JOC Article

Regiochemistry of [70]Fullerene: Preparation of $C_{70}(OO^tBu)_n$ (n = 2, 4, 6, 8, 10) through Both Equatorial and Cyclopentadienyl Addition Modes

Zuo Xiao,[†] Fudong Wang,[†] Shaohua Huang,[†] Liangbing Gan,*[,†,‡] Jiang Zhou,[§] Gu Yuan,[§] Mujian Lu,[§] and Jinqi Pan[§]

Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

gan@pku.edu.cn

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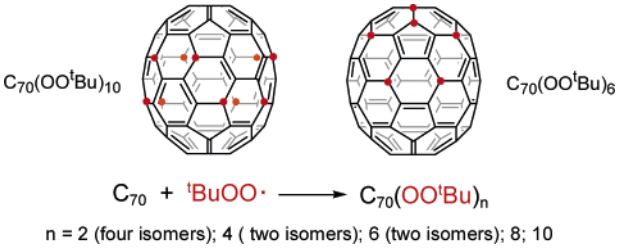

tert-Butylperoxy radicals add to [70]fullerene to form a mixture of adducts $C_{70}(OO^tBu)_n$ (n = 2, 4, 6, 8, 10). Four isomers were isolated for the bis-adduct with the two *tert*-butylperoxo groups attached at 1,2-, 5,6-, 7,23-, and 2,5-positions, respectively. Two isomers were isolated for the tetrakis-adduct with the *tert*-butylperoxo groups located along the equator in C_s symmetry and on the side in C_1 symmetry, respectively. Similarly, two isomers were isolated for the hexakis-adducts with a structure related to the tetrakis-adducts, one of which has the cyclopentadienyl substructure. No isomer was detected for the octakis- and decakis-adducts. The C_s-symmetric octakis- and C_2-symmetric decakis-adducts have all the *tert*-butylperoxo groups located along the equator. The decakis-adduct is the major product under optimized conditions. The compounds were characterized by their spectroscopic data. Chemical correlation through further addition of *tert*-butylperoxy radicals to isolated pure derivatives confirmed the structure assignment. Mechanisms of the *tert*-butylperoxy radical addition to C_{70} follow two pathways: equatorial addition along the belt and cyclopentadienyl addition on the side.

Introduction

Regiochemistry of fullerene multiaddition is unprecedented in organic chemistry because of the unique spherical structure of fullerenes. Several prototypes of multiple-addition modes have been reported, some of which are highly regioselective.[1] For the icosahedral [60]-fullerene, both the octahedral T_h-symmetric addition[2] and the cyclopentadienyl addition modes[3] have been observed. Multiadditions of the D_{5h}-symmetric [70]fullerene are more complex and less understood.[4] The pole carbons with relatively high pyramidalization show greater reactivity in some reactions. Selective additions at the less pyramidalized carbons have also been reported. Compounds with the general formula $C_{70}X_{8/10}$ have all the addends at the equator.[5] Such an equatorial addition

[†] Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University.

[‡] Chinese Academy of Sciences.

[§] College of Chemistry and Molecular Engineering, Peking University.

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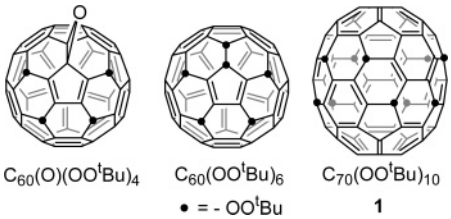
mode probably undergoes a sequential 1,4-adition, but a detailed mechanism remains unknown. Cu(I)-mediated addition of Grignard reagents to [70]fullerene forms the tris-adducts $C_{70}R_3H$. The reaction takes place 100% selectively on the side of [70]fullerene and stops at the tris-addition without the expected pentakis-adduct.[6] So far, the cyclopentadienyl mode has not been observed for [70]fullerene.

We have recently reported that *tert*-butylperoxy radicals add to fullerenes selectively to form $C_{60}(O)(OO^tBu)_4$, $C_{60}(OO^tBu)_6$, and $C_{70}(OO^tBu)_{10}$ **1**.[7] Further investigation of the [60]fullerene reactions have resulted in the isolation of various key intermediates $C_{60}(O)_n(OO^tBu)_m$ (n = 0−3, m = 0−6) and confirmed the stepwise cyclopentadienyl addition mechanism. Here we report a detailed investigation of the reaction between *tert*-butylhydroperoxide (TBHP) and [70]fullerene. Characterization of all the isolable products and their chemical correlation reveals both equatorial addition and cyclopentadienyl addition modes for [70]fullerene.

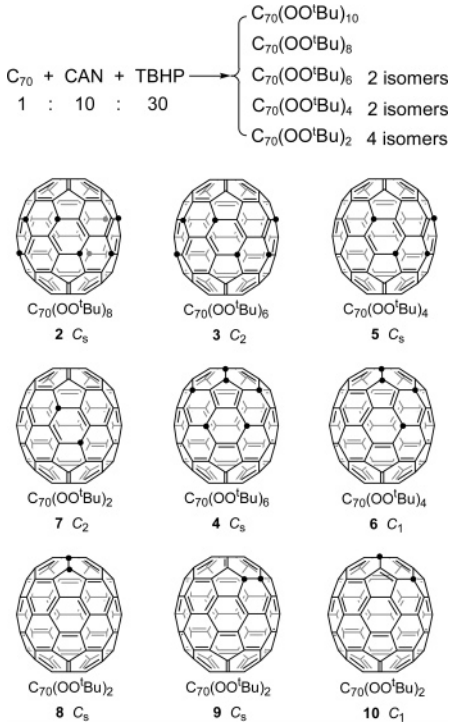


Results and Discussion

Synthesis. Various methods were tested for the reaction between [70]fullerene and TBHP. When a catalyst such as ruthenium(II or III) or iron(III) complex was used, the reaction was relatively slow and a large amount of TBHP was necessary. The yield of decakis-adduct $C_{70}(OO^tBu)_{10}$ **1** was 8%. The stoichiometric reaction with ammonium cerium(IV) nitrate (CAN)[8] needed much less TBHP and also resulted in better selectivity. The extent of multiaddition could be controlled by the amount of CAN. When the molar ratio between C_{70}, CAN, and TBHP was 1:20:40, the reaction gave the decakis-adduct **1** as the main product (30% on the basis of converted C_{70}). When the molar ratio was 1:10:30, the reaction gave products with fewer addends (Scheme 1).

