

Selective Preparation of Oxygen-Rich [60]Fullerene Derivatives by Stepwise Addition of *tert*-Butylperoxy Radical and Further Functionalization of the Fullerene Mixed Peroxides

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tert-Butylperoxy radicals add to C₆₀ selectively to form multi-adducts C₆₀(O)_m(OO^tBu)_n ($m = 0, n = 2, 4, 6; m = 1, n = 0, 2, 4, 6$) in moderate yields under various conditions. Visible light irradiation favors epoxide formation. High concentration of *tert*-butylperoxy radicals mainly produces the hexa-homoadduct C₆₀(OO^tBu)₆ **6**; low concentration and long reaction time favor the epoxy-containing C₆₀(O)(OO^tBu)₄ **7**. The reaction can be stopped at the bis-adducts with limited TBHP. A stepwise addition mechanism is discussed involving mono-, allyl-, and cyclopentadienyl C₆₀ radical intermediates. *m*-CPBA reacts with the 1,4-bis-adduct to form C₆₀(O)(OO^tBu)₂ and C₆₀(O)₃(OO^tBu)₂. The C–O bond of the epoxy ring in **7** can be cleaved with HNO₃ and CF₃COOH. Nucleophilic addition of NaOMe to **7** follows the S_N1 and extended S_N2' mechanism, from which four products are isolated with the general formula C₆₀(O)_a(OH)_b(OMe)_c(OO^tBu)_d. Visible light irradiation of the hexa-adduct **6** results in partial cleavage of both the C–O and O–O bonds of peroxide moieties and formation of the cage-opened compound C₆₀(O)(O)₂(OO^tBu)₄. All the fullerene derivatives are characterized by spectroscopic data. A single-crystal structure has been obtained for an isomer of C₆₀(O)(OH)₂(OMe)₄(OO^tBu)₂.

Introduction

Oxygenation of fullerenes has received much attention since the early days of fullerene chemistry due to their bioactivity and possible applications in materials chemistry. Various methods have been reported to generate multioxygenated fullerene compounds. Mixtures of C₆₀O_n can be formed by electrochemical oxidation,¹ photolysis,² and ozonation.³ Polyhydroxylated fullerenes (fullerenols) usually containing more than six hydroxyl groups are prepared mainly through the use of aqueous HNO₃/H₂-SO₄,⁴ nitronium tetrafluoroborate,⁵ and fuming sulfuric

acid.⁶ Alkoxides can add to fullerenes to form complex multiadducts.⁷ Separation and characterization of such mixtures are difficult, and the reaction mechanism remains uncertain in some cases.

Isomerically pure oxygenated fullerene derivatives are still relatively rare compared to other fullerene derivatives. Epoxidation is among the intensively studied fullerene reactions. The [6,6]-closed monoepoxide C₆₀(O) was one of the first fullerene derivatives.⁸ The [5,6]-open oxidoannulene isomer of C₆₀(O) was characterized recently.⁹ The structure of one isomer of the diepoxide

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$C_{60}(O)_2$ has been determined by X-ray analysis.¹⁰ Three isomers of the triepoxide $C_{60}(O)_3$ were identified.¹¹ The simple fullerene diols $C_{60}(OH)_2$ and $C_{70}(OH)_2$ were prepared by addition of RuO_4 followed by acid hydrolysis.¹² A number of alkoxy [60]fullerene derivatives¹³ were purified including the 1,4-(MeO)₂ C_{60} .¹⁴ Yields of these isomerically pure oxygenated fullerene derivatives are low in most cases, and tedious purification processes by HPLC is often required.

We have found that excess *tert*-butyl hydroperoxide (TBHP) reacts with C_{60} and C_{70} to form fullerene mixed peroxides $C_{60}(O)(OO^tBu)_4$ **7** and $C_{70}(OO^tBu)_{10}$, respectively, under the catalysis of metal compounds such as $Ru(PPh_3)_3Cl_2$.¹⁵ A radical addition mechanism was proposed to explain their formation. Here we report a detailed investigation of the reaction between TBHP and C_{60} under various conditions and isolation of several key intermediates leading to **7**. The reactivity of the C_{60} mixed peroxides toward some acids and nucleophiles and under photolysis is also described here.

Results and Discussion

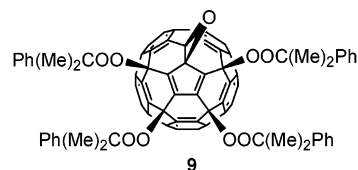
Metal-Catalyzed Reaction of Alkyl Hydroperoxides with C_{60} . Fullerenes have been known as efficient radical scavengers. Various radicals can add easily to C_{60} such as boron, carbon, sulfur, oxygen,¹⁶ and halogen radicals.¹⁷ TBHP has been used extensively in organic synthesis and in biochemical studies as a radical source. The reaction of alkenes with TBHP is well established and yields mainly epoxides. *tert*-Butylperoxy radical adducts are formed as the major product for some alkenes.¹⁸ Thus, both fullerene mixed peroxides and fullerene epoxides could be expected from the reaction of TBHP with C_{60} .

As in other cases, the presence of a catalyst is essential for the addition of TBHP to C_{60} . There is hardly any reaction when a C_{60} benzene solution is mixed with excess TBHP at rt in the dark after 3 days. The first catalyst we tested was the ruthenium complex $Ru(PPh_3)_3Cl_2$, which has been applied successfully in other TBHP reactions.¹⁹ Benzene was chosen as the reaction solvent instead of the more commonly used toluene in fullerene chemistry because toluene could produce benzyl radical

with TBHP under the reaction conditions.¹⁶ The scale of C_{60} was varied from 5 to 500 mg with essentially the same results. To avoid possible photosensitized decompositions, the reaction flask was wrapped with aluminum foil. The reaction was carried out at room temperature. Lowering the temperature to 0 °C did not improve the selectivity. The progress of the reaction could be followed by HPLC. At the beginning, the bis-adducts are formed together with some monoepoxide $C_{60}(O)$. After 2 days, most of the C_{60} had been converted and compound **7** was the major product. At this point, a significant amount of other products was also formed which could not be eluted by benzene/petroleum ether. Benzene and a mixture of benzene and ethyl acetate could further elute two bands, which showed complex ¹H NMR spectra.

In an effort to improve the yield of **7**, we tried $FeCl_3$ as the catalyst. Iron complexes are active catalyst for TBHP and well studied in Gif chemistry.²⁰ The result is similar to the ruthenium-catalyzed reaction in terms of products formed and their relative yields, but the reaction was slower and some pyridine has to be added to accelerate the reaction. $Fe(NO_3)_3$ and $(NH_4)_2Fe(SO_4)_2$ show activity similar to that of $FeCl_3$. The greenish $Ru(PPh_3)_4Cl_2$ shows essentially the same result as the black $Ru(PPh_3)_3Cl_2$ discussed above. $Pb(OAc)_4$ ²¹ and $(NH_4)_2Ce(NO_3)_6$ (CAN)²² have been reported to react with TBHP in a stoichiometric ratio to give *tert*-butylperoxy radicals. When these two salts were used, compound **6** was the major product with hardly any **7**. In these two cases, the molar ratio between C_{60} and TBHP was around 1:15 and the reaction was complete in less than 30 min. Interestingly a combination of catalytic amount of $Ru(PPh_3)_4Cl_2$ and excess of $K_3Fe(CN)_6$ gave the same results as CAN, i.e., the major product was **6**. $K_3Fe(CN)_6$ alone was inactive for the reaction between TBHP and C_{60} . Changing the solvent from benzene to CS_2 sped up the ruthenium-catalyzed reaction significantly and resulted in mainly the hexa-homoadduct **6**.

Cumene hydroperoxide reacts similarly with C_{60} in the presence of catalytic amount of $Ru(PPh_3)_3Cl_2$ to give **9** in 15% yield. Purification of **9** is quite difficult due to the presence of some oily byproducts which has close R_f value with **9**.



(Diacetoxymethyl)benzene (DIB)-Promoted Reaction of TBHP with C_{60} . It has been well-established that DIB reacts with TBHP producing *tert*-butylperoxy radicals efficiently.²³ To isolate reactive intermediates leading to the final hexahydrofullerene adducts **6** and **7**,

