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Boomerang-Type Substitution Reaction: Reactivity of Fullerene Epoxides and a Halofullerenol

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Abstract: The C_s-symmetric fullerene chlorohydrin $C_{60}(Cl)(OH)(OOtBu)_4$ reacts with 4-dimethylaminopyridine (DMAP) and 1,4-diazabicyclo-[2.2.2]octane (DABCO) to yield two isomers with the formula $C_{60}(O)$-$(OOtBu)_4$ in good yields. These isomers differ with respect to the location of the epoxy functionality. The one from DMAP is C_s symmetric, whereas that from DABCO is C_1 symmetric with the epoxy group on the central pentagon. Two different mechanisms are proposed to explain the chemoselectivity of these reactions. The reaction with DMAP involves single-electron transfer as the key step; DMAP acts as the electron donor. A combination of an oxygen-atom shift and S_N2'' processes (boomerang substitution) are responsible for the formation of isomer with DACBO. Various related reactions support the proposed mechanisms. The structures of new fullerene derivatives were determined by spectroscopy, single-crystal X-ray analysis, and chemical correlation experiments.

Keywords: epoxides · fullerenes · halohydrins · peroxides · single-electron transfer

Introduction

The chemistry of fullerenes has attracted much attention during the past decade. Numerous fullerene derivatives have been prepared through various addition reactions to the fullerene double bonds. The results have revealed a series of reactivity principles, such as the mode of cyclopentadiene addition to the fullerene cage.[1a] In the light of these established principles, functional fullerene derivatives can be designed rationally and synthesized for investigations towards their application in biological and materials sciences.[1]

In spite of the rich chemistry already developed, fullerenes remain an exciting young field. New reactions and mechanisms are still being reported.[1b,c] In particular, the further transformation of fullerene derivatives can be expected to produce novel structures and reveal reactivity principles unobserved for classical organic compounds. For example, a number of unusual reactions were reported in the preparation of cage-opened fullerene derivatives[2] and azafullerene[3] derivatives. Recently, Wong and Diederich reported the first diastereoselective synthesis of enantiomeric bis- and tetrakisadducts of C_{70} by tether-directed remote functionalization.[4] Inherently stereoselective addition patterns were observed. Tajima et al. transformed the fullerene epoxide $C_{60}(O)$ into a *para* bisadduct $C_{60}Ar_2$ through Lewis acid assisted nucleophilic substitution.[5] Wang et al. reported the unexpected formation of cyclopentafullerenes from C_{60}, Et_3N, and aldehydes.[6]

We have prepared a number of fullerene mixed peroxides through the addition of $tBuOO^{\bullet}$ radicals to C_{60} and C_{70}.[7] The fullerene peroxo bonds exhibit versatile reactivity when treated with Lewis acids or irradiated.[8] As part of our continued investigation of such oxygen-rich fullerene derivatives, we report herein the conversion of a fullerene halohydrin into the fullerene epoxide by a boomerang-type mechanism, which is a combination of S_N2'' and oxygen-shift processes.

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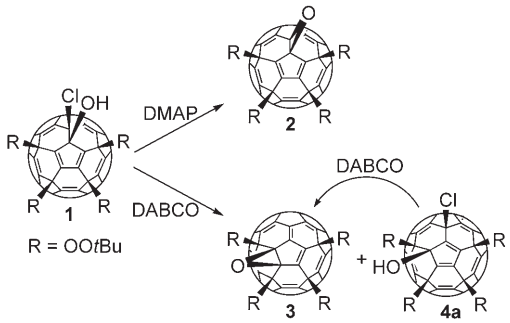
Results and Discussion

Base-Induced Reactions of Fullerene Chlorohydrins

trans Halohydrins (or *anti* halohydrins) are common precursors to epoxides in classical organic reactions. The transformation is usually performed by treating the halohydrin with a base. The base reacts with the hydroxy group to form an alkoxide, which replaces the adjacent halogen substituent. The process is an intramolecular S_N2 reaction, that is, an example of the Williamson ether synthesis.

Fullerene **1** has a rigid *cis*-chlorohydrin moiety (Scheme 1). The spherical fullerene skeleton rules out the possibility of an S_N2 process. Cleavage of the peroxo bonds appeared to be an alternative way to form the epoxy group from **1**. However, halogen replacement still took place to afford products **2** and **3** when **1** was treated with a base (Scheme 1). The four *t*BuOO groups remained unchanged in these products.



Scheme 1. Base-induced intramolecular substitution and rearrangement.

The selectivity of epoxide-formation reactions depends strongly on the choice of base. 4-Dimethylaminopyridine (DMAP) gave the C_s-symmetric epoxide **2**. 1,4-Diazabicyclo[2.2.2]octane (DABCO) mainly gave compound **3** with the epoxy moiety on the central pentagon. The isomerized product **4a** could be isolated if the reaction was stopped before all of the starting material **1** was consumed. The 1,3-chlorohydroxy functionality in **4a** showed analogous reactivity upon treatment with a base. The treatment of compound **4a** with DABCO led to epoxide **3**. In contrast to the reactions of **1**, compound **4a** reacted to give the same product **3** when treated with other bases, such as DMAP.

To optimize the yields and gather information about the reaction mechanism, various bases were tested (Table 1). Among them, pyridine, proton sponge, and sodium acetate did not give any characterizable product. Prolonged reaction times resulted in complex mixtures. Some bases promoted the formation of **3** together with **4a**. DABCO was found to be the best base for the preparation of epoxide **3**. The concentration of the solution also affects the reaction time. The reaction is slower at lower concentrations. For similar conversion and yields, reaction times of 8 min and 30 min were required for 360 mg of **1** in 4 mL of CH_2Cl_2 and 200 mg of **1** in 20 mL of CH_2Cl_2, respectively. (In both cases DABCO (3 equiv) was used.)

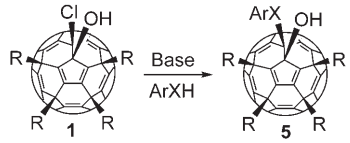
Table 1. Reaction of **1** with different bases in CH_2Cl_2.

Base[a]	Yield [%][b]		
	2	**3**	**4a**
DMAP	50	–[c]	–
DABCO	–	81	4
DBU	–	12	8
Et_3N	–	12	38
NaOH	–	59	12
pyridine	–	–	–

[a] Three equivalents of base were used in the first four entries; a larger excess of base was used for the last two entries. [b] Yield of isolated product. [c] Not detected by TLC. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

The presence of phenols or anilines in the above reactions resulted in the formation of completely different products. Instead of epoxides, only the products **5** of halogen replacement were isolated with both DABCO and DMAP (Table 2). The functional group at the *para* position of the aromatic substrates plays an important role in the reaction. In the case of phenols, unsubstituted phenol and *para*-nitrophenol did not give any observable product under the same conditions. Aniline derivatives with an electron-donating group gave products **5** in good yields. To avoid the possible formation of **2** or **3**, an excess of the phenol or aniline was added, and the mixture was stirred for 10 min before the ad-

Table 2. Base-induced intermolecular substitution reactions.



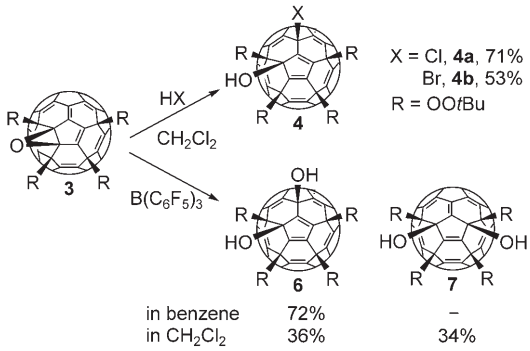
Compound	ArXH	DABCO [%]	DMAP [%]
5a	*p*-(MeO)C_6H_4OH	74	82
5b	*p*-(CHO)C_6H_4OH	84	86
5c	*p*-(MeOOC)C_6H_4OH	76	84
5d	*p*-(MeO)$C_6H_4NH_2$	70	56
5e	*p*-$MeC_6H_4NH_2$	47	60

Abstract in Chinese:
富勒烯衍生物 C_{60}(Cl)(OH)(OO*t*Bu)$_4$与 DMAP 和 DABCO 反应可以分别得到分子式均为 C_{60}(O)(OO*t*Bu)$_4$的两个同分异构体。它们的不同之处在于环氧基团的位置。DMAP 的反应可以用单电子转移反应机理来解释；而 DABCO 的反应包括氧迁移以及 S_N2"两个过程，反应机理类似“回旋镖”的飞行路线。通过谱学数据、X-射线衍射晶体结构以及相关化学反应确定了所合成新富勒烯衍生物的结构。

dition of DMAP or DABCO. No detectable product was formed with the phenols and anilines in the absence of DABCO or DMAP.

