Oxyfunctionalization of Non-Natural Targets by Dioxiranes. 3.[1] Efficient Oxidation of Buckminsterfullerene C_{60} with Methyl(trifluoromethyl)dioxirane

Caterina Fusco, Roberta Seraglia,[†] and Ruggero Curci*

Centro C.N.R. "M.I.S.O.", Dipartimento Chimica, Università di Bari, v. Amendola 173, I-70126 Bari, Italy

Vittorio Lucchini

Dipartimento Scienze Ambientali, University of Venice, Dorsoduro 2137, I-30123 Venice, Italy

Received August 20, 1999

By employing methyl(trifluoromethyl)dioxirane (**1b**), the stepwise oxyfunctionalization of C_{60} can be carried out with high conversions (>90%) under mild conditions (0 °C); the products have been compared with those produced by the oxidation of C_{60} with *m*-chloroperoxybenzoic acid. Along with the previously characterized oxide $C_{60}O$, a wider set of higher oxidation products is obtained by using **1b**; among these, regioisomeric dioxides $C_{60}O_2$ are isolated in good overall yield (40%). One of the dioxides is predominant (yield 23%), corresponding to a C_s-symmetry dioxide previously well characterized and presenting the epoxide functionalities in close proximity over the 6:6 ring junctions. The oxidation with dioxirane **1b** also produces sufficient quantities of trioxides, so that mixtures of $C_{60}O_3$ regioisomers can be isolated. The main trioxide fraction was found amenable to spectroscopic characterization; the ^{13}C NMR spectra indicates that the sample consists of two possible regioisomers, one having C_s, and the other C_2 symmetry. In both, the three epoxide rings are assembled over 6:6 ring junctions and in close proximity to each other; this shows that, in the ensuing sequential O-transfers from the dioxirane to the fullerene framework, the 6:6 carbon−carbon double bonds adjacent to an existing epoxide functionality are more easily oxidized. The whole of the spectroscopic data indicate that the fullerene core remains intact and no rupture of the cage occurs following oxidation at the trioxide level.

Introduction

The feat of fullerene C_{60}[2] preparation in gram quantities[3] has recently brought these remarkable target molecules from the province of electric arc experiments into the realm of organic synthesis.[2,3] In particular, the oxidation of the fullerenes—and especially C_{60}—with dioxygen and other oxidizing agents is of relevance in view of the technological application of these substances.[2] For instance, electrochemically active films can be grown on electrode surfaces upon reduction of fullerene oxide $C_{60}O$;[2,4] the latter could also serve as a convenient starting material for fullerene derivatives,[5] such as the enlarged ion C_{119}^{-} [5c] and oxo- or methylene-bridged C_{60} dimers.[5e]

It is generally recognized that, although it reacts readily with nucleophiles and is amenable to reduction, fullerene C_{60} is rather resistant to oxidation.[6] Thus, the reactivity of this target has been tested in a range of oxidations,[7] including photooxidation[8] and ozonation,[9] with a varied degree of success. A number of papers

---

[†] CNR-Laboratorio Spettrometria di Massa, Padova, Italy.

(1) Part 1: Kuck, D.; Schuster, A.; Fusco, C.; Fiorentino, M.; Curci, R. *J. Am. Chem. Soc.* **1994**, *116*, 2375. Part 2: Fusco, C.; Fiorentino, M.; Dinoi, A.; Curci, R.; Krause, R. A.; Kuck, D. *J. Org. Chem.* **1996**, *61*, 8681.

(2) For recent reviews, see: (a) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317. (b) Maggini, M.; Prato, M. *Chim. Ind. (Milan)* **1996**, *78*, 1085. (c) Tetrahedron Symposia-in-Print Number 60. *Fullerene Chem.* (Smith, A. B., Guest Ed.) **1996**, *52*, 14. (d) *The Chemistry of Fullerenes*; Taylor, R., Ed.; Word Scientific, Singapore, 1995. (e) Hirsch, A. *The Chemisry of the Fullerenes*; Thieme: Stuttgart, 1994. (c) *Acc. Chem. Res.* **1992**, *25*, 5. Special Issue 3. See also references therein.

(3) (a) Kroto, H. W.; Heath, J. R.; O'Brieu, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. *Nature* **1991**, *353*, 149. (c) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, C.; Koch, A. *Science* **1991**, *232*, 548. (d) Peters, G.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 223.

