ORGANIC
LETTERS

2007
Vol. 9, No. 9
1741−1743

From Fullerene-Mixed Peroxide to Open-Cage Oxafulleroid $C_{59}(O)_3(OH)_2(OO^tBu)_2$ Embedded with Furan and Lactone Motifs

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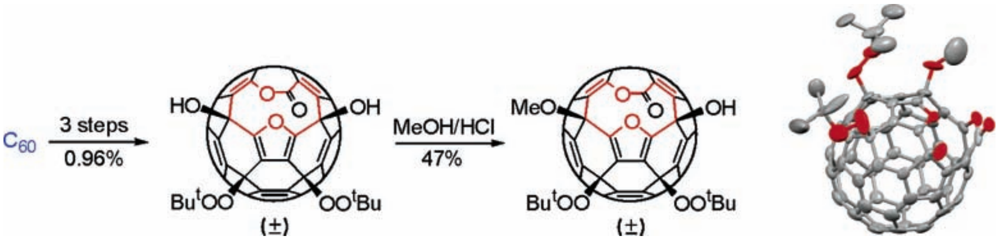
Received February 21, 2007

ABSTRACT



Removal of one carbon atom from the C_{60} cage is achieved under mild conditions. The process involves the formation of fullerene-mixed peroxide, subsequent Lewis acid induced cleavage of O–O and C–O bonds, and thermolysis at 75 °C. In the proposed mechanism, the carbon atom is deleted as CO and an oxygen atom occupies the vacancy to form a furan ring. Single-crystal X-ray analysis confirmed the results.

Cluster modification of fullerenes could generate many fulleroids with either open- or close-cage structures. Exciting chemical and physical properties can be expected for such compounds. This area has proven to be a challenging problem in fullerene chemistry. Nevertheless, remarkable progress has been made. Rubin et al. discovered the photochemical [4+4] intramolecular cycloaddition and retro [2+2+2] reaction.[1] The strategy has been successfully employed to make a number of bisfulleroids.[2] Komatsu et al. reported a landmark endohedral fullerene $H_2@C_{60}$ through a molecular surgery pathway.[3] The largest orifice among cage-opened fulleroids was reported by Iwamatsu et al., through which water and carbon monoxide can be inserted.[4]

Replacement of fullerene cage carbons with other non-carbon atoms forms heterofullerenes. Preparative heterofullerene chemistry is so far still restricted to azafullerenes. In 1995, Mattay[5] and Hirsch,[6] respectively, discovered that

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(1) (a) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775. (b) Qian, W.; Bartberger, M. D.; Pastor, S. J.; Houk, K. N.; Wilkins, C. L.; Rubin, Y. *J. Am. Chem. Soc.* **2000**, *122*, 8333.

(2) (a) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67. (b) Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2973, and references therein.

(3) (a) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238. (b) Murata, Y.; Murata, M.; Komatsu, K. *Chem.*−*Eur. J.* **2003**, *9*, 1600. (c) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152.

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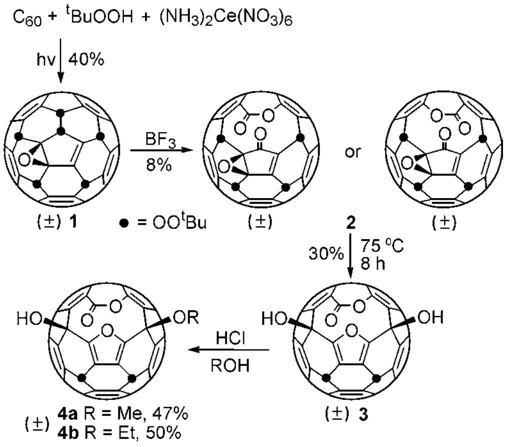
10.1021/ol070386j CCC: $37.00

certain nitrogen-containing fullerene derivatives generate azafullerenium such as $C_{59}N^+$ and $C_{69}N^+$ in the gas phase. In the same year, Wudl accomplished the first synthesis of azafullerene $C_{59}NR$ in bulk quantities.[7] Shortly after, Hirsch also reported its synthesis using a different method.[8] Rich exohedral chemistry of the azafullerene has been developed over the past 10 years. Several other heterofullerenes were observed in gas-phase experiments.[9]

We have reported the synthesis of a number of fullerene-mixed peroxides such as **1** through the addition of *t*-butylperoxo radicals to C_{60}.[10] Recently, several oxahomofullerenes were prepared starting from these fullerene-mixed peroxides.[11] Further investigation revealed that the fullerene-mixed peroxides can also serve as precursors for the controlled replacement of cage carbons to form fulleroids. Here, we report the synthesis of the title oxafulleroid with one carbon atom deleted from the C_{60} cage.

