JOC Article

Lewis Acid Promoted Preparation of Isomerically Pure Fullerenols from Fullerene Peroxides $C_{60}(OO\textit{t}\text{-Bu})_6$ and $C_{60}(O)(OO\textit{t}\text{-Bu})_6$

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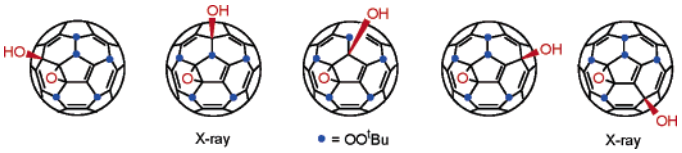

Fullerene mixed peroxides $C_{60}(\textit{t}\text{-BuOO})_6$ and $C_{60}(O)(\textit{t}\text{-BuOO})_6$ react with Lewis acids to form various fullerenols through the partial fragmentation of *t*-BuOO groups. Two monohydroxyl fullerenols with the general formula $C_{60}(OH)(\textit{t}\text{-BuOO})_5$ and six monohydroxyl fullerenols with the general formula $C_{60}(O)(OH)(\textit{t}\text{-BuOO})_5$ were prepared, which are essentially the same except the location of the OH group. An additional reaction of the monohydroxyl fullerenols gave bis- and trishydroxyl fullerenols. Single-crystal X-ray structures have been obtained for the two monohydroxyl fullerenols. Other compounds are characterized by chemical correlation and their spectroscopic data. Cuprous bromide could protect the most reactive *t*-BuOO group from being attacked by stronger Lewis acids. The proposed mechanism mainly involves Lewis acid induced heterolysis of the peroxo O−O bond.

Introduction

Polyhydroxylated fullerenes (fullerenols) have been intensively studied for their biological activities.[1] Various methods have been developed for their synthesis, such as the acidic preparation using aqueous HNO_3/H_2SO_4[2] and the basic preparation using phase-transfer catalysis.[3] These methods usually give a high level of hydroxylation and inseparable complicated mixtures of isomers. Hemiketal moieties have been shown to be present in addition to tertiary hydroxyl groups.[4] Recently, polyhydroxylated fullerenols prepared by the basic method were shown to be mixtures of radical anions.[5] Despite the importance of fullerenols, the preparation of isomerically pure fullerenols remains a challenging problem. Isomerically pure fullerenols are still rare. RuO_4-assisted hydroxylation gave simple fullerene diols $C_{60}(OH)_2$ and $C_{70}(OH)_2$.[6] The C_{2v} symmetric penta-adduct $C_{60}(C(COOEt)_2)_5$ may be oxidized with $KMnO_4$ to give a diol moiety.[7] We have found that *tert*-butylperoxo radicals add readily to fullerene to form isomerically pure fullerene mixed peroxides.[8] Peroxo groups in these compounds are potential

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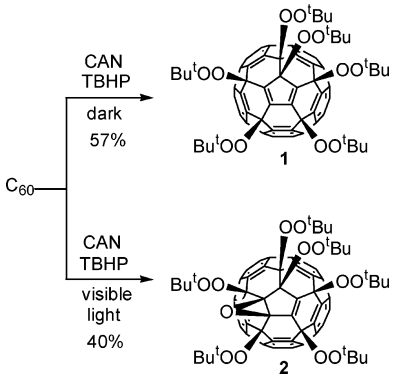
SCHEME 1. Preparation of Compounds 1 and 2



precursors for further transformation in analogy to the rich chemistry of organic peroxides. Here we report the controlled cleavage of peroxo bonds and the formation of isomerically pure fullerenols from fullerene peroxides.

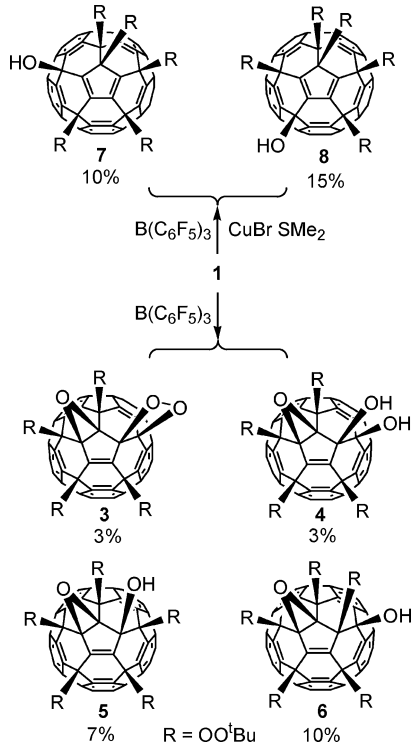
Results and Discussion

Improved Preparation of C_{60}(OO*t*-Bu)$_6$ and C_{60}(O)(OO*t*-Bu)$_6$. Compounds **1** and **2** were previously isolated from the reaction between C_{60} and *t*-BuOOH in 32 and 16% yield, respectively, with (diacetoxyiodo)benzene (DIB) as the oxidant.[8b] When DIB was changed to ammonium cerium(IV) nitrate (CAN), the corresponding yields increased to 57 and 40% (Scheme 1). Visible light is an important factor affecting the selectivity of the reaction. Compound **1** was prepared under total darkness, whereas visible light irradiation is necessary for the formation of **2**. Light-induced cleavage of the peroxo O−O bond is probably responsible for the epoxide formation. A small amount of **1** was also formed in the preparation of **2**. Both of the two compounds were purified on a silica gel column wrapped with aluminum foil to avoid light-induced decomposition. Purified samples can be stored for weeks at rt in the dark with little change.

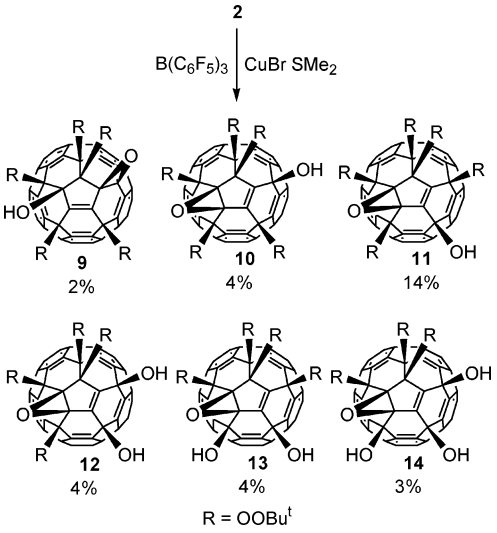
Reaction between C_{60}(OO*t*-Bu)$_6$, C_{60}(O)(OO*t*-Bu)$_6$, and $(C_6F_5)_3B$/CuBr·SMe$_2$. It is well-known that Lewis acids can initiate cleavage of peroxo bonds in organic peroxides. Hemiketal fullerene derivatives were obtained when C_{60}(OH)Cl(OO*t*-Bu)$_4$ was treated with $AlCl_3$.[9] Under similar conditions, treatment of **1** with $AlCl_3$ resulted in uncharacterizable mixtures. When compound **1** was treated with $(C_6F_5)_3B$, four products were isolated, as shown in Scheme 2.[10] The dioxetane containing derivative **3** is relatively unstable and slowly decomposes to a complex mixture of products. Compounds **5** and **6** are regioisomers and differ at the location of the hydroxyl group. The more acidic Lewis acid BF_3 gave compounds **3**−**6** with slightly different yields. A combination of CuBr·SMe$_2$ and $(C_6F_5)_3B$ cleaves the peroxo bonds of **1** smoothly yielding two monohydroxyl isomers **7** and **8**.