All the purifications were carried out on a silica gel column. A mixture of CS_2, benzene, and petroleum ether was used for the separation of isomeric bis-adducts. CS_2 was necessary due to their relatively low solubility. Bis-adduct isomers with *tert*-butyl groups closer to the poles are more polar than isomers with *tert*-butyl groups closer to the equator, as indicated by their R_f values. Adducts with four or more *tert*-butylperoxo groups are very soluble. All the [70]fullerene mixed peroxides are very stable. A solid sample of **1** showed only 50% decomposition after being stored for two years at rt under ambient atmosphere.

SCHEME 1. Addition of *tert*-Butylperoxo Radical to C_{70}



Characterization. The decakis-adduct **1** is C_2 symmetric as shown by NMR spectra. At rt, the NMR signals are relatively broad due to hindered rotation of the addends. At 283 K, the ^1H NMR shows four methyl signals with an integral ratio 1:1:1:2, the last of which is due to overlapping of two *tert*-butyl groups. The ^{13}C NMR spectrum at 283 K shows five different *tert*-butyl signals for the 10 *tert*-butyl groups. There are five separate tertiary C signals and four methyl signals with an intensity ratio of 1:2:1:1, the second of which is due to overlapping of two signals. The [70]fullerene skeleton carbons are well resolved at 283 K with no overlapping. There are 35 fullerene signals, 30 of which are in the sp^2 C region (all with equal intensity) and five in the sp^3 C region (84.23, 83.88, 83.79, 83.55, 81.33 ppm all with equal intensity). This is in agreement only with a C_2-symmetric structure. The C_s structure requires 32 signals in the sp^2 region, four of which should be half intensity compared to the rest (these four sp^2 carbons are on the symmetry plane).

The octakis-adduct $C_{70}(OO^tBu)_8$ **2** is C_s symmetric, in agreement with other octakis-adducts such as $C_{70}Ph_8$, $C_{70}Cl_8$, and $C_{70}H_8$.[5] The ^1H NMR showed four *tert*-butyl methyl signals. On the ^{13}C NMR, the [70]fullerene skeleton carbons appeared as four sp^3 signals and 33 sp^2 signals, four of which are half intensity at 154.56, 152.10,

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151.29, 144.29 ppm. There would be 31 sp^2 signals, all with equal intensity should it have C_2 symmetry.

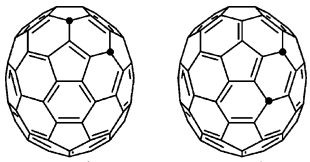
Isomers **3** and **4** were isolated for the hexakis-adduct $C_{70}(OO^tBu)_6$. Compound **3** has all the *tert*-butylperoxo groups at the equator. There are 3 sp^3 and 31 sp^2 signals for the C_{70} skeleton, one of which shows double intensity due to overlapping of two signals. This is consistent with C_2 symmetry. The other isomer **4** is C_s symmetric. It shows four *tert*-butyl signals in a 1:2:2:1 ratio on the ^1H NMR spectrum. The ^{13}C NMR comprises four sp^3 skeleton carbons in a 1:1:2:2 ratio. For the sp^2 carbons, there are 33 signals (the one at 151.46 ppm is due to two overlapping signals). The two signals at 151.80 and 149.58 ppm are half intensity and can be assigned to the two sp^2 carbons on the mirror plane.

The tetrakis-adduct $C_{70}(OO^tBu)_4$ also has two isomers **5** and **6**. Isomer **5** is C_s symmetric. The four *tert*-butylperoxo groups are located on the equator. There are 2 sp^3 and 35 sp^2 signals for the C_{70} skeleton. The four signals at 150.60, 149.24, 148.46, and 146.88 ppm are half intensity and can be assigned to the four carbons on the mirror plane. The other isomer **6** is C_1 symmetric. All the fullerene carbons show different chemical shifts except that three sp^2 signals were overlapped. The structure of **6** was further confirmed by its further addition reaction (see Chemical Correlation).

The bis-adducts are more complicated with four isomers **7**−**10**. Isomer **7** is C_2 symmetric. Its ^{13}C NMR spectrum comprises 1 sp^3 and 34 sp^2 fullerene signals. Isomer **8** is C_s symmetric. There are 2 sp^3 and 35 sp^2 fullerene signals, two of which are half-intensity sp^2 signals (147.33 and 151.12 ppm, the latter one was overlapped with another signal). This pattern suggests C_s symmetry for **8** with the two sp^3 fullerene carbons connecting the *tert*-butylperoxo groups on the mirror plane. Isomer **9** is also C_s symmetric. It has the two *tert*-butylperoxo groups on the two sides of the mirror plane. There are one sp^3 and 36 sp^2 fullerene carbon signals. The signals at 155.11, 150.11, 148.97, and 146.61 ppm are on the mirror plane with half intensity. It was difficult to purify isomer **10**. Its NMR data were derived from spectra obtained with a mixture containing **9** and **10** by comparison with those of pure isomer **9**. The data obtained this way were sufficient to identify the C_1-symmetric nature for isomer **10**. The number of ^{13}C NMR signals defined the C_1 symmetry without any doubt.

