

Efficient Cage-Opening Cascade Process for the Preparation of Water-Encapsulated [60]Fullerene Derivatives

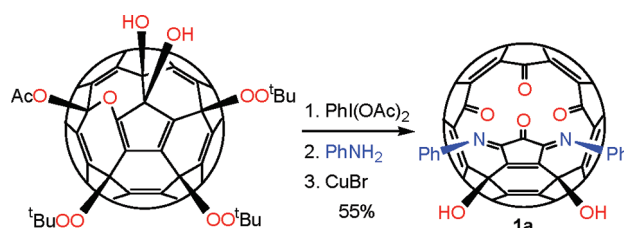
Qianyan Zhang,[†] Zhenshan Jia,[†] Shuming Liu,[†] Gang Zhang,[†] Zuo Xiao,[‡]
Dazhi Yang,[‡] Liangbing Gan,^{*,†,‡} Zheming Wang,^{*,‡} and Yuliang Li[†]

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory for Organic Solids, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, China, and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

gan@pku.edu.cn; zmw@pku.edu.cn

Received April 29, 2009

ABSTRACT



Cage-opened fullerenes with 18-membered-ring orifices have been prepared starting from fullerene-mixed peroxides. The key transformation involves a cascade sequence including a deketalization, a $\text{S}_{\text{N}}2'$ epoxide opening reaction, and a formal 3,3- σ rearrangement. The 18-membered-ring orifice is big enough for water encapsulation under mild conditions. Single crystal X-ray structures were obtained for both the empty and water-encapsulated fullerene derivatives.

Cage-opened fullerene derivatives with suitable orifice could allow incorporation of atoms or small molecules inside the cavity to form endohedral fullerene derivatives. Several molecules such as He , H_2 , H_2O , CO , NH_3 and CH_4 have been incorporated into cage-opened fullerene derivatives.^{2–10} Pure $\text{H}_2@\text{C}_{60}$ has been prepared through the opening-insertion-closing pathway (the molecular surgery method).¹¹

To fully explore such a strategy, efficient cage-opening methods are still needed. At present the number of known cage-opened fullerene derivatives is quite limited, especially those with an orifice large enough for encapsulation purposes.

We have been studying the chemistry of fullerene-mixed peroxides and prepared several cage-opened fullerene derivatives starting from the hexa-adduct $\text{C}_{60}(\text{OO}^t\text{Bu})_6$.^{6a} Here we report the formation of new cage-opened derivatives **1** and **2** through an unexpected cascade process as the fullerene

[†] Chinese Academy of Science.

[‡] Peking University.

(1) (a) Rubin, Y. *Chem.—Eur. J.* **1997**, *3*, 1009. (b) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67. (c) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083.

(2) Stanisky, C. M.; Cross, R. J.; Saunders, M.; Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2005**, *127*, 299.

(3) Rubin, Y.; Jarrosson, T.; Wang, G.-W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders, M.; Cross, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543.

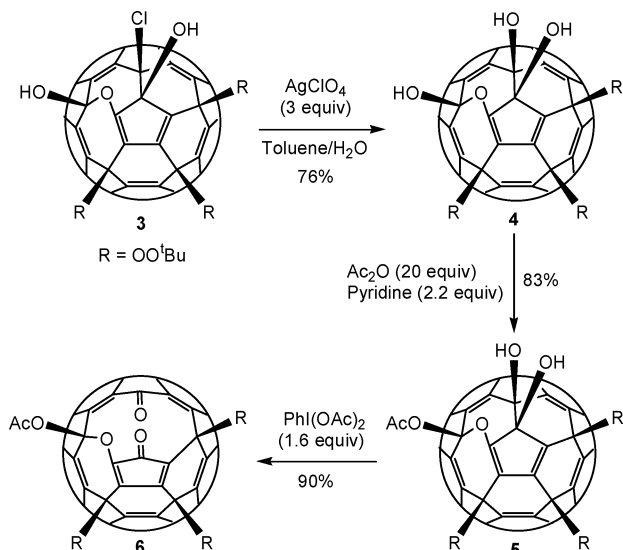
(4) (a) Iwamatsu, S.-i.; Uozaki, T.; Kobayashi, K.; Re, S.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668. (b) Iwamatsu, S.-i.; Murata, S. *Synlett* **2005**, *14*, 2117.

(5) Iwamatsu, S.-i.; Stanisky, C. M.; Cross, R. J.; Saunders, M.; Mizorogi, N.; Nagase, S.; Murata, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5337.

C–C bond cleavage steps. The orifices in these compounds are suitable for the formation of water-encapsulated complexes.