Compound **2** was isolated from the reaction of **1** with boron trifluoride. Heating **2** for 8 h at 75 °C led to the oxafulleroid **3** (Scheme 1). One of the two hydroxyl groups in **3** could be converted to an alkoxyl group catalyzed by hydrogen chloride. The compounds are stable under atmospheric conditions for weeks without noticeable decomposition. Slow evaporation of **4a** in CS_2/EtOH gave suitable crystals.

Scheme 1. Preparation of Compounds **2**−**4**



The crystal structure of **4a** (Figure 1) showed clearly the presence of the furan moiety, which is isolated from other double bonds by the two *t*-butylperoxo, hydroxyl, and methoxyl addends.[12] The space-filling model indicates that the furan oxygen is in close contact with the lactone moiety in the 11-membered opening. As a result, the lactone is pushed outward (dihedral angle C39−C54, C41−C55B is 141°) and the furan oxygen is also slightly above the furan plane (dihedral angle C58−C59, C56−O1 is 6.3°).

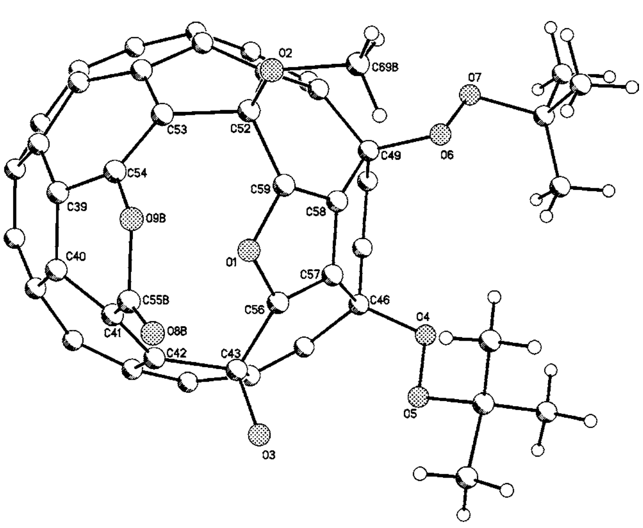


Figure 1. Single-crystal X-ray structure of **4a** (one enantiomer is shown, and for clarity, some atoms of the cage were omitted).[12]

The presence of *t*-butylperoxo groups in these compounds improves their solubility and facilitates spectroscopic data measurements. The data clearly reveal the formula and functional groups present in the compounds. In light of the X-ray analysis data, structures of other compounds were deduced. Compound **3** is the precursor of **4**. It should have the same cage skeleton as **4** because they exhibit the same ^{13}C NMR pattern. The characteristic C═O stretching band of the lactone moiety is also very similar at 1775, 1772, and 1770 cm^{-1} for **3**, **4a**, and **4b**, respectively. Their UV−vis spectra are almost identical. There is no sharp peak in the region 300−800 nm.

The ^{13}C NMR of compound **2** showed two characteristic signals at 189.5 and 159.1 ppm indicating the presence of ketone and lactone moieties. This is further supported by its IR spectrum which showed two bands at 1798 and 1743 cm^{-1}. Because compound **2** is the precursor of **3**, it is reasonable to position the lactone moiety of **2** in the same way as that in **3**. Locations of the epoxy and *t*-butylperoxo groups in **2** are assigned according to its precursor compound **1** which was established previously on the basis of closely related single-crystal X-ray analysis.[10] The remaining ketone moiety can only be on the central pentagon as drawn in Scheme 1. Switching the lactone moiety by 180° would give

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(9) (a) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191. (b) Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. *Top. Curr. Chem.* **1999**, *199*, 93. (c) Hirsch, A. *Acc. Chem. Res.* **1999**, *32*, 795.