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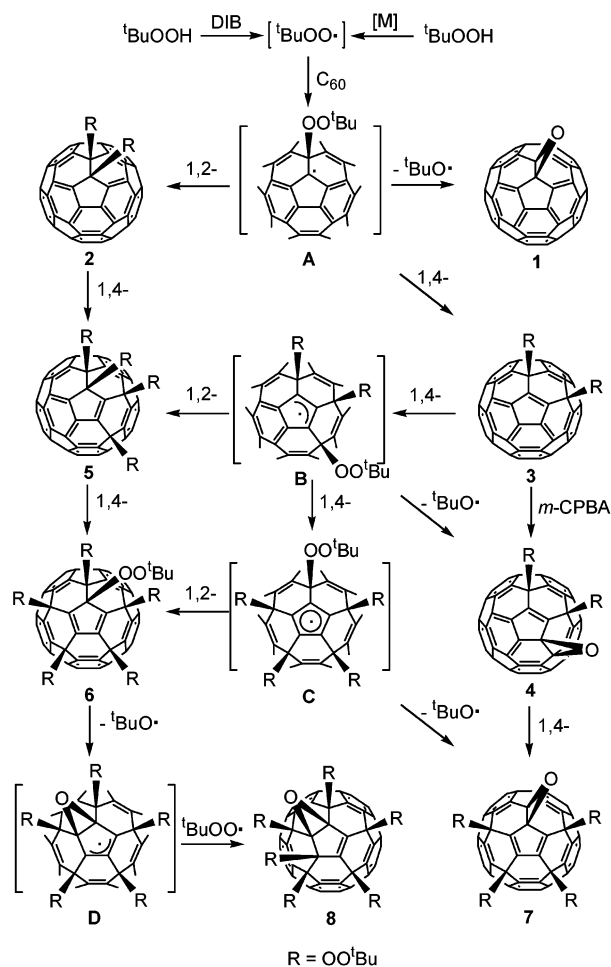
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TABLE 1. Reaction between C₆₀, DIB and TBHP under Different Conditions

entry	molar ratio of C ₆₀ /DIB/TBHP	T (°C)	dark or <i>hν</i>	time (h)	products (isolated yields ^c)								C ₆₀ ^f
					1	2	3	4	5	6	7	8	
1	1:5:15	0	dark	6	— ^d	X ^e	—	—	X	32	—	—	X
2		20	dark	6	—	X	—	—	X	30	—	—	X
3		0	<i>hν</i> (i) ^a	0.25	—	X	—	—	X	15	—	—	X
4	1:1.2:3.6	20	<i>hν</i> (ii)	54	7	X	—	—	—	—	—	—	31
5	1:0.8:2.4	20	<i>hν</i> (ii) ^b	8	4	10	20	—	3	—	—	—	57
6		40	dark	15	—	6	23	—	3	—	—	—	40
7		50	<i>hν</i> (ii)	16	6	6	24	X	6	—	—	—	55
8		60	<i>hν</i> (ii)	15	6	5	31	X	—	—	X	—	63
9	1:1.3:3.9	80	<i>hν</i> (ii)	15	5	5	7	X	—	—	—	—	32

^a *hν*(i): luminescent light bulb (12 W). ^b *hν*(ii): laboratory light. ^c Based on converted C₆₀. ^d —: not detected. ^e X: yield too low to be determined accurately. ^f Recovered C₆₀.

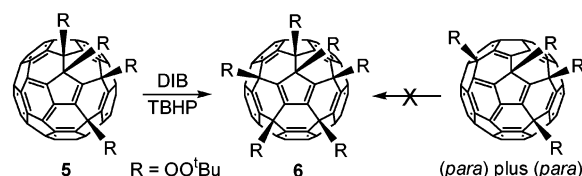
SCHEME 1. Addition of *tert*-Butylperoxy Radical to [60]Fullerene



we treated C₆₀ with TBHP and DIB (Scheme 1). Various conditions were tested as shown in Table 1. In a 1:5:15 molar ratio of C₆₀/DIB/TBHP and under total darkness, the hexakis-adduct **6** was the major isolable product. The results are essentially the same when the temperature of the reaction was changed from 0 to 20 °C (Table 1, entries 1 and 2). When a luminescent light bulb was placed beside the reaction flask, the reaction was complete in just 15 min and compound **8** was isolated in addition to **6** (Table 1, entry 3).

Two less polar minor products **2** and **5** were noticed under the above conditions. To maximize their yields, the amount of *tert*-butylperoxy radical was decreased and the

SCHEME 2. Formation of Compound 6 from 5



reaction temperature was increased. Under the new conditions, epoxide **1** and the 1,4-isomer **3** were also isolated. Formation of epoxide **1** needs light irradiation, similar to that of **8**. Under total darkness, no compound **1** could be detected (Table 1, entry 6). Separation of the isomeric **2** and **3** is not possible by column chromatography. Pure isomer **2** was obtained under the conditions in entry 2. A mixture containing mainly the 1,4-isomer **3** could be produced at 60 °C (Table 1, entry 8).

The selective formation of the 1,2-isomer **2** or the 1,4-isomer **3** under different conditions can be rationalized as follows. It is known that the spin density of RC₆₀[•] is highest at position 2.²⁴ MM2 calculations show the 1,4-isomer **3** is 6.0 kcal/mol more stable than the 1,2-isomer **2**. Thus, **2** is the kinetic product and **3** is the thermodynamic product. At higher temperatures, **3** is favored (Table 1, entries 5–9). When excess TBHP is present, further *tert*-butylperoxy radical addition takes place. The 1,4-isomer **3** is apparently more reactive, due to the formation of the relatively stable allyl radical intermediate. Under this condition only the 1,2-isomer **2** is detected (Table 1, entries 1–3). A mixture of 1,2- and 1,4-isomers has been reported for C₆₀Me₂.²⁵

Treating isolated **2** with DIB and TBHP in a 1:1.8:6.9 molar ratio for 20 min could yield **5** and **6**, indicating that further addition of **2** does occur and **6** could be formed through **5** (see below). But the reaction is slower than that of a mixture of **2** and **3** containing mainly **3** (1:2). In the later case more **5** and **6** could be detected in 20 min with less *tert*-butylperoxy radical (molar ratio 1:0.5:2.3 for (**2** + **3**)/DIB/TBHP). This preliminary kinetic test proves that the 1,4-isomer **3** is indeed more reactive toward further addition than the 1,2-isomer **2**.

Calculations²⁶ have predicted that the structure depicted for **5** and another stable C₁ symmetric isomer named as (*para*) plus (*para*) (Scheme 2) are among the

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three exceptionally stable isomers for $C_{60}X_4$, the other one being the C_s symmetric pseudofulvene which is easily ruled out by the NMR data of **5**. To distinguish between the two possible C_1 isomers, pure **5** was treated with DIB and TBHP in a 1:2:6 ratio for 5 min in dark at room temperature. Compound **6** was the only isolated product. This result confirms the assignment of **5** as depicted. The (*para*) plus (*para*) isomer should not give **6**.

Mechanism Considerations. ESR studies have provided unequivocal identification of radical intermediates in fullerene radical reactions.¹⁶ Radical mono-adducts ROC_{60}^{\bullet} , allyl $Bz_3C_{60}^{\bullet}$, and cyclopentadienyl $Bz_5C_{60}^{\bullet}$ radicals have been verified. Diamagnetic 1,4-bis-adduct Bz_2C_{60} ²⁷ and the C_s -symmetric tetrakis-adduct Bz_4C_{60} were deduced in the proposed successive 1,4-addition pathway leading to $Bz_5C_{60}^{\bullet}$. The present work provides complementary information to the ESR study in a synthetic way.

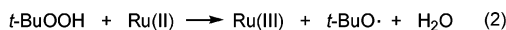
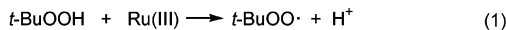
Isolation of products **1–3** indicates the formation of the monoaddition radical $t\text{-BuOOC}_{60}^{\bullet}$ **A**. Further addition of the allyl radical $(t\text{-BuOO})_3C_{60}^{\bullet}$ **B** should give the C_s -symmetric pseudofulvene $(t\text{-BuOO})_4C_{60}$ according to the suggested benzyl addition pattern. Pseudofulvene fullerene derivatives have been isolated in other systems.²⁸ But such C_s -symmetric tetra-adduct was not detected in the present reaction. It must be very reactive toward further addition to form the resonance-stabilized cyclopentadienyl radical. Instead the less reactive isomer **5**, the other possible tetra-adduct from **B**, was isolated here in low yield (Table 1).

The penta-*tert*-butylperoxy [60]fullerene radical **C** is a perfect precursor to both **6** and **7**. Addition of another *tert*-butylperoxy radical affords the hexa-adduct **6**, whereas cleavage of one of the five O–O peroxy bonds affords the neutral **7** with an epoxide unit as in many classical epoxidation reactions. Oxygen may be produced in the solution by the combination of two *tert*-butylperoxy radicals. It may react with a neutral C_s -symmetric tetra-adduct $C_{60}(OO-t\text{Bu})_4$ to form **7** as well. In the presence of oxygen, some secondary amines react with C_{60} to give epoxide derivatives with structures analogous to **7**.²⁹

A possible pathway leading to **8** is the loss of a *tert*-butoxy radical from **6** to form the new ally radical **D** with an epoxide on the same pentagon. Like other radical intermediates in the DIB reaction, this new ally radical adds another *tert*-butylperoxy radical to form **8** instead of losing a *tert*-butoxy radical to form the bisepoxide derivative **10**. Compound **10** is stable and could be prepared from pure **7** with *m*-CPBA (see below).

The concentration of *tert*-butylperoxy radical appears to be the key factor in the formation of the epoxide unit. At a relatively high concentration, *tert*-butylperoxy radicals trap fullerene radical intermediates efficiently before they lose a *tert*-butoxy radical to form an epoxide product. At a low concentration, the fullerene radical intermediates have enough time to break the O–O bond to form

SCHEME 3. Ruthenium-Catalyzed Formation of *tert*-Butylperoxy Radical



epoxide products. DIB, $\text{Pb}(\text{OAc})_4$, and CAN are all strong oxidants and can react with TBHP almost instantly to produce *tert*-butylperoxy radicals, thus resulting a relatively high *tert*-butylperoxy radical concentration and affording mainly *tert*-butylperoxy homo-adducts. $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ can generate *tert*-butylperoxy radical through catalytic cycles with TBHP (see below), but it is much less efficient compared to the three strong oxidants and can only maintain a low *tert*-butylperoxy radical concentration. So even though a much larger excess of TBHP was used in this catalytic process, the reaction is slow and epoxide containing compound like **7** is the major product.