(4) For instance, see: Fedurco, M.; Costa, D.; Balch, A. L.; Fawcett, W. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 194.

(5) (a) Deng, J.-P.; Mou, Ju, D.-D.; Her, G.-R.; Mou, C.-Y.; Chen, C.-J.; Lin, Y.-Y.; Han, C.-C. *J. Phys. Chem.* **1993**, *97*, 11575. (b) McElvany, S. W.; Callahan, J. H.; Ross, M. M.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632. (c) Taylor, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1629. (d) Beck, R. D.; Bräuchle, G.; Stoermer, C.; Kappes, M. M. *J. Chem. Phys.* **1995**, *102*, 540. (e) Smith, A. B., III; Tokuyama, H.; Strongin, R. M.; Furst, G. T.; Romanov, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 9359.

(6) (a) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. (b) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (c) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (d) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2780. (e) Jehoulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456. (f) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(7) Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363.

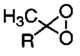
(8) (a) Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907. (b) Creegan, K. M.; Robbins, J. L.; Robbins, K. W.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCanley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103. (c) Millar, J. M.; Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M. *Synth. Met.* **1993**, *59*, 317.

(9) (a) Heymann, D.; Chibante, L. P. F. *Chem. Phys. Lett.* **1993**, *207*, 339. (b) Malhotra, R.; Kumar, S.; Satyam, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1339.

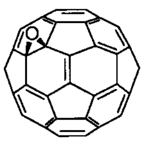
10.1021/jo9913309 CCC: $18.00

describe the formation of $C_{60}O$ when C_{60} is made to react with organic peracids,[10] Murray's methyltrioxorhenium/hydrogen peroxide oxidant,[11] and some model systems for monooxygenase enzymes (cytochrome P450).[12] The fullerene oxide is also formed as a byproduct during fullerene synthesis.[8]

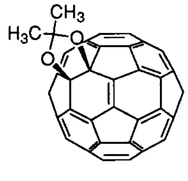
On the other hand, Foote et al. have showed that the application of a simple representative of the dioxirane family, such as dimethyldioxirane (**1a**), to fullerene C_{60} (**2**) results in low conversions and minor yields (ca. 6%) of fullareno-1,3-dioxolane **3′** (8%), along with $C_{60}O$ oxide (**3**) in ca. 6% yield.[13]



1a: R = CH_3
1b: R = CF_3



3



3′

Balch and co-workers have carefully studied the products obtained by the oxidation of C_{60} with *m*-chloroperoxybenzoic acid (*m*-CPBA).[10a] By using a substantial (10- to 30-fold) excess of peracid over the C_{60} substrate in toluene at 80 °C, these authors were able to achieve a conspicuous 30% yield of the previously characterized[8b,13,14] $C_{60}O$ oxide **3**, in which the epoxide oxygen is positioned over a 6:6 ring junction. These authors also reported that the *m*-CPBA oxidation produces sufficient quantities of the higher oxide $C_{60}O_2$ (8% yield), so that the latter could be isolated and structurally characterized.

Dioxiranes (**1**)[15] have been proven to be useful reagents for the selective oxidation of a variety of organic compounds under mild conditions, including polycyclic aromatic hydrocarbons (PAH).[16,17] We have shown that, in carrying out these oxidations, methyl(trifluoromethyl)dioxirane (**1b**)[17] provides higher substrate conversions and much shorter reaction times with respect to dimethyldioxirane (**1a**),[15] and with no loss in selectivity.[15a] Since the similarity of C_{60} to strained members of the PAH series is only superficial, we deemed it worthwhile to undertake a study on the oxidation of fullerene C_{60} with the powerful dioxirane **1b** (TFD) and to compare the efficiency of this process with previously reported oxygenations.[7−13] We describe herein that the application of TFD (**1b**) efficiently affords the oxide $C_{60}O$ in high yield and with high substrate conversion; significantly, it also leads to products of sequential oxidation $C_{60}O_2$ and $C_{60}O_3$, in sufficient amount to be separated and characterized.