Epoxide-Opening Reactions of 3

There are many methods for opening epoxides to give various functional groups. Lewis acid catalyzed epoxide opening usually leads to the generation of carbon cations followed by nucleophilic addition. When **3** was treated with $B(C_6F_5)_3$, the bishydroxy derivatives **6** and **7** were produced (Scheme 2). The solvent is a key factor in this reaction. In

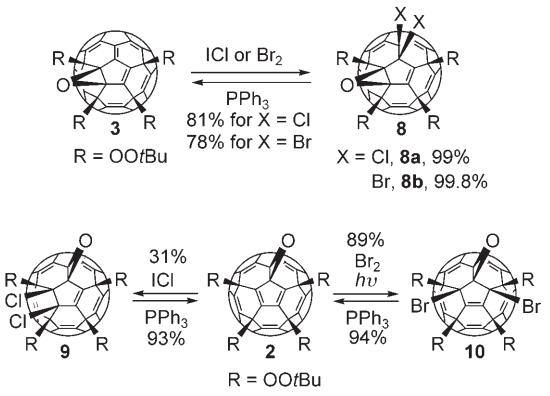


Scheme 2. Epoxide-opening reactions of **3**.

dichloromethane, both **6** and **7** were isolated in 36 and 34% yield, respectively. In benzene, compound **6** was the major product. A trace amount of water in the solvent was necessary for the formation of **6** and **7**. Gaseous hydrogen halides are also effective in opening the epoxy group in **3** to give compounds **4**. The reaction of aqueous hydrochloric acid with **3** gave a complex mixture. The reaction of compound **2** with hydrogen halides and $B(C_6F_5)_3$ gave C_s-symmetric halohydrin or fullerenediol derivatives.[8c,d]

Halogenation of 2 and 3

The halogenation of fullerenes has been well-studied.[9] Complex multihalofullerene adducts have been characterized by single-crystal X-ray analysis. In an effort to grow suitable crystals for X-ray analysis and also to test their reactivity towards further addition, compounds **2** and **3** were treated with ICl and Br_2 (Scheme 3). The reaction gave the two analogous dihalofullerene derivatives **8a** and **8b** for compound **3**. The dichloro derivative **8a** is very stable and can be stored for months with little change, but the dibromo analogue **8b** decomposes slowly during storage. In the case of compound **2**, both chlorination and bromination occurred on the central cyclopentadiene moiety to yield the vicinal dichloro adduct **9** and the C_s-symmetric dibromo adduct **10**, respectively. The C_s-symmetric dibromo derivative **10** is the thermodynamic product. Steric hindrance would be very



Scheme 3. Halogenation and dehalogenation reactions of **2** and **3**.

high for the formation of the vicinal dibromo analogue of **9**. All four dihalofullerenes reacted with PPh_3 to return to the corresponding halogen-free precursors in good yields (>70%). As expected, the dihalofullerene derivatives showed better crystallization properties. Single crystals of compounds **8a** and **10** were obtained (see next section).

X-ray Crystal Structure of Compounds 6, 8a, and 10

Various methods were used to grow suitable crystals. The slow evaporation of a mixture of solvents appeared to be the most-efficient method for the present compounds. Single crystals were obtained from CH_2Cl_2/EtOH for **6**, and CS_2/EtOH for **8a** and **10**. There is no disorder in the crystals except for the presence of one ethanol solvent molecule in the lattice of compound **10**.

The X-ray crystal structures[10,11,12] are in agreement with the assignments made on the basis of NMR spectroscopy (Figure 1). The bonding distances show the expected pattern. The double bonds on the unique central pentagon (around 1.34 Å) are slightly shorter than the other fullerene double bonds on the cage (around 1.4 Å). Single bonds with two adjacent addends are relatively longer. For example, the single bond in **8a** with the two adjacent Cl atoms has a length of 1.579 Å. The two Br–C bonds in **10** have slightly different lengths as a result of the crystal packing (1.987 and 2.022 Å). These Br–C bonds are essentially the same length as those reported for $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$, which appear in the narrow range of 1.98–2.02 Å.[13]

Space-filling models show that the central pentagon is quite crowded in these compounds. The distance between the two Br atoms is 3.52 Å, which indicates a close contact. Relative to those of the other pyramidalized sp^2-hybridized fullerene carbon atoms, the sp^2 orbitals of the unsaturated carbon atoms on the central pentagon show less deviation from planar geometry. The torsion angles of the sp^2 orbitals of the unsaturated carbon atoms on the central pentagon range from 160° for **7** to 173° for **10**; these torsion angles are considerably larger than those of the other sp^2-hybridized fullerene carbon atoms (around 140°).

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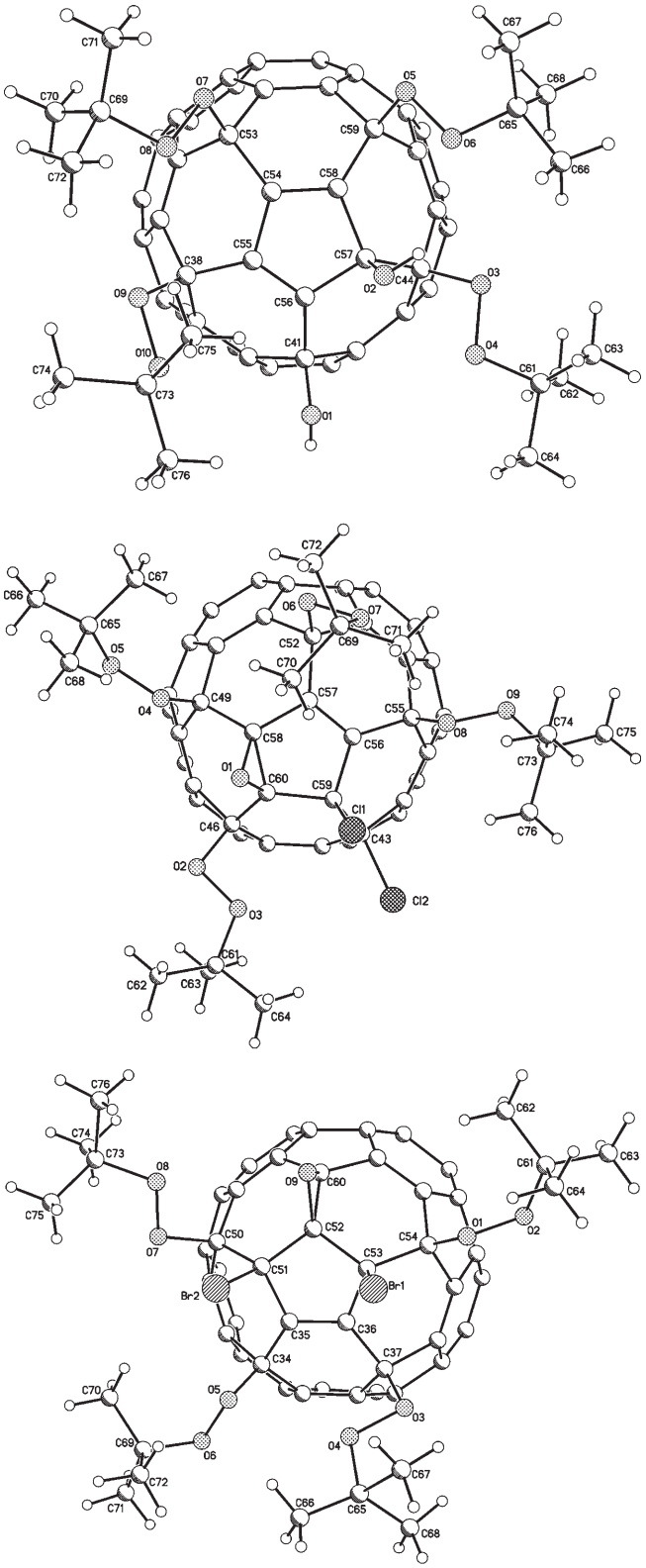


Figure 1. Single-crystal molecular structures of **6** (top), **8a** (middle), and **10** (bottom); for clarity, some atoms of the C_{60} cages are omitted.