Scheme 3 shows the mechanism for formation of *tert*-butylperoxy radicals for the ruthenium catalyzed reaction, which is the same as those proposed by Barton and Le Gloahec for FeCl_3 .²⁰ *tert*-Butoxyl radical can also add to C_{60} as shown by Lunazzi et al.^{16b} In a toluene solution, the *tert*-butoxyl radical abstracts a methyl hydrogen atom from the solvent and addition of the resulting benzyl radical to C_{60} is the only observed reaction.^{16a} In the present ruthenium-catalyzed reaction, TBHP, used in a large excess, reacts apparently more rapidly with the *tert*-butoxyl radical than C_{60} (but unidentified products may involve the *tert*-butoxyl radical). By increasing the amount of trapping agent, Barton and Le Gloahec were able to trap the *tert*-butoxyl radical in the Fe(III) and TBHP system.²⁰ If less TBHP is added in the present reaction or if toluene is used as the solvent, more complicated products are observed perhaps as a result of competing reactions of *tert*-butoxyl radicals.

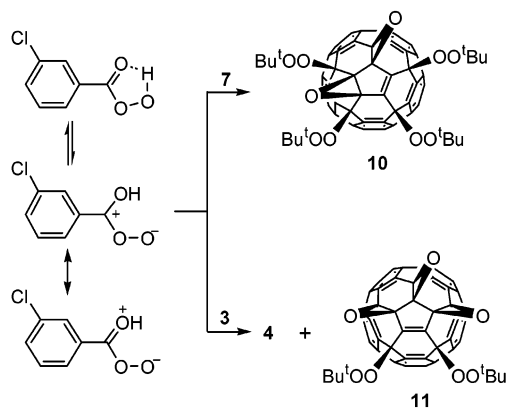
As mentioned previously, an excess amount of $\text{K}_3\text{Fe}(\text{CN})_6$ could greatly accelerate the ruthenium catalyzed reaction and gives **6** as the major product. This may indicate that the rate-limiting step of the ruthenium catalyzed reaction is the reoxidation of Ru(II) to Ru(III) by TBHP. $\text{K}_3\text{Fe}(\text{CN})_6$ is an effective one electron oxidant. It may simply accelerate the regeneration of Ru(III) from Ru(II) . $\text{K}_3\text{Fe}(\text{CN})_6$ itself can not react with TBHP to give *tert*-butylperoxy radicals and was used to maintain the Fe(III) state in the mechanism study of Gif chemistry.²⁰ Further investigation is necessary to verify our explanation.

Epoxidation of **3 and **7** with *m*-CPBA.** All the above reactions yield predominantly peroxide products containing only peroxy groups or multiperoxy groups with just one epoxy group. To prepare derivatives with more epoxy groups, we then tested the reaction of *m*-CPBA with the above fullerene mixed peroxides. *m*-CPBA has been used to prepare fullerene epoxides $C_{60}(\text{O})_n$ with n up to 12, which could be detected by mass spectra. But the reaction is not selective. Separation and characterization of the multiperoxides is difficult due to their poor solubility. Presence of the *tert*-butyl groups greatly enhances the solubility of the fullerene mixed peroxides prepared here. The already attached *tert*-butylperoxy groups could also serve as directing groups for further addition reactions.

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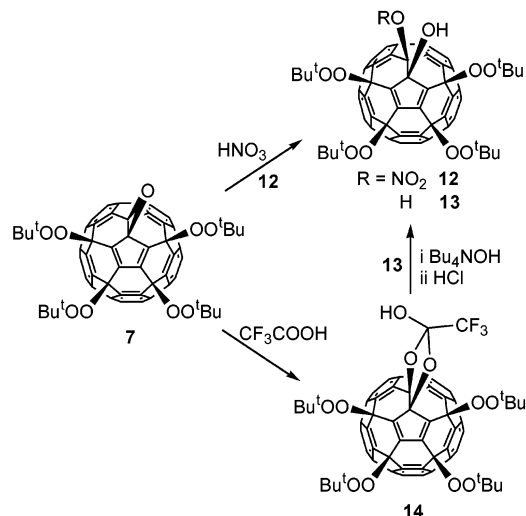
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SCHEME 4. Reaction of *m*-CPBA with **3** and **7**

Treating **7** with excess *m*-CPBA gave compound **10** in 62% yield, which has one more epoxy group than **7** located on the center pentagon (Scheme 4). Various efforts were unsuccessful in trying to epoxidate the remaining double bond in the center pentagon, such as prolonged reaction time, heating the solution, and treating isolated **10** with peroxy acids. Steric hindrance is probably too big in the center pentagon of **10**. These failed efforts support the structure of **10** as depicted. Should the new epoxy group be on the outskirts of the center pentagon, addition of more epoxy groups must be possible. The structure of **10** is isostructural with the unsymmetric hydroxyepoxide C₆₀Me₅(O)(OH) and C₆₀Ph₄(O)(C₆H₄O) (which contains a furanoid ring), reported by Taylor's group from the reaction of C₆₀Cl₆ with LiMe followed by hydrolysis.³⁰ Taylor's group also identified the symmetric hydroxydiepoxide C₆₀Me₅(O)₂(OH) with two epoxy groups in the center pentagon from the same reaction.

The reaction of **3** with *m*-CPBA afforded two products, **4** and **11**. Yields of these two compounds are very low and vary slightly on different runs. To get enough material for characterization the reaction was repeated many times. The structure of **4** was verified by treating **4** with DIB and TBHP which yields **7**, thus ruling out *C_s*-symmetric structures for **4** in agreement with the NMR data.

There are several different double bonds adjacent to the two *tert*-butylperoxy groups in **3** which may react with *m*-CPBA. The double bond on the pentagon would be the most reactive. Just like the stepwise radical addition mechanism, steric hindrance and allyl-type intermediate formation should be responsible for the observed selectivity. The initial step of alkene epoxidation by peracids is the electrophilic attack by the resonant species having negative peroxy oxygen (Scheme 4). To form the *C_s*-symmetric triepoxy derivative **11**, the *C_s*-symmetric diepoxy compound C₆₀(O)₂(OO^tBu)₂ is the most likely precursor. Such a diepoxy product is not detected. It must be too reactive toward further epoxidation with the activation effect of two neighboring epoxy groups toward the remaining double bond connected to the center pentagon. As mentioned earlier, the *C_s*-

SCHEME 5. Epoxy-Opening Reactions of Compound **7**

symmetric tetra-adduct C₆₀(OO^tBu)₄ was not detected in the radical addition reaction. The arrangement of the three epoxy groups in **11** is the same as that in the T-shaped isomer of C₆₀(O)₃.¹¹

Epoxyde Ring-Opening Reactions. Functional groups on fullerene derivatives usually exhibit unique chemical reactivity due to the influence of the fullerene cage. Trivial transformations readily achieved in classical organic synthesis may not take place or drastic conditions are needed in fullerene chemistry. To explore the reactivity of the epoxy group prepared here, we treated the readily available **7** with various acids. Acid-induced ring opening of epoxides is one of the major reactions in epoxide transformations.

Among the inorganic acids tested only concentrated nitric acid gave the nitratofullerenol **12** in 58% yield (Scheme 5). Two regioisomers are possible for **12** with the position of OH and ONO₂ exchanged. Only one isomer was produced under our conditions. The exact relative location of the OH and ONO₂ cannot be determined with the present NMR data. The depicted structure is preferred in light of the sodium methoxide reaction, in which nucleophilic addends attack from the outskirts of the center pentagon (see the next section). In addition, an unfavorable 4π electron antiaromatic carbocation would be involved to form the other regioisomer of **12**. The pentaaryl[60]fullerene carbocation C₆₀(Ar)₅⁺ exists mainly as the *C_s*-symmetrical rather than the *C₅* cyclopentadienyl carbocation.³¹

It is known that CAN is able to open different epoxides effectively to give vicinal nitrate alcohol.³² But treating **7** with CAN did not give **12** or any other characterizable product. Both HCl and H₂SO₄ do not react with **7**. Treating **7** with a mixture of KI and HCl could give the fullerendiol **13** in very low yield. A better method for the preparation of **13** is shown in Scheme 5.