The oxahomofullerene **3** was prepared in three steps as we reported previously.¹² Treatment of **3** with AgClO₄ and water converted the chlorine atom into a hydroxyl group and resulted in the formation of **4**. The hemiketal hydroxyl group in **4** could be selectively acylated with acetic anhydride to form the diol **5**, which was oxidized with diacetoxyiodobenzene (DIB) to give the corresponding diketone derivative **6** (Scheme 1). Protection of the hemiketal moiety was

Scheme 1. Preparation of Cage-Opened Precursor



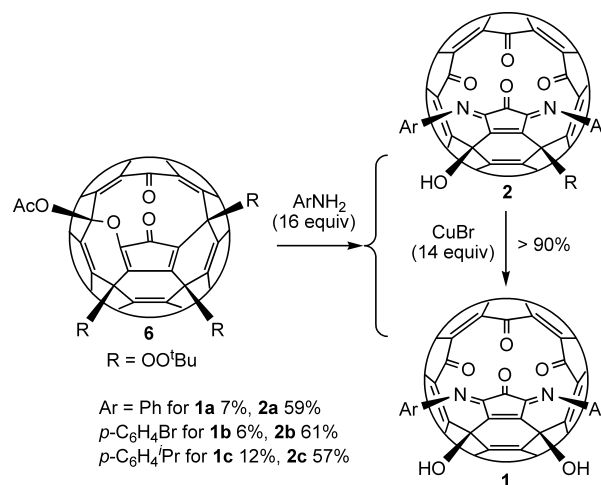
necessary for oxidation with DIB. Direct oxidation of **4** gave complicated mixture of products.

The structure of compound **3** was previously confirmed by single crystal X-ray analysis.¹² Compounds **4** and **5** are analogous to **3**. Their NMR spectra show similar pattern. The unique hemiketal fullerene carbon appears at 108.0, 107.8, and 107.7 ppm on the ¹³C NMR spectrum for compounds **3**, **4**, and **5**, respectively. The diketone derivative **6** showed two carbonyl groups at 194.6 and 192.0 ppm. Its

hemiketal fullerene carbon is slightly shifted to lower field at 110.2 ppm compared with its precursor **5**.

We have previously investigated the reaction between fullerene diketones and anilines. The resulting fullerene hemiketal amino-ketal derivatives were proved to be useful precursors for cage-opened fullerene derivatives.^{6a} However, to our surprise, the reaction of **6** and aniline directly led to the formation of two orifice-enlarged compounds **1a** and **2a** (Scheme 2). In the formation of **1a**, all three *t*-butoxyl groups

Scheme 2. Cage-Opening by Cascade Process



in **6** were removed. The remaining *t*-butylperoxy group in compound **2a** could be reduced to the hydroxyl group in **1a** with CuBr in excellent yield. Further optimization showed that isolation of **6** was not necessary before the addition of aniline. The DIB oxidation and the amination could be carried out in one pot with improved overall yield (54% for **2a**). Other aniline derivatives such as the 4-bromo and 4-isopropyl anilines gave similar results with slightly different yields. The more electron rich 4-isopropyl aniline gave relatively higher yield of the dihydroxyl derivative **1**.

A possible mechanism for the amine-initiated cage-opening process is shown in Scheme 3. The first step is the aminolysis of the hemiketal ester to form the allyl anion intermediate **A** with four carbonyl groups. Loss of *t*-butoxide ion from **A** results in the formation of **B** with an epoxy moiety. Addition of another amine molecule to **B** opens the epoxide through the S_N2' mechanism. The resulting intermediate **C** undergoes a formal 3,3-σ rearrangement process to cleave another fullerene C–C bond to form intermediate **D**. This step is probably driven mainly by ring strain. Cleavage of the fullerene C–C bond in this step allows the central pentagon to be lifted up from the spherical surface and become completely planar (see crystal structure of **1a** below). In the final step, a third amine molecule reacts with the less hindered carbonyl group on the lifted pentagon to form compound **2**. Activation of this carbonyl group by H-bond from the adjacent OH group must play a key role for the observed selective imination besides steric preference.

(6) (a) Xiao, Z.; Yao, J. Y.; Yang, D. Z.; Wang, F. D.; Huang, S. H.; Gan, L. B.; Jia, Z. S.; Jiang, Z. P.; Yang, X. B.; Zheng, B.; Yuan, G.; Zhang, S. W.; Wang, Z. M. *J. Am. Chem. Soc.* **2007**, *129*, 16149. (b) Pankewitz, T.; Kloppe, W. *Chem. Phys. Lett.* **2008**, *465*, 48.

(7) Whitener, K. E., Jr.; Frunzi, M.; Iwamatsu, S. -i.; Murata, S.; Cross, R. J.; Saunders, M. J. *Am. Chem. Soc.* **2008**, *130*, 13996.

(8) Stanisky, C. M.; Cross, R. J.; Saunders, M. J. *Am. Chem. Soc.* **2009**, *131*, 3392.

