.) 963 [M^-]; Found: C. 87.52, H. 2.04, N. 4.24%. Calcd for $C_{70}H_{17}N_3O_4$: C. 87.22, H. 1.78, N. 4.36%.
10   a) J. E. Kuder, *Tetrahedron*, **28**, 1973 (1981). b) F. M. Soliman, El-S. M. Yakout, and M. M. Said, *Bull. Chem. Soc. Jpn.*, **67**, 2162 (1994).