

Fullerene peroxides in cage-opening reactions*

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Abstract: Fullerene-mixed peroxides $C_{60}(O)(OO^tBu)_4$ and $C_{60}(OO^tBu)_6$ are effective precursors for cage-opened fullerene derivatives. Lewis acids induce the heterolysis of peroxo O–O bond in $C_{60}(O)(OO^tBu)_4$. Subsequent Hock-type rearrangement affords both [5,6]- and [6,6]-fullerene hemiketals—oxahomofullerene. Photolysis of $C_{60}(OO^tBu)_6$ results in the homolysis of O–O and C–O bonds, affording fullerene diketone as the major product. Spectroscopic data and single-crystal analysis confirmed the cage-opening reactions.

Keywords: fullerenes; peroxide; hemiketals; epoxides; ketones.

INTRODUCTION

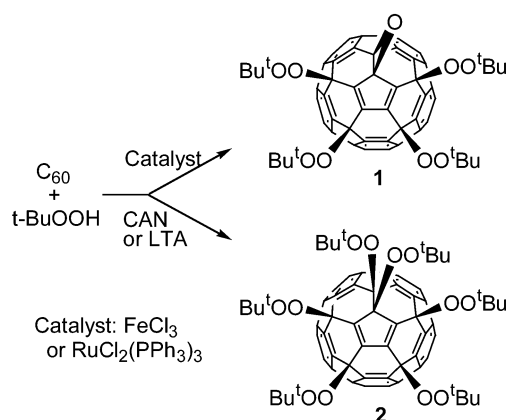
Remarkable progress [1] has been made since the first observation of a fullerene cage-opening reaction by Wudl and coworkers [2]. Several groups have used azides and nitrenes to make cage-opened fullerene derivatives [3]. Cobalt-covered opening was reported by Rubin et al. through a series of bond scissions involving pericyclic and metal insertion reactions [4]. Taylor et al. found that spontaneous oxidation of fullerene derivatives leads to openings containing lactone and ketone moieties [5]. Recently, Komatsu's group succeeded in making the hydrogen-containing endohedral fullerene $H_2@C_{60}$ through a molecular surgery pathway [6], a landmark work in fullerene chemistry. In spite of these achievements, cage opening remains a young field compared to the rich exohedral fullerene chemistry. Existing methods need to be modified, and new methods are necessary to explore many other fascinating targets, such as various heterofullerenes [7] and truncated fullerenes [8]. We have recently reported the preparation of some fullerene-mixed peroxides [9]. These peroxides are good precursors for selective cage-opened fullerene derivatives [10]. This review summarizes some of the cage-opening results.

PREPARATION OF FULLERENE-MIXED PEROXIDES

Fullerene-mixed peroxides can be readily prepared through the stepwise addition of peroxo radicals to fullerene. Various methods may be used to generate *t*-butylperoxo radicals. When a catalytic amount of ruthenium complex $RuCl_2(PPh_3)_2$ or ferric chloride was used, the reaction mainly gave the epoxy-containing fullerene peroxide **1**. When $Pb(OAc)_4$ (LTA) or $(NH_4)_2Ce(NO_3)_6$ (CAN) was used as the oxidant, the reaction gave mainly the fullerene peroxide **2** without an epoxy moiety. (Diacetoxyiodo)benzene (DIB) can give both **1** and **2**. Visible light irradiation favors the formation of **1**. Preparation of **2** was carried out in total darkness. While compound **1** can be stored in air for several months without no-

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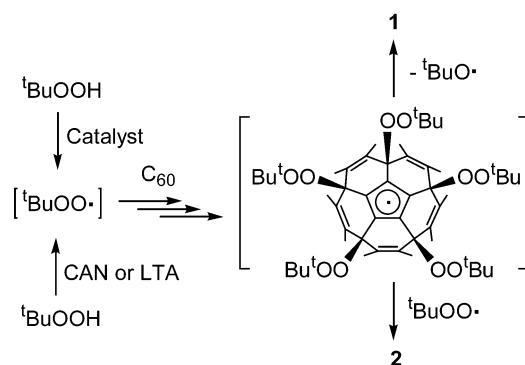
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Scheme 1 Preparation of compounds **1** and **2**.

ticeable change, compound **2** slowly decomposes when exposed to ambient light (see Photolysis Section below).