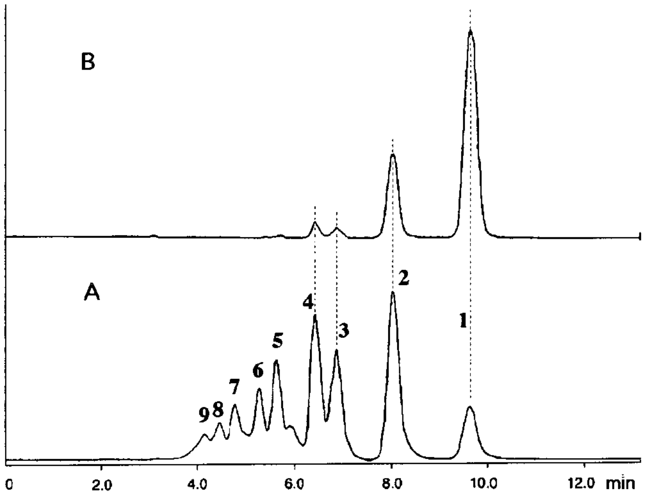


Figure 1. HPLC reversed-phase chromatograms (Inertisil ODS-2 5U, MeOH/toluene 55:45) for the reaction mixtures resulting from the oxidation of C_{60} with (A) TFD (in 1,2-dichlorobenzene, 0 °C, 5 min) and (B) *m*-CPBA (in toluene, 80 °C, 1 h).

Results

Oxidation of C_{60} with Methyl(trifluoromethyl)dioxirane. Starting with commercial C_{60} fullerene, pure samples were obtained by column chromatography on alumina[8b,10a] as described by Diederich et al.[3b] for the purification of analytical quantities. To pure C_{60} dissolved in 1,2-dichlorobenzene, dioxirane **1b** was applied in the isolated form (i.e., as 0.5−0.6 M solution in 1,1,1-trifluoropropanone (TFP), the parent ketone); the latter was obtained according to described protocols.[17a,b]

In the simple general procedure, an aliquot of a standardized cold solution of dioxirane (**1b**) was added to a stirred solution of 1 equiv of C_{60} (0.28 mmol) in 1,2-dichlorobenzene (50 mL) at 0 °C. Under these conditions, with only a 4-fold excess oxidant, the reaction proceeds quite rapidly and the initially purple solution turns reddish-brown within 5−6 min.

Analysis of the reaction mixture by analytical HPLC on an octadecylsilica (ODS) column gave the profile shown by trace A in Figure 1. It can be seen that nine separated peaks are present.

The product mixture can be compared with that obtained by oxidation of C_{60} with *m*-CPBA (30-fold excess) in toluene (1 h, 80 °C), i.e., under conditions identical to those reported by Balch et al.;[10a] this yields the HPLC profile shown by trace B.

In the reversed-phase HPLC runs shown in Figure 1, unreacted C_{60} is the last substance to elute (peak 1), preceded by the known oxide $C_{60}O$ (peak 2) and dioxides $C_{60}O_2$ (peak 3 and 4).[10a] The latter give a MALDI signal at *m*/*z* 752 (M^+) and *m*/*z* 753 for the $[M + H]^+$ ion, respectively. One of the dioxides $C_{60}O_2$ (peak 4) has been

---

(10) (a) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 8926. (b) Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem.* **1996**, *35*, 458. See references therein.

(11) Murray, R. W.; Iyanar, K. *Tetrahedron Lett.* **1997**, *38*, 335.

(12) Hamano, T.; Okuda, K.; Mashino, T.; Hirobe, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1537.

(13) Elemes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.

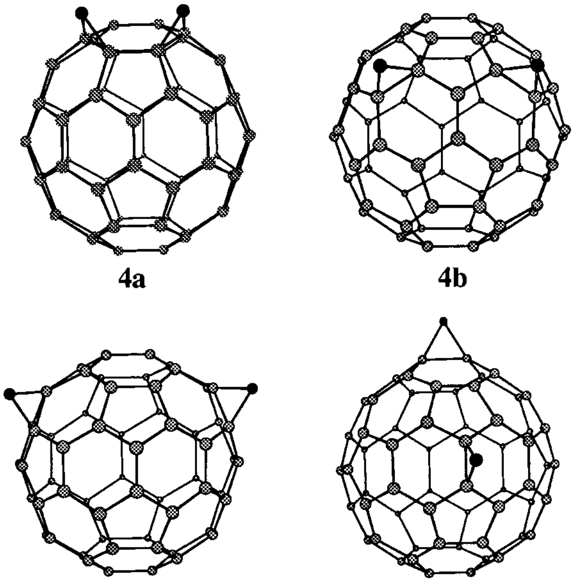
(14) Balch, A. L.; Costa, D. A.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem.* **1994**, *33*, 2071.