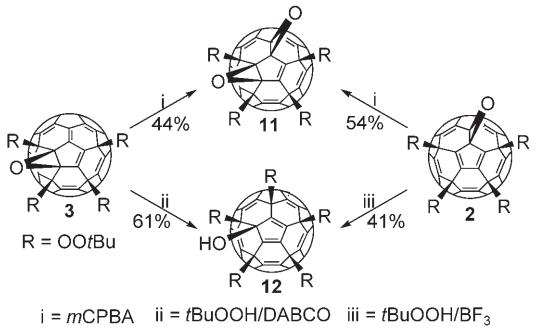
Spectroscopic Data and Structure Assignment

Except for the above three compounds, the structures of all new fullerene derivatives reported herein were assigned on the basis of their spectroscopic data. Chemical correlation experiments were also carried out to confirm the structures. It was relatively easy to deduce the correct structural formulae. In the ESIMS spectra, the most intense signal was usually that of the molecular ion. A combination of ^{1}H and ^{13}C NMR spectroscopic data indicated which groups were attached to the fullerene cage. The relative locations of the addends were assigned by comparison of the NMR spectra with those of analogous compounds whose structure had been determined by X-ray crystallography, and by chemical correlation experiments.

*Compounds **3**, **8**, **9**, and **10***

For the C_1-symmetric compounds **3**, **8**, and **9**, NMR spectroscopic data alone could not be used to determine the relative locations of the addends. The single-crystal structure of the dichloro adduct **8a** was a breakthrough. The treatment of **8a** with PPh_3 reproduced its precursor **3**. Similarly, the treatment of the dibromo analogue **8b**, dichloro isomer **9**, and dibromo isomer **10** with PPh_3 led to dehalogen1ation and the formation of the corresponding precursor **3** or **2** (Scheme 3). These results support the structure of **3** as depicted.

The structure of **3** was further confirmed by the chemical correlation reactions shown in Scheme 4. Compounds **2** and **3** both reacted to give the same bisepoxide derivative **11**



Scheme 4. Correlation reactions of **2** and **3**.

when treated with *m*-chloroperbenzoic acid (*m*CPBA). Similarly, the known compound **12**[8a] could be obtained from both **2** and **3**. Isomer **3** exhibits more facile reactivity than **2** in these reactions. The unique 6,6-junction double bond connected to the central pentagon appears to be the more-reactive site, in agreement with the general pattern of fullerene addition reactions. For example, the formation of **11** in 54% yield from **2** took 30 h, whereas only 10 min was needed for **11** to form in 44% yield from **3** under similar conditions. These data are in agreement with the structure of **3** as depicted.

The ^{13}C NMR chemical shifts of the epoxy moiety in **3** appeared at 66.8 and 68.4 ppm, at higher field than those for C_s-symmetric **2** (71.4 and 75.8 ppm). This difference may be due to the shielding effect of the adjacent *t*BuOO groups in

3. The dichlorofullerene derivative **9** is an isomer of **8a**, which was characterized by X-ray crystallography. In the ^{13}C NMR spectrum of **9**, there are two signals due to sp^3-hybridized fullerene carbon atoms at 56.9 and 57.7 ppm, which may be assigned to the two chloro-substituted carbon atoms. These signals appear at higher field than the corresponding signals for isomer **8a**. This difference can also be explained by the shielding effect of surrounding *t*BuOO groups.

*Compounds **5***

The structures of compounds **5** were deduced from the pattern in their NMR spectra characteristic of compounds with C_s symmetry and from their HMBC spectra. As expected, there were 28 signals (a few of which overlapped) in the ^{13}C NMR spectra in the region for sp^2-hybridized fullerene carbon atoms and four C(sp^3) fullerene signals. The HMBC spectrum of **5a** showed a correlation between the OH hydrogen atom and the sp^2-hybridized fullerene carbon atom on the central pentagon at 155.3 ppm (Figure 2). An analogous HMBC spectrum was reported previously for compound **1**, which has been characterized by X-ray crystallographic analysis.[8c]

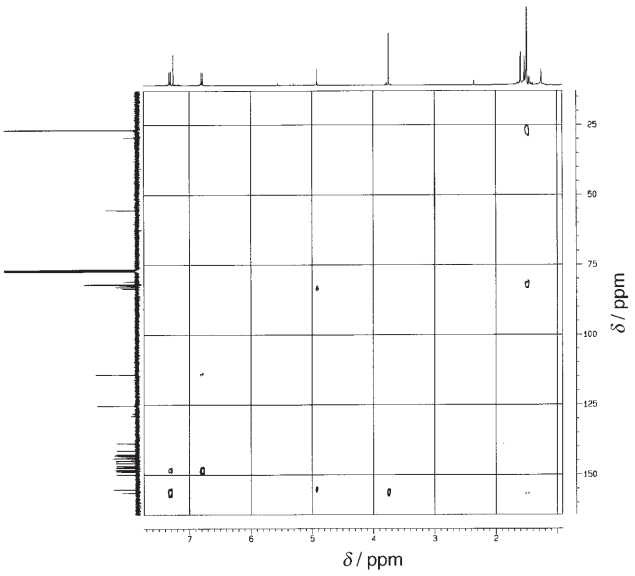
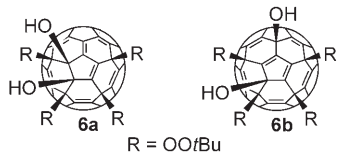


Figure 2. HMBC spectrum of compound **5a**.

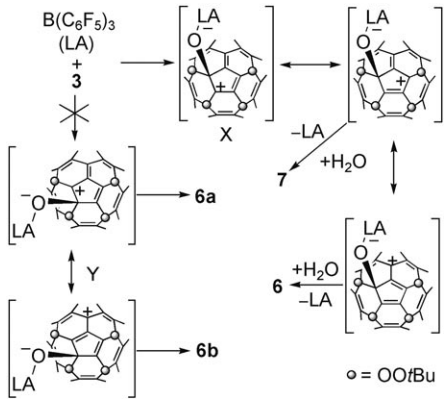
*Compounds **4**, **6**, and **7***

There are two OH signals at 3.4 and 5.1 ppm in the ^1H NMR spectrum of the fullerenediol derivative **6**. These signals correlate to sp^2 fullerene signals at 140.6 and 155.9 ppm, respectively, in the HMBC spectrum. The signal at 5.1 ppm should correspond to the OH group on the central pentagon. This hydroxy group forms a hydrogen bond with the adjacent *t*BuOO group, which results in the downfield shift with respect to the other OH signal. The NMR spectroscopic data agree with the structure depicted for **6**, but did not rule out isomers **6a** and **6b** (Scheme 5). Compound **6b**, in particular, could have a similar pattern in the NMR spectrum. Fortunately, the X-ray crystal structure of **6** was obtained, as discussed above.



Scheme 5. Possible isomeric structures of compound **6**.

The preference for the formation of **6** and **7** over **6a** and **6b** may be due to the different stabilities of the corresponding fullerene-cation precursors shown in Scheme 6. Both



Scheme 6. Proposed cationic intermediates in the epoxide-opening reactions of **3**. LA = Lewis acid.

steric hindrance and the resonance-stabilization energy favor the opening of the epoxide to form X rather than Y. Cation X has three resonance structures, whereas Y has two resonance structures (without considering the conjugation effect outside the central-pentagon area, which is the same for both X and Y). The bulky Lewis acid tris(pentafluorophenyl)boron is further away from the crowded center in X than in Y.