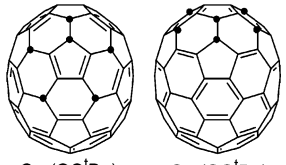
Chemical shifts of the bis-adducts increase in the order 7,23-isomer **7**, 5,6-isomer **9** to 1,2-isomer **8**. The ^1H NMR chemical shifts are 1.26 for **7**, 1.34 for **9**, and 1.35, 1.63 for **8**. The ^{13}C NMR chemical shifts of the sp^3 fullerene carbon are 80.77 for **7**, 86.57 for **9**, and 88.68, 90.42 for **8**. Such an order of chemical shifts is in good agreement with the fact that the pole carbons of [70]fullerene are more electron deficient than those on the equator.[5d,e]

There are two possible structures for the C_1-symmetric bis-adduct: 2,5-isomer **10** and 5,21-isomer **10a** (other structures can be ruled out by chemical correlation; see the following section). Kepert and Clare have calculated all possible isomers for the bis-adduct $C_{70}H_2$ and related adducts $C_{70}R_2$.[9] The calculation indicates that the most stable isomers for $C_{70}H_2$ are 5,6-$C_{70}H_2$, 1,2-$C_{70}H_2$, 7.23-$C_{70}H_2$, and 2,5-$C_{70}H_2$. Their formation enthalpies differ by only 3 kcal/mol. The 2,5-$C_{70}H_2$ is 18.5 kcal/mol more stable than the 5,21-isomer. Thus the C_1-symmetric bis-adduct observed here is more likely to be the 2,5-isomer **10** rather than the 5,21-isomer **10a**. The ^1H NMR signals for **10** appear at 1.25 and 1.58 ppm. The sp^3 fullerene ^{13}C signals appear at 77.10 and 82.34 ppm. These chemical shifts do not follow the order observed for isomers **7**−**9**. The phenomena may due to the newly formed double bond on the pentagon, which is unique for **10** and not present in isomers **7**−**9**.



UV−vis spectra of the 1,2-isomer **8** and 5,6-isomer **9** show exactly the same pattern as those reported for other C_{70} bis-adducts such as $C_{70}H_2$ and $C_{70}(H)(CH_2COOMe)$ reported by Meier et al.[10] The UV−vis spectrum of **9** rules out the C_s-symmetric 1,4-isomer **11** (see Mechanism Consideration), which would show the same NMR pattern as **9**. Various methods were tested to obtain the mass spectra. ESI proved to be the best for these fullerene mixed peroxides. All the compounds except the bis-adducts showed a molecular ion signal as the base peak. The bis-adducts were not soluble in the mixture solvent $CHCl_3$/MeOH required for ESI measurement.

Chemical Correlation. The above assignments are mainly based on the number of NMR signals. There are other C_2- and C_s-symmetric structures that could also explain the NMR data. For example, the C_s-symmetric compound **4a** with the addends on the poles would have the same NMR pattern as that of **4**. To confirm the NMR-derived structures, we carried out a series of correlation experiments starting with isolated pure species.

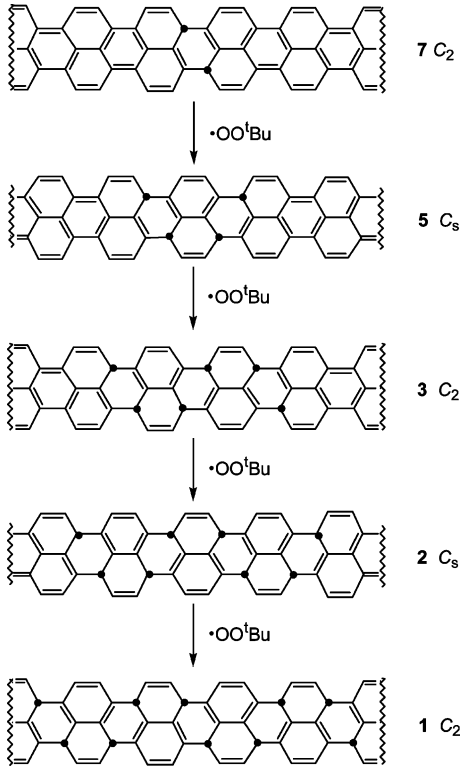


Addition of *tert*-butylperoxo radical, generated from TBHP and CAN, to pure C_s-symmetric octakis-adduct **2** resulted in decakis-adduct **1**. Addition of *tert*-butylperoxo radical to pure C_2-symmetric hexakis-adduct **3** gave both **1** and **2**. Similarly, **5** yielded **1**−**3**, whereas **7** yielded **1**−**3** and **5** (Scheme 2). The reactions were more selective than those starting from [70]fullerene. There was hardly any other product formed except the equator products in this series of experiments. Progress of the reactions was easily monitored by TLC, and the products were confirmed by ^1H NMR spectra.

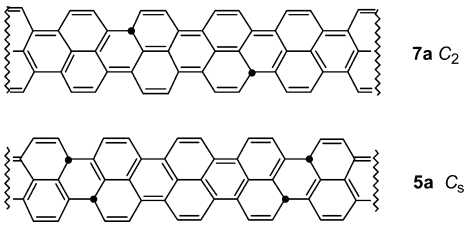
(9) Clare, B. W.; Kepert, D. L. *J. Mol. Struct.: THEOCHEM* **1999**, *491*, 249−264.

(10) (a) Wang, Z. W.; Meier, M. S. *J. Org. Chem.* **2003**, *68*, 3043−3048. (b) Wang, Z. W.; Meier, M. S. *J. Org. Chem.* **2004**, *69*, 2178−2180.

SCHEME 2. Chemical Correlation of the Equatorial Derivatives



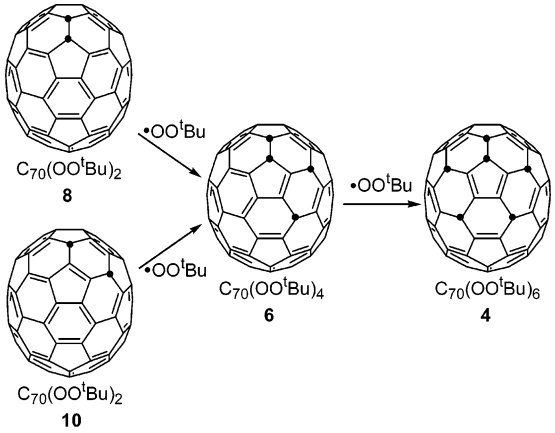
The above experiments confirm that *tert*-butylperoxo groups are adjacent to each other along the equator rather than separated in these compounds. The bis-adduct isomer **7a** would show the same NMR pattern as that of **7**. However, **7a** would not give **5** as the only tetrakis-adduct and thus can be ruled out. Similarly, isomer **5a** for the tetrakis-adduct can be ruled out since only one hexakis-adduct **3** was observed from further addition of the tetrakis-adduct.