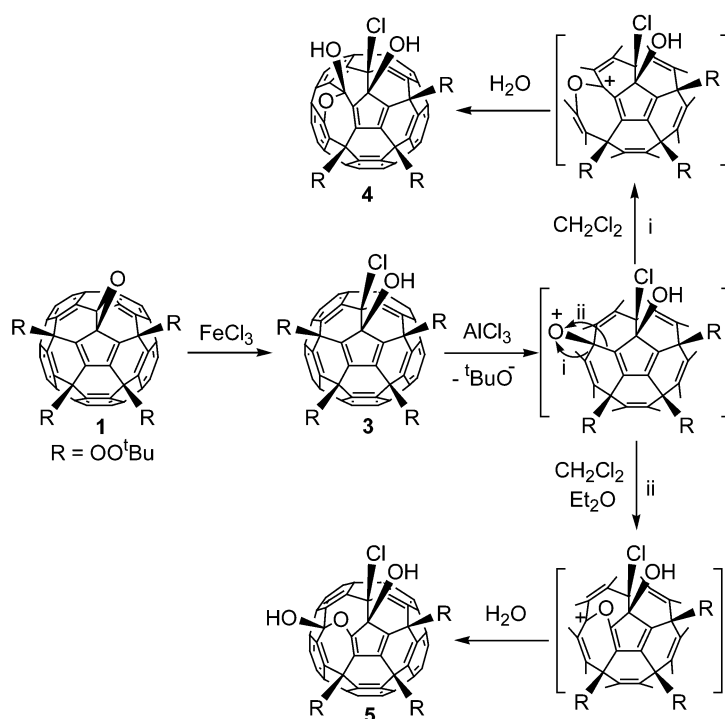
The selective formation of **1** and **2** is probably a result of the different concentration of the *t*-butylperoxy radicals. In the catalytic reaction, the concentration of *t*-BuOO \cdot is relatively low. Thus, the cyclopentadienyl radical intermediate tends to lose a *t*-butoxy radical to form **1** before it can catch another *t*-butylperoxy radical. Oxidation of *t*-butyl hydrogen peroxide by CAN or LTA rapidly forms a relatively high concentration of *t*-butyl peroxy radicals. Thus, addition of another *t*-butylperoxy radical to the cyclopentadienyl radical is favored, giving the hexa-adduct **2**. Unlike the heterogeneous reactions with CAN and LTA, the ruthenium and iron catalysts are soluble in the reaction media benzene. It is possible that ruthenium and iron form a weak η^5 -type coordination complex with the pentakis-adduct intermediate, effectively preventing further radical addition.



Scheme 2 The cyclopentadiene mode of radical addition.

HETEROLYSIS OF O–O BOND AND FORMATION OF OXAHOMOFULLERENE

The chemistry of peroxides has been well established [11]. It is known that Lewis acid can initiate heterolysis of the O–O bond in organic peroxides. When compound **1** was treated with ferric chloride, the epoxy moiety was opened selectively to form the chlorohydrin derivative **3** [10b]. The peroxy groups remain unchanged if the reaction is stopped properly. Prolonged reaction results in complex mixture of products.



Scheme 3 Formation of compounds **3**, **4**, and **5**.

Further treatment of the epoxide-opened derivative **3** with aluminum chloride led to the expected heterolysis of the peroxo bond and formation of isomers **4** and **5**. In pure dichloromethane, **4** is the major product. If some ether is added as the cosolvent, compound **5** becomes the major product. Under ambient light and in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$, **4** can slowly isomerize to **5**. The cleavage and subsequent rearrangement process are similar to the Hock rearrangement [11]. The structure of **5** was confirmed by single-crystal analysis (Fig. 1). It shows that the two double bonds on the central pentagon are the shortest among all the fullerene double bonds in the molecule.