Compound **7** was isolated when CH_2Cl_2 was used as the solvent, but not from the reaction in benzene. The polar solvent could stabilize the cationic intermediate and thus accelerate the opening of the epoxide and the addition of water. Therefore, the intermediate could be trapped to form the sterically disfavored compound **7** in CH_2Cl_2. The reaction time was 50 min and 26 h, respectively, in CH_2Cl_2 and benzene. Stable fullerene cations have been reported.[14]

The chemical shifts for the OH hydrogen atoms in the ^1H NMR spectra of **4a** and **4b** are almost identical at 5.1 and 5.2 ppm, and essentially the same as that of the analogous OH group in **6**. Furthermore, the ^{13}C NMR spectra of these three compounds show the same pattern (Figure 3). The only major difference lies in the chemical shifts of the sp^3-hybridized fullerene carbon atoms bonded to the OH, Cl, and Br groups. These signals appear at 73.7, 57.6, and

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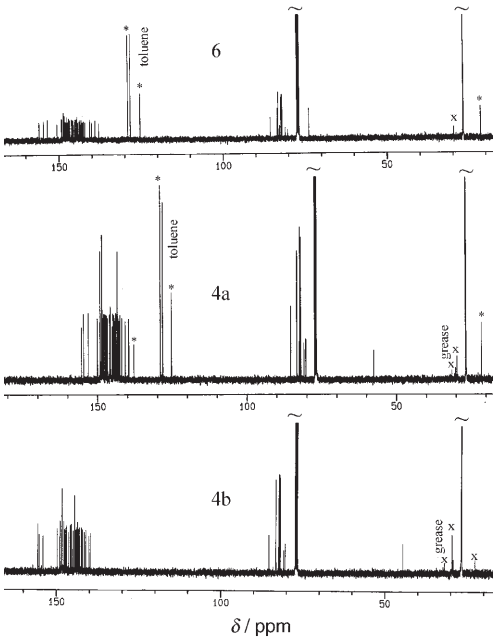


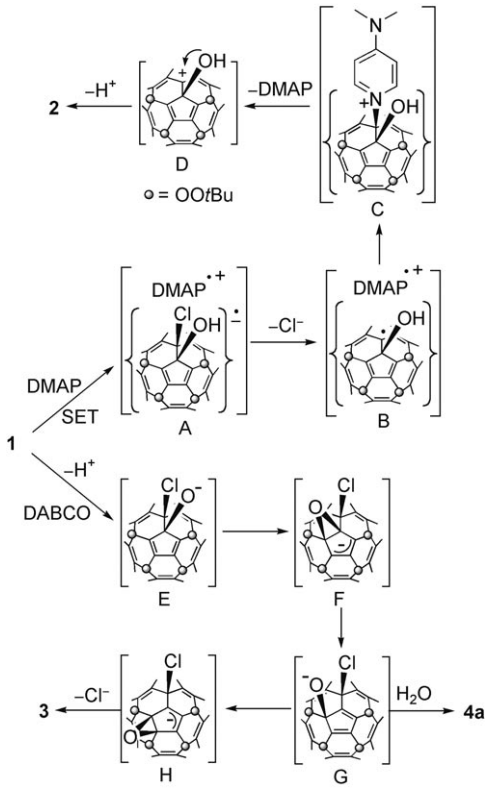
Figure 3. ^{13}C NMR spectra of compounds **6**, **4a**, and **4b**.

44.5 ppm, respectively, for compounds **6**, **4a**, and **4b**. It is reasonable to assume that the structures of **4a** and **4b** are analogous to that of **6**. The fullerenediol isomer **7** has C_s symmetry. The signal for the hydrogen atoms of the OH groups appears at 5.3 ppm in the ^1H NMR spectrum. This chemical shift is comparable to that of the OH group on the central pentagon of **6**.

Mechanistic Considerations

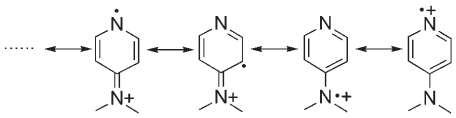
Compounds **2** and **3** are isomers that differ only with respect to the location of the epoxy group. To explain their formation, two possible pathways are proposed in Scheme 7. The DMAP-induced formation of **2** involves a single-electron transfer (SET) as the key step to form the radical-ion-pair intermediate A. Cleavage of a chloride ion from A then results in the fullerene-radical species B, which couples with the DMAP radical cation to form C. Cleavage of neutral DMAP from C results in the fullerene cation D. Deprotonation in the final step leads to compound **2**. Thus, DMAP acts as both the SET initiator and the base that neutralizes the hydrochloride by-product.

The SET pathway above is reminiscent of the $S_{RN}1$ mechanism, in which a radical R· is formed through the reductive cleavage of an R–X bond and then reacts with the nucleophile.[15] Fullerenes are known electron acceptors and could react with amines through SET processes. Komatsu and coworkers reported the $S_{RN}1$ mechanism in substitution reactions of alkylated fullerene chloride $C_{60}(R)Cl$ with 1,8-bis(dimethylamino)naphthalene.[16] In their proposed mechanism, the C–Cl bond is cleaved to form a fullerene-radical intermediate by an SET process between $C_{60}(R)Cl$ and 1,8-bis(dimethylamino)naphthalene. In the present reaction,



Scheme 7. Possible pathways for the formation of **2** and **3**.

DMAP donates the electron to form the DMAP cation radical, which may be stabilized through several resonance structures, as shown in Scheme 8.

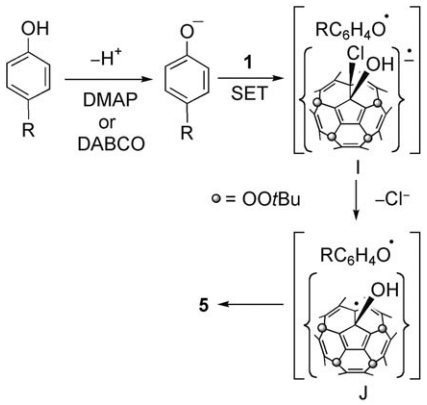


Scheme 8. Resonance structures of the DMAP cation radical.

Unlike DMAP, the aliphatic tertiary amine DABCO simply acts as a base in the reaction with **1**. There is no resonance structure to stabilize a DABCO cation radical. Therefore, instead of SET, the first step is deprotonation of the hydroxy group to form the fullerene oxide intermediate E (Scheme 7). The oxygen-centered anion adds to a neighboring double bond to form the fullerene-centered allyl anion F. The opening of the epoxy group in F generates another oxygen-centered anion G. The isolation of **4a** is a clear indication of the presence of G. In a similar way to the formation of F, H is formed through G. Loss of a chloride ion from H completes the boomerang-type substitution and formation of epoxide **3**. The formation of epoxide **3** from intermediate G is a typical S_N2'' process. The fluorine atom in fluorofullerenes can be replaced in an S_N2'' process, as reported by Taylor and co-workers.[17]

The SET process that leads to **2** is faster than the boomerang substitution that leads to **3**. As mentioned earlier, the reaction rate depends on the concentration of the reaction mixture. To eliminate the concentration effect, **1** was treated with an excess of a 1:1 mixture of DMAP and DABCO. Only **2** was observed as a product. This phenomenon is in agreement with the fact that none of compound **3** was detected in the DMAP reaction, even though DMAP, like DABCO, is basic enough to deprotonate **1**.

In the presence of an excess of a phenol or aniline, the SET process is the preferred key step regardless of the base. Both DMAP and DABCO induce the replacement of the chloro substituent with the aromatic group. The formation of compounds **5** may be considered to be an $S_{RN}1$ reaction (Scheme 9). The first step is probably the deprotonation of



Scheme 9. Possible pathway for the formation of **5**.

the phenol to form the phenoxide, which is a stronger electron donor. The acidity of the phenol should be in the right range to achieve the required balance between facile deprotonation of the phenol and the electron-donating ability of the resulting phenoxide. Unactivated phenols, such as PhOH, are not acidic enough to be deprotonated efficiently for the reaction described. Strongly acidic phenols, such as *p*-nitrophenol, can be deprotonated readily, but the corresponding anion could not be oxidized by **1** and is also a weak nucleophile. The electron-donating methoxy group in 4-methoxyphenol is not beneficial for the deprotonation step. However, the methoxy group may stabilize the phenoxy radical through resonance and thus provide the driving force for the formation of **5a**.

In the reactions with anilines, SET may be the first step to form an amino radical cation, which is less basic and may be deprotonated by DMAP or DABCO. In the absence of a strong base, anilines hardly reacted with **1**, which indicates the importance of the deprotonation step. Aliphatic amines are very reactive towards the fullerene halohydrin **1** and cause cleavage of peroxo bonds as well as halogen replacement.[18] Reactions of aliphatic amines with pristine fullerene have been well documented and have been shown to involve SET processes.[19]

Epoxides **2** and **3** were not observed under the conditions used for the formation of **5**. It is unlikely that the epoxides were formed as intermediates in the formation of **5**. The treatment of the pure epoxide **2** with a phenol or aniline and DMAP also gives **5**, but in much lower yields. For example, **5a** was prepared in 45% yield from **2** and 82% yield from **1**. The much higher yield of **5** when prepared from **1** indicates that the pathway shown in Scheme 9 is the major, if not the only, route.