The cyclopentadienyl hexakis-adduct $C_{70}(OO^tBu)_6$ can have either structure **4** or **4a** on the basis of the NMR data. To establish the structure, we treated the C_s-symmetric 1,2-adduct **8** with *tert*-butylperoxo radical (Scheme 3). The reaction afforded the C_1-symmetric tetrakis-adduct **6**. Addition of *tert*-butylperoxo radical to **6** yielded the C_s-symmetric hexakis-adduct **4**. This result confirmed the structure of the C_1-symmetric tetrakis-adduct **6**.

The structure of **4** was established by the conversion of C_1-symmetric **10** to **6** and then to **4**. Assuming the two *tert*-butylperoxo groups are attached to C_{70} in an ortho (1,2-) or para (1,4-) relative position, there is no C_1-symmetric bis-adduct that could yield the cap isomer **4a** by further addition of *tert*-butylperoxo radicals. The formation of **4** from **10** thus rules out the cap isomer **4a**.

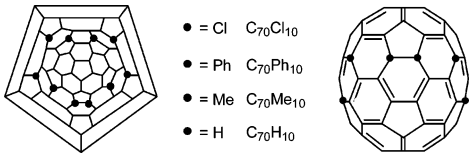
SCHEME 3. Chemical Correlation of the Cyclopentadienyl Derivatives



The reactivity shown in these cyclopentadienyl series is quite similar to that observed for the C_{60} analogues. For both C_{60} and C_{70}, further addition of the *ortho*-bisadduct (1,2-) is much slower than that of the *para*-bisadduct (1,4-). For the *para*-bisadduct, the double bond on the pentagon can form an allyl radical upon the addition of a third radical, which may be the main reason for the observed difference.

Mechanism Consideration. Compounds characterized above follow two types of addition patterns for [70]-fullerene: a stepwise para addition (1,4-) pathway along the equator and a cyclopentadienyl mode on the side. The equatorial mode is favored over the cyclopentadienyl mode, as indicated by the higher yields of equator products than cyclopentadienyl products. Preliminary tests with a mixture of C_{60} and C_{70} indicated that C_{60} reacted faster than C_{70} toward *tert*-butylperoxo addition.

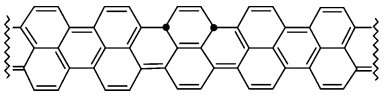
Equatorial Addition. Multiaddition along the equator has been reported for several other [70]fullerene derivatives. The structure of $C_{70}Cl_{10}$, $C_{70}Ph_{10}$, $C_{70}Me_{10}$, and $C_{70}H_{10}$ were derived from spectroscopic data.[5] Later, the X-ray structure of $C_{70}Me_8$ was reported.[11] Recently, the structure of $C_{70}Br_{10}$ was solved by X-ray analysis.[5f] For these C_s-symmetric decakis-adducts the last step of addition is an ortho (1,2-) addition rather than para (1,4-) addition. Even though two groups are adjacent in these multiadducts, the C_s structure is the most stable isomer according to theoretical calculation. As the size of the addend increases, the C_2 structure becomes favored. Theory predicts that the C_2 isomer of $C_{70}(^tBu)_{10}$ is about 55 kcal mol^{-1} more stable than the corresponding C_s isomer.[9] The *tert*-butylperoxy group in the present system is apparently bulky enough and leads to the C_2 addition pattern.



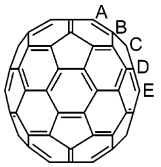
Two bis-adducts can be envisioned for the first step of addition along the equator, the C_2-symmetric **7** and the

(11) Darwish, A. D.; de Guio, P.; Taylor, R. *Fullerenes Nanotubes Carbon Nanostruct.* **2002**, *10* (4), 261−272.

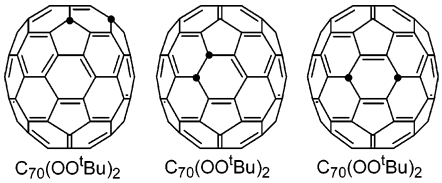
C_s-symmetric **7b**. The latter was not observed and probably not formed. Formation of **7** eliminates a double bond on the pentagon, but the number of double bonds on the pentagons remains the same in the formation of **7b**. Calculation indicates that the thermodynamically most stable isomer of $C_{70}H_2$ with nonadjacent hydrogens is the 7,23-isomer.[9,12] The bis-benzyl adduct $C_{70}Bn_2$ was shown to be the 7,23-iosmer.[13]



The *tert*-butylperoxo groups already in place have a strong directing effect for incoming new *tert*-butylperoxo groups as shown in the correlation reactions. The first addition site determines the structure of the final multiadduct. If the first *tert*-butylperoxo group adds at one of the 20 D carbons on the C_{70} surface, the second addition will form the bis-adduct **7**. The tetrakis-adduct **5** is the only product starting from the bis-adduct **7**, **3** is the only hexakis-adduct starting from **5**, and so forth up to the decakis-adduct **1**.