The reaction of compound **2** was more complicated. A rather complex mixture was obtained when **2** was treated with $(C_6F_5)_3B$ alone. The combination of CuBr·SMe$_2$ and $(C_6F_5)_3B$ afforded three monohydroxyl isomers **9**, **10**, and **11**, two bishydroxyl isomers **12** and **13**, and the trishydroxyl derivative **14** (Scheme 3). Treating **1** or **2** with CuBr·SMe$_2$ alone did not give noticeable product. To avoid the formation of uncharacterizable polar products, the reactions were stopped before the starting material was completely consumed. A large amount of **2** was recovered (48%) for the reaction in Scheme 3. Some starting material **1** was also recovered for the reactions in Scheme 2 (40% for the preparation of **7** and **8**, 9% for the preparation of **3**−**6**). The separation of the products is not easy but can be carried out on a silica gel column because of their different polarity and solubility. The number of OH and *tert*-butylperoxo groups attached on the C_{60} cage has much effect on the solubility. For example, solubility of the trishydroxyl derivative **14** was measured as: 1,4-dioxane (100 mg/mL), THF (60 mg/mL), ethyl acetate (10 mg/mL), acetone (6 mg/mL), methanol (2 mg/mL), chloroform (1 mg/mL), carbondisulfide, benzene (0.9 mg/mL), acetonitrile (0.5 mg/mL), and water (insoluble). Compounds

SCHEME 2. Lewis Acid Induced Reactions of 1



SCHEME 3. Lewis Acid Induced Reactions of 2



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(10) A fifth compound was noticed, but its structure remains to be determined.

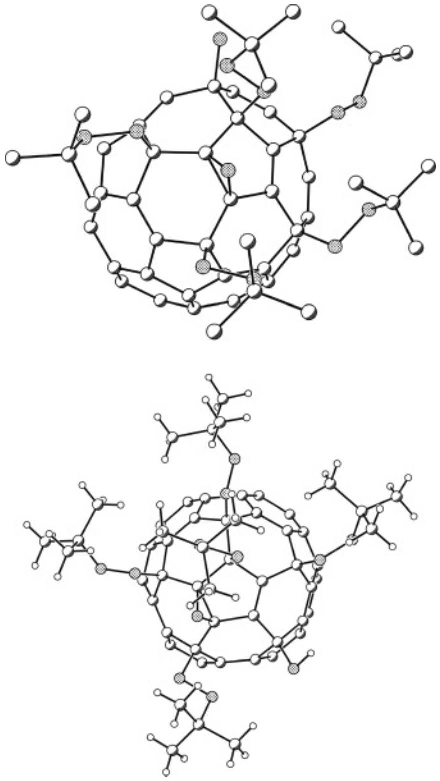


FIGURE 1. Single-crystal molecular structure of **6** (top) and **11** (bottom); for clarity, H atoms for **6** and some atoms of the C_{60} cage are omitted.

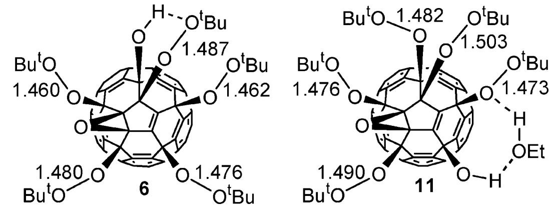
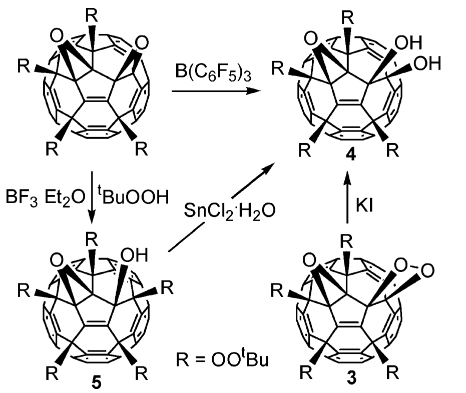


FIGURE 2. Peroxo O−O bond length and H-bonding for **6** and **11**.

SCHEME 4. Formation of Fullerendiol 4



with fewer OH groups are more soluble in chloroform (>20 mg/mL) than in methanol (<1 mg/mL).

Single-Crystal X-ray Analysis of Compounds 6 and 11. To establish the structure of the above fullerenols, various methods were tried to grow suitable crystals for X-ray diffraction analysis. Slow evaporation of a CCl_4 solution of compound **6** yielded rectangular crystals, but they did not show a clear X-ray diffraction pattern. The crystals were then redissolved in CS_2, and some ethanol was added. Slow evaporation of the CS_2/ethanol solution gave suitable crystals for X-ray analysis. A solvent CCl_4 molecule was still present in the lattice. Crystals of compound **11** were also obtained from the slow evaporation of a CS_2/ethanol solution.

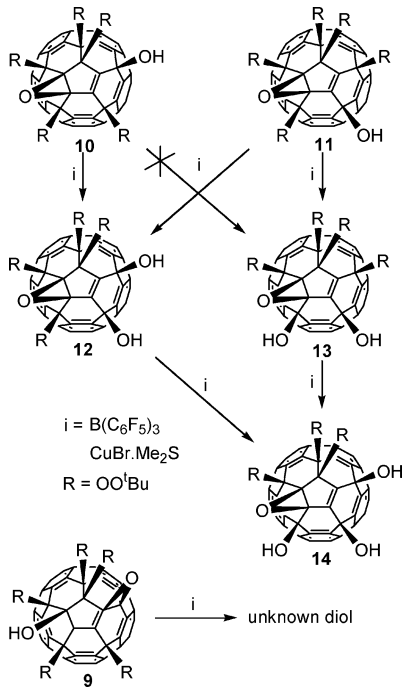
Crystal structures of **6** and **11** (Figure 1) show a strong hydrogen bond for the fullerenol OH group. Compound **6** forms an intramolecular H bond between the OH and the adjacent peroxo oxygen atom connected to the CMe_3 group. Such intramolecular H bonding is not possible for **11** because the OH and *t*-BuOO groups are relatively far away from each other. Instead, a solvent ethanol molecule connects the fullerenol OH and the *t*-BuOO on the same hexagon by forming two H bonds, C_{60}OH···O(Et)H···OO*t*-Bu. The double bond on the central pentagon is the shortest on the fullerene cage at 1.339 and 1.333 Å for **6** and **11**, respectively.

The O−O bond of the *t*-BuOO group on the central pentagon is the longest among all O−O bonds at 1.487 and 1.503 Å, respectively (Figure 2). The two *t*-BuOO groups meta to the *t*-BuOO group on the central pentagon have essentially the same O−O bond length, which is slightly shorter than the O−O bonds of the *t*-BuOO groups located further away from the *t*-BuOO group on the central pentagon. Such different O−O bond length patterns suggest that the *t*-BuOO on the central pentagon is the most reactive, followed by the *t*-BuOO further away from the crowded center. The observed different reactivities of the *t*-BuOO groups are in accord with such O−O bond lengths. The yield of **8** is higher than **7** (Scheme 2), and the yield of **11** is higher than **10** (Scheme 3). Lewis acids interact with the *t*-BuOO on the central pentagon in the first step, as discussed in the mechanism section.

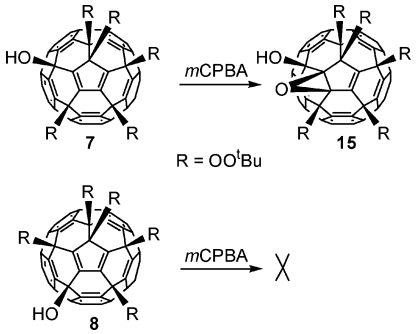
Chemical Correlation and Structure Assignment. Except the above two compounds **6** and **11**, structures of other compounds are deduced from chemical correlation experiments and their spectroscopic data. The NMR and ESI-MS data reveal the number of OH, *t*-BuOO, and epoxy groups attached on the C_{60} cage (see next section), but the spectroscopic data alone cannot assign the structures for sure, in particular, about the relative location of the OH groups in the regioisomers. Correlation of related products was, thus, carried out. The previously reported bisepoxy derivative $C_{60}(O)_2$(*t*-BuOO)$_4$[8b] opens its epoxy moiety at the less-crowded 6,6-junction to yield **4** when treated with $B(C_6F_5)_3$, whereas in the presence of BF_3·Et_2O, addition of *t*-BuOOH converts it to **5**, as shown in Scheme 4. Treatment of **3** with potassium iodide produced the corresponding dihydroxyl fullerene **4**. The ESI-MS spectrum of **3** showed C_{60}(O)(OH)$_2$(*t*-BuOO)$_4$ as the most intensive signal, indicating hydrolysis of the dioxetane moiety. Reduction of the monohydroxyl derivative **5** with $SnCl_2$·H_2O also yielded compound **4**, which indicates that the hydroxyl group of **5** is on the central pentagon because the other possible isomer **6** was determined by X-ray analysis. Compound **6** is relatively inert and could not be converted to **4** or any characterizable product under similar conditions.

