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Preparation of Fullerendione through Oxidation of Vicinal Fullerendiol and Intramolecular Coupling of the Dione To Form Hemiketal/Ketal Moieties

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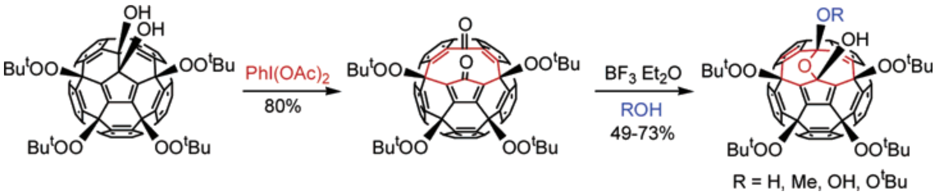
ABSTRACT



Vicinal fullerendiol is oxidized to fullerendione in good yield by (diacetoxy)iodobenzene. The resulting cage-opened fullerendione reacts with oxygen nucleophiles in the presence of $BF_3 \cdot Et_2O$ to form fullerene hemiketal/ketal derivatives through coupling of the two carbonyl groups. Fullerene-mixed peroxide derivatives are involved in all these reactions. The compounds are characterized by spectroscopic data and single-crystal X-ray analysis.

Selective cleavage of fullerene skeleton bonds has proven to be a challenging problem.[1] Compared to the rich exohedral fullerene chemistry,[2] cage-opening reactions are still limited. Addition of azides and nitrenes results in azafulleroids with an opening bridged by a nitrogen atom.[3] Rubin et al. discovered the photochemical [4 + 4] intramolecular cycloaddition and retro [2 + 2 + 2] reaction.[4] The strategy has been successfully employed to make a number of fulleroid derivatives.[5] Singlet oxygen was involved in several cage-opening reactions [6] including the first cage-opening reaction reported by Wudl and co-workers.[7] Recently Ko-

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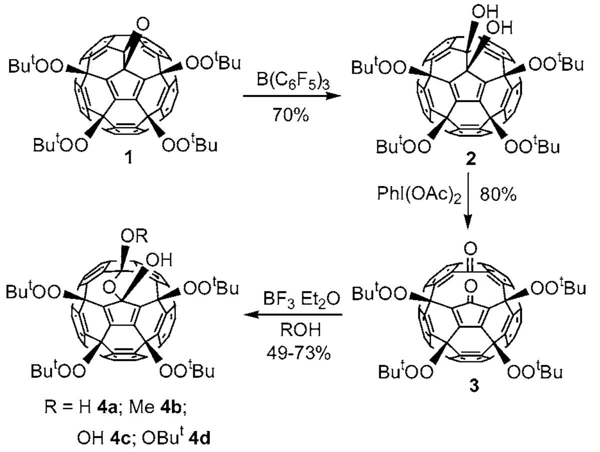
matsu et al. succeeded in making the landmark endohedral fullerene $H_2@C_{60}$ through a molecular surgery pathway,[8] in which singlet oxygen was also employed in the cage-opening process.

Oxidation of vicinal diol is a classical method for the cleavage of C−C bond and formation of carbonyl groups. It is reasonable to expect the formation of cage-opened fullerenes through oxidation of vicinal fullerendiol, but so far there is no successful report using such an approach. Recently we have reported the preparation of some fullerene-mixed peroxides,[9] which exhibit interesting reactions.[10] Here we report the oxidation of fullerendiol and formation of cage-opened products.