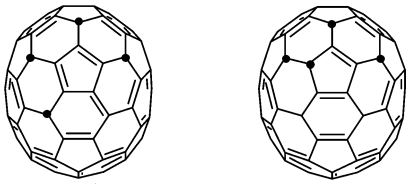


Cyclopentadienyl Addition. The cyclopentadienyl addition mode is well-known for [60]fullerene but has not been reported for [70]fullerene. In the formation of the cyclopentadienyl-type hexakis-adduct **3**, all the A, B, C, and E carbons on the C_{70} surface may act as the first addition site. Addition at A can lead to either **8** or **10**. Addition at B can lead to **8** or **11**; addition at C can lead to **9**, **10**, or **10a**; and addition at E can lead to **10a**, **12**, and the C_{2v}-symmetric **13**. ESR study by Preston et al. has shown that three regioisomeric monoadducts were formed in the addition of a bulky radical to C_{70}, one of which was assigned as the addition at position A on the basis of its C_{60}-like *g* value.[14]



It is somewhat surprising that all four of the predicted most stable bis-adducts,[9] i.e., compounds **7**−**10**, were isolable and also characterizable in the present system. Isomer **11** is unlikely because it has an unfavorable double bond on the cap between two pyramidalized A carbons that are not effective for π bonding. Isomer **12** is unlikely because two *tert*-butylperoxo groups are adjacent to each other on the relatively planar equator.[15] Both the 1,2-isomer **8** and 5,6-isomer **9** have *ortho-tert*-butylperoxo groups. They are relatively stable because the groups are attached to more pyramidalized carbons on the pole and are thus further apart. Isomer **13** is much less stable than the 7,23-iosmer **7** since **13** has two more double bonds on the pentagon than **7** does. Calculated results also indicate that these isomers are much less stable.[9]

Only one tetrakis-adduct, compound **6**, was isolated in the cyclopentadienyl addition series. **6** may be formed from **8** or **10**. Another tetrakis-adduct isomer, **6a**, is quite likely also formed from **10** but probably too reactive toward further addition, yielding the hexakis-adduct **3**. In the *tert*-butylperoxo radical addition to C_{60}, there was no C_s-symmetric pseudofulvene $C_{60}(OO^tBu)_4$ detected either,[7] which reacted further to give the epoxy derivative $C_{60}(O)(OO^tBu)_4$.[16] Unlike the C_{60} reaction, there is no epoxy group in the present C_{70} derivatives.



Further addition of the 5,6-isomer **9** would give the tetrakis-adduct **6b**, but the reaction was very slow and did not give any characterizable product. Nakamura and co-workers prepared $C_{70}R_3H$, the structure of which is analogous to **6b**, with the three R groups symmetrically located on the side and H filling the other site. The 2,5-$C_{70}R_2$ isomer was proposed as an intermediate leading to $C_{70}R_3H$. This result supports the earlier assignment of the C_1-symmetric bis-adduct as the 2,5-isomer **10** rather than the 5,21-isomer **10a**.

Conclusion

The regiochemistry of [70]fullerene is more complicated than that of [60]fullerene. Unlike the exclusively cyclopentadienyl addition mode to C_{60}, addition of *tert*-butylperoxo radical to C_{70} follows two pathways: equatorial addition along the belt and cyclopentadienyl addition on the side. All five different types of carbon on [70]fullerene may be functionalized, including carbons on the equator line. *tert*-butylperoxo radical exhibits excellent reactivity toward fullerenes. The reaction yields isolable stepwise intermediates leading to multiadducts under mild conditions. Fullerene mixed *tert*-butyl peroxides could be easily separated by column chromatography. Their stability and solubility in common solvents facilitate characterization by spectroscopic data. We have reported that C_{60} peroxides are good starting materials for further functional-

(12) Henderson, C. C.; Rohlfing, C. M.; Cahill, R. A. *Chem. Phys. Lett.* **1993**, *213*, 383−388.
(13) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. W. *J. Org. Chem.* **2002**, *67*, 5946−5952.
(14) Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Chem. Soc., Chem. Common*. **1992**, 1259.
(15) Monoadducts of cycloaddition have been reported at the 7,21-positions; e.g.: (a) Herman, S. P.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 344−354. (b) *J. Am. Chem. Soc*. **1998**, *120*, 2337−2342.
(16) Pseudofulvene fullerene derivatives have been isolated in other systems: Murata, Y.; Shiro, M.; Komatsu, K. *J. Am. Chem. Soc.* **1997**, *119*, 8117−8118.

ization. Preliminary tests indicate that the decakis-adduct **1** may also be functionalized. Work is underway to prepare open-cage and/or heterofullerenes from the fullerene mixed peroxides.

Experimental Section

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

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

Synthesis of Decakis-adduct 1. C_{70} (98% pure, 50 mg, 0.06 mmol) was dissolved in benzene (100 mL). $(NH_4)_2Ce(NO_3)_6$ (CAN) (656 mg, 1.2 mmol, dissolved in 0.6 mL 0.1 mol/L H_2SO_4) and *tert*-butyl hydroperoxide (TBHP) (310 mg, 70%, 2.4 mmol) were added. The resulting solution was stirred for 10 min. The solution was evaporated. The residue was dissolved in 3 mL of CS_2 and chromatographed on a silica gel column (200−300 mesh, 4 × 15 cm), eluting with benzene/petroleum ether (60−90 °C) (2:1). C_{70} was recovered as the first band (7 mg). Several intermediate bands were collected together (10 mg). The decakis-adduct **1** was eluted as an orange-red band (27 mg, 30% yield on the basis of converted C_{70}).

Procedure for the Synthesis of Compounds 2−10. C_{70} (98% pure, 100 mg, 0.12 mmol) was dissolved in benzene (200 mL). $(NH_4)_2Ce(NO_3)_6$ (CAN) (658 mg, 1.2 mmol, dissolved in 0.6 mL 0.1 mol/L H_2SO_4) and *tert*-butyl hydroperoxide (TBHP) (463 mg, 70%, 3.6 mmol) were added. The resulting solution was stirred for 10 min. The solution was evaporated. The residue was dissolved in 5 mL of CS_2 and chromatographed on a silica gel column (200−300 mesh, 4 × 20 cm), eluting with benzene, petroleum ether (60−90 °C), and carbon disulfide (1:5:5). C_{70} was recovered as the first band (32 mg). The second, dark brown band was a mixture containing four bis-adducts (10 mg): **7**−**10**. The third, wine-red band was the tetrakis-adduct **6** (10 mg, yield 10% on the basis of converted C_{70}). After these three bands were eluted, the solvent was changed to benzene and petroleum ether (60−90 °C) (1:1). The fourth, black band was then eluted as a mixture containing **5** and **4** (8 mg). The fifth, black band was a mixture containing **3** and some unidentified products (6 mg). At this stage, the eluting solvent was changed to benzene and petroleum ether (60−90 °C) (2:1). The sixth, brown band was eluted and found to contain **2** (6 mg, yield 5% on the basis of converted C_{70}). The seventh, orange-red band was **1** (20 mg, yield 14% on the basis of converted C_{70}).