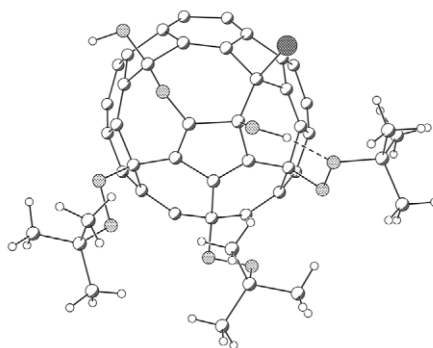
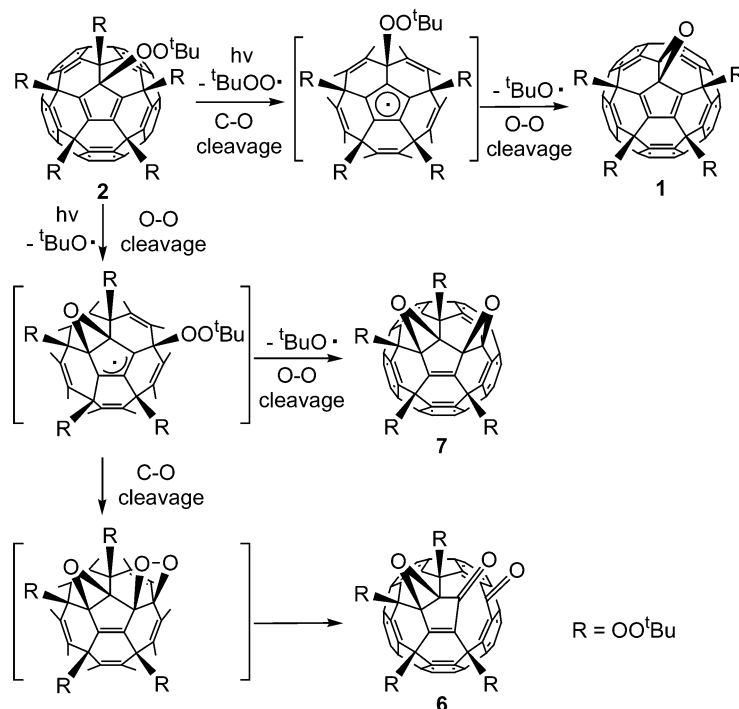


Fig. 1 X-ray single-crystal structure of compound **5**.

PHOTOLYSIS OF FULLERENE PEROXIDE

Cage-opened product **6** was obtained as the major product when compound **2** was irradiated with visible light [10a]. Compounds **1** and **7** were also isolated as by-products. In a separate experiment, compound **1** showed little decomposition under the same photolysis conditions. Addition of some iodine is necessary to improve the selectivity of the photolysis reaction, but the exact role of iodine is not known. It probably traps radical species produced in the fragmentation of the *t*-butylperoxy groups, thus preventing their addition to the fullerene cage to form complicated multi-adducts.



Scheme 4 Proposed mechanism for the photolysis of compound **2**.

The proposed mechanism involves both O–O and C–O bond cleavage processes to form radical intermediates. Decomposition of organic peroxides usually results in homolytic O–O bond cleavage. C–O bond cleavage of organic peroxides is rare under photolysis, but has been observed in some cases and is common in acid- or base-catalyzed decompositions [11]. When compound **2** was treated with Lewis acid, fulleranol was obtained as shown in a preliminary study.

CONCLUSION

Fullerene-mixed peroxides are readily prepared through stepwise radical addition reactions. Some of their reactions are analogous to classical organic peroxides. Lewis acids usually result in heterolysis of the O–O bond, followed by cage-opening rearrangement processes. Homolysis of both O–O and C–O bonds is observed under photolysis. The fullerene-mixed peroxides are potential precursors for effectively large openings considering the presence of multi-peroxy groups around the central pentagon. Truncated fullerene can also be envisioned starting from the fullerene-mixed peroxides. Work is in progress toward such directions.

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