Further hydroxylation confirms the structures for compounds **9** to **14** (Scheme 5). The X-ray characterized compound **11** can be further hydrolyzed to bishydroxyl derivatives **12** and **13**. Compound **10** gave just the bishydroxyl derivative **12**. This indicates that the location of the hydroxyl group in **10** is as depicted. Compound **14** is the only trishydroxyl derivative detected from the reaction of **12** and **13**. Under the same conditions, it was not possible to hydrolyze the remaining three

SCHEME 5. Hydroxylation of Compounds 9−14



SCHEME 6. Preparation of Compound 15



t-butylperoxo groups in **14**. Further hydroxylation of **9** gave an unknown bishydroxyl fullerenol.

The reactivities of **7** and **8** toward *m*CPBA support their structure assignments. While compound **7** formed **15**, compound **8** did not give any characterizable product under the same conditions (Scheme 6). It is known that the reactive sites of ordinary 1,3-dienes are the two ends of the conjugated diene. Likewise, the reactive sites of the central cyclopentadienyl moiety in compounds **7** and **8** are the two positions next to the unique *tert*-butylperoxo on the central pentagon. Thus, the steric hindrance of compound **7** with a *tert*-butylperoxo group and a hydroxyl group next to the reactive site is relatively small for the incoming *m*CPBA as compared to the same position in compound **8**, which has two *tert*-butylperoxo groups next to the reactive site. The same steric consideration also explains the fact that compound **10** with the epoxy moiety further away from the OH group is not detected in the reaction of **7** with *m*CPBA. This phenomenon indicates that steric factors play an important role for the present reactions.

Spectroscopic Data. The composition of the compounds is established by spectroscopic data. Most compounds are quite soluble in chloroform, and their NMR spectra were obtained in $CDCl_3$. A mixture of $CS_2/CDCl_3$ (1:1) had to be used for **6** and **9** and CS_2/dioxane-d_8 (3:1) was used for **14** to get decent ^{13}C NMR spectrum because of their relatively low solubility. The ^1H NMR clearly indicates the number of OH and *t*-BuOO groups in the molecule. The number of sp^3 fullerene signals on the ^{13}C NMR then shows whether an epoxy group is present or not. For example, the ^1H NMR spectrum of compound **5** showed one hydroxyl group and five *t*-butylperoxo groups. Its ^{13}C NMR spectrum showed eight sp^3 fullerene signals, indicating the presence of an epoxy moiety, because the hydroxyl group and the five *tert*-butylperoxo groups can only account for six sp^3 fullerene signals. Such NMR data derived the formula $C_{60}(OH)(O)(OO\textit{t}\text{-}Bu)_5$, which is further confirmed by its ESI-MS spectra. The HMBC spectrum of the fullerendiol **4** confirmed the vicinal diol moiety.

Intramolecular hydrogen bonding is a key feature affecting the chemical shift of the OH groups in the present fullerenols. Compound **6** has a strong intramolecular bond between the OH and the adjacent *t*-BuOO groups, as seen from the X-ray structure. Its OH group appears at the lowest field at 6.11 ppm among all the monohydroxyl fullerenols from compounds **5** to **11**. Its OH stretching also appears at the lowest frequency at 3449 cm^{-1}. Both compound **5** and compound **9** have the OH adjacent to *t*-BuOO group, thus, may also form an intramolecular H bond. Compared to **6** the OH groups of **5** and **9** appear at relatively higher fields (4.78 and 5.02 ppm for **5** and **9**, respectively). This is probably due to the shielding effect of neighboring *t*-BuOO groups, because the OH groups of these two compounds are on the central pentagon and are well-surrounded by the bulky *t*-butyl groups. The downfield shift effect of the H bond can also explain the difference between **7** (4.53 ppm) and **8** (3.55 ppm), assuming weak H bonding between the OH and the meta *t*-BuOO group in **7**.

In contrast to H bonding, the epoxy moiety causes an upfield shift of the OH group. Compound **7** without an epoxy moiety has the OH signal at 4.53 ppm, whereas the corresponding compound **15**, with an epoxy moiety, has the OH signal at 3.57 ppm. In addition, the closer the epoxy moiety is to the OH group, the stronger the upfield shift is. The different chemical shifts between **5** (4.78 ppm) and **9** (5.02 ppm) follow such a trend. Such a phenomenon is probably due to local steric strain caused by the epoxy moiety. To form the three-membered epoxy ring, the fullerene sp^3 carbons must be distorted compared to other sp^3 fullerene carbons. The chemical shifts of the bis- and trishydroxyl fullerenes can be assigned tentatively by considering H-bonding and the effect of epoxy moiety (Figure 3). The dioxane-d_8 used for **14** may be partially responsible for its downfield shift compared to other fullerenols. The H-bonding of the OH groups with solvent molecules is likely to occur in dioxetane. It is well-known that the chemical shift of the OH group is sensitive to many factors such as concentration, temperature, and solvent. The assignment of the OH shifts is speculative for compounds with more than one OH group, namely, **4**, **12**, **13**, and **14**.

The present chemical shifts of the hydroxyl groups are comparable to those reported for other monohydroxylated and bishydroxylated fullerenes. In the methylated hydroxyepoxides $C_{60}Me_5O_2(OH)$, $C_{60}Me_5O(OH)$, and $C_{60}Me_4PhO_2(OH)$, the hydroxyl protons appear at 4.25, 3.59, and 4.29 ppm, respectively.[11] The cyanofullerenol $C_{60}(CN)(OH)$ shows a broad OH signal at 4.9 ppm.[12] The symmetric vicinal fullerendiol deriva-

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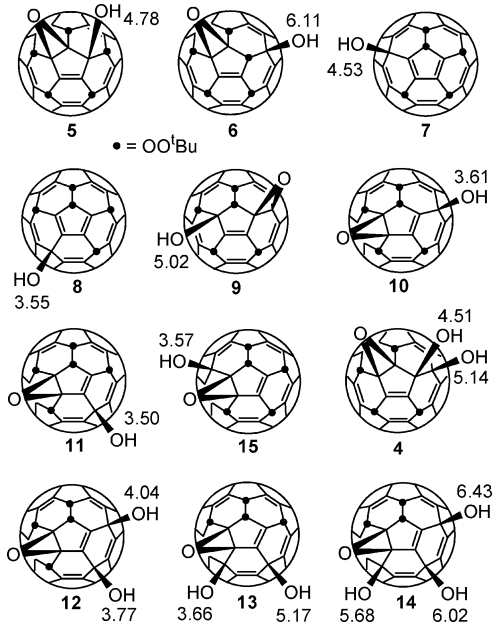