The reaction was repeated several times with the same scale to produce enough sample for characterization.

Purification of Bis-adducts. The mixture containing bis-adducts **7**−**10** from above was rechromatographed on a silica gel column eluting with benzene, petroleum ether (60−90 °C), and carbon disulfide (1:10:10). The first, dark brown band was pure **7**. The second, wine-red band was pure **8**. The third, dark brown band was a mixture of **9** and **10**.

Separation of 4 and 5 The mixture containing **4** and **5** from above was rechromatographed on silica gel column eluting with carbon tetrachloride. The first, black band was pure **5**. The second, light brown-red band was an uncharacterized minor product. The third, brown band was pure **4**.

Preparation of Pure 3. Pure **3** could not be obtained directly by column chromatography as described above: it contained some unidentified products. To obtain pure **3**, we treated pure **5** (10 mg, 8.4×10^{-6} mol) with CAN (20 mg, 36×10^{-6} mol) and TBHP (20 mg, 160×10^{-6} mol). The reaction gave pure **3** (2 mg, yield 44% on the basis of converted **5**; 6 mg **5** was recovered) as the main product, which was easily purified by chromatography eluting with benzene and petroleum ether (60−90 °C) (1:1).

Preparation of Pure 9. Pure **9** could not be obtained directly by column chromatography as described above. Both **9** and **10** were eluted together as a single band. To obtain pure **9**, we treated the mixture containing **9** and **10** with CAN and TBHP. **9** was relatively inert compared to **10**. The reaction thus gave pure **9** after **10** was converted to **6**, which could be easily separated from **9** (see below).

Conversion of 10 to 6. A stock NMR solvent was prepared by mixing $CDCl_3$ (5 mL), CS_2 (5 mL), and CH_2Cl_2 (2 drops). CS_2 was needed to improve the solubility. The ^1H NMR signal of CH_2Cl_2 at 5.31 ppm was used as an integral reference. A mixture containing **9** and **10** (10 mg) was dissolved in the stock solvent (0.6 mL), and its ^1H NMR was measured. The integral ratio between CH_2Cl_2, **9**, and **10** was 1:4.8:10.8 (total ^1H signals of two peaks for **10**)

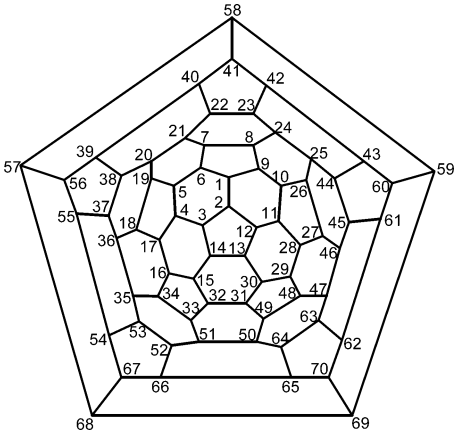
After the NMR was measured, the solvent was evaporated and the solid was dissolved in 20 mL benzene. Then, TBHP (50 mg, 0.39 mmol) and CAN/H_2SO_4 (12 μL, 1 mg/μL, 0.022 mmol) were added. The resulting solution was stirred for 10 min and concentrated, and the residue was chromatographed on a silica gel column, eluting with benzene and petroleum ether (60−90 °C) and carbon disulfide (1:2:2). The first, dark brown band was unreacted bis-adducts. The second band was the major product. There was only a trace amount of other byproducts.

The first and second bands were evaporated and dissolved separately in the stock solvent (0.6 mL). ^1H NMR spectra of the two samples were measured. The spectrum of the first band showed that the integral ratio between CH_2Cl_2, **9**, and **10** was 1:4.0:5.4. The spectrum of the second band showed that **6** was the major product, and the ratio between CH_2Cl_2 and **6** was 1:4.4 (total ^1H signals of four peaks for **6**).

The above results indicated that **10** was converted to **6** since most **9** was unchanged and the consumed **9** was not sufficient to give the isolated amount of **6**.

When the mixture of **9** and **10** was treated with more CAN and TBHP, **10** could be consumed completely, leaving pure **9**. In a separate experiment, pure **6** was converted to **4**.

C_2- and C_1-symmetric compounds prepared here are enatiomeric pairs. Only the ^fC enantiomer[4] was drawn and named according to the following numbering: [17]



7,19,23,27,33,37,44,49,53,63-Decakis-*tert*-butylperoxy-7,19,23,27,33,37,44,49,53,63-decakishydro[70]fullerene $C_{70}(OO^tBu)_{10}$ (1). For characterization data, see Supporting Information of ref 7a. The name has been corrected as above.

7,19,23,27,33,37,44,53-Octakis-*tert*-butylperoxy-7,19,-23,27,33,37,44,53-octakishydro[70]fullerene $C_{70}(OO^tBu)_8$

(17) For the IUPAC nomenclature system for fullerenes, see: Godly, E. W.; Taylor, R. *Pure Appl. Chem.* **1997**, *69*, 1411−1434.