We reported previously the preparation of alkoxy analogues of **5** through Lewis acid catalyzed ring opening of epoxide **2** in the presence of an alcohol, such as methanol.[8a] The mechanism involves a fullerene cation. The phenoxy derivative **5** could not be obtained under the same conditions. Phenol is apparently not an efficient nucleophile under acidic conditions. The greater nucleophilicity of alkoxy anions relative to phenoxy anions towards these fullerene derivatives is consistent with that observed in classical nucleophilic-substitution reactions.[20]

Conclusions

The reactivity of the fullerene chlorohydrin **1** towards a base depends on the redox potential and basicity of the base. SET is the dominant process if the base can be oxidized by the chlorofullerenol. Weak bases, such as anilines, are relatively inert unless assisted by another base. Strong bases react with the chlorofullerenol to form a fullerene epoxide through a boomerang-type substitution mechanism, which combines S_N2'' and oxygen-atom-shift pathways. To our knowledge, such a mechanism is unprecedented. The unique spherical structure of **1** and the isolated 1,4-diene moiety on the central pentagon are essential for such a mechanism. Further studies on the chemical reactivity of the new fullerene peroxide derivatives are in progress.

Experimental Section

General

NMR spectra were recorded on a Bruker ARX 400 spectrometer at room temperature (298 K). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESIMS spectra were recorded on a LCQ Decaxp Plus Spectrometer with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent; positive-mode spectra were recorded, unless otherwise noted. FTIR spectra were recorded on a Nicolet Magna-IR 750 instrument in the microscope mode. All reagents were used as received. The reactions were carried out in air. The TLC plates used were Macherey–Nagel silica gel 60 UV254. Chromatographic purifications were carried out with silica gel of mesh 160–200 or 200–300. Compound **1** was prepared as in reference [8a].

Caution: A large amount of peroxide is involved in some reactions; therefore, care must be taken to avoid possible explosions.

Syntheses

2:[21] DMAP (20 mg, 0.18 mmol) was added to a solution of **1** (58 mg, 0.05 mmol) in CH_2Cl_2 (8 mL), and the resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 70 min, the solution was transferred directly

onto a short column of silica gel and eluted quickly with toluene. The eluted mixture was concentrated and dissolved in toluene. The solution in toluene was purified by column chromatography on silica gel with toluene as the eluent to give **2** (28 mg, 50%) as the first band. The remaining starting material **1** was eluted as the second band (13 mg). The product **2** was characterized by comparing its R_f and ^{1}H NMR spectrum with those reported; see reference [7a] for full characterization data. Note: the reaction rate depends on the concentration of the solution. A complex mixture resulting from overreaction was obtained in less than 3 min at a concentration of 200 mg of **1** in 5 mL of CH_2Cl_2.

3: DABCO (99 mg, 0.88 mmol) was added to a solution of **1** (335 mg, 0.30 mmol) in freshly distilled CH_2Cl_2 (3 mL), and the resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 8 min, the solution was transferred directly onto a short column of silica gel and eluted quickly with toluene. The eluted mixture was concentrated and dissolved in toluene. The solution in toluene was purified by column chromatography on silica gel column with toluene as the eluent to give **3** (262 mg, 81%) as the first band. A small amount of **1** (3 mg) was eluted as the second band, and **4a** was eluted as the third band (12 mg, 4%; for the preparation of **4a**, see below). FTIR (microscope): $\tilde{\nu}$ = 2978, 2928, 1462, 1387, 1363, 1261, 1243, 1193, 1141, 1104, 1045, 1015, 872 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.50 (s, 9H), 1.455 (s, 9H), 1.452 (s, 9H), 1.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 150.6, 150.1, 149.4, 148.9, 148.9, 148.8, 148.7, 148.6, 148.4, 148.0, 148.0, 147.9, 147.8, 147.7 (4C), 147.5, 147.3, 147.3, 147.0, 146.8, 146.6, 146.6, 146.5, 146.4 (2C), 146.2, 145.5, 145.1, 144.7, 144.7, 144.6, 144.6, 144.5, 144.2 (2C), 144.2, 144.2, 144.0, 143.8, 143.6, 143.4 (2C), 143.3, 143.2, 143.0, 142.6, 142.5, 141.8, 141.1, 138.8, 138.0, 137.6, 84.9, 82.4, 82.0 (C-$(CH_3)_3$), 82.0 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 81.4, 81.1, 68.4, 66.8, 26.8 ($3CH_3$), 26.8 ($3CH_3$), 26.7 ($3CH_3$), 26.7 ppm ($3CH_3$); MS (ESI): m/z (%): 1110 (100) $[M+NH_4]^+$.

4a: Anhydrous HCl was bubbled into a solution of **3** (87 mg, 0.08 mmol) and Bu_4NCl (20 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (10 mL), and the resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 4 h, petroleum ether (60–90 °C; 10 mL) was added, and the mixture was transferred onto a column of silica gel and eluted with toluene and petroleum ether (2:1). A small amount of the starting material **3** (6 mg) was eluted as the first band. The product **4a** (64 mg, 71%) was eluted as the second band. FTIR (microscope): $\tilde{\nu}$ = 3511, 2979, 2930, 2871, 1387, 1364, 1192, 1120, 1100, 1085, 1051, 1020, 1008, 909, 872, 841, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.15 (s, 1H), 1.51 (s, 9H), 1.48 (s, 9H), 1.45 (s, 9H), 1.41 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 155.3, 154.6, 153.1, 150.1, 149.1, 149.1 (2C), 149.0, 148.6, 148.5 (3C), 148.5, 148.4 (2C), 148.4, 148.1, 147.9, 147.9, 147.5, 147.5, 147.4, 147.3, 147.3, 147.0, 147.0, 146.7, 145.9, 145.8, 145.7 (2C), 145.6, 145.1, 144.9, 144.8, 144.5, 144.4, 144.3, 144.2, 143.9, 143.9, 143.8, 143.4 (2C), 143.3, 143.0, 143.0, 143.0, 142.8, 142.5, 141.9, 140.7, 139.7, 139.6, 85.4, 83.3, 83.3 ($C(CH_3)_3$), 82.6, 82.3 ($C(CH_3)_3$), 82.2 (C-$(CH_3)_3$), 82.0 ($C(CH_3)_3$), 80.9, 80.4, 57.6, 26.8 ($3CH_3$), 26.8 ($6CH_3$), 26.7 ppm ($3CH_3$); MS (ESI): m/z (%): 1146 (100) $[M+NH_4]^+$.

4b: An excess of a saturated solution of HBr in anhydrous CH_2Cl_2 (2 mL; freshly prepared by bubbling HBr into CH_2Cl_2) was added to a solution of **3** (126 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 5 min, petroleum ether (60–90 °C; 10 mL) was added, and the mixture was transferred onto a column of silica gel and eluted with toluene and petroleum ether (2:1). A small amount of the starting material **3** (5 mg) was eluted as the first band. The product **4b** (72 mg, 53%) was eluted as the second band. FTIR (microscope): 3512, 2979, 2929, 1473, 1456, 1387, 1364, 1192, 1104, 1051, 1020, 1008, 872, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.16 (s, 1H), 1.52 (s, 9H), 1.47 (s, 9H), 1.45 (s, 9H), 1.42 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 155.7, 155.4, 154.1, 149.9, 149.0, 149.0, 149.0 (2C), 148.5 (2C), 148.4 (2C), 148.4 (3C), 148.3, 147.9, 147.8, 147.8, 147.5, 147.4, 147.3, 147.2, 147.2, 147.0, 146.9, 146.4, 145.8, 145.8, 145.7, 145.6, 145.5, 145.0, 144.6 (2C), 144.5, 144.5, 144.3, 144.2, 144.0, 143.9, 143.7, 143.7, 143.5, 143.3, 143.0, 143.0, 142.5, 142.2, 142.1, 141.6, 141.2, 140.2, 139.8, 85.4, 83.3 ($C(CH_3)_3$), 83.3, 82.5, 82.3 ($C(CH_3)_3$), 82.2 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 80.9, 80.4, 44.6, 26.8 ($6CH_3$), 26.7 ($3CH_3$), 26.7 ppm ($3CH_3$); MS (ESI): m/z (%): 1190 (85) $[M+NH_4]^+$, 1192 (100).