(15) For reviews, see: (a) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811. (b) Adam, W.; Hadjiarapoglou, L. *Top. Curr. Chem.* **1993**, *164*, 4552. (c) Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. in *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; Chapter 4, pp 195−219. (d) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT, 1990; Vol. 2, Chapter I, 1−59. (e) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (f) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205. See references therein.

(16) (a) Jeyaraman, R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 2462. (b) Murray, R. W.; Singh, M. *Polycycl. Aromat. Compd.* **1997**, *12*, 51. See references therein.

(17) (a) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890. (b) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749. (c) Mello, R.; Ciminale, F.; Fiorentino, M.; Fusco, C.; Prencipe, T.; Curci, R. *Tetrahedron Lett.* **1990**, *31*, 6097. (d) Curci, R.; Dinoi, A.; Fusco, C.; Lillo, M. A. *Tetrahedron Lett.* **1996**, *37*, 249. See references therein.

Chart 1



4a 4b 4c 4d

completely characterized by Balch et al. via ^{13}C NMR spectra and through X-ray crystallographic analysis of its crystalline adduct with Vaska's complex Ir(CO)Cl-$(PPh_3)_2$; this revealed that the most abundant dioxide has the C_s symmetry of isomer **4a**.[10a] Ensuing epoxidation at the 6:6 ring junctions in C_{60}, this is one of the eight possible $C_{60}O_2$ regioisomers that could arise;[10a] the four having C_s symmetry are shown from a common perspective in Chart 1.

Inspection of Figure 1 reveals that oxidation of C_{60} by the powerful dioxirane **1b** is characterized by a significantly larger substrate conversion than using *m*-CPBA (i.e., 92% vs 37%), and this under remarkably milder conditions (0 vs 80 °C). This ranks among the highest conversions attained in direct oxidative transformations of fullerene C_{60}. Indeed, in separate experiments we verified that a higher yield of the monooxide can be attained simply by limiting the dioxirane excess. For instance, upon reduction of dioxirane equivalents from 4 to 2 in the title oxidation under identical conditions, HPLC monitoring allowed us to determine a 72% conversion of C_{60} and a 67% yield of monooxide $C_{60}O$, accompained by the $C_{60}O_2$ regioisomers above (in a combined yield of ca. 25%).

Returning to the experiments carried out with a substantial (4-fold) excess of dioxirane **1b**, based on the substrate reacted, the combined yield in diepoxides $C_{60}O_2$ (peak 3 plus 4) is ca. 40% for TFD; this again compares favorably with the 23% yield of the same compounds attained using *m*-CPBA. It is also worthy of note that at least four additional products are seen in the TFD oxidation (trace A). By using column flash chromatography (silica gel, gradient *n*-hexane/CS_2, 0 °C), it was possible to collect samples of most components in the reaction mixture. Unreacted C_{60} and the oxide $C_{60}O$ gave MS and ^{13}C NMR spectra in full agreement with literature.[8,13] The sample corresponding to peak 4 (yield 23%) turned out to be the regioisomerically pure dioxide **4a** described by Balch et al.;[10] it had $[M + H]^+$ *m*/*z* 753 (MALDI) and ^{13}C NMR [CS_2/benzene-d_6 95:5, with Cr-$(acac)_3$ as relaxation agent] in all identical to that reported by these authors. The collected material that is related to peak 3 (yield 17%) again gives a MALDI M^+ at *m*/*z* 752, also corresponding to $C_{60}O_2$. However, its ^{13}C NMR spectrum presented a very complex pattern; for instance, in the epoxide region from δ 75 to δ 85 more than 10 signals are present, ruling out that we are dealing with a single isomer. Thus, we can endorse the conclusion by Balch et al.[10a] that this fraction consists of several isomers of $C_{60}O_2$.

The material corresponding to peak 6 (yield 8%) was isolated as a dark brown powder; it gave $[M + H]^+$ at *m*/*z* 769, which is consistent with trioxide $C_{60}O_3$. So far, our attempts at obtaining a suitable crystalline adduct of this material with the complex $Ir(CO)Cl(PPh_3)_2$ have failed, thus precluding conclusive X-rays structural analysis. However, spectroscopic studies (^{13}C NMR, in particular) turned out to be quite telling concerning the structure of the material isolated.