Fullerene-mixed peroxides are involved in the reactions. Compound **1** is transformed to the vicinal fullerendiol **2** in 70% yield through $B(C_6F_5)_3$-promoted hydrolysis of the epoxy moiety.[11] Various oxidants were tested to oxidize the fullerendiol **2**. Classical reagents such as $Pb(OAc)_4$ and $NaIO_4$ did not give any characterizable product. (Diacetoxyiodo)benzene (DIB) reacted smoothly with **2** to give the expected dione **3** in good yield. Treatment of **3** with $BF_3{\cdot}Et_2O$ in the presence of water results in coupling of the carbonyl groups and formation of compound **4a** with two hemiketal moieties bridged by an oxygen atom. Similarly, addition of CH_3OH, H_2O_2, and ${}^tBuOOH$ leads to analogous compounds **4b**, **4c**, and **4d**, respectively. Compounds **3** and **4** are all very soluble in common organic solvents and can be easily purified on silica gel column.

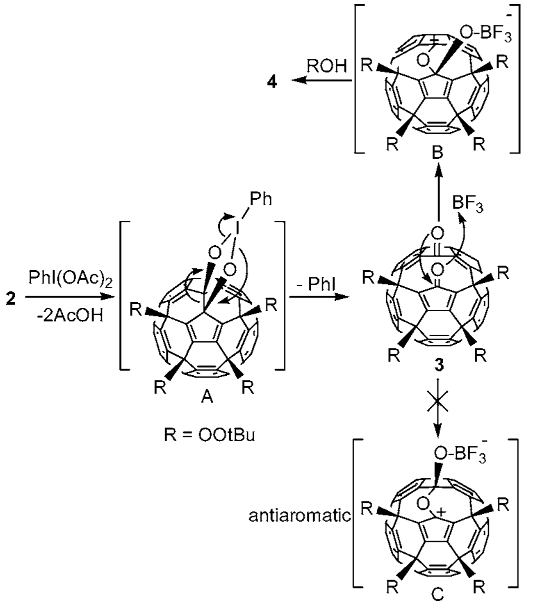
The coupling reactions are highly regio- and chemoselective. Only one isomer is formed with the OR group on the outside and the OH group on the central pentagon as shown in Scheme 1. The regioselectivity is similar to the epoxy-opening reaction of **1** with $BF_3{\cdot}Et_2O$ and ROH (R = Me, OH and O^{t}Bu).[10] Carbonyl groups in **3** do not undergo Bayer−Villiger reaction. There is no fullerene lactone derivative detected in the preparation of **4c** and **4d**.

Scheme 1. Preparation of Compounds **2**, **3**, and **4**



A possible mechanism is shown in Scheme 2 for the cage-opening and -closing processes. Formation and rearrangement of intermediate A is the same as those for classical vicinal diol oxidations by hypervalent iodine reagents.[12] Formation of **4** involves fullerene cations.[13] Selectivity of the $BF_3{\cdot}Et_2O$-catalyzed coupling is due to the antiaromatic nature of intermediate C. The observed high regioselectivity also indicates that coordination of the carbonyl oxygen with BF_3 and attack of the other carbonyl at the coordinated carbonyl maybe be a synchronized process, but the present data cannot rule out the stepwise process.

Scheme 2. Proposed Mechanism for the Formation of **3** and **4**



Compound **3** has a 10-membered ring opening, which is relatively small compared to those in the literature.[4,8] Simple modeling shows that the two carbonyls of **3** are in close contact, thus facilitating the above coupling reaction, but the distance is apparently still long enough to prevent the cyclization and formation of a dioxetane moiety. $Pb(OAc)_4$-

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(11) This is an improved method over the two step-reaction reported earlier in ref 10a.

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mediated oxidation of an octahedral adduct with a vicinal fullerendiol moiety leads to a dioxetane instead of dione as reported by Hirsch et al.[14] The closed dioxetane structure is more favorable in the highly symmetric octahedron adduct. The four *tert*-butylperoxo groups in **3** are all located on the same side of one carbonyl group. Such an unsymmetrical geometry probably provides the driving force for the formation of dione instead of dioxetane in the present case.