5a: Method A: 4-Methoxyphenol (28 mg, 0.23 mmol) was added to a solution of **1** (50 mg, 0.04 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 10 min, then DMAP (27 mg, 0.22 mmol) was added, and the resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 2 h, the solution was transferred directly onto a short column of silica gel and eluted quickly with chloroform. The eluted mixture was concentrated and dissolved in toluene. The solution in toluene was purified by column chromatography on silica gel with toluene as the eluent to give **5a** (44 mg, 82%) as the major product. Method B: The major difference from method A was that DABCO was used in place of DMAP. 4-Methoxyphenol (11 mg, 0.09 mmol) was added to a solution of **1** (20 mg, 0.02 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 10 min, then DABCO (4 mg, 0.04 mmol) was added, and the resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 8 h, the solution was transferred directly onto a short column of silica gel and eluted quickly with chloroform. The eluted mixture was concentrated and dissolved in toluene. The solution in toluene was purified by column chromatography on silica gel with toluene as the eluent to give **5a** (16 mg, 74%) as the major product. FTIR (microscope): $\tilde{\nu}$ = 3527, 2979, 2931, 1504, 1387, 1364, 1246, 1205, 1194, 1099, 1046, 1021, 993, 908, 872, 836, 733 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.31 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 9.0 Hz, 2H), 4.91 (s, 1H), 3.75 (s, 3H), 1.492 (s, 18H), 1.489 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; a few signals overlapped, and it was not possible to assign the aromatic carbon atoms unambiguously): δ = 156.4, 155.3, 149.9, 149.0, 149.0, 148.8, 148.6, 148.5, 148.4, 148.4, 148.3, 147.6, 147.5, 147.4, 147.3, 147.2, 146.9, 145.8, 145.1, 144.9, 144.4, 144.4, 144.3, 143.9, 143.8, 143.3, 143.0, 142.7, 141.3, 138.7, 125.4, 114.2, 83.6, 82.9, 82.4, 82.1 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 80.9, 55.4, 26.8 ($6CH_3$), 26.8 ppm ($6CH_3$); MS (ESI): m/z (%): 1239 (100) $[M+Na]^+$.

5b: Method A: The same procedure was used as for **5a**. Reactants: **1** (50 mg, 0.04 mmol), 4-hydroxybenzaldehyde (27 mg, 0.22 mmol), DMAP (27 mg, 0.22 mmol); reaction time: 2.5 h; yield of **5b**: 46 mg, 86%. Method B: The same procedure was used as for **5a**. Reactants: **1** (20 mg, 0.02), 4-hydroxybenzaldehyde (11 mg, 0.09 mmol), DABCO (4 mg, 0.04 mmol); reaction time: 5 h; yield of **5b**: 18 mg, 84%. FTIR (microscope): 3528, 2979, 2931, 1701, 1597, 1502, 1387, 1364, 1241, 1222, 1192, 1159, 1098, 1048, 1020, 1000, 865 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.95 (s, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 4.82 (s, 1H), 1.52 (s, 18H), 1.51 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; a few signals overlapped, and it was not possible to assign the aromatic carbon atoms unambiguously): δ = 190.9 (CHO), 161.6, 155.2, 149.8, 149.1, 149.1, 148.6, 148.6, 148.5, 148.4, 148.4, 147.7, 147.6, 147.4, 147.3, 147.1, 146.9, 145.8, 144.9, 144.7, 144.6, 144.5, 144.2, 144.0, 143.4, 142.9, 142.9, 141.2, 138.6, 132.1, 131.4, 122.3, 83.9, 82.6 ($C(CH_3)_3$), 82.4, 82.0 (C-$(CH_3)_3$), 80.9, 26.8 ($6CH_3$), 26.8 ppm ($6CH_3$); MS (ESI): m/z (%): 1237 (100) $[M+Na]^+$.

5c: Method A: The same procedure was used as for **5a**. Reactants: **1** (50 mg, 0.04 mmol), 4-hydroxybenzoic acid methyl ester (35 mg, 0.23 mmol), DMAP (27 mg, 0.22 mmol); reaction time: 2 h; yield of **5c**: 45 mg, 84%. Method B: The same procedure was used as for **5a**. Reactants: **1** (50 mg, 0.04), 4-hydroxybenzoic acid methyl ester (35 mg, 0.23 mmol), DABCO (10 mg, 0.09 mmol); reaction time: 2 h; yield of **5c**: 42 mg, 76%. FTIR (microscope): $\tilde{\nu}$ = 3529, 2980, 2932, 1722, 1602, 1504, 1435, 1388, 1364, 1278, 1224, 1192, 1169, 1111, 1099, 1050, 1020, 1001, 909, 869, 770, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 4.79 (s, 1H), 3.87 (s, 3H), 1.50 (s, 18H), 1.49 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; a few signals overlapped, and it was not possible to assign the aromatic carbon atoms unambiguously): δ = 166.6, 160.1, 155.2, 149.8, 149.1, 149.0, 148.6, 148.5, 148.5, 148.4, 148.4, 147.7, 147.6, 147.4, 147.3, 147.1, 146.9, 145.8, 144.7, 144.7, 144.7, 144.4, 144.4, 144.2, 143.9, 143.4, 143.0, 142.8, 141.2, 138.7,

131.2, 125.7, 122.5, 83.8, 82.5, 82.5 ($C(CH_3)_3$), 82.4, 81.9 ($C(CH_3)_3$), 80.9, 52.0, 26.8 ppm (12 CH_3); MS (ESI): *m/z* (%): 1267 (100) $[M+Na]^+$.

5d: Method A: The same procedure was used as for **5a**. Reactants: **1** (20 mg, 0.02 mmol), 4-methoxyphenylamine (11 mg, 0.09 mmol), DMAP (11 mg, 0.09 mmol); reaction time: 3 h; yield of **5d**: 12 mg, 56%. Method B: The same procedure was used as for **5a**. Reactants: **1** (20 mg, 0.02 mmol), 4-methoxyphenylamine (11 mg, 0.09 mmol), DABCO (4 mg, 0.04 mmol); reaction time: 2 h; yield of **5d**: 15 mg, 70%. FTIR (microscope): $\tilde{\nu}$ = 3499, 3332, 2979, 2931, 2833, 1510, 1464, 1387, 1364, 1243, 1193, 1101, 1046, 1021, 1006, 909, 870, 830, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.23 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 5.86 (s, 1H), 4.75 (s, 1H), 3.73 (s, 3H), 1.50 (s, 18H), 1.49 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; a few signals overlapped, and it was not possible to assign the aromatic carbon atoms unambiguously): δ = 155.9, 155.3, 150.4, 150.3, 149.1, 148.9, 148.5, 148.5, 148.4, 148.3, 147.5, 147.3, 147.2, 146.9, 145.9, 145.0, 144.8, 144.3, 144.1, 143.8, 143.4, 142.9, 142.4, 141.5, 137.5, 137.3, 124.6, 114.3, 82.6, 82.3, 82.1 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 81.0, 69.1, 55.3, 26.8 (6 CH_3), 26.8 ppm (6 CH_3); MS (ESI): *m/z* (%): 1216 (100) $[M+H]^+$.

5e: Method A: The same procedure was used as for **5a**. Reactants: **1** (20 mg, 0.02 mmol), 4-methylphenylamine (9 mg, 0.08 mmol), DMAP (10 mg, 0.08 mmol); reaction time: 3 h; yield of **5d**: 13 mg, 60%. Method B: The same procedure was used as for **5a**. Reactants: **1** (20 mg, 0.02 mmol), 4-methylphenylamine (9 mg, 0.08 mmol), DABCO (4 mg, 0.04 mmol); reaction time: 3 h; yield of **5e**: 10 mg, 47%. FTIR (microscope): $\tilde{\nu}$ = 3499, 3382, 2978, 2928, 2867, 1514, 1465, 1387, 1364, 1243, 1193, 1110, 1070, 1047, 1020, 1007, 909, 868, 813, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.24 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 5.74 (s, 1H), 4.87 (s, 1H), 2.26 (s, 3H), 1.50 (s, 18H), 1.49 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; a few signals overlapped, and it was not possible to assign the aromatic carbon atoms unambiguously): δ = 155.1, 150.4, 150.4, 149.1, 148.9, 148.5, 148.4, 148.4, 148.4, 147.6, 147.3, 147.3, 146.9, 145.9, 145.0, 145.0, 144.9, 144.3, 144.2, 143.8, 143.4, 143.0, 142.4, 141.7, 141.5, 137.5, 132.4, 129.7, 122.0, 82.6, 82.3, 82.1 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 81.0, 68.8, 26.8 (6 CH_3), 26.8 (6 CH_3), 20.8 ppm (CH_3); MS (ESI): *m/z* (%): 1200 (100) $[M+H]^+$.