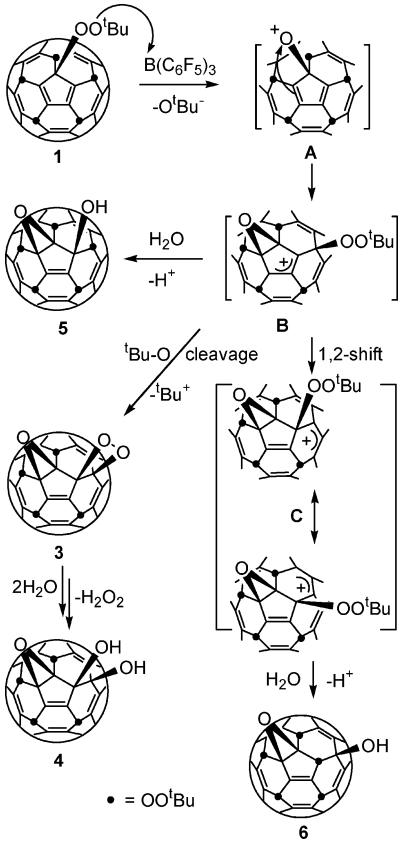
FIGURE 3. Proposed chemical shift assignment of the OH groups.

tive $C_{60}(C(COOEt)_2)_5(OH)_2$ has the OH signal at 5.13 ppm.[7] We have reported the Lewis acid promoted opening of the epoxy moiety in $C_{60}(O)(t\text{-BuOO})_4$ to form monohydroxyl derivatives $C_{60}(OH)X(t\text{-BuOO})_4$ (X = F, Cl, OMe, OOH, *t*-BuOO), OH signals of which range from 4.46 to 5.54 ppm.[9] (all the literature shifts cited here were from data obtained in $CDCl_3$)

Mechanism Consideration. Scheme 7 shows a possible pathway for the $B(C_6F_5)_3$ induced reaction of **1**. The first step is the Lewis acid induced heterolysis of the *tert*-butylperoxo group on the central pentagon to form the oxonium cation A, which then adds to the neighboring double bond on the central pentagon to form the allyl cation B. The addition of water to B forms fullerenol **5**. Heterolysis of the *t*-Bu-O bond adjacent to the allyl radical forms the dioxetane derivative **3**. Formation of the diol **4** may result from hydrolysis of the dioxetane **3**, but other pathways cannot be ruled out such as the hydrolysis of **5**. Formation of the isomeric fullerenol **6** suggests a 1,2-shift process from intermediate B to C. The driving force for such a 1,2-shift is probably the extra resonance structure present for C compared to that of B. The addition of water to the allyl cation of intermediate C is regioselective, yielding just compound **6**. Addition at the other end of the ally cation moiety would result in an unfavorable double bond on the adjacent pentagon. Cleavage of O−O and *t*-Bu-O bonds has been reported before in classical organic peroxide chemistry.[13] The shift of the *t*-BuOO group to form a more stable carbocation has also been suggested in organic peroxide chemistry.[14]

In accord with its longest O−O bond length, the *tert*-butylperoxo group on the central pentagon is the most reactive toward Lewis acid, as indicated in the above reaction mechanism with just $B(C_6F_5)_3$. So when excess cuprous salt is added, the *tert*-butylperoxo group on the central pentagon coordinates to the cuprous ion to form a complex above the central pentagon

SCHEME 7. Proposed Mechanism for $B(C_6F_5)_3$ Induced Reactions



(Scheme 8), thus preventing the *tert*-butylperoxo group on the central pentagon from being attacked by $B(C_6F_5)_3$. The epoxy moiety of compound **2** may also form a weak coordination bond with the cuprous ion, leading to the *tert*-butyl groups next to the epoxy groups to be more crowded than the *tert*-butylperoxo groups further away from the epoxy moiety. Cuprous salt is a weak Lewis acid for the present reactions. The addition of CuBr·Me_2S alone did not result in a noticeable change.

The further interaction of intermediate D with $B(C_6F_5)_3$ results in the heterolysis of the less-crowded *tert*-butylperoxo groups to form E or G (Scheme 8). The resulting oxonium E and G are reduced by cuprous bromide to form a cupric complex, hydrolysis of which gave fullerenol **10** and **11**, respectively. The oxonium group in E can also add to the neighboring double bond on the central pentagon, opening the epoxy moiety on the central pentagon to form the new oxonium intermediate F. Hydrolysis of F affords compound **9**. The relatively higher yield observed for **11** compared to that of **9** and **10** suggests that intermediate G is formed preferentially over intermediate E. So the *t*-BuOO group further away from the crowded center is cleaved more easily. A similar mechanism can also explain the reaction of compound **1** with CuBr·$Me_2S/B(C_6F_5)_3$ and the formation of compounds **7** and **8**.

Conclusion

The peroxo O−O bond in fullerene-mixed peroxides can be readily cleaved by Lewis acids. Steric hindrance is the key factor affecting the O−O bond length and relative reactivity in the cyclopentadienyl-type adducts $C_{60}(OOt\text{-Bu})_6$ and $C_{60}(O)(OOt\text{-Bu})_6$. The *t*-BuOO group on the central pentagon has the

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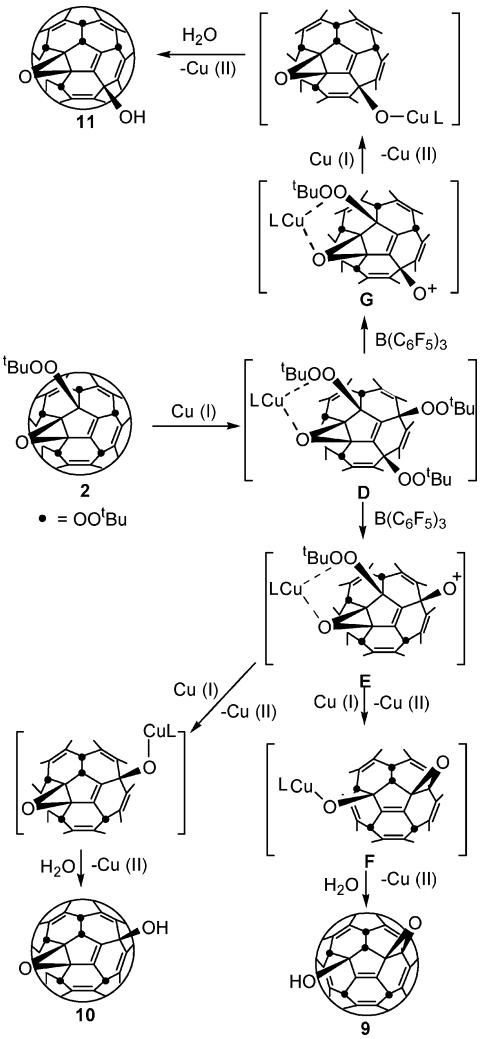
SCHEME 8. Proposed Mechanism for $CuBr \cdot SMe_2/B(C_6F_5)_3$ Induced Reactions



longest O−O bond length and is the most reactive toward Lewis acids. The relatively mild Lewis acid cuprous bromide can act as a protecting group for the peroxo bond and also as a reducing agent for the formation of fullerenols. A number of fullerenols have been prepared and characterized in the present work with low yields. Selectivity of the reactions still needs to be improved. Further study is in progress to hydrolyze all the *t*-BuOO groups completely and make isomerically pure multihydroxyl fullerenols.

Experimental Section

Benzene, used for the reactions, was distilled from potassium under nitrogen. Other solvents and reagents were used as received. Chromatographic purifications were carried out with 200−300 mesh silica gel. NMR spectra were recorded at 298 K. ESI-MS spectra were recorded with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent. Positive mode ESI-MS spectra were cited for most compounds.

Caution: a large amount of peroxide is involved in some of the reactions; care must be taken to avoid possible explosion.