Control experiments revealed that the given dioxides and trioxides are chiefly formed by the sequential oxidation of the initially formed mono oxide **3**. For instance, when a sample of isolated $C_{60}O$ was made to react with 1 equiv. TFD (**1b**) under identical conditions, HPLC analysis revealed that the latter was transformed (54% conv.) in the same dioxide mixtures, i.e., the materials corresponding to peak 3 (yield 34%) and peak 4 (yield 38%); the trioxide $C_{60}O_3$ mixtures conforming to peaks 5 and 6 were also formed in ca. 12 and 10% yield, respectively (cf., HPLC run in the Supporting Information).

Spectroscopic Characterization of Trioxides $C_{60}O_3$. The CS_2 solutions of material corresponding to peak 6 are reddish. In *n*-hexane, its visible absorption spectrum presents broad bands at 554 (broad) and 372 nm; apparently, the former absorption is red-shifted relative to its counterparts in the spectrum of diepoxide $C_{60}O_2$ (λ_{max} 466 and 424).[10a] In the UV region, the spectrum shows typical fullerene absorptions[8] at λ_{max} 326, 254, and 238 nm.

The FTIR spectrum of the product (deposited from CS_2 solution as a film on a KBr plate) revealed no bands in the C−H or C=O units region, while fullerene-like broad bands were present at 1433, 1182, 580, and 527 cm^{-1}. At least 22 bands are discernible in the region 850−450 cm^{-1}; this cluster is dominated by an intense absorption (broad) centered at about 796 cm^{-1}.

Important clues concerning the composition of the trioxide $C_{60}O_3$ mixture isolated came from ^{13}C NMR analysis of this material; a sample is shown in Figure 2.

Forty-nine resonances occur in the fullerene cage region, i.e., 152−138 ppm. Six of these (those at 147.1, 146.6, 145.2, 145.0, 142.7, and 142.6 ppm) have intensities that are approximately double the intensities of the remaining individual resonances, thus representing six accidentally degenerate resonances.

The remaining seven upfield resonances in the region from 83 to 65 ppm are assigned to carbon atoms in epoxide units. For comparison, $C_{60}O$ has a single resonance at 90.2 ppm[8b,13] and the diepoxide $C_{60}O_2$ C_s regioisomer **4a** two resonances at 82.3 and 78.4 ppm in this upfield region.[10a] These seven peaks could be classified into two groups. One group presents five resonances at 82.6, 80.2, 77.0, 75.3, and 69.1 (peak height ratio, 1:1: 1: 1: 1), while the other consists of two signals at 73.1 and 65.9, both of peak height (1/2). These results suggest a mixture composed in roughly equal amounts (as judged

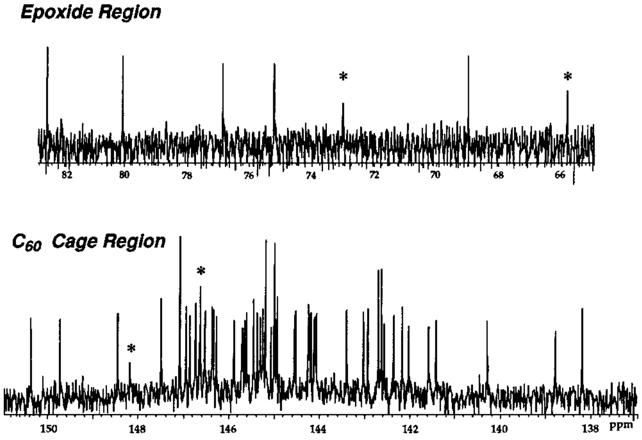
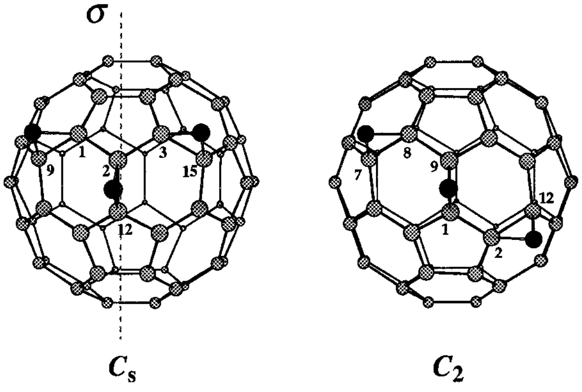


Figure 2. ^{13}C NMR spectrum of the mixture composed of regioisomeric trioxides $C_{60}O_3$ in CS_2 in the presence of Cr(acac)$_3$ as relaxation agent.