(2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 18H), 1.44 (s, 18H), 1.40 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$), all signals represent 2C except where noted: δ 154.56 (1C), 153.43, 153.00, 152.73, 152.40, 152.10 (1C), 151.29 (1C), 150.78, 150.21, 150.10, 149.96, 149.76, 149.63, 148.96, 148.49, 148.39, 148.22, 146.98, 146.87, 146.65, 145.74, 145.70, 145.67, 145.11, 144.29 (1C), 144.13, 142.49, 140.17, 135.43, 135.12, 134.43, 133.39, 132.92, 84.21 (2C, sp^3), 83.84 (2C, sp^3), 83.48 (2C, sp^3), 82.22 (2C, sp^3), 81.72 (2*C*-$(CH_3)_3$), 81.61 (2*C*-$(CH_3)_3$), 81.50 (2*C*-$(CH_3)_3$), 81.49 (2*C*-$(CH_3)_3$), 26.92 ($6CH_3$), 26.82 ($12CH_3$), 26.76 ($6CH_3$). ESI-MS: *m/z* (rel intensity) 1570 (100, $M^+ + H_2O$).

7,19,23,27,37,44-Hexakis-*tert*-butylperoxy-7,19,23,27,-37,44-hexakishydro[70]fullerene $C_{70}(OO^tBu)_6$ (3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 18H), 1.38 (s, 18H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$), all signals represent 2C except where noted: δ 154.44, 152.44, 152.40, 151.51, 151.46, 151.11, 150.10, 149.49, 149.43, 148.42, 147.95, 147.84 (4C), 147.80, 147.41, 146.42, 146.28, 146.19, 145.72, 145.34, 144.79, 143.59, 143.00, 142.45, 141.39, 141.20, 138.22, 137.19, 135.57, 133.46, 132.63, 132.04, 83.95 (2C, sp^3), 83.46 (2C, sp^3), 81.85 (2C, sp^3), 81.76 (2*C*-$(CH_3)_3$), 81.61 (2*C*-$(CH_3)_3$), 81.49 (2*C*-$(CH_3)_3$), 26.84 ($6CH_3$), 26.79 ($6CH_3$), 26.74 ($6CH_3$). ESI-MS: *m/z* (rel intensity) 1392 (100, $M^+ + H_2O$).

1,2,5,10,21,24-Hexakis-*tert*-butylperoxy-1,2,5,10,21,24-hexakishyro[70]fullerene $C_{70}(OO^tBu)_6$ (4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 9H), 1.47 (s, 18H), 1.41 (s, 18H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$), all signals represent 2C except where noted: δ 152.64, 152.61, 151.80 (1C), 151.51, 151.46 (4C), 151.06, 150.92, 150.74, 150.23, 150.20, 149.82, 149.70, 149.58 (1C), 149.24, 148.73, 148.03, 147.68, 145.98, 145.93, 145.43, 145.42, 145.40, 145.36, 145.13, 145.10, 144.99, 139.98, 135.14, 135.10, 134.92, 134.21, 133.05, 89.63 (1C, sp^3), 84.86 (1C, sp^3), 82.62 (2C, sp^3), 81.49 (2*C*-$(CH_3)_3$), 81.22 (2*C*-$(CH_3)_3$), 80.98 (1*C*-$(CH_3)_3$), 80.97 (1*C*-$(CH_3)_3$), 79.90 (2C, sp^3), 26.86 ($9CH_3$), 26.80 ($6CH_3$), 26.69 ($3CH_3$). ESI-MS: *m/z* (rel intensity) 1392 (100, $M^+ + H_2O$).

7,19,23,37-Tetrakis-*tert*-butylperoxy-7,19,23,37-tetrakishydro[70]fullerene $C_{70}(OO^tBu)_4$ (5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 18H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$), all signals represent 2C except where noted: δ 154.28, 151.21, 151.13, 150.60 (1C), 150.50, 150.32, 149.24 (1C), 149.18, 149.14, 148.96, 148.54, 148.46 (1C), 146.88 (1C), 146.86, 146.77, 146.53, 146.17, 146.07, 145.68, 145.29, 145.03, 144.86, 143.91, 143.86, 143.62, 143.19, 143.15, 143.06, 142.97, 140.18, 137.63, 136.05, 135.50, 131.71, 130.46, 83.38 (2C, sp^3), 81.74 (2*C*-$(CH_3)_3$), 81.57 (2*C*-$(CH_3)_3$), 81.38 (2C, sp^3), 26.78 ($6CH_3$), 26.70 ($6CH_3$). ESI-MS: *m/z* (rel intensity) 1214 (100, $M^+ + H_2O$).

1,2,5,21-Tetrakis-*tert*-butylperoxy-1,2,5,21-tetrakishyro-[70]fullerene $C_{70}(OO^tBu)_4$ (6). ^{1}H NMR (400 MHz, C_6D_6:CS_2 = 1:1): δ 1.61 (s, 9H), 1.40 (s, 9H), 1.38 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6:CS_2 = 1:1), all signals represent 1C except where noted: δ 157.16, 155.48, 152.51, 152.26, 150.98, 150.66, 150.17, 150.05, 149.75, 149.65, 149.61, 149.35, 149.28, 149.13, 149.06, 148.96 (2C), 148.79, 148.61, 148.56, 148.47, 148.37, 148.11, 148.07 (2C), 147.86, 147.49, 147.39, 147.26, 147.12, 146.97, 146.95, 146.78, 146.73, 146.56, 146.30, 146.12, 146.01, 145.59, 145.37, 145.32, 145.24, 145.17, 145.01 (2C), 144.77, 144.75, 144.23, 143.86, 143.25, 143.12, 142.46, 140.65, 140.22, 139.76, 137.21, 133.83, 133.61, 132.23, 131.90, 131.65, 131.53, 130.47, 129.81, 128.66, ? (buried in C_6D_6 solvent signals), 85.29 (1C, sp^3), 83.20 (1C, sp^3), 82.99 (1C, sp^3), 81.21 (1*C*-$(CH_3)_3$), 81.06 (1*C*-$(CH_3)_3$), 80.93 (1*C*-$(CH_3)_3$), 80.74 (1*C*-$(CH_3)_3$), 77.50 (1C, sp^3), 26.85 ($3CH_3$), 26.57 ($3CH_3$), 26.54 ($3CH_3$), 26.45 ($3CH_3$). ESI-MS: *m/z* (rel intensity) 1214 (100, $M^+ + H_2O$).