Synthesis of 1,2,4,11,15,30-Hexa-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (1). C_{60} (99% pure, 200 mg, 0.28 mmol) was dissolved in 200 mL of benzene. *tert*-Butyl hydroperoxide (TBHP; 540 mg, 70%, 4.2 mmol) was added. The flask was wrapped with aluminum foil. $(NH_4)Ce(NO_3)_6$ (CAN; 1.32 g, 2.4 mmol, dissolved in 1.3 mL of 0.1 mol/L H_2SO_4) was added slowly (about 3 min). The resulting solution was stirred for another 5 min. The organic layer was separated and evaporated in the dark. The residue was dissolved in 10 mL of benzene and petroleum ether (60−90 °C; 1:2) and chromatographed on a silica gel column, eluting with benzene and petroleum ether (60−90 °C; 1:2). To avoid decomposition, the column was wrapped with aluminum foil and opened occasionally to check the progress of elution. The first band was collected and evaporated with the bottle wrapped with aluminum foil. Yield: 200 mg, 57%. For characterization data, see ref 8b.

Synthesis of 1,2,4,11,15,30-Hexa-*tert*-butylperoxy-3,14-epoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2). C_{60} (99% pure, 100 mg, 0.14 mmol) was dissolved in 100 mL of benzene. TBHP (350 mg, 70%, 2.8 mmol) was added. The flask was cooled with an ice−water bath and stirred for 5 min. The solution was then transferred into a Dewar container, the inside surface of which can reflect light just like a mirror. Two household luminescent light bulbs (12 W, commercial household light bulb) were placed above the container. CAN (660 mg, 1.2 mmol, dissolved in 0.7 mL of 0.1 mol/L H_2SO_4) was added slowly (about 2 min). The resulting solution was stirred for another 7 min. The organic phase was separated and evaporated in the dark. The residue was dissolved in 4 mL of benzene and petroleum ether (60−90 °C; 1:2) and chromatographed on a silica gel column, eluting with benzene and petroleum ether (1:2). The first red band was a small amount of compound **1**. The second red band was collected and evaporated with the bottle wrapped with aluminum foil. Yield: 70 mg, 40%. For characterization data, see ref 8b.

Procedure for the Synthesis of Compounds 3−6. Compound **1** (200 mg, 0.16 mmol) was dissolved in 50 mL CH_2Cl_2. The flask was wrapped with aluminum foil. $BF_3 \cdot Et_2O$ solution (128 μL, 1 mol/L in CH_2Cl_2) was added. The resulting solution was stirred for 2.5 h in a water bath at 30 °C. The solution was washed with 50 mL of brine and 50 mL of water. The organic layer was separated and evaporated. The residue was dissolved in 3 mL of benzene and petroleum ether (1:1) and chromatographed on a silica gel column (200−300 mesh). Unreacted compound **1** was collected as the first band (18 mg, 9%). The second band was compound **3** (16 mg, 8%). The third band was compound **6** (16 mg, 8%). After these three bands were eluted, the solvent was changed to benzene. The fourth band was compound **5** (18 mg, 9%). The last band was compound **4** (12 mg, 6%). The reaction was repeated with the same scale to obtain enough samples for characterization.

Note: Compound **3** was very unstable. Its spectra should be measured immediately.

4,11,15,30-Tetra-*tert*-butylperoxy-1,2-peroxy-3,14-epoxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (3). ^{1}H NMR (400 MHz, $CDCl_3$): 1.42 (s, 18H), 1.48 (s, 9H), 1.53 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 149.55, 149.49, 149.46, 149.27, 148.70, 148.66, 148.51 (2C), 148.48 (2C), 148.37, 148.22, 148.20, 148.12 (2C), 148.04 (2C), 147.95, 147.91, 147.87, 147.78 (2C), 147.67, 146.81, 146.34, 146.02, 145.38, 144.86, 144.83, 144.72, 144.45, 144.27, 144.20, 144.16, 144.07, 144.04 (3C), 143.93, 143.87, 143.82, 143.76, 143.74 (2C), 143.66, 143.59, 143.13 (2C), 142.94, 139.82, 139.06, 138.53, 89.15 (sp^3), 83.57 (sp^3), 82.49 (*C*-$(CH_3)_3$), 82.44 (sp^3), 82.42 (*C*-$(CH_3)_3$), 82.20 (*C*-$(CH_3)_3$), 82.13 (*C*-$(CH_3)_3$), 81.84 (sp^3), 81.03 (sp^3), 80.61 (sp^3), 74.36 (sp^3), 71.07 (sp^3), 26.75 ($3CH_3$), 26.72 ($9CH_3$). ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1144 (100, M + 2H + NH_4^+). Negative mode: *m*/*z* (rel intens) 1126 (100, M^- + 2H).

4,11,15,30-Tetra-*tert*-butylperoxy-3,14-epoxy-1,2-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (4). ^{1}H NMR (400 MHz, $CDCl_3$): 1.37 (s, 9H), 1.41 (s, 9H), 1.43 (s, 9H), 1.50 (s, 9H), 4.51 (s, 1H), 5.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 154.17, 149.35, 149.02, 148.87, 148.70, 148.55, 148.53, 148.36 (2C), 148.27, 148.21, 148.16, 148.14, 148.11, 148.09 (2C), 148.06, 148.01, 147.91(3C), 147.72, 146.93, 146.32, 146.17, 145.08, 145.01, 144.76, 144.72,

144.63, 144.39, 144.27, 144.21, 144.02, 143.99, 143.89, 143.81, 143.77, 143.75, 143.55, 143.49 (2C), 143.37, 143.31, 143.20, 143.06, 143.01, 142.40, 141.45, 140.65, 138.72, 137.79, 82.09 (*C*-$(CH_3)_3$), 81.96 (2*C*-$(CH_3)_3$), 81.94 (*C*-$(CH_3)_3$), 81.81 (sp^3), 80.99 (sp^3), 80.59 (sp^3), 80.44 (sp^3), 80.32 (sp^3), 77.11 (*C*-OH), 74.92 (*C*-OH), 73.63 (sp^3), 26.64 ($3CH_3$), 26.62 ($3CH_3$), 26.58 ($6CH_3$). Assignment was obtained from HMBC. FT-IR (microscope): 3473, 2980, 2929, 2869, 1471, 1456, 1388, 1364, 1193, 907, 871, 733 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1144 (100, M + NH_4^+).

1,4,11,15,30-Penta-*tert*-butylperoxy-3,14-epoxy-2-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (5). ^1H NMR (400 MHz, $CDCl_3$): 1.35 (s, 9H), 1.37 (s, 9H), 1.40 (s, 9H), 1.41 (s, 9H), 1.53 (s, 9H), 4.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 153.66, 150.03, 149.45, 149.03, 148.72, 148.66, 148.54, 148.51, 148.49 (2C), 148.46 (3C), 148.33 (2C), 148.28 (2C), 148.25, 148.19, 148.14, 148.08, 147.95, 146.65, 146.26, 146.10, 145.95, 145.60, 144.66, 144.53, 144.44, 144.10, 144.08, 143.97, 143.91, 143.89 (3C), 143.81 (2C), 143.70, 143.67, 143.60, 143.59, 143.39, 142.95, 142.93, 142.48, 141.66, 141.57, 140.55, 139.32, 130.67, 84.82 (sp^3), 82.71 (*C*-$(CH_3)_3$), 82.25 (*C*-$(CH_3)_3$), 81.93 (*C*-$(CH_3)_3$), 81.79 (*C*-$(CH_3)_3$), 81.61 (*C*-$(CH_3)_3$), 81.28 (sp^3), 81.24 (sp^3), 81.21 (sp^3), 81.02 (sp^3), 80.43 (sp^3), 79.09 (*C*-OH), 72.58 (sp^3), 26.82 ($3CH_3$), 26.77 ($3CH_3$), 26.75 ($3CH_3$), 26.73 ($3CH_3$), 26.70 ($3CH_3$). FT-IR (microscope): 3520, 2978, 2926, 2852, 1469, 1388, 1364, 11936, 909, 871, 732 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1221 (100, M + Na^+).