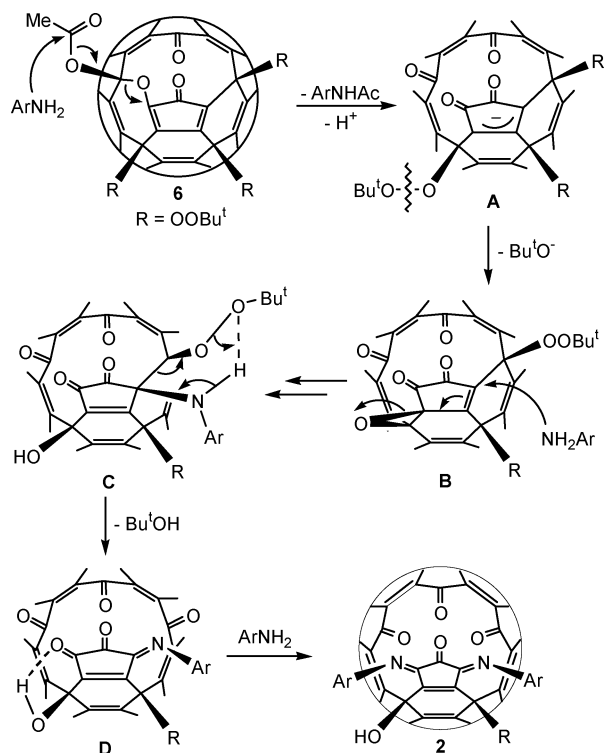
(9) Wang, G. W.; Wu, P.; Tian, Z. G. *Eur. J. Org. Chem.* **2009**, *7*, 1032.

(10) Whitener, Jr., K. E.; Cross, R. J.; Saunders, M.; Iwamatsu, S. -i.; Murata, S.; Mizorogi, N.; Nagase, S. *J. Am. Chem. Soc.* **2009**, *131*, 6338.

(11) (a) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238. (b) Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2006**, *128*, 8024. (c) Matsuo, Y.; Isobe, H.; Tanaka, T.; Murata, Y.; Murata, M.; Komatsu, K.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 17148. (d) Murata, Y.; Maeda, S.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *130*, 6702.

(12) Huang, S. H.; Xiao, Z.; Wang, F. D.; Zhou, J.; Yuan, G.; Zhang, S. W.; Chen, Z. F.; Thiel, W.; Schleyer, P. R.; Zhang, X.; Hu, X. Q.; Chen, B. C.; Gan, L. B. *Chem.-Eur. J.* **2005**, *11*, 5449.

Scheme 3. Possible Pathway for the Formation of **2**



In agreement with the above explanation for the selectivity of the last step, the ^1H NMR spectra of compounds **1** and **2** indicate a strong intramolecular H-bond between the imino and OH groups. Their chemical shifts (7.9 ppm for **1a** and 7.6 ppm for **2a**) appear at a much lower field than those of OH groups attached to a normal fullerene carbon such as the vicinal diol moiety of **4** and **5** which are less than 6 ppm. The ^{13}C NMR spectra of compounds **1** and **2** showed the expected number of carbonyl signals. But resolution of the IR spectrum is not high enough, and just one intense band around 1745 cm^{-1} was observed for the four carbonyl groups.

Crystals of **1a** and $\text{H}_2\text{O}@\mathbf{1a}$ were obtained by slow evaporation of their CS_2/EtOH solution. Their X-ray structures are essentially the same in terms of the unit cell parameters and the molecular geometries (Figure 1). The intramolecular H-bonds between the imino and the hydroxyl groups are clearly observed from the single crystal structures

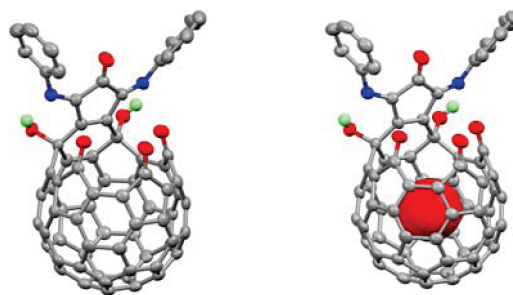


Figure 1. Molecular structures of **1a** (left) and $\text{H}_2\text{O}@\mathbf{1a}$ (right). The oxygen atom of the encapsulated water molecule was drawn as the spacefill model. For clarity only the hydrogen atoms of the OH groups were shown. Color scheme: gray, C; red, O; blue, N; green, H.

of **1a** and $\text{H}_2\text{O}@\mathbf{1a}$, with the H-bond of $\text{O}-\text{H}\cdots\text{N}$ geometry: 2.71 to 2.78 Å and 131 to 133°. The encapsulated water molecule does not have noticeable effect on the cage structure. Water content was estimated to be 38% as determined from the refined occupancy in the structure refinement, which is close to the ^1H NMR determined value (40%) for the same sample. This sample was obtained by heating the solution of **1a** in toluene/water for 5 h. Further heating for 24 h could increase the water content up to 87%.

In summary, fullerene-mixed peroxides have been converted to cage-opened fullerenes with an 18-membered orifice, suitable for water encapsulation. The key transformation involves a cascade sequence including a deketalization, a $\text{S}_{\text{N}}2'$ epoxide opening reaction, and a formal 3,3- σ rearrangement. Work is in progress to further modify the orifice and to incorporate other atoms or molecules into the cavity of the cage-opened fullerene derivatives.

Acknowledgment. Financial support is provided by NNSFC (Grants 20632010, 20772004, and 20821062) and MOST (2006CB806201).

Supporting Information Available: Experimental procedure and spectroscopic data for all new compounds and cif files for compounds **1a** and $\text{H}_2\text{O}@\mathbf{1a}$ with lattice solvents, 1.2 CS_2 and 0.3 EtOH. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL9009305