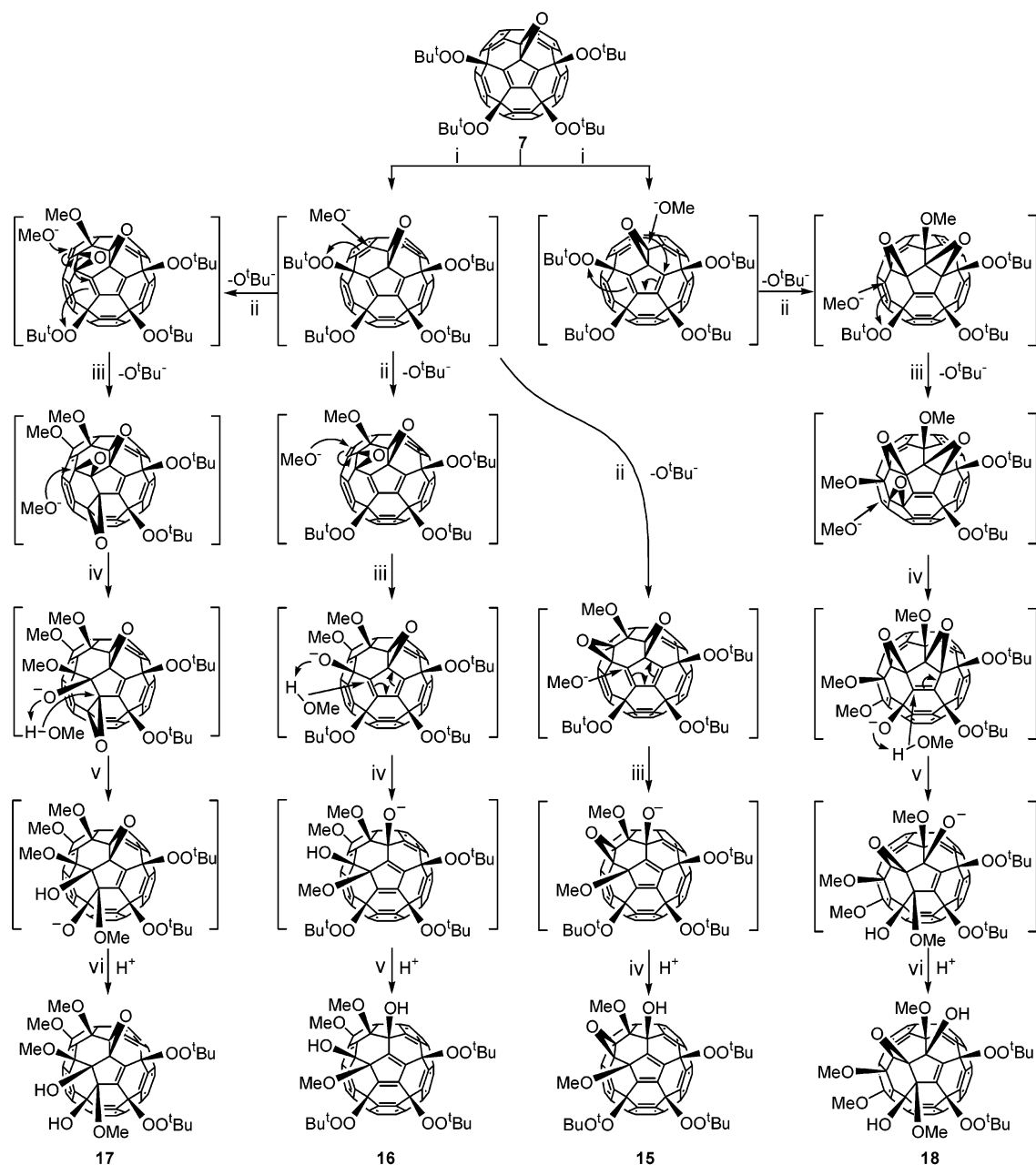
Trifluoroacetic acid is the only organic acid which reacted with **7** smoothly (Scheme 5). The product **14** contains an ortho acid moiety (hydrates of carboxylic

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SCHEME 6. Nucleophilic Additions of Methoxide to 7



acids). Ortho acids are intermediates postulated in many reactions but rarely isolable. The trifluoromethyl group may play an important role in stabilizing such an unusual structure besides the C_{60} cage. A related compound is the $CF_3C(OEt)_2ONa$ prepared from the addition of sodium ethoxide to ethyltrifluoroacetate.³³ Compound **14** is surprisingly stable toward strong acids such as HCl. Treating **14** with tetrabutylammonium hydroxide did cleave the 1,3-dioxolanol moiety and gave the fullerendiol **13** after acidification with dilute HCl. The mechanism of this base-catalyzed hydrolysis must be the same as that in classical organic reactions.

Nucleophilic Addition of NaOMe to 7 and 3. Base-induced epoxide opening is also a common reaction. Various attempts failed to open the epoxy group with

hydroxides to make the diol **13**. Alkoxides have been shown to dehalogenate halofullerenes to give isomerically pure alkoxy fullerene derivatives.^{13a} To improve the selectivity of base-induced epoxide opening, we then turned our attention to alkoxide and treated **7** with a mixture of sodium methoxide and methanol. As expected, the reaction is successful, yet it is much more complicated than the above acid-induced reactions. Four methoxylated products, namely compounds **15–18**, were isolated. To form these derivatives, the O–O bond of one or two *tert*-butylperoxy groups is cleaved. An epoxy group is still present in compounds **15**, **17**, and **18**. All the hydroxyl groups are adjacent to a methoxy group, a motif originally expected for the epoxy ring opening by methoxide.

Scheme 6 shows possible pathways for the methoxide reaction. As expected, methoxide ion does attack the epoxide ring carbon to open the ring as in the first step

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for the formation of **18** and step iv of **17**. Sodium cation may coordinate to the epoxy oxygen and initiates the ring opening to leave a positive fullerene carbon for the incoming methoxide group, similar to the classical S_N1 reaction. The positive fullerene carbon is not on the center pentagon, similar to the $C_{60}(Ar)_5^+$.³¹ Because of the strong electron-withdrawing nature of the fullerene cage, the S_N1 mechanism is rarely observed in fullerene chemistry. Ferric chloride catalyzed dehalogenation reactions are proven to involve the S_N1 mechanism.^{31,34}

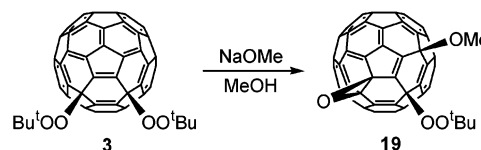
The methoxide ion also attacks α and β carbons of the fullerene double bond adjacent to the epoxy group. The resulting carbon anion then either approaches the epoxy carbon to form a double bond thus opening the epoxide as in step ii of **16** and **17** and step iv of **18** or reaches its *tert*-butylperoxy neighbor and forms an epoxy ring by replacing a *tert*-butyl oxide as in the first step in the formation of **15–17** and step iii of **18**. This process is similar to the S_N2' mechanism observed for the hydroxy-defluorination for fluorofullerenes.³⁵ Anionically induced decompositions of β,γ -unsaturated peroxides also follow a similar pathway.³⁶

The oxygen anion resulting from the methoxide-induced epoxide opening follows three different routes for further transformation: attaches to a neighboring sp^2 cage carbon and causes the loss of a *tert*-butoxide ion through an electron relay process and eventually formation of two epoxy groups as in step ii of **18**; opens another epoxide ring by trapping a neutral methanol molecule to form a hydroxyl group and a vicinal methoxy group as in iv of **16**, v of **17** and **18**; and becomes protonated in the final workup procedure with HCl. The electron relay process across the isolated double bonds on the center pentagon is analogous to the extended S_N2' mechanism (defined as S_N2'' mechanism) in the formation of trans annulenes from fluorofullerenes.³⁵

Scheme 6 only shows possible pathways leading to the four isolated products. The combined yield of the four products is less than 50%. Other pathways may have resulted in more reactive intermediate species and complicated final products. Steric hindrance of the bulky *tert*-butylperoxy groups plays a key role in the regioselectivity of the reactions. In most cases, the methoxide ion approaches its target site from a position far away from the sterically hindered center pentagon. Fullerene carbons around the epoxy moiety are more reactive than those around the peroxy groups.

The 1,4-bis-adduct **3** reacts with sodium methoxide under the same conditions as above (Scheme 7). The yield here is much better at 44%. The mechanism here should be similar to that for the reaction between **3** and

SCHEME 7. Nucleophilic Addition of Methoxide to **3**



m-CPBA mentioned earlier. In the *m*-CPBA reaction the *m*-chlorobenzoate ion is a better leaving group than the *tert*-butoxide ion, and the two *tert*-butylperoxy groups remain in the products **4** and **11**.

Characterization

Mass Spectra. Three methods, ESI, MALDI-TOF, and SIMS, have been employed to obtain the mass spectra. Solubility in methanol (as required for ESI) is an important factor to observe the molecular ion peak. Molecular ion peaks are observed for compounds with more than two *tert*-butylperoxy groups. For the less soluble compounds with only one or two *tert*-butylperoxy groups, namely compounds **2**, **3**, **4**, **11**, and **19**, it is not possible to observe the molecular ion peak under the same conditions.

The type of ESI instrument is another factor to observe the molecular ion peak. On the Bruker Esquire MS instrument molecular ion signals are observed as the most prominent signals in the positive mode. The base peak is $M + Na^+$ together with $M + K^+$ signal with less intensity as commonly observed with other types of compounds. On the VG-platform II instrument the ESI base peak is usually the $M^+ + H_2O$ or $M^+ + OH$ (resolution of the instrument is not as good as the Bruker Esquire). No meaningful signals were detected when exactly the same sample was measured on the Bruker ApexII FT-ICR instrument.