6: Method A: Tris(pentafluorophenyl)boron (72 mg, 0.14 mmol) was added in three portions at 12-h intervals to a solution of **3** (152 mg, 0.14 mmol) in benzene (30 mL), and the resulting mixture was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 26 h, the solution was transferred directly onto a column of silica gel and eluted with toluene. The remaining starting material **3** (25 mg) was eluted as the first band. The eluent was then changed to toluene/ethyl acetate (20:1), and **6** (111 mg, 72%) was eluted as the second band. Method B: Tris(pentafluorophenyl)boron (22 mg, 0.04 mmol) was added to a solution of **3** (50 mg, 0.046 mmol) in freshly distilled CH_2Cl_2 (3 mL), and the resulting mixture was stirred at room temperature in the dark in air. The progress of the reaction was monitored by TLC. After about 50 min, the solution was transferred directly onto a column of silica gel and eluted with CH_2Cl_2. The remaining starting material **3** (8 mg) was eluted as the first band, **7** (17 mg, 34%) as the second band, and **6** (18 mg, 36%) as the third band. FTIR (microscope): $\tilde{\nu}$ = 3508, 2979, 2928, 1464, 1387, 1364, 1243, 1192, 1122, 1099, 1047, 1023, 1007, 909, 872, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.05 (s, 1H), 3.41 (s, 1H), 1.51 (s, 9H), 1.49 (s, 9H), 1.44 (s, 9H), 1.39 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 155.9, 154.6, 153.4, 150.5, 149.1, 149.1, 149.1, 149.0, 148.6, 148.5, 148.5, 148.4, 148.2, 148.2, 148.2, 147.9, 147.7, 147.6, 147.5, 147.4, 147.4, 147.3, 147.2, 146.9, 146.8, 146.7, 146.6, 146.0, 145.8, 145.7, 145.5, 145.1, 145.1, 144.9, 144.6, 144.5, 144.4, 144.4, 144.2, 143.8, 143.7, 143.5, 143.4, 143.3, 143.0, 143.0, 143.0, 142.7, 142.4, 142.0, 140.6, 139.9, 138.9, 85.5, 83.3 , 83.1 ($C(CH_3)_3$), 82.6, 82.2 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 80.9, 80.3, 73.8, 26.8 (3 CH_3), 26.7 (6 CH_3), 26.7 ppm (3 CH_3); MS (ESI): *m/z* (%): 1128 (100) $[M+NH_4]^+$.

7: See method B for the preparation of **6**. FTIR (microscope): $\tilde{\nu}$ = 3518, 2979, 2931, 1463, 1387, 1364, 1243, 1191, 1109, 1084, 1064, 1019, 1005, 908, 871, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.30 (s, 2H), 1.43 (s, 18H), 1.41 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 2C unless otherwise noted): δ = 149.8, 149.2, 149.1, 148.9, 148.8, 148.7 (3C), 148.7, 148.3 (1C), 148.3, 148.0 (1C), 147.9, 147.7, 147.7, 147.1, 146.8, 145.3, 144.9, 144.9, 144.7, 144.3, 144.3, 143.3 (4C), 143.3, 143.2, 141.1, 138.4, 125.9 (1C), 86.7, 82.8, 81.9 ($C(CH_3)_3$), 81.7 ($C(CH_3)_3$), 80.8, 26.7 ppm (12 CH_3); MS (ESI): *m/z* (%): 1128 (100) $[M+NH_4]^+$.

8a: An anhydrous solution of ICl (160 mg, 0.99 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **3** (268 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 3 min, a saturated aqueous solution of $Na_2S_2O_3$ (15 mL) was added, and the mixture was stirred until its color changed from purple to red. The organic phase was then separated and washed with water (20 mL), and the inorganic phase was extracted with CH_2Cl_2 (10 mL).The combined organic solutions were transferred onto a very short column of silica gel and eluted with CH_2Cl_2. The eluted solution was concentrated to afford **8a** (283 mg, 99%). FTIR (microscope): $\tilde{\nu}$ = 2980, 2929, 2854, 1472, 1458, 1388, 1384, 1193, 1132, 1108, 1096, 1019, 909, 871, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.55 (s, 9H), 1.51 (s, 9H), 1.40 (s, 9H), 1.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 152.0, 149.7, 149.5, 149.0, 148.7, 148.7, 148.6, 148.5 (2C), 148.4 (2C),148.4, 148.3, 148.3 (3C), 148.2, 148.2, 148.2, 148.1, 148.0, 147.9, 146.1, 146.0, 145.4, 145.3, 145.0, 144.7, 144.5, 144.4, 144.3, 144.2, 144.1, 144.1, 143.9, 143.9, 143.8, 143.8 (2C), 143.8, 143.6, 143.6, 143.2, 143.2, 143.0, 142.7, 142.1, 140.9, 139.9, 138.9, 138.6, 137.9, 82.8, 82.8 ($C(CH_3)_3$), 82.4 ($C(CH_3)_3$), 82.1 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 81.1, 80.8, 80.5, 80.4, 73.9, 73.1, 68.8, 26.7 (3 CH_3), 26.7 (3 CH_3), 26.7 (3 CH_3), 26.6 ppm (3 CH_3); MS (ESI): *m/z* (%): 1180 (90) $[M+NH_4]^+$, 910 (100).

8b: An anhydrous solution of Br_2 (76 mg, 0.48 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **3** (216 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 3 min, a saturated aqueous solution of $Na_2S_2O_3$ (15 mL) was added, and the mixture was stirred until it turned bright red. The organic phase was then separated and washed with water (20 mL), and the inorganic phase was extracted with CH_2Cl_2 (10 mL).The combined organic solutions were transferred onto a very short column of silica gel and eluted with CH_2Cl_2. The eluted solution was concentrated to afford **8b** (247 mg, 99.8%). All operations must be carried out in the dark. FTIR (microscope): 2978, 2929, 2868, 1471, 1456, 1387, 1363, 1243, 1193, 1133, 1096, 1017, 872, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.57 (s, 9H), 1.55 (s, 9H), 1.43 (s, 9H), 1.39 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 152.3, 149.9, 149.5, 148.9, 148.7, 148.7, 148.5, 148.5, 148.5, 148.4, 148.3 (3C), 148.3, 148.2 (2C), 148.2, 148.2, 148.1, 148.0, 148.0, 147.9, 146.4, 146.0, 145.8, 145.1, 144.9 (2C), 144.5, 144.4, 144.3, 144.3, 144.0 (2C), 143.8 (2C), 143.8, 143.8, 143.7, 143.5, 143.4 (2C), 143.1, 142.9, 142.5 (2C), 142.2, 140.5, 139.1, 138.7, 137.5, 136.7, 83.1, 82.9 ($C(CH_3)_3$), 82.4 ($C(CH_3)_3$), 82.1 ($C(CH_3)_3$), 80.0 ($C(CH_3)_3$), 81.1, 80.7, 80.7, 80.6, 74.5, 67.1, 61.5, 26.9 (3 CH_3), 26.7 (3 CH_3), 26.7 (3 CH_3), 26.6 ppm (3 CH_3); MS (ESI): *m/z* (%): 1270 (82) $[M+NH_4]^+$, 936 (100).