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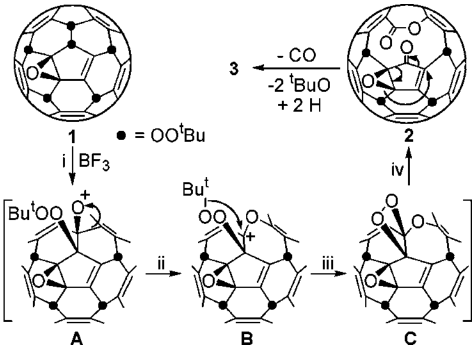
(12) All the products in Scheme 1 are racemates. Two enantiomers occupy the same position in the lattice of **4a** resulting in disorder. Monoclinic; *C*2/*c*; unit cell dimensions, $a = 35.284(7)$ Å, $\alpha = 90°$, $b = 14.200(3)$ Å, $\beta = 116.70(3)°$, $c = 18.567(4)$ Å, $\gamma = 90°$; $Z = 8$; $V = 8311(3)$ Å^3; $T = 143(2)$ K; final R indices [$I > 2\sigma(I)$] R1 = 0.0617, wR2 = 0.1470.

an alternative structure for **2** which can also satisfy all the spectroscopic data. It is not possible to distinguish between the two at present.

Scheme 2. Proposed Pathway



Scheme 2 shows a possible pathway for the present reactions. Lewis acid induces the heterolysis of the O−O bond on the relatively crowded *t*-butylperoxo group to form the oxonium intermediate **A**, which rearranges to the carbon-centered cation **B** through the cleavage of a 5,6-junction. The dioxetane moiety in the neutral intermediate **C** was then formed through heterolysis of the ^{t}Bu−O bond on the adjacent *t*-butylperoxo group. Ring-opening rearrangement of the dioxetane gave compound **2**. Competing pathways are possible for steps i and ii. For example, O−O bond heterolysis of the *t*-butylperoxo group on the central pentagon should be possible. The other 5,6-junction could also be cleaved in the rearrangement process of oxonium intermediate **A**. Uncharacterized products isolated from the reaction may be formed through these competing pathways.

The above pathway is a combination of similar steps in the literature.[7,11] We have reported conversions of the *t*-butylperoxo group in fullerene-mixed peroxides into the hydroxyl group and hemiketal and dioxetane moieties by various Lewis acids, which also involve heterolysis of the O−O bond as the key step.[11] The last step of the above mechanism and formation of oxafulleroid **3** from **2** are reminiscent of the formation of the first azafullerene derivative reported by Wudl et al., where the dioxetane intermediate was formed through singlet oxygen addition to the azafulleroid.[7] The ketolactone opening in **2** is essentially the same as the 11-membered ketolactam opening in Wudl's compound (Figure 2).

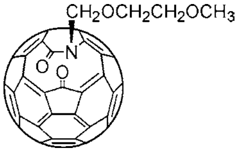


Figure 2. Structure of the first cage-opened fullerene.[7]

Formation of oxafulleroid **3** from ketolactone **2** results from the loss of CO and conversion of two ^{t}BuOO groups into two OH groups. It is not quite clear which occurred first. Release of steric strain and furan aromatization may be the driving force for elimination of the carbonyl group from the central pentagon. Loss of CO is also suggested in the ketolactam (Figure 2) to azafullerene $(C_{59}N)_2$ transformation.[7]

Selective monoalkoxylation of **3** should involve a cation intermediate formed by the HCl-catalyzed cleavage of the OH group. The extra stabilization effect of the lactone oxygen on the cation intermediate explains the regioselective formation of **4**. Komatsu et al. have reported stable fullerene cations.[13]

The present work demonstrates that cleavage of C−C, C−O, and O−O bonds in fullerene-mixed peroxides can be achieved under mild conditions. Fullerene-mixed peroxides have much potential for the preparation of cluster-modified fullerenes such as homo-, seco-, nor-, and heterofullerenes. To facilitate future multistep synthesis, selectivity of the reactions remains to be improved even though separation of the present products could be achieved by column chromatography. Work is in progress to investigate the chemical reactivity of fullerene-mixed peroxides in detail and to prepare new cage-modified fullerene derivatives.[14]

Acknowledgment. Financial support is provided by NNSFC (Grants 20632010, 20521202, and 20472003), the Ministry of Education of China, and the Major State Basic Research Development Program (2006CB806201).

Supporting Information Available: Experimental procedures; selected NMR, MS, IR, and UV−vis spectra; and crystallographic data in CIF format for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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