The laser at 337 nm used in the MALDI-TOF is very effective at breaking peroxide bonds.³⁷ MALDI-TOF spectra show only the fullerene multioxides $C_{60}(O)_n$. For compound **7**, oxides with n up to 12 can be detected with successive loss of O, and the most intense peak is n equal to 4. SIMS spectra did not show the molecular ion signal either, but signals resulting from fragmentation of the fullerenes become evident besides the fullerene multioxides. For **7** fragmentation peaks range from 576 to 720 at 24 amu intervals. Multioxide signals similar to the MALDI-TOF spectrum are also present. In addition, several other intriguing signals resulting from successive loss of 28 amu (CO) are observed in the SIMS spectrum. These peaks seem to indicate the presence of $C_{58}O$, $C_{58}O_2$, $C_{58}O_3$, $C_{59}O_2$, $C_{59}O_3$, and $C_{59}O_4$. Similar $C_{58}(O)_{1-3}$ species have been observed in the LDI spectrum of $C_{60}(O)$.³⁸

NMR Spectra. The presence of the *tert*-butyl groups in the present compounds greatly enhances their solubility and facilitates the NMR measurement. Less than 50 scans were enough to get a decent ^{13}C NMR spectrum for **7** on a DMX600 spectrometer. Both the 1H and ^{13}C NMR chemical shifts of the *tert*-butyl group show little change for different compounds. A high-resolution

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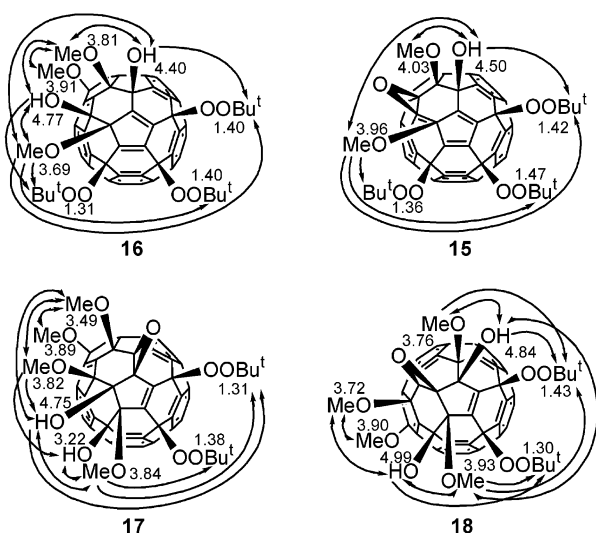


FIGURE 1. NOE couplings of compounds 15–18.

spectrum and low temperature are necessary in some cases to observe the expected number of signals. For example, all four tertiary *tert*-butyl carbons appear as a single peak at 81.90 ppm at rt on the 600 MHz spectrum. It is separated into two peaks (81.92 and 81.94 ppm) at 283 K as expected for the C_3 -symmetric structure. Hindered rotation of the anionic intermediate $t\text{-BuC}_{60}^-\text{Li}^+$ and in the radical $t\text{-BuC}_{60}^\cdot$.³⁹ The rotation is fast in all the present compounds. MM2 modeling indicates that the two peroxy oxygen atoms keep the *tert*-butyl group far enough away from the C_{60} cage to allow free rotation.

Product characterization is a difficult task for the methoxide reaction. The C_1 symmetric nature of these compounds makes the routine 1D ^1H and ^{13}C NMR spectra useless in assigning the exact locations of the different addends. Extensive NOE measurements and 2D NMR spectra were obtained to clarify the structure. Figure 1 shows the NOE results for the four compounds. All the methoxy and hydroxyl groups were irradiated to find their relevant NOE couplings. The *tert*-butyl groups were not irradiated because they have too similar chemical shifts for accurate selective irradiation.

The NOE results indicate that H-containing groups on the same hexagon or pentagon have NOE couplings in all cases except one pair of methoxy groups in each compound. The chemical shifts of these pairs, one of which is on the center pentagon, are at 3.96 and 4.03 ppm in **15**, 3.69 and 3.81 ppm in **16**, 3.82 and 3.84 ppm in **17**, 3.72 and 3.93 ppm in **18**. This phenomenon may result from the opposite orientation of the two methoxy groups and the H-bonding with the adjacent hydroxyl group, which prevents the free rotation of the methoxy group. The X-ray crystal structure of **18** (see Figure 3) supports this interpretation. The methoxy group on the center pentagon shows NOE coupling with all the *tert*-butyl groups present in the molecule including the one separated by three fullerene carbon bonds. Irradiation

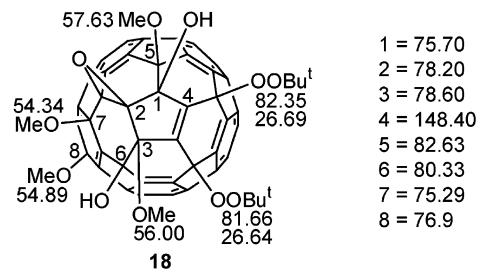


FIGURE 2. Partial assignment of ^{13}C NMR chemical shifts of **18**.

of the hydroxyl groups at 3.22 ppm in **17** indicates NOE just for its vicinal methoxy group at 3.84 ppm and no NOE for the *p*-*tert*-butyl group at 1.38 ppm and the *p*-methoxy group at 3.82 ppm. This may be due to the decreased sensitivity of the measurement for this hydroxyl group which exhibits a broad peak. Irradiation of the methoxy group at 3.82 ppm does show NOE coupling with this hydroxyl group.

A combination of HSQC and HMBC spectra agrees with the NOE-derived structures. ^{13}C NMR chemical shifts for **18** can be also partially assigned from these spectra (Figure 2). On the HMBC spectrum, all four relevant fullerene carbon signals were detected for the hydroxyl group at 4.84 ppm including the one directly bonded to the hydroxyl group. Three were observed for the other hydroxyl group at 4.99 ppm, one of which is the hydroxyl carbon as confirmed from the HSQC spectrum. Intensities of hydroxyl fullerene carbons are almost twice as strong as other sp^3 cage carbons on the ^{13}C NMR spectrum apparently due to enhancement by the hydroxyl proton.

X-ray Diffraction Analysis of 18. The NMR-derived structure of **18** was further verified by single-crystal X-ray diffraction analysis. Crystals suitable for diffraction were obtained from a mixture of CS_2 and ethanol. Each unit cell contained two fullerene molecules and one solvent CS_2 molecule. The IR spectrum showed the characteristic CS_2 band at 1512 cm^{-1} for the crystal sample.⁴⁰ The hydroxyl proton on O3 forms a strong hydrogen bond with the vicinal methoxy oxygen O2 (Figure 3). The other one on O11 forms a weaker bond with the peroxy oxygen O9 instead of the vicinal methoxy oxygen. The two double bonds on the hexagon with the two remaining *tert*-butylperoxy groups are the shortest at $1.301(7)\text{ \AA}$ (C3–C4) and $1.328(7)\text{ \AA}$ (C17–C25); the former is at the 6,5-conjunction of the center pentagon. The longest bond is between C(2) and C(11) at $1.630(6)\text{ \AA}$, which is considerably longer than the average (1.474 \AA) of the C–C single bonds in the *tert*-butyl groups.

Photolysis of 6: Cage-Opening Process. A major target of our present work is to open the fullerene cage partially.⁴¹ Theoretical calculations indicate that ring-opened structures are the most stable isomers for $\text{C}_{60}(\text{O})_6$ and $\text{C}_{60}(\text{O})_9$.⁴² As discussed earlier, the MALDI-TOF spectra of the fullerene mixed peroxides show intense peaks for fullerene multioxides. To isolate such com-

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(40) Obtained with pure CS_2 .

(41) For an overview of this topic, see: Rubin, Y. *Top. Curr. Top.* **1999**, *99*, 67–91.

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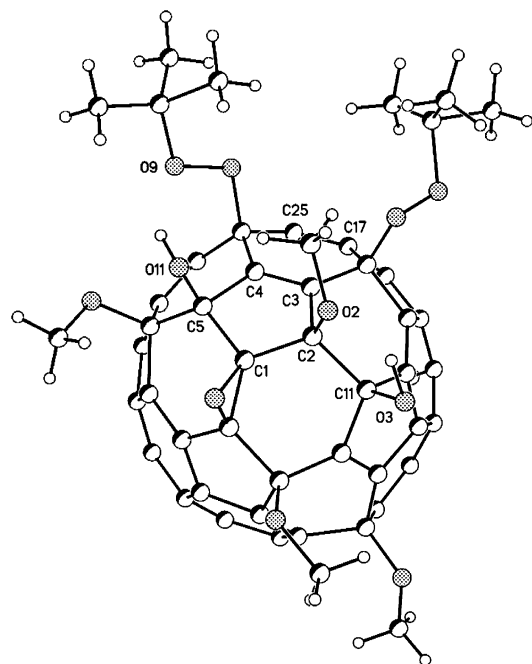
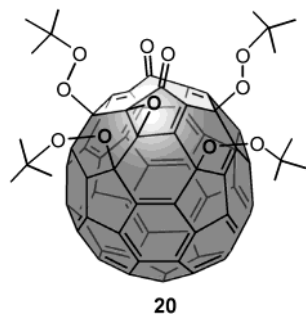


FIGURE 3. Single-crystal molecular structure of **18**; for clarity, some atoms of C_{60} cage were omitted.

pounds, we treated compound **7** under various conditions such as heating to 150 °C and irradiate its solution with visible light source, but without any success. It is too stable. A sample of **7** showed about 50% decomposition after storage at rt for 1 year.