9: An anhydrous solution of ICl (25 mg, 0.154 mmol) in CH_2Cl_2 (2 mL) was added to a solution of **2** (45 mg, 0.041 mmol) in anhydrous CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature in the dark. The progress of the reaction was monitored by TLC. After about 10 min, a saturated aqueous solution of $Na_2S_2O_3$ (15 mL) was added, and the mixture was stirred for 5 min. The organic phase was then separated and washed with water (20 mL), and the inorganic phase was extracted with CH_2Cl_2 (10 mL).The combined organic solutions were concentrated, and the residue was dissolved in toluene and petroleum ether (1:1; 2 mL), then transferred onto a column of silica gel and eluted with toluene and petroleum ether (60–90 °C; 1:1). Compound **9** (15 mg, 31%) was eluted as the first band. FTIR (microscope): 2979, 2928, 2869, 1473, 1457, 1387, 1364, 1242, 1192, 1088, 1050, 1019, 870, 833 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.45 (s, 9H), 1.37 (s, 9H), 1.34 (s, 9H), 1.31 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 1C unless otherwise noted): δ = 152.2, 150.3, 149.8, 149.7, 149.5, 149.4, 149.1, 148.9, 148.9 (2C), 148.5, 148.4, 148.0, 148.0, 148.0 (2C), 147.9, 147.8, 147.7, 147.6 (2C), 147.5, 147.4, 147.4, 147.3, 147.2, 147.1 (2C), 147.0, 146.9, 146.6,

146.5, 146.4, 146.0, 145.9, 145.8, 145.8, 145.6, 145.5, 145.5, 145.0, 144.8, 144.6, 144.3, 143.8, 143.0, 142.1, 141.9, 139.0, 138.9, 138.7, 136.9, 84.8, 83.6, 82.0 ($C(CH_3)_3$), 82.0 ($C(CH_3)_3$), 81.9 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 80.7, 80.2, 78.7, 73.5, 57.7, 57.0, 26.7 ($3CH_3$), 26.6 ($6CH_3$), 26.5 ppm ($3CH_3$); MS (ESI): *m/z* (%): 1180 (100) $[M+NH_4]^+$.

10: Excess bromine (75 mg) was added to a solution of **2** (59 mg, 0.05 mmol) in benzene (5 mL). The solution was stirred during irradiation by a luminescent lamp (15 W). The progress of the reaction was monitored by TLC. After 15 min, petroleum ether (60–90 °C; 10 mL) was added. The resulting solution was transferred directly onto a column of silica gel and eluted with a mixture of toluene and petroleum ether (1:2). Bromine was eluted as the first band, **10** (60 mg, 89 %) as the second. FTIR (microscope): $\tilde{\nu}$ = 2980, 2931, 1470, 1455, 1387, 1365, 1261, 1244, 1192, 1112, 1093, 1019, 908, 865, 734 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.42 (s, 18H), 1.32 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz; signals represent 2C unless otherwise noted): δ = 149.2, 148.7, 148.5, 148.3 (4C), 148.3 (1C), 148.1, 148.0, 147.9, 147.7, 147.6, 147.4, 147.1 (1C), 145.6, 145.1, 145.0, 144.7, 144.6, 144.5, 144.1, 143.8, 143.7, 143.5, 143.3, 141.1, 138.6, 135.5, 86.2, 82.3 (1C), 82.0 ($C(CH_3)_3$), 81.8 ($C(CH_3)_3$), 80.5, 68.6 (1C), 62.7, 26.8 ($6CH_3$), 26.7 ppm ($6H_3$); MS (ESI): *m/z* (%): 1275 $[M+Na]^+$.

Reactions of Dihalofullerene Derivatives with Triphenylphosphane

The reactions of **8a**, **8b**, **9**, and **10** with PPh_3 were carried out in a similar way. The products were formed in 81, 78, 93, and 94 % yield, respectively. The reaction time was about 5 min for all four reactions. The following is an example.

PPh_3 (70 mg, 0.27 mmol) was added to a solution of **8a** (283 mg, 0.24 mmol) in freshly distilled benzene (12 mL), and the resulting solution was stirred in the dark. The progress of the reaction was monitored by TLC. After 5 min, petroleum ether (60–90 °C; 10 mL) was added. The resulting solution was transferred directly onto a column of silica gel and eluted with a mixture of toluene and petroleum ether (1:1) to give **3** (216 mg, 81 %) as the only major band. The identity of the product was confirmed by comparing its ^1H NMR spectrum with that of **3** prepared above.

*Epoxidation of **3** with m*CPBA

Excess *m*CPBA (70 %, 120 mg, 0.5 mmol) was added to a solution of **3** (20 mg, 0.02 mmol) in CH_2Cl_2 (5 mL), and the resulting solution was stirred in the dark. The progress of the reaction was monitored by TLC. After 12 h, the solution was transferred onto a short column of silica gel and eluted with CH_2Cl_2. The eluted band was concentrated and purified by column chromatography on silica gel (eluent: toluene/petroleum ether (60–90 °C) 1:1). The remaining starting material **3** (4 mg) was eluted as the first band, **11** (9 mg, 44 %) as the second. The identity of the products was confirmed by comparing their ^1H NMR spectra with those of authentic samples (for the ^1H NMR spectrum of **11**, see reference [7b]).

*Preparation of **12** from **3***

Excess *tert*-butylhydroperoxide (TBHP; 5 drops) was added to a solution of **3** (50 mg, 0.05 mmol) in CH_2Cl_2 (10 mL), and the resulting solution was stirred for 10 min. DABCO (15 mg, 0.13 mmol) was then added, and the resulting solution was stirred in the dark. The progress of the reaction was monitored by TLC. After 5 h, the solution was transferred onto a short column of silica gel and eluted with CH_2Cl_2. The eluted band was concentrated and purified by column chromatography on silica gel (eluent: toluene). The remaining starting material **3** (6 mg) was eluted as the first band, **11** (33 mg, 61 %) as the second. The identity of the product was confirmed by comparing its ^1H NMR spectrum with that reported in reference [8a].

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[10] Crystal data for **6** ($C_{78}H_{42}Cl_4O_{10}$, M_r = 1280.92): triclinic, $P\bar{1}$, a = 14.204(3), b = 14.679(3), c = 14.867(3) Å, α = 90.40(3), β = 97.88(3), γ = 114.35(3)°, V = 2774.4(10) Å^3, T = 143(2) K, Z = 2, ρ_{calcd} = 1.533 Mg m^{-3}, graphite-monochromated $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, crystal size 0.50 × 0.35 × 0.10 mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 9285 unique reflections (R_{int} = 0.0577). Refinement on F^2, final residuals $R1$ = 0.0880 for 4441 reflections with $I > 2\sigma(I)$, $wR2$ = 0.2336 for all data. CCDC-289585 contains the supplementary crystallographic data for this compound.

[11] Crystal data for **8a** ($C_{77}H_{36}Cl_2O_9S_2$, M_r = 1240.08): monoclinic, $P21/n$, a = 14.620(3), b = 13.968(3), c = 26.487(5) Å, α = 90, β = 101.70(3), γ = 90°, V = 5296.6(18) Å^3, T = 143(2) K, Z = 4, ρ_{calcd} = 1.555 Mg m^{-3}, graphite-monochromated $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, crystal size 0.50 × 0.20 × 0.14 mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 9340 unique reflections (R_{int} = 0.0516). Refinement on F^2, final residuals $R1$ = 0.0457 for 5093 reflections with $I >$

$2\sigma(I)$, $wR2 = 0.0916$ for all data. CCDC-289586 contains the supplementary crystallographic data for this compound.

[12] Crystal data for **10** ($C_{80}H_{48}Br_2O_{11}$, $M_r = 1345.00$): monoclinic, $P21/c$, $a = 22.264(5)$, $b = 13.809(3)$, $c = 18.716(4)$ Å, $\alpha = 90$, $\beta = 100.64(3)$, $\gamma = 90°$, $V = 5655(2)$ Å^3, $T = 143(2)$ K, $Z = 4$, $\rho_{calcd} = 1.555$ Mg m^{-3}, graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.50 \times 0.25 \times 0.08$ mm^3. Data collected on a Rigaku RAXIS RAPID IP diffractometer, 9505 unique reflections ($R_{int} = 0.0813$). Refinement on F^2, final residuals $R1 = 0.0783$ for 3903 reflections with $I > 2\sigma(I)$, $wR2 = 0.1629$ for all data. CCDC-289585 (**6**), -289586 (**8a**), and -290715 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK (fax: (+44) 1223-366-033; e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/data_request/cif.

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[21] C_1-symmetric compounds were prepared as racemates.

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