^{1}H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1): δ 1.54 (s, 9H), 1.34 (s, 9H), 1.32 (s, 9H), 1.21 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$:CS_2 = 1:1), all signals represent 1C except where noted: δ 156.89, 155.36, 152.45, 152.01, 150.81, 150.49, 150.09, 149.99, 149.69, 149.46 (2C), 149.28, 149.20, 148.99, 148.96, 148.83, 148.70, 148.63, 148.52, 148.40, 148.38, 148.26, 148.00, 147.97 (2C), 147.70, 147.42, 147.30, 147.10, 147.04, 146.85, 146.74, 146.71, 146.52, 146.47, 146.17, 146.03, 145.92, 145.49, 145.24, 145.16 (2C), 145.09, 144.92, 144.89, 144.69, 144.63, 144.15, 143.73, 143.13, 142.82, 142.26, 140.55, 139.77, 139.66, 137.03, 133.75, 133.53, 132.16, 131.85, 131.48, 131.42, 130.66, 129.69, 128.52, 128.14, 85.11 (1C, sp^3), 82.86 (1C, sp^3), 82.72 (1C, sp^3), 81.32 (1*C*-$(CH_3)_3$), 81.22 (1*C*-$(CH_3)_3$), 81.05 (1*C*-$(CH_3)_3$), 80.80 (1*C*-$(CH_3)_3$), 77.26 (1C, sp^3), 26.85 ($3CH_3$), 26.60 ($3CH_3$), 26.59 ($3CH_3$), 26.45 ($3CH_3$).

7,23-Bis-*tert*-butylperoxy-7,23-dihyro[70]fullerene $C_{70}(OO^tBu)_2$ (7). ^{1}H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1): δ 1.26 (s). ^{13}C NMR (100 MHz, $CDCl_3$:CS_2 = 1:1), all signals represent 2C except where noted: δ 151.99, 151.88, 151.74, 150.92, 150.48, 149.01, 148.62, 148.40 (4C), 148.37, 147.40, 147.22 (4C), 146.86, 146.66, 146.18, 145.96, 145.53, 145.45, 145.29, 144.73, 144.54, 144.35, 144.09, 143.79, 143.37, 141.93, 140.98, 137.98, 136.81, 134.13, 133.92, 133.75, 132.25, 81.17 (2*C*-$(CH_3)_3$), 80.77 (2C, sp^3), 26.59 ($6CH_3$).

1,2-Bis-*tert*-butylperoxy-1,2-dihyro[70]fullerene $C_{70}(OO^tBu)_2$ (8). ^{1}H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1): δ 1.35 (s, 9H), 1.63 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$:CS_2 = 1:1), all signals represent 2C except where noted: δ 154.96, 154.75, 151.53, 151.34, 151.12 (3C), 150.64, 150.06, 149.78, 149.26, 149.22, 149.06 (4C), 148.69, 148.38, 148.17, 147.42, 147.37, 147.33 (1C), 146.56, 145.92, 145.71, 144.14, 143.86, 143.78, 143.50, 143.27, 141.71, 139.91, 138.44, 133.52, 132.40, 132.07, 131.53, 131.38, 90.42 (1C, sp^3), 88.68 (1C, sp^3), 81.77 (1*C*-$(CH_3)_3$), 81.47 (1*C*-$(CH_3)_3$), 26.97 ($3CH_3$), 26.58 ($3CH_3$).

5,6-Bis-*tert*-butylperoxy-5,6-dihyro[70]fullerene $C_{70}(OO^tBu)_2$ (9). ^{1}H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1): δ 1.34 (s). ^{13}C NMR (100 MHz, $CDCl_3$:CS_2 = 1:1), all signals represent 2C except where noted: δ 155.11 (1C), 151.59, 150.11 (1C), 150.02, 149.89, 149.54, 149.30, 149.02, 148.97 (1C), 148.93, 148.16, 148.04, 148.00, 147.80, 147.05, 146.91, 146.61 (1C), 146.17, 145.98, 145.80, 145.77, 145.33, 145.15, 145.01, 144.92, 144.81, 144.07, 143.93, 143.86, 143.01, 140.46, 132.54, 132.39, 130.69, 129.54, 127.29, 86.57 (2C, sp^3), 81.32 (2*C*-$(CH_3)_3$), 26.58 ($6CH_3$).

5,21-Bis-*tert*-butylperoxy-5,21-bishyro[70]fullerene $C_{70}(OO^tBu)_2$ (10). ^{1}H NMR (400 MHz, $CDCl_3$:CS_2 = 1:1): δ 1.58 (s, 9H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$:CS_2 = 1:1), all signals represent 1C except where noted: δ 159.38, 154.97, 154.83, 154.51, 152.19, 152.08, 152.02, 150.72, 150.22 (2C), 150.04, 149.81, 149.66, 149.29, 149.19, 149.08, 148.68, 148.54, 148.52, 148.24, 148.22, 148.08, 148.07, 147.93, 147.79, 147.52 (2C), 147.25, 146.82, 146.72 (2C), 146.70, 146.61, 146.34, 146.16, 145.92, 145.89 (2C), 145.69, 145.10, 144.87, 144.74 (2C), 144.68, 144.56, 144.31, 143.58, 143.47, 143.22, 143.13, 142.75, 142.00 (2C), 141.97, 139.71, 138.10, 136.16, 135.82, 133.97, 133.51, 133.34, 133.26, 132.80, 131.31, 131.20, 130.57, 129.17, 129.14, 82.34 (1C, sp^3), 81.78 (1*C*-$(CH_3)_3$), 81.38 (1*C*-$(CH_3)_3$), 77.10 (1C, sp^3), 26.98 ($3CH_3$), 26.52 ($3CH_3$).

Acknowledgment. Financial support was provided by NNSFC (Grants 20232010 and 20472003) and the Ministry of Education of China.

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

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