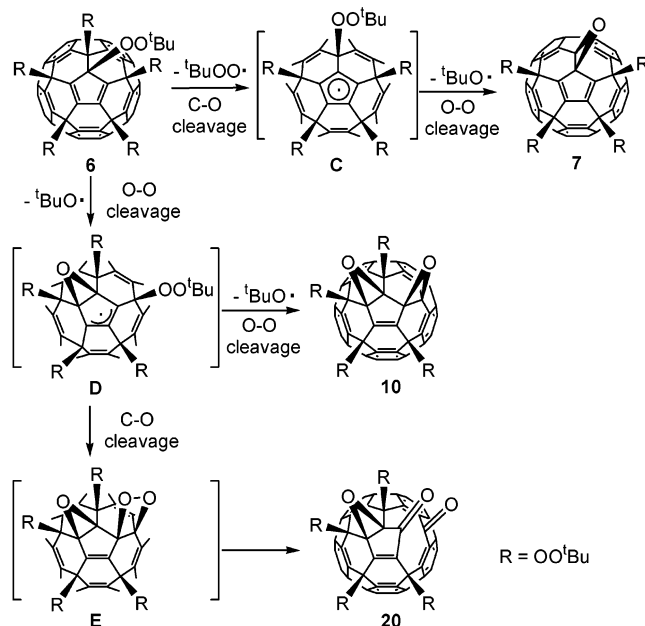


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The hexa-adduct **6** appears to be a promising candidate for cage opening. It was purified with the silica gel column wrapped with an aluminum foil to avoid light-induced decomposition. Even though its $CDCl_3$ solution for NMR could be stored in the refrigerator for a few days without noticeable decomposition, the solid sample of **6** decomposes slowly at rt. The cage-opened compound **20** was first isolated from a complex decomposition mixture of **6** after the powder sample was stored at rt for 2 months. The yield was ~1%, too low to be determined accurately. It was found that iodine can improve the yield of **20**. Visible light irradiation of an iodine added solution of **6** gave **20** in 27% yield in 40 h. Compounds **7** and **10** were also isolated as byproducts (Scheme 8).

Scheme 8 shows possible pathways of the photochemical reaction leading to the observed products. The two intermediates **C** and **D** are the same as those proposed in Scheme 1. Under the conditions in Scheme 1, **C** is the precursor to both **6** and **7**, and **D** forms **8** instead of **10**. Rearrangement of the 1,2-dioxetane-containing interme-

SCHEME 8. Photolysis of Compound **6**



diolate **E** to **20** is analogous to that for the formation of the holey keto-lactam reported by Wudl.⁴³ Cleavage of both C–O and O–O bonds of the peroxide moiety are involved in Scheme 8. Decomposition of peroxides mainly results in homolytic O–O bond cleavage. C–O bond cleavage of peroxides is rare under photolysis or pyrolysis but has been observed in some cases and is common in acid- or base-catalyzed decompositions.⁴⁴

The exact role of iodine is not known yet. Iodine can stabilize **6** and does not react with fullerene mixed peroxides itself. An iodine-added benzene solution of **6** can be stored at rt in dark for weeks with little change. It probably traps radical species produced in the fragmentation of the *tert*-butylperoxy groups, thus preventing their addition to the fullerene cage to form complicated products. Radical induced decomposition of *tert*-butylperoxy compounds has been well studied, which involves the formation of methyl and *tert*-butoxy radicals.⁴⁵

Spectroscopic data suggests the cage-opened structure for **20** as depicted. The molecule is C_1 symmetric. There are four sets of 1H and ^{13}C NMR signals due to the *tert*-butyl groups. The C_{60} skeleton shows 52 sp^2 and six sp^3 carbon signals. In addition, there are two carbonyl signals at 193.11 and 192.08 ppm. The location of the epoxide cannot be assigned for sure with the NMR data. It is assumed to be located on the center pentagon in comparison with compounds **8**, **10**, $C_{60}Me_5(O)(OH)$, and $C_{60}Ph_4(O)(C_6H_4O)$.³⁰ Location of the carbonyl groups should be on pentagons rather than hexagons according to the IR spectrum. It shows a strong C=O stretching band at 1748 cm^{-1} , which is close to that of cyclopen-

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tanone (1743 cm⁻¹).⁴⁶ Essentially the same wavenumbers were reported in several open-cage fullerene derivatives reported by Komatso's⁴⁷ and Iwamatsu's groups.⁴⁸ Carbonyl bands of other cage-opened fullerene derivatives are lower, 1722 and 1726 cm⁻¹ for some fullerenols reported by Chiang,⁵ 1727 cm⁻¹ for the holey keto-lactam reported by Wudl,⁴³ and 1703 cm⁻¹ for the bisepoxide ketone C₆₀Me₅O₃H reported by Taylor.⁴⁹

Conclusions

The unique cyclopentadiene mode of fullerene reactions has been reported in the successful preparation of several fullerene multi-adducts. The present work provides another example for such a highly regioselective multi-addition mode. Characterization of various intermediates verifies the proposed stepwise addition mechanism. Fullerene-mixed peroxides are shown to be stable and can be used as starting materials for further derivatization. Chemical reactivity of the fullerene peroxides is analogous to the classical S_N1 and extended S_N2' reactions. The [60]fullerene cage may be opened upon controlled cleavage of peroxy bonds. Work is in progress to improve yields of the reactions and to open up a bigger hole on the C₆₀ surface.

Experimental Section

All the reagents were used as received. Benzene used for reactions was distilled from potassium under nitrogen; other solvents were used as received. The reactions were carried out under atmospheric conditions. Compounds not shown below are included in the Supporting Information.

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

1,2,4,11,15,30-Hexa-tert-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (C₆₀(OO^tBu)₆, **6).** C₆₀ (99% pure, 100 mg, 0.14 mmol) was dissolved benzene (100 mL). DIB (224 mg, 0.70 mmol) in 2 mL of CH₂Cl₂ was added. The flask was wrapped with aluminum foil and cooled with an ice bath. TBHP (270 mg, 70%, 2.1 mmol) in 2 mL of CH₂Cl₂ was added. The resulting solution was stirred in the dark. Progress of the reaction was monitored by TLC. The reaction was stopped when the desired product **6** reached its maximum (6 h). Longer reaction time resulted in more polar unidentified products and less **6**. The solution was concentrated to about 3 mL on a rotovap keeping the flask wrapped with aluminum foil. The residue was chromatographed on silica gel column (3 × 30 cm, wrapped with aluminum foil), eluting with benzene and petroleum ether (60–90 °C) (1:1). Before the major product band of **6**, two minor bands (compounds **2** and **5**) were collected. The eluted solution of **6** was evaporated and dried under atmosphere at rt with the bottle wrapped with aluminum foil. Yield: 56 mg, 32%. ¹H NMR (600 MHz, CDCl₃): δ 1.33 (s, 9H), 1.35 (s, 18H), 1.46 (s, 18H), 1.57 (s, 9H). ¹³C NMR (150 MHz, CDCl₃; all signals represent 2C except as noted): δ 151.77 (4C), 148.99, 148.89, 148.53, 148.35, 148.18, 148.07 (1C), 147.61, 147.59, 147.45 (1C), 147.37, 147.33, 146.98, 146.91, 146.50, 146.00, 145.71, 145.39, 144.45, 144.38, 144.10, 143.66, 143.04, 142.92, 142.21, 141.31, 137.91, 90.48 (sp³), 85.01 (sp³), 82.51 (2C, sp³), 81.35 (2C-(CH₃)₃), 81.02 (2C-(CH₃)₃), 80.95 (C-(CH₃)₃), 80.91 (C-(CH₃)₃), 80.62 (2C, sp³),

26.85 (3CH₃), 26.80 (12CH₃), 26.72 (3CH₃). FT-IR (microscope): 2977, 2929, 2870, 1474, 1456, 1386, 1363, 1260, 1242, 1195, 1098, 1045, 1023, 1008, 876, 755 cm⁻¹. ESI-MS (Bruker Esquire): *m/z* (rel intens) 1277 (100, M⁺ + Na), 1273 (68, M⁺ + H + H₂O). UV-vis (CHCl₃): 388, 432, 470 nm. Anal. Calcd for C₆₀(OO^tBu)₆: C, 80.37; H, 4.34. Found: C, 80.32; H, 4.33.

1,2,4,11,15,30-Hexa-tert-butylperoxy-3,14-epoxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (C₆₀(O)(OO^tBu)₆, **8).** C₆₀ (99% pure, 100 mg, 0.14 mmol) was dissolved in freshly distilled benzene (100 mL). DIB (224 mg, 0.70 mmol) in 4 mL of CH₂Cl₂ was added. The flask was cooled with an ice bath and stirred. A household luminescent light bulb (12 W, commercial household light bulb) was placed next to the reaction flask. TBHP (270 mg, 70%, 2.1 mmol) in 2 mL of CH₂Cl₂ was added dropwise in 2 min. The reaction was stopped after another 13 min. The solution was concentrated to about 3 mL on a rotovap keeping the flask wrapped with aluminum foil. The residue was chromatographed on a silica gel column, eluting with benzene and petroleum ether (60–90 °C) (1:1). Compounds **2** and **5** were eluted first as two separate minor bands, followed by **6** and **8** as another two major bands. Yield: compound **6**: 26 mg, 15%; compound **8**: 28 mg, 16%. ¹H NMR (600 MHz, CDCl₃): δ 1.30 (s, 9H), 1.31 (s, 9H), 1.34 (s, 9H), 1.43 (s, 9H), 1.54 (s, 9H), 1.61 (s, 9H). ¹³C NMR (150 MHz, CDCl₃; all signals represent 1C except as noted): δ 149.96, 149.39, 149.06, 148.99, 148.85, 148.69, 148.48, 148.46, 148.39, 148.37, 148.34 (3C), 148.28, 148.24, 148.22, 148.18, 148.15, 148.12, 148.05, 148.02, 147.94, 147.73, 146.80, 145.74, 145.69, 145.51, 144.63 (2C), 144.41, 144.29, 144.27, 144.16 (2C), 144.02, 143.85, 143.81, 143.77 (2C), 143.61, 143.54, 143.51, 143.09 (2C), 143.05, 142.89, 142.26, 141.86, 141.85, 141.23, 138.34, 137.84, 87.37 (sp³), 84.68 (sp³), 83.18 (2C, sp³), 82.01 (C-(CH₃)₃), 81.66 (C-(CH₃)₃), 81.49 (C-(CH₃)₃), 81.35 (C-(CH₃)₃), 81.26 (sp³), 80.91 (C-(CH₃)₃), 80.82 (C-(CH₃)₃), 80.63 (sp³), 80.26 (sp³), 72.17 (sp³), 27.19 (3CH₃), 26.90 (6CH₃), 26.84 (3CH₃), 26.72 (3CH₃), 26.59 (3CH₃). FT-IR (microscope): 2978, 2930, 1473, 1456, 1387, 1363, 1260, 1243, 1196, 1122, 1111, 1094, 1046, 1023, 1003, 874, 755, 675 cm⁻¹. ESI-MS (Bruker Esquire): *m/z* (rel intens) 1293 (100, M⁺ + Na). UV-vis (CHCl₃): 388, 431, 464 nm.