2,4,11,15,30-Penta-*tert*-butylperoxy-3,14-epoxy-1-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (6). ^1H NMR (400 MHz, $CDCl_3/CS_2$ = 1:1): 1.28 (s, 9H), 1.32 (s, 9H), 1.41 (s, 9H), 1.52 (s, 9H), 1.64 (s, 9H), 6.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1:1; all signals represent 1C, except where noted): 149.65, 149.26, 148.89, 148.85, 148.44, 148.40, 148.34, 148.29, 148.27, 148.21, 148.19, 148.16, 148.14 (3C), 148.05, 147.98 (2C), 147.94 (2C), 147.88, 147.84, 147.34, 146.67, 145.71, 145.55, 145.19 (2C), 145.17, 144.75, 144.65, 144.45, 144.38, 144.19, 144.16, 144.03, 144.01, 143.69 (2C), 143.61, 143.56, 143.36, 143.30, 143.27, 143.03, 142.97 (2C), 142.13, 141.80, 139.57, 138.11, 137.26, 87.42 (sp^3), 83.11 (*C*-$(CH_3)_3$), 82.32 (sp^3), 81.88 (*C*-$(CH_3)_3$), 81.48 (*C*-$(CH_3)_3$), 81.33 (*C*-$(CH_3)_3$), 81.31 (*C*-$(CH_3)_3$), 81.15 (sp^3), 80.77 (sp^3), 80.37 (sp^3), 81.21 (sp^3), 77.80 (sp^3), 71.93 (sp^3), 26.82 ($3CH_3$), 26.72 ($6CH_3$), 26.60 ($3CH_3$), 26.44 ($3CH_3$). FT-IR (microscope): 3449, 2980, 2930, 2870, 1471, 1456, 1387, 1364, 1194, 1112, 874, 736 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1216 (100, M + NH_4^+).

Crystals suitable for diffraction were obtained by the slow evaporation of compound **6** in a mixture of CS_2 and CCl_4 (1:1) to form the crystalline solids, which were redissolved in a mixture of CS_2 and ethanol (1:1). The resulting solution was then evaporated slowly under atmosphere. Crystal system, space group: monoclinic, P2(1)/c. Unit cell dimensions: a = 24.233(5) Å, α = 90°, b = 13.861(3) Å, β = 107.50(3)°, c = 18.487(4) Å, γ = 90°, volume = 5922(2) $Å^3$. Final R indices [I > 2σ(I)] R_1 = 0.0820, wR_2 = 0.1931.

Procedure for Compounds 7 and 8. Compound **1** (200 mg, 0.16 mmol) was dissolved in 20 mL of CH_2Cl_2. The flask was wrapped with aluminum foil. $CuBr{\cdot}SMe_2$ (130 mg, 0.63 mmol) and $(C_6F_5)_3B$ (82 mg, 0.16 mmol) were added. The resulting solution was stirred for 7 h at room temperature. The solution was filtered through a short silica gel column to remove the solids. The solution was evaporated. The residue was chromatographed on a silica gel column with benzene as the eluent. Unreacted compound **1** was collected as the first band (80 mg, 40%). The second band was compound **7** (20 mg, 10%). After these two bands were collected, the solvent was changed to CH_2Cl_2 and compound **8** was collected as another band (30 mg, 15%).

Note: These compounds were unstable under light. Light should be avoided throughout the experimental procedure.

1,2,4,15,30-Penta-*tert*-butylperoxy-11-hydroxy-1,2,4,11,15,30-hexahydro[60]fullerene (7). ^1H NMR (400 MHz, $CDCl_3$): 1.34 (s, 9H), 1.40 (s, 9H), 1.43 (s, 9H), 1.52 (s, 9H), 1.62 (s, 9H), 4.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 160.37, 152.01, 151.26, 149.28, 149.09 (3C), 149.03, 148.99, 148.77, 148.69, 148.40, 148.38, 148.34, 148.30, 148.22, 147.95 (2C), 147.69, 147.67, 147.60, 147.58, 147.56, 147.43, 147.35, 147.10, 147.07, 146.92, 146.50, 145.97, 145.78, 145.74, 145.35, 145.21, 144.75, 144.41, 144.39, 144.35, 144.23, 144.08, 143.98, 143.96, 143.76, 143.48, 143.40, 143.16, 142.97, 142.88, 142.85, 142.49, 141.59, 141.46, 140.80, 136.95, 91.73 (sp^3), 83.88 (sp^3), 83.21 (*C*-$(CH_3)_3$), 82.28 (sp^3), 81.81 (*C*-$(CH_3)_3$), 81.55 (*C*-$(CH_3)_3$), 81.42 (*C*-$(CH_3)_3$), 81.32 (*C*-$(CH_3)_3$), 80.90 (sp^3), 80.77 (sp^3), 73.02 (*C*-OH), 26.98 ($3CH_3$), 26.89 ($3CH_3$), 26.84 ($3CH_3$), 26.79 ($3CH_3$), 26.77 ($3CH_3$). FT-IR (microscope): 3509, 2978, 2930, 1473, 1458, 1387, 1363, 1194, 872 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1200 (100, M + NH_4^+).

1,2,4,11,30-Penta-*tert*-butylperoxy-15-hydroxy-1,2,4,11,15,30-hexahydro[60]fullerene (8). ^1H NMR (400 MHz, $CDCl_3$): 1.33 (s, 9H), 1.36 (s, 9H), 1.39 (s, 9H), 1.50 (s, 9H), 1.58 (s, 9H), 3.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 152.83, 151.81, 150.38, 149.38, 149.19, 149.10 (2C), 148.98 (2C), 148.73, 148.71, 148.53 (2C), 148.37 (4C), 148.21, 147.75, 147.67, 147.64, 147.61, 147.58, 147.44 (2C), 147.37, 147.34, 147.07, 146.89, 146.04, 145.97, 145.71, 145.63, 145.57, 145.45, 145.33, 144.70, 144.63 (2C), 144.58, 143.94, 143.90, 143.77 (2C), 143.72, 143.38, 143.28, 143.22, 142.71, 142.51, 142.31, 141.22, 137.54, 137.07, 90.36 (sp^3), 85.39 (sp^3), 82.85 (sp^3), 82.24 (sp^3), 82.06 (*C*-$(CH_3)_3$), 81.58 (*C*-$(CH_3)_3$), 81.27 (*C*-$(CH_3)_3$), 81.18 (*C*-$(CH_3)_3$), 80.92 (*C*-$(CH_3)_3$), 80.22 (sp^3), 71.91 (*C*-OH), 26.90 ($3CH_3$), 26.86 ($3CH_3$), 26.82 ($3CH_3$), 26.77 ($3CH_3$), 26.72 ($3CH_3$). FT-IR (microscope): 3556, 2977, 2930, 2871, 1473, 1457, 1387, 1363, 1195, 874 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1200 (100, M + NH_4^+).

Procedure for the Synthesis of Compounds 9−14. Compound **2** (200 mg, 0.16 mmol) was dissolved in 50 mL of CH_2Cl_2. $CuBr{\cdot}SMe_2$ (160 mg, 0.78 mmol) and $(C_6F_5)_3B$ (100 mg, 0.20 mmol) were added. The flask was wrapped with aluminum foil. The resulting solution was stirred for 3 h at 15 °C. The solution was filtered through a short silica gel column to remove the solids. The filtered solution was evaporated under vacuum. The residue was chromatographed on silica gel column with CH_2Cl_2. A mixture of compounds **2** and **9** were collected as the first band. The second band was compound **11** (35 mg, 12%). The third band was compound **10** (10 mg, 4%). After these three bands were collected, the eluent was changed to benzene and ethyl acetate (1:1). Compound **13** (10 mg, 4%) and compound **12** (9 mg, 4%) were collected as the fourth and fifth band. Then the eluent was changed to benzene and ethyl acetate (1:1). Compound **14** (7 mg, 3%) was collected as the last band.