Spectroscopic data confirms the structures as depicted. Due to the presence of a mirror plane, NMR spectra are relatively simple. On the ^{1}H NMR spectrum of **3**, there are two singlets for the four *tert*-butylperoxo groups. The ^{13}C NMR of **3** showed two carbonyl signals at 196.88 and 196.64 ppm. The two sp^{3} fullerene carbon signals connecting the *tert*-butylperoxo groups are well resolved and appear as separate signals at 88.37 and 78.23 ppm. A total of 28 signals are expected for the remaining 54 fullerene skeleton sp^{2} carbons, two of which are on the mirror plane. There are 27 signals observed with a half-intensity signal at 148.92 ppm and another half-intensity overlapped at 149.28 ppm. The IR spectrum of **3** exhibits a strong C═O stretching band at 1751 cm^{-1}, which is close to cyclopentanone (1743 cm^{-1}) and nearly the same as other open-cage fullerene derivatives reported by Komatsu et al. (1747 and 1748 cm^{-1}).[8b] The ESI-MS spectrum of **3** shows a molecular ion peak at 1126 (M + NH_4) as the base peak.

The hemiketal/ketal moieties in derivative **4** are verified by the ^{13}C NMR spectra. Two clear signals appear in the range from 100 to 110 ppm corresponding to the two hemiketal/ketal carbons. There are also two unique sp^{2} carbon signals on the ^{13}C NMR spectrum of **4**, one at around 162 ppm and the other at around 133 ppm. HMBC spectrum of **4b** indicates that these carbons are probably on the central pentagon. As expected the two equivalent central pentagon carbons (162.61 ppm) closer to the OH group show a clear correlation signal with the OH proton.

The relative location of the OH and OR (R = Me, OH, and O^{t}Bu) groups in compounds **4b**, **4c**, and **4d** is further confirmed by X-ray analysis. Single crystal of **4d** was obtained by slow evaporation of its toluene solution at 5 °C. The X-ray structure shows that the OO^{t}Bu group is on the outside and the OH group is on the central pentagon. The bridging oxygen O(1) is about the same distance from the two fullerene ketal carbons at 1.377(5) and 1.394(5) Å. The bond angle (121.1°) around the bridging oxygen (C59−O1−C60) is distorted as a result of steric strain.

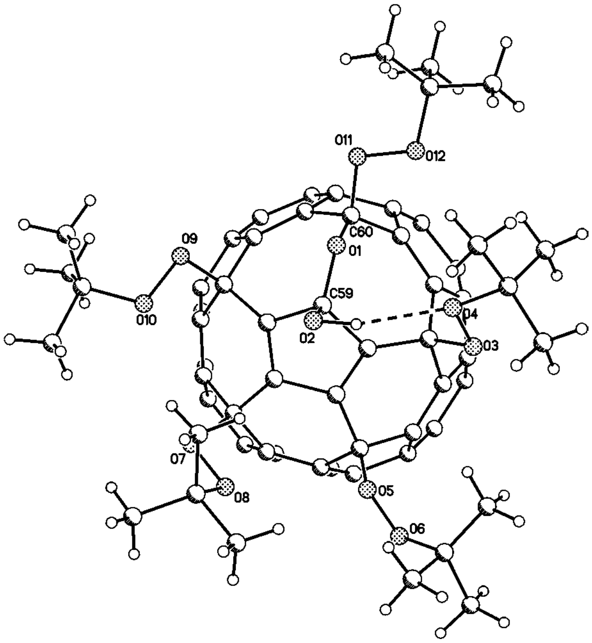

Figure 1. Single-crystal X-ray structure of **4d**.

In summary the classical diol to dione conversion is shown to be an effective method for fullerene cage-opening. Close proximity and strain of the resulting dione leads an unique coupling reaction when it was treated with Lewis acid and an oxygen nucleophile. Oxidation of isomerically pure multi-hydroxylated fullerenols may lead to a large opening on the fullerene cage or even truncated fullerenes with fewer carbons.[15] Efforts are in progress toward this direction.

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Supporting Information Available: Detailed experimental procedure; selected NMR, MS, and IR spectra; and crystallographic data in CIF format for **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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