Chart 2



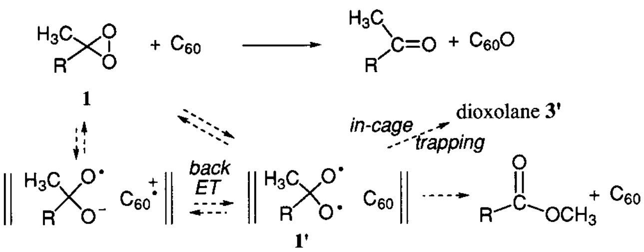
5a **5b**

by peak heights) by two trioxides $C_{60}O_3$, one having a C_s and the other a C_2 symmetrical structure. There are 46[18] possible regioisomers $C_{60}O_3$ that can exist with three oxygen atoms lying across 6:6 ring junctions. The observed ^{13}C NMR spectrum shown in Figure 2 strongly suggests that the given mixture consists of the two regioisomers **5a** and **5b** presented in Chart 2.

In fact, the pattern of resonances denoted by asterisks, with four resonances in the epoxide region and two resonances in the fullerene cage region, are consistent with **5a** being one of the two isomers. Indeed, this C_s regioisomer uniquely presents two nonequivalent *pairs* of carbons (each pertaining to a different epoxide moiety) placed across the symmetry plane σ, plus two nonequivalent epoxide carbons laying in the same plane that would give intensity approximately half of the others. In the downfield region, two resonances (δ 146.6 and 148.2) are ascribed to the two fullerene cage carbons also in the σ plane in juxtaposition to the epoxide carbons mentioned last; the signal at δ 148.2 has intensity one-half, while the signal at δ 146.6 integrates approximately 1.5 due to accidental degeneration with the resonance of another fullerene sp^2 carbon.

Considering how pairs of sp^3 carbons relate to the C_2 axis, in the epoxide region isomer **5b** is expected to give rise to three signals (1:1:1), which sum up with the above four resonances (1:1:0.5:0.5) of **5a** in accounting for the observed pattern (Figure 2). In addition, **5b** is expected to give rise to 27 resonances in the fullerene cage region, while **5a** should yield 28; taking into account the six accidental degenerations observed, this uniquely matches with the observed spectrum. On the basis of our estimates, the combination of **5a** with C_2 regioisomers other than **5b** cannot adequately explain the observed assembly of ^{13}C NMR resonances (Figure 2).

Scheme 1



Discussion

The results above suggest that the powerful methyl(trifluoromethyl)dioxirane **1b** is the oxidant of choice to transform fullerene C_{60} into its oxides $C_{60}O$, $C_{60}O_2$, and $C_{60}O_3$, with high conversions (>90%) and in mild conditions. Inspection of Figure 1 reveals that—with only a modest oxidant excess (ca. 4-fold)—along with the oxide $C_{60}O$, one is able to obtain the corresponding mixtures of dioxides $C_{60}O_2$ in good overall yield (ca. 40%); of these, dioxide **4a** could be obtained in regioisomerically pure form with ca. 20% yield, which poses a distinct advantage over classic oxidizing agents such as peracids.

Also, the trifluoromethyl dioxirane **1b** is obviously more efficient than its methyl counterpart **1a** (cf., Introduction); for instance, substrate conversion and $C_{60}O$ yields are much improved, and with remarkably shorter reaction times (5 min vs 12 h[10a]). It is also worthy of note that no 1,3-dioxolane derivative is observed in the TFD case herein. Hence, the reported[13] formation of fullareno-1,3-dioxolane **3′** in the DMD oxidation of C_{60} might be due to the long reaction time (12 h), during which competitive dioxirane decomposition can occur via the corresponding bis(oxy)methylene diradical **1′**(Scheme 1).[17d]

Actually—similar to what we proposed[17c] for the reaction of higher homologues PAH with dioxiranes—the latter process might be induced by the fullerene itself, for instance as sketched in Scheme 1. In this context, it is should be recalled that a mechanism involving a C_{60} cation radical has been invoked for the reaction of buckminsterfullerene with perfluoroalkanoyl peroxides.[19]

Whatever the mechanistic details, C_{60} oxidation by TFD apparently stands alone by the ease and efficiency of formation of products of higher oxidation, as is clearly shown by MS. Most fractions collected consist of regiosomers in mixtures that are difficult to resolve, so then their full characterization is in order. However, it is recognized that preparative-scale chromatographic separations of these fullerene derivatives can be quite laborious,[10a] and satisfactory separation of regioisomers of higher oxides is hard to accomplish. Nevertheless, in

---

[18] Hirsh, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437.