The mixture of compounds **2** and **9** was evaporated and chromatographed on a silica gel column with benzene and petroleum (1:1) as the eluent. Compound **2** was recovered as the first band (120 mg, 48%). Compound **9** was collected as the second band (5 mg, 2%).

1,2,4,15,30-Penta-*tert*-butylperoxy-11,12-epoxy-3-hydroxy-1,2,3,4,11,12,1,30-octahydro[60]fullerene (9). ^1H NMR (400 MHz, $CDCl_3/CS_2$ = 1:1): 1.32 (s, 9H), 1.38 (s, 9H), 1.46 (s, 9H), 1.50 (s, 9H), 1.65 (s, 9H), 5.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$ = 1:1; all signals represent 1C, except where noted): 156.98, 150.86, 149.40, 148.95, 148.79, 148.47 (2C), 148.44 (3C), 148.38 (3C), 148.36, 148.22 (2C), 148.16, 148.00, 147.98, 147.96, 147.85, 146.46, 146.42, 145.67, 145.60, 145.29, 144.32, 144.28, 144.22, 144.04, 143.94 (2C), 143.87, 143.83, 143.82 (3C), 143.61, 143.59, 143.48, 143.45 (2C), 143.18, 143.04, 142.97, 142.66, 142.41, 142.29, 142.23, 141.56, 141.40, 138.93, 88.57 (sp^3), 84.11 (*C*-$(CH_3)_3$), 83.40 (sp^3), 82.74 (sp^3), 81.74 (1sp^3, 1*C*-$(CH_3)_3$), 81.64 (*C*-$(CH_3)_3$), 81.50 (*C*-$(CH_3)_3$), 81.19 (*C*-$(CH_3)_3$), 80.97 (sp^3), 80.26 (sp^3), 73.15 (sp^3), 71.62 (sp^3), 26.88 ($3CH_3$), 26.82 ($3CH_3$), 26.80

($3CH_3$), 26.67 ($6CH_3$). FT-IR (microscope): 3480, 2978, 2930, 1472, 1455, 1387, 1363, 1195, 1112, 876 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1216 (100, M + NH_4^+).

1,2,4,15,30-Penta-*tert*-butylperoxy-3,14-epoxy-11-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (10). ^1H NMR (400 MHz, $CDCl_3$): 1.30 (s, 9H), 1.31 (s, 9H), 1.36 (s, 9H), 1.56 (s, 9H), 1.62 (s, 9H), 3.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 150.63, 149.38, 148.97, 148.86, 148.75, 148.69, 148.49, 148.43 (2C), 148.40 (2C), 148.33, 148.32, 148.28, 148.26, 148.18, 148.15, 148.11 (2C), 148.07, 148.02, 147.82, 146.37, 146.29, 145.70, 145.49, 145.32, 144.55, 144.50, 144.43, 144.25, 144.16 (2C), 144.12, 144.09 (2C), 144.04, 144.02, 143.93, 143.70, 143.64, 143.38, 143.14, 143.02, 142.99, 142.97, 142.89, 142.28, 141.76, 140.77, 138.71, 137.17, 87.61 (sp^3), 85.55 (sp^3), 84.83 (sp^3), 82.33 (*C*-$(CH_3)_3$), 81.59 (*C*-$(CH_3)_3$), 81.50 (*C*-$(CH_3)_3$), 81.16 (sp^3), 81.01 (*C*-$(CH_3)_3$), 80.90 (*C*-$(CH_3)_3$), 80.80 (sp^3), 74.77, 71.60 (*C*-OH), 27.18 ($3CH_3$), 26.88 ($3CH_3$), 26.76 ($3CH_3$), 26.64 ($3CH_3$), 26.56 ($3CH_3$). Assignment was obtained from HMBC. One sp^3 fullerene carbon signal is missing, probably as a result of overlapping with the signal at 82.33 ppm, which is lightly broad. FT-IR (microscope): 3551, 2978, 2928, 2855, 1470, 1456, 1387, 1363, 1195, 1088, 907, 874, 733 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1216 (100, M + NH_4^+).

1,2,4,11,15-Penta-*tert*-butylperoxy-3,14-epoxy-30-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (11). ^1H NMR (400 MHz, $CDCl_3$): 1.31 (s, 9H), 1.32 (s, 9H), 1.40 (s, 9H), 1.52 (s, 9H), 1.61 (s, 9H), 3.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 149.97, 149.55, 149.09, 148.95, 148.67 (2C), 148.58, 148.48, 148.43 (3C), 148.37 (2C), 148.35, 148.32, 148.27, 148.20, 148.05 (2C), 147.98, 147.96 (2C), 147.45, 147.30, 146.60, 145.70, 145.47, 145.35, 145.16, 144.49, 144.31, 144.29 (3C), 144.08, 143.94 (2C), 143.87, 143.84, 143.79, 143.36, 143.24, 143.19, 143.16, 143.02 (2C), 142.35, 141.84, 141.30, 141.13, 140.86, 136.85, 87.36 (sp^3), 84.63 (sp^3), 83.67 (sp^3), 82.20 (*C*-$(CH_3)_3$), 81.70 (*C*-$(CH_3)_3$), 81.54 (*C*-$(CH_3)_3$), 81.32 (sp^3), 81.12 (*C*-$(CH_3)_3$), 80.78 (*C*-$(CH_3)_3$), 80.30 (sp^3), 80.10 (sp^3), 72.84 (*C*-OH), 71.89 (sp^3), 27.09 ($3CH_3$), 26.87 ($3CH_3$), 26.81 ($3CH_3$), 26.79 ($3CH_3$), 26.56 ($3CH_3$). FT-IR (microscope): 3556, 2978, 2930, 2870, 1471, 1456, 1387, 1363, 1196, 1091, 875 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1216 (100, M + NH_4^+).

Crystals suitable for X-ray diffraction were obtained from the slow evaporation of **11** in a mixture of CS_2 and ethanol (1:1). Crystal system, space group: triclinic, P-1. Unit cell dimensions: a = 13.301 (3) Å, α = 99.32(3)°, b = 14.292(2) Å, β = 94.56-(3)°, c = 18.349(4) Å, γ = 108.96(3)°, volume = 3222.5(11) $Å^3$. Final R indices [I > 2σ(I)] R_1 = 0.0773, wR_2 = 0.2138.[15]

1,2,4,15-Tetra-*tert*-butylperoxy-3,14-epoxy-11,30-dihydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (12). ^1H NMR (400 MHz, $CDCl_3$): 1.31 (s, 18H), 1.43 (s, 9H), 1.61 (s, 9H), 3.77 (s, 1H), 4.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 149.48, 149.30, 149.04, 148.64, 148.57, 148.53, 148.50, 148.49, 148.45 (3C), 148.35, 148.33, 148.27, 148.20 (2C), 148.17, 148.12, 148.05 (2C), 148.03, 147.79, 147.49, 146.41, 146.29, 145.66, 145.44, 145.34, 145.30, 145.17, 144.45 (2C), 144.16 (2C), 144.04, 143.98 (2C), 143.96, 143.93, 143.89, 143.25 (2C), 143.18, 143.05, 142.99, 142.95, 142.84, 142.36, 141.47, 140.94, 140.34, 135.85, 87.79 (sp^3), 85.48 (sp^3), 84.81 (sp^3), 81.97 (*C*-$(CH_3)_3$), 81.72 (*C*-$(CH_3)_3$), 81.22 (*C*-$(CH_3)_3$), 81.16 (sp^3), 80.94 (*C*-$(CH_3)_3$), 79.90 (sp^3), 74.20 (sp^3), 72.79 (*C*-OH), 71.62 (*C*-OH), 27.09 ($3CH_3$), 26.83 ($3CH_3$), 26.77 ($3CH_3$), 26.64 ($3CH_3$). Assignment was obtained from HMBC. FT-IR (microscope): 3550, 3388, 2978, 2930, 1471, 1455, 1387, 1363, 1195, 1112, 1089, 907, 877, 733 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1144 (100, M + NH_4^+).

