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

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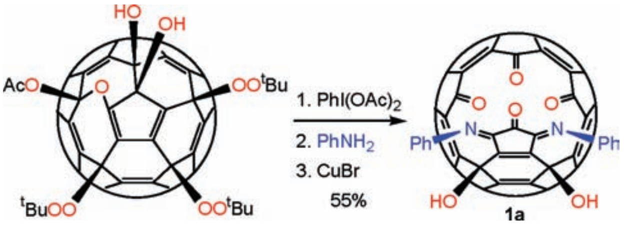
ABSTRACT



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 S_N2' 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 $H_2@C_{60}$ 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 $C_{60}(OO^tBu)_6$.[6a] Here we report the formation of new cage-opened derivatives **1** and **2** through an unexpected cascade process as the fullerene

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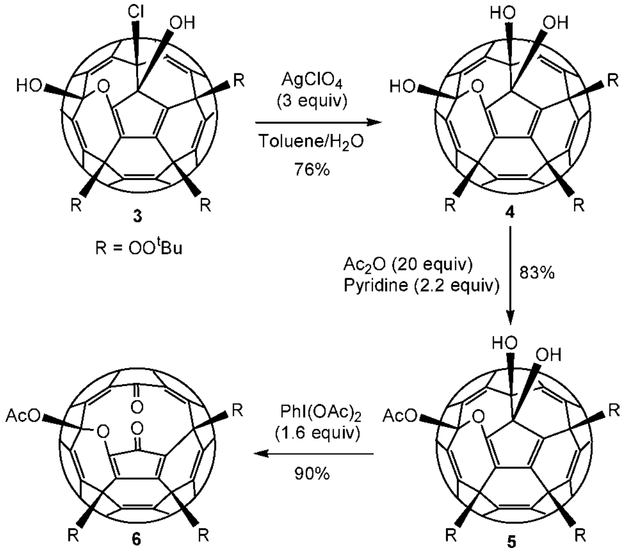
C−C bond cleavage steps. The orifices in these compounds are suitable for the formation of water-encapsulated complexes.

The oxahomofullerene **3** was prepared in three steps as we reported previously.[12] Treatment of **3** with $AgClO_4$ 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 diacetoxyliodobenzene (DIB) to give the corresponding diketone derivative **6** (Scheme 1). Protection of the hemiketal moiety was necessary for oxidation with DIB. Direct oxidation of **4** gave complicated mixture of products.

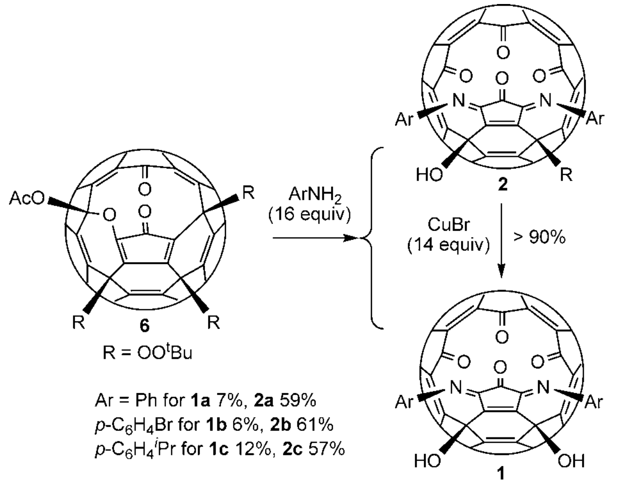
Scheme 1. Preparation of Cage-Opened Precursor



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 ^{13}C 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 in **6** were removed. The remaining *t*-butylperoxo 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**.

Scheme 2. Cage-Opening by Cascade Process



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.

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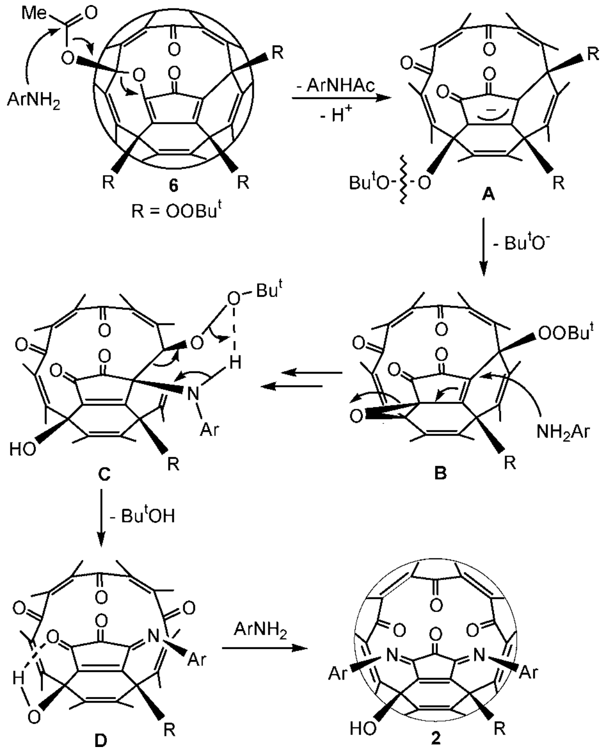
Scheme 3. Possible Pathway for the Formation of **2**



In agreement with the above explanation for the selectivity of the last step, the ^{1}H 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.

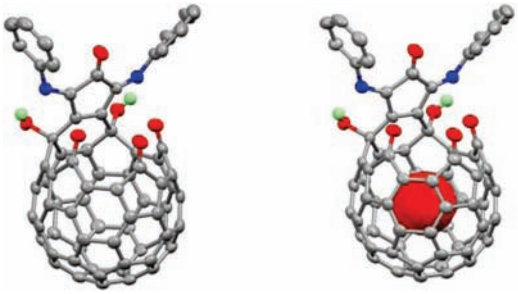


Figure 1. Molecular structures of **1a** (left) and H_2O@**1a** (right). The oxygen atom of the encapsulated water molecule was drawn as the spacefill model. For clarity only the hydrogen atoms of the OH groups were shown. Color scheme: gray, C; red, O; blue, N; green, H.

Crystals of **1a** and H_2O@**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 of **1a** and H_2O@**1a**, with the H-bond of O−H···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 ^{1}H 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 S_N2' 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.

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Supporting Information Available: Experimental procedure and spectroscopic data for all new compounds and cif files for compounds **1a** and H_2O@**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.

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