[19] Yoshida, M.; Morinaga, Y.; Iyoda, M.; Kikuchi, K.; Ikemoto, I.; Achiba, Y. *Tetrahedron Lett.* **1993**, *34*, 7629.

one favorable circumstance we were able to separate clean $C_{60}O_3$ fractions; for one of these, the ^{13}C NMR spectra were sufficiently clear-cut to provide strong evidence concerning the structure of the two trioxides in the admixture, i.e., **5a** and **5b** (in combined yield of ca. 8%). The whole of the spectroscopic data show that these higher oxidation products retain intact the essential framework of the parent compound. Thus, the expectation[20] that the transfer of two or more oxygen atoms to C_{60} would bring about the rupture of the fullerene cage is not fulfilled. It is interesting that the trioxides **5a** and **5b** have been detected (MALDI, SORI)[21] also in the product mixture resulting from the oxidation of C_{60} with excess peracid.

It should be noted that triepoxides **5a** and **5b** are likely to derive from the further oxidation of diepoxides **4a** and/or **4b**. Namely, **5b** could be formed from **4a**, while **5a** might arise from epoxidation of either **4a** or **4b**. Although this anticipation is still circumstantial, the proximity of epoxide moieties in the trioxides (and in dioxide **4a**) brings one to the conclusion that—in the fullerene framework—6:6 double bonds adjacent to an existing epoxide functionality are more easily oxidized than the others. It also confirms that, in carrying out sequential oxyfunctionalization of target molecules, the powerful dioxirane **1b** can be quite selective despite its high reactivity.[15a] It worth mentioning that Hirobe et al.[12] have recently proposed that a mixture of fullerene trioxides **5a** and **5b** is formed (yield unspecified) in the oxidation of C_{60} with certain cytochrome P450 chemical models. If this is the case, it would provide further support to the view[15a] that selectivity of dioxirane oxidations can be biomimetic.

Experimental Section

Materials and Methods. Commercial 1,1,1-trifluoro-2-propanone (TFP) (bp 22 °C), carbon disulfide, *n*-hexane, and 1,2-dichlorobenzene were purified by standard methods, stored over 5 Å molecular sieves at 2−5 °C, and routinely redistilled prior to use. Curox triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ (a gift by Peroxid-Chemie GmbH, Munich, Germany) was our source of potassium peroxymonosulfate employed in the synthesis of dioxirane.[15] Solutions of 0.8−1.0 M methyl(trifluoromethyl)dioxirane (**1b**) in TFP were obtained by following described[17] procedures, equipment, and precautions. Commercial [5,6]-fullerene-60-I_h (**2**) (fullerene C_{60}) was repeatedly purified by column chromatography on alumina (*n*-hexane).[8b]

Reactions were monitored by HPLC using an Inertisil ODS-2 5U column [25 cm × 5 mm, 4.6 mm id., isocratic MeOH/toluene 55:45, 320 nm detection]. Column flash chromatography was performed at 0−2 °C using 230−400 mesh silica gel with *n*-hexane/carbon disulfide gradient eluent. The ^{13}C NMR spectra were recorded at 100.562 MHz in CS_2, with 10% benzene-d_6 as internal lock; chemical shifts (δ) are given in ppm and referred to tetramethylsilane. The FTIR spectra are relative to fullerene oxides films, deposited on KBr plates from CS_2 solutions.[8b] Matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained in a positive linear or reflection mode at 30 KV acceleration voltage on a mass spectrometer reflex time-of-flight, using 2,5-dihydroxybenzoic acid as matrix. For each sample several calibrated MALDI-MS runs were performed and data averaged; mass accuracy was about +0.05%.