1,2,4,11-Tetra-*tert*-butylperoxy-3,14-epoxy-15,30-di-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (13). ^1H NMR (400 MHz, $CDCl_3$): 1.33 (s, 9H), 1.51 (s, 9H), 1.53 (s, 9H), 1.67 (s, 9H), 3.66 (s, 1H), 5.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 154.55, 151.03, 149.54, 148.94, 148.76, 148.53, 148.49 (3C), 148.47, 148.45, 148.43, 148.39, 148.38, 148.35, 148.20, 148.18, 148.16, 148.03, 147.86, 147.84, 147.82, 146.75, 146.45, 146.00, 144.79, 144.43, 144.17 (2C), 144.14, 144.09, 144.06, 144.01, 143.94 (2C), 143.92, 143.85 (3C), 143.57, 143.54, 143.49, 143.36, 143.15, 142.98, 142.76, 142.36, 142.25, 141.75 (2C), 141.62, 141.15, 88.59 (sp^3), 84.20 (*C*-$(CH_3)_3$), 83.94 (sp^3), 82.72 (sp^3), 82.59 (*C*-$(CH_3)_3$), 81.90 (*C*-$(CH_3)_3$), 81.31 (*C*-$(CH_3)_3$), 81.05 (sp^3), 80.02 (sp^3), 73.24 (*C*-OH), 73.04 (sp^3), 71.61 (*C*-OH), 26.89 ($3CH_3$), 26.81 ($3CH_3$), 26.64 ($3CH_3$), 26.60 ($3CH_3$). Assignment was obtained from HMBC. FT-IR (microscope): 3555, 3467, 2978, 2930, 2871, 1471, 1455, 1388, 1363, 1194, 1108, 1101, 1084, 1026, 874, 732 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1144 (100, M + NH_4^+).

1,2,4-Tri-*tert*-butylperoxy-3,14-epoxy-11,15,30-trihydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (14). ^1H NMR (400 MHz, dioxane-d_8/CS_2 = 1:3): 1.49 (s, 9H), 1.59 (s, 9H), 1.79 (s, 9H), 5.18 (s, 1H), 6.02 (s, 1H), 6.43 (s, 1H). ^{13}C NMR (100 MHz, dioxane-d_8/CS_2 = 1:3; all signals represent 1C, except where noted): 156.15, 152.40, 151.12, 150.70, 150.49, 150.31 (4C), 150.20, 150.18, 150.16 (2C), 150.11, 150.00 (2C), 149.98, 149.95, 149.92, 149.79, 149.76, 149.58 (2C), 149.42, 148.24, 147.92, 146.99, 146.60, 146.25, 146.17, 146.13, 145.74 (2C), 145.72, 145.68, 145.66, 145.59, 145.50, 145.31, 145.24, 145.13, 145.07, 145.03, 144.91, 144.83, 144.72, 144.69, 143.97, 143.91, 143.78, 143.28, 143.17, 90.26 (sp^3), 86.63 (sp^3), 85.03 (*C*-$(CH_3)_3$), 84.85 (sp^3), 83.25 (*C*-$(CH_3)_3$), 82.95 (sp^3), 82.63 (*C*-$(CH_3)_3$), 76.70 (sp^3), 75.13 (*C*-OH), 73.52 (*C*-OH), 73.49 (*C*-OH), 28.51 ($3CH_3$), 28.44 ($3CH_3$), 28.42 ($3CH_3$). Assignment was obtained from HMBC. FT-IR (microscope): 3394, 2978, 2930, 1471, 1455, 1388, 1364, 1193, 1116, 1099, 1085, 1042, 1029, 757 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1072 (100, M + NH_4^+).

Preparation of Compound 15. Compound **7** (50 mg, 0.04 mmol) was dissolved in 10 mL of CH_2Cl_2. The flask was wrapped with aluminum foil. *m*CPBA (250 mg, 1.45 mmol) was added. The resulting solution was stirred for 22 h at room temperature. $Na_2S_2O_3$ solution (500 mg, 3.16 mmol, dissolved in 10 mL of H_2O) was added to reduce the unreacted *m*CPBA. The organic phase was evaporated. The residue was chromatographed on a silica gel column with benzene. Unreacted compound **7** (12 mg, 14%) was collected as the first band. Compound **15** (13 mg, 26%) was collected as the second band.

1,2,11,15,30-Penta-*tert*-butylperoxy-3,14-epoxy-4-hydroxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (15). ^1H NMR (400 MHz, $CDCl_3$): 1.31 (s, 9H), 1.35 (s, 9H), 1.42 (s, 9H), 1.55 (s, 9H), 1.63 (s, 9H), 3.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; all signals represent 1C, except where noted): 149.89, 149.46, 149.44, 149.09, 148.97, 148.89, 148.61, 148.51 (2C), 148.47, 148.41 (2C), 148.37 (3C), 148.31, 148.30 (2C), 148.28, 148.17, 148.15, 148.10, 147.86, 146.24, 145.76, 145.46, 145.34, 145.12, 144.62, 144.59, 144.23 (2C), 144.11, 143.98, 143.93, 143.83 (2C), 143.78, 143.75, 143.70, 143.66, 143.55 (2C), 143.19, 143.06, 142.99, 142.96, 142.17, 141.98, 141.32, 138.46, 137.79, 87.84 (sp^3), 86.04 (sp^3), 84.35 (sp^3), 82.23 (*C*-$(CH_3)_3$), 81.89 (*C*-$(CH_3)_3$), 81.83 (*C*-$(CH_3)_3$), 81.61 (*C*-$(CH_3)_3$), 81.37 (sp^3), 81.20 (*C*-$(CH_3)_3$), 80.69 (sp^3), 79.98 (sp^3), 74.86 (sp^3), 72.50 (*C*-OH), 27.20 ($3CH_3$), 26.96 ($3CH_3$), 26.89 ($6CH_3$), 26.70 ($3CH_3$). FT-IR (microscope): 3551, 2978, 2931, 1472, 1456, 1387, 1364, 1194, 908, 872, 734 cm^{-1}. ESI-MS (VGPlatform II): *m*/*z* (rel intens) 1216 (100, M + NH_4^+).

Chemical Correlation Experiments. Similar conditions were used in the correlation experiments. Products were isolated by column chromatography and their ^1H NMR spectra were compared

(15) CCDC-285046 and CCDC− 285047 contains the supplementary crystallographic data for compounds **6** and **11**, respectively. The crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (+44)1223−366−033; or e-mail: deposit@ccdc.cam.ac.uk).

to the above compounds to confirm their identity. The main purpose of these experiments was to identify what product could be formed, not to identify the optimal yield of the individual products. The following is an example: Compound **11** (33 mg, 0.028 mmol) was dissolved in 8 mL CH_2Cl_2. $CuBr \cdot SMe_2$ (23 mg, 0.11 mmol) and $(C_6F_5)_3B$ (14 mg, 0.028 mmol) were added. The flask was wrapped with aluminum foil. The resulting solution was stirred at 13 °C. The progress of the reaction was monitored by TLC. The reaction was stopped when a significant amount of products were formed (2.5 h). The solution was filtered through a short silica gel column to remove the solids. The filtered solution was evaporated under vacuum. The residue was chromatographed on a silica gel column with CH_2Cl_2. The first band was unreacted compound **11** (15 mg, 45%). After this band was collected, the eluent was changed to benzene and ethyl acetate (1:1). Compound **13** (4 mg, 12%) and compound **12** (5 mg, 15%) were collected as the second and third band. Then the eluent was changed to benzene and ethyl acetate (1:1). Compound **14** (5 mg, 17%) was collected as the last band.

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Supporting Information Available: Selected NMR, MS, IR, and UV−vis spectra and cif data. This material is available free of charge via the Internet at http://pubs.acs.org.

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