4,11,15,30-Tetra-tert-butylperoxy-(1,2),(3,14)-bisepoxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene (C₆₀(O)₂(OO^tBu)₄, **10).** Compound **7** (100 mg, 0.092 mmol) was dissolved in 25 mL of CH₂Cl₂. *m*-CPBA (600 mg, 70–75%, ~2.5 mmol) was added. The flask was wrapped with aluminum foil and stirred at rt. Progress of the reaction was monitored by TLC. The reaction was stopped after 30 h. The solution was treated with saturated NaHCO₃ (15 mL) twice to remove excess *m*-CPBA. The organic layer was separated, dried with Na₂SO₄, and evaporated. The residue was chromatographed on silica gel column eluting with benzene and petroleum ether (60–90 °C) (1:1). Unreacted **7** was eluted as the first band (12 mg), followed by compound **10**. Yield: 55 mg, 62% based on converted **7**. ¹H NMR (400 MHz, CDCl₃): δ 1.37 (s, 9H), 1.44 (s, 18H), 1.48 (s, 9H). ¹³C NMR (100 MHz, CDCl₃; all signals represent 1C except as noted): δ 149.57, 149.54 (2C), 149.23, 148.47 (2C), 148.41, 148.35, 148.32 (2C), 148.14 (2C), 148.10, 148.06, 147.95, 147.89(2C), 147.85, 147.72, 147.40, 147.22, 147.01, 146.71, 146.68, 146.25, 145.64, 145.55, 145.47, 145.18, 144.77, 144.74 (2C), 144.57, 144.44, 144.40, 144.30, 144.27 (2C), 144.22, 144.10, 144.07, 144.04, 143.79, 143.56, 143.52 (2C), 143.48, 143.15, 143.13, 140.03, 138.94, 138.49, 83.97 (sp³), 83.57 (sp³), 82.20 (C-(CH₃)₃), 82.09 (C-(CH₃)₃), 82.02 (C-(CH₃)₃), 81.90 (C-(CH₃)₃), 81.20 (sp³), 81.00 (sp³), 72.47 (sp³), 71.01 (sp³), 69.68 (sp³), 64.16 (sp³), 26.79 (3CH₃), 26.76 (3CH₃), 26.70 (3CH₃), 26.68 (3CH₃). FT-IR (microscope): 2979, 2920, 2850, 1463, 1387, 1364, 1261, 1244, 1193, 1108, 1095, 1048, 1018, 900, 871, 757 cm⁻¹. ESI-MS (Bruker Esquire): *m/z* (rel intens) 1109 (100, M⁺ + H), 1131 (80, M⁺ + Na), 1125 (24, M⁺ + H + O). UV-vis (CHCl₃): 389 nm.

15,30-Tetra-tert-butylperoxy-(1,2),(3,4),(11,12)-triepoxy-1,2,3,4,11,12,15,30-octahydro[60]fullerene (C₆₀(O)₃(OO^tBu)₂,

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11). Compound **3** (50 mg, 0.51 mmol) was dissolved in 35 mL of benzene, and *m*-CPBA was added (500 mg, 70–75%, ~2.1 mmol). The solution was wrapped with aluminum foil and stirred at rt for 20 h. The solution was treated with NaHCO₃ (0.5 g in 20 mL of H₂O) to remove excess *m*-CPBA. The organic layer was separated, dried with Na₂SO₄, and concentrated to 5 mL. Chromatography on silica gel column eluting with benzene and petroleum ether (60–90 °C) (1:2) afforded unreacted **3** (5 mg), **4** (5 mg), and **11** (5 mg, 10%).

¹H NMR (400 MHz, C₆D₆/CS₂ = 1:5): δ 1.36 (s, 18H). ¹³C NMR (150 MHz, C₆D₆/CS₂ = 1:5; all signals represent 2C except as noted): δ 150.13, 148.63, 148.43, 148.33, 147.92, 147.70, 147.40, 147.13 (1C), 146.99, 146.29, 146.18 (1C), 146.17, 146.07, 145.66, 145.48, 144.81, 144.79, 144.75, 144.74, 144.72, 144.65, 144.56, 144.48, 144.08, 144.02, 143.66, 141.82, 83.74 (2C, sp³), 81.78 (2C-(CH₃)₃), 71.42 (2C, sp³), 71.00 (sp³), 69.15 (2C, sp³), 64.72 (sp³), 26.94 (6CH₃). FT-IR (microscope): 2956, 2920, 2850, 1462, 1386, 1363, 1192, 1091, 1041, 1021, 866, 829, 795, 730 cm⁻¹. MALDI-TOF: *m/z* (rel intens) 817 (33, C₆₀(O)₆⁺ + H), 801 (62, C₆₀(O)₅⁺ + H), 785 (100, C₆₀(O)₄⁺ + H), 769 (71, C₆₀(O)₃⁺ + H), 753 (26, C₆₀(O)₂⁺ + H). UV-vis (CHCl₃): 385 nm.

4,11,15,30-Tetra-tert-butylperoxy-2-hydroxy-1-nitroso-1,2,4,11,15,30-hexahydro[60]fullerene (C₆₀(ONO₂)(OH)(OOBu)₄, **12)**. Compound **7** (100 mg, 0.092 mmol) was dissolved in benzene (20 mL). Concentrated nitric acid (2 mL) was added. The flask was wrapped with aluminum foil and stirred at rt. Progress of the reaction was monitored by TLC. Petroleum ether (60–90 °C, 20 mL) was added when **12** reached its maximum (around 8 h); the mixture was chromatographed on silica gel column. Elution with benzene–petroleum ether (60–90 °C) (1:1) gave some unreacted **7** as the first band, followed by compound **12**. Yield: 62 mg, 58%. ¹H NMR (400 MHz, CDCl₃): δ 5.31 (s, 1H), 1.48 (s, 18H), 1.48 (s, 18H). ¹³C NMR (100 MHz, CDCl₃; all signals represent 2C except as noted): δ 155.00, 149.77, 149.17, 149.16, 148.71, 148.49, 148.41 (3C), 148.36, 147.90, 147.63 (1C), 147.49, 147.29, 146.83, 145.71, 145.05, 145.03, 144.61, 144.58, 144.54, 144.49, 144.10, 144.01, 143.47, 143.33, 142.99, 141.09, 139.97, 85.46 (sp³), 82.96 (2C-(CH₃)₃), 82.23 (2C, sp³), 82.00 (2C-(CH₃)₃), 81.82 (2C, sp³), 80.83 (sp³), 26.77 (6CH₃), 26.75 (6CH₃). FT-IR (microscope): 3484, 2979, 2932, 1662, 1474, 1456, 1388, 1364, 1291, 1193, 1101, 1048, 1022, 984, 873, 826 cm⁻¹. ESI-MS (Bruker Esquire): *m/z* (rel intens) 1178 (100, M + Na⁺). Anal. Calcd for C₆₀(ONO₂)(OH)(OOBu)₄: C, 78.96; H, 3.23; N, 1.21. Found: C, 78.37; H, 3.11; N, 1.08.

4,11,15,30-Tetra-tert-butylperoxy-1,2-dihydroxy-1,2,4,11,15,30-hexahydro[60]fullerene (C₆₀(OH)₂(OOBu)₄, **13)**. Compound **14** (110 mg, 0.1 mmol) was dissolved in benzene (10 mL). Tetrabutylammonium hydroxide solution (200 μL, 10% aqueous solution) was added. The flask was wrapped with aluminum foil. The resulting solution was stirred at room temperature. After 6 h, HCl (10 drops, 6 M) was added to the solution. The organic layer was separated and chromatographed on silica gel column (160–200 mesh). Unreacted compound **14** (25 mg) was eluted with benzene. Further elution with benzene–ethyl acetate (15:1) yielded **13** (21 mg). Yield: 36%, based on converted **14**. ¹H NMR (400 MHz, CDCl₃): δ 5.26 (s, 1H), 4.82 (s, 1H), 1.47 (s, 18H), 1.46 (s, 18H). ¹³C NMR (100 MHz, CDCl₃; all signals represent 2C except as noted): δ 156.10, 150.21, 149.19, 149.14, 149.025, 148.75, 148.72, 148.52 (1C), 148.45, 148.24, 147.52, 147.50 (1C), 147.45, 147.35, 147.15, 145.77, 145.26, 145.22, 145.11, 144.49, 144.45 (4C), 144.04, 143.44, 142.82, 142.72, 141.08, 137.21, 82.80 (2C-(CH₃)₃), 82.24 (sp³), 81.92 (2C-(CH₃)₃), 81.03 (sp³), 80.97 (2C, sp³), 75.49 (2C, sp³), 26.76 (6CH₃), 26.75 (6CH₃). FT-IR (microscope): 3356 (broad), 2978, 2926, 2853, 1579, 1454, 1388, 1364, 1192, 1092, 1046, 1023, 877, 672 cm⁻¹. ESI-MS (VG-Platform II): *m/z* (rel intens) 1128 (100, M⁺ + H₂O), 1172 (15). UV-vis (CHCl₃): 383, 470 nm.

4,11,15,30-Tetra-tert-butylperoxy-1,2-((2-hydroxy-2-trifluoromethyl)-1,3-dioxolano)-1,2,4,11,15,30-hexahydro-

[60]fullerene (C₆₀((O)(O)C(OH)CF₃)(OOBu)₄, **14)**. Compound **7** (110 mg, 0.1 mmol) was dissolved in benzene (6 mL). Trifluoroacetic acid (99%, 1 mL) was added. The mixture was stirred at room temperature. After 40 min, petroleum ether (60–90 °C, 6 mL) was added to the mixture. Column chromatography on silica gel (160–200 mesh) eluting with petroleum ether (60–90 °C)–benzene (1:1) gave compound **14**. Yield: 105 mg, 86%. ¹H NMR (400 MHz, CDCl₃): δ 1.37 (s, 9H), 1.41 (s, 9H), 1.48 (s, 9H), 1.50 (s, 9H), 6.36 (s, 1H). ¹³C NMR (100 MHz, CDCl₃; all signals represent 1C except as noted): δ 151.39, 149.35, 149.29, 149.24 (2C), 149.15, 148.75, 148.61, 148.33 (3C), 148.24 (2C), 148.06, 147.82, 147.72, 147.37, 147.30, 147.29, 147.23, 147.17 (2C), 147.12, 147.04, 146.97, 146.84, 146.82, 146.66, 145.63, 145.43, 145.32, 145.24, 145.08, 144.94, 144.79, 144.72, 144.66, 144.61, 144.57, 143.89, 143.83, 143.79, 143.67, 143.44, 143.34, 143.16 (2C), 143.11, 142.96, 142.28, 141.22, 140.35, 139.68, 136.84, 119.20 (q, *J* = 283.4 Hz, CF₃), 116.07 (q, *J* = 37.3 Hz, C-CF₃), 90.46 (sp³), 85.15 (sp³), 83.30 (C-(CH₃)₃), 82.98 (sp³), 82.89 (sp³), 82.25 (C-(CH₃)₃), 82.19 (C-(CH₃)₃), 81.75 (C-(CH₃)₃), 80.73 (sp³), 80.52 (sp³), 26.79 (6CH₃), 26.55 (3CH₃), 26.46 (3CH₃). FT-IR (microscope): 3396, 2979, 2926, 2852, 1459, 1388, 1365, 1197, 1159, 1102, 1067, 1023, 1002, 871, 749 cm⁻¹. ESI-MS (VG-Platform II): *m/z* (rel intens) 1224 (M⁺ + H₂O), 1126 (30), 616 (24). UV-vis (CHCl₃): 383, 472 nm.

5,30-Bis-tert-butylperoxy-1,2-epoxy-3,11-dihydroxy-4,9,12,25-tetramethoxy-1,2,3,4,9,11,12,15,25,30-decahydro[60]fullerene (C₆₀(O)(OH)₂(OMe)₄(OOBu)₂, **18)**. Compound **7** (50 mg, 0.046 mmol) was dissolved in freshly distilled benzene (50 mL). The flask was cooled in an ice–water bath. Sodium methoxide (10 mg, 0.185 mmol) and CH₃OH (1 mL) were added. Progress of the reaction was monitored by TLC. After 1.5 h, the reaction was quenched with four drops of concentrated HCl. The solvent was removed under vacuum. The residue was chromatographed on silica gel column eluting with benzene and dioxane (20:1). Unreacted **7** was eluted as the first band (22 mg), followed by compounds **15**, **16**, and **18** (10 mg). Further elution with benzene–dioxane (10:1) gave compound **17**. The yield of compound **18** was 36% on the basis of converted **7**. ¹H NMR (600 MHz, CDCl₃): δ 1.30 (s, 9H), 1.43 (s, 9H), 3.72 (s, 3H), 3.76 (s, 3H), 3.90 (s, 3H), 3.93 (s, 3H), 4.84 (s, 1H), 4.99 (s, 1H). ¹³C NMR (150 MHz, CDCl₃; all signals represent 1C except as noted): δ 152.80, 152.73, 152.32, 150.60, 150.22, 149.64, 149.57, 149.55, 149.46, 149.41, 149.29, 148.88, 148.85, 148.82, 148.79, 148.71, 148.40, 148.25, 148.11, 148.07, 147.93, 147.89, 147.41, 147.40, 147.33, 147.10, 147.09, 146.93, 146.84, 146.79, 146.51, 146.40, 146.32, 146.05, 146.01, 145.77, 145.65, 145.64, 145.49, 145.11, 144.60, 144.58, 144.46, 144.29, 144.12, 141.43, 140.78, 137.56, 137.43, 136.92, 82.63 (sp³), 82.35 (C-(CH₃)₃), 81.66 (C-(CH₃)₃), 80.33 (sp³), 79.58 (sp³), 79.30 (sp³), 78.60 (sp³), 78.20 (sp³), 76.96 (sp³), 75.70 (sp³), 75.29 (sp³), 57.63 (OMe), 56.00 (OMe), 54.89 (OMe), 54.34 (OMe), 26.69 (3CH₃), 26.64 (3CH₃), for detailed assignment see Figure 3. FT-IR (microscope): 3495, 3431, 2980, 2951, 2932, 1512 (CS₂), 1456, 1364, 1192, 1137, 1113, 1094, 1083, 1018 cm⁻¹ (crystal); 3468 (broad), 2985, 2944, 1458, 1365, 1191, 1095 cm⁻¹ (powder). ESI-MS (VG-Platform II): *m/z* (rel intens) 1090 (100, M⁺ + H₂O), 1040 (23). UV-vis (CHCl₃): 368 nm.

A single crystal suitable for X-ray diffraction study was obtained from CS₂–C₂H₅OH (1:1): crystal system; space group: triclinic, *P*-1; unit cell dimensions: *a* = 10.124(2) Å, *α* = 98.93(3)°, *b* = 10.340(2) Å, *β* = 96.53(3)°, *c* = 23.975(5) Å, *γ* = 105.99(3)°; volume = 2350.9(8) Å³. Final *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0829, *wR*₂ = 0.2149.

Open-Cage [60]Fullerene Derivative (C₆₀(O)(O)₂(OOBu)₄, **20)**. Compound **6** (200 mg, 0.16 mmol) was dissolved in 100 mL of benzene, and I₂ (2 g, 7.9 mmol) was added. The solution was stirred and irradiated with two luminescent light bulbs (12 W, commercial household bulbs). After 40 h, the solution was treated with Na₂S₂O₃ (4 g in 20 mL H₂O) to reduce excess iodine. The organic layer was separated. The aqueous layer was extracted with benzene (2 × 20 mL). The

combined benzene solution was concentrated to 5 mL and chromatographed on silica gel with the column wrapped with an aluminum foil. Benzene eluted a mixture of unreacted **6**, **7**, and **10** as the first band and then the second band of product **20**. Yield: 55 mg, 27%. ^1H NMR (400 MHz, CDCl_3): δ 1.29 (s, 9H), 1.33 (s, 9H), 1.34 (s, 9H), 1.47 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3 ; all signals represent 1C except as noted): δ 193.11, 192.08, 154.44, 150.02, 149.35, 149.22, 148.97, 148.78, 148.76, 148.75 (2C), 148.34, 148.30, 148.18, 148.14, 148.03, 147.80, 147.77, 147.75, 147.62, 147.61, 147.46, 147.38, 147.27, 147.21, 147.16, 147.13, 147.00, 146.61, 146.06, 145.68, 145.13 (4C), 145.09, 145.03, 144.99, 144.98, 144.73, 143.77, 143.38, 143.25, 143.08, 141.84, 141.08, 140.84, 140.64, 140.55, 140.30, 138.90, 138.56, 138.21, 137.95, 92.18 (sp^3), 92.02 (sp^3), 88.12 (sp^3), 83.91 (sp^3), 82.43 ($\text{C}-(\text{CH}_3)_3$), 82.36 ($\text{C}-(\text{CH}_3)_3$), 82.22 ($\text{C}-(\text{CH}_3)_3$), 82.21 ($\text{C}-(\text{CH}_3)_3$), 68.17 (sp^3), 66.60 (sp^3), 26.73 (3 CH_3), 26.71

(3 CH_3), 26.70 (3 CH_3), 26.62 (3 CH_3). FT-IR (microscope): 2978, 2925, 2852, 1748, 1458, 1388, 1364, 1193, 1098, 1053, 1020, 892, 870 cm^{-1} . ESI-MS (Bruker Esquire): m/z (rel intens) 1125 (14, $\text{M} + \text{H}^+$), 1147 (100, $\text{M} + \text{Na}^+$), 1163 (38, $\text{M} + \text{K}^+$), 1123 (12, $\text{M} + \text{O} + \text{K}^+$). UV-vis (CHCl_3): 379, 468 nm.

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Supporting Information Available: Experimental procedure and characterization data for compounds not listed in the Experimental Section, crystallographic data for **18** and selected NMR, MS, IR, UV-Vis spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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