Oxidation of C_{60} with Methyl(trifluoromethyl)dioxirane. To a stirred solution of C_{60} (200 mg, 0.277 mmol) in 1,2-dichlorobenzene (50 mL) at 0 °C was added 1.6 mL of a cold solution of 0.7 M methyl(trifluoromethyl)dioxirane (**1b**) (1.1 mmol) in trifluoropropanone (TFP) during 5 min. The initially purple solution was observed to turn dark brown. The mixture was then analyzed by HPLC using a Inertisil octadecylsilica (ODS) analytical column with a MeOH/toluene 55:45 v/v mixture as eluent, affording the chromatogram shown in Figure 1 (trace A). The reaction solution was filtered in order to remove tiny amounts of suspended material (if any), and the brown solution is evaporated in vacuo (15 mmHg) with a stream of dry N_2 in order to eliminate most of the solvent. Column chromatography (silica gel, *n*-hexane/CS_2 gradient) at subambient temperature (0−2 °C) allowed recovery of C_{60} starting material (12 mg, 7%); the procedure also afforded fractions corresponding (HPLC analysis) to peaks 2−6 (Figure 1). Each fraction was evaporated to dryness under vacuum, affording (by MALDI and ^{13}C NMR) $C_{60}O$ (**3**) (peak 2, 38 mg, 52 μmol, 20% yield), a regioisomeric $C_{60}O_2$ mixture (peak 3, 28 mg, 37 μmol, 14.5% yield), regioisomerically pure dioxide **4a**[10a] (peak 4, 40 mg, 53 μmol, 21% yield), a mixture of $C_{60}O_3$ isomers (peak 5, 20 mg, 26 μmol, 10% yield), and a mixture constituted by trioxides **5a** and **5b** in nearly equal amount (peak 6, 14 mg, 18 μmol, 7% yield). It should be noted that, based on 92% substrate conversion, percent product distribution and isolated yields do not match exactly the data derived by HPLC analysis (Figure 1). This might be ascribed to the fact that, similar to $C_{60}O$,[8b] also the higher oxides $C_{60}O_2$ and $C_{60}O_3$ may slowly undergo deoxygenation during column chromatography on alumina or silicagel; this phenomenon is minimized by carrying out their separation by flash column chromatography at subambient temperatures. **[5,6]Fullereno-C_{60}-I_h-[1,9-*b*]oxirene** (fullerene C_{60} epoxide) (**3**)[8b] and **[5,6]-Fullereno-C_{60}-I_h-[1,9-*b*:2,12-*b*′]bisoxirene** (fullerene C_{60} diepoxide) (**4a**)[10] gave MS and ^{13}C NMR in agreement with literature.

Mixture of [5,6]Fullereno-C_{60}-I_h-[1,9-*b*:2,12-*b*′:3,15-*b*″]-trisoxirene (5a) and [5,6]Fullereno-C_{60}-I_h-[1,9-*b*:2,12-*b*′:7,8-*b*″]trisoxirene (5b): dark reddish-brown amorphous solid; R_f 0.13 (*n*-hexane/CS_2 5:1); [MALDI-MS $C_{60}O_3$ (MW 768)] *m/z* 769 $[M + H]^+$); ^{13}C NMR (100.562 MHz, CS_2, 10% C_6D_6, [Cr(acac)$_3$] as relaxation reagent, 35000 scans) δ (no. of carbon atoms) 150.37 (2), 149.72 (2), 148.45 (2), 148.18 (1), 147.49 (2), 147.08 (4), 146.95 (2), 146.85 (2), 146.73 (2), 146.65 (2), 146.62 (3), 146.53 (2), 146.37 (2), 146.34 (2), 146.28 (2), 145.88 (2), 145.70 (2), 145.66 (2), 145.62 (2), 145.46 (2), 145.38 (2), 145.31 (2), 145.25 (2), 145.20 (4), 145.07 (2), 145.01 (4), 145.00 (2), 144.98 (2), 144.54 (2), 144.52 (2) 144.24 (2), 144.22 (2), 144.18 (2), 144.11 (2), 144.06 (2), 143.38 (2), 143.01 (2), 142.92 (2), 142.68 (4), 142.63 (4), 142.55 (2), 142.34 (2), 142.14 (2), 142.00 (2), 141.56 (2), 141.39 (2), 140.27 (2), 138.78 (2), 138.19 (2), 82.61 (2), 80.19 (2), 76.96 (2), 75.29 (2), 73.08 (1), 69.06 (2), 65.88 (1).

In a separate run under conditions identical to the above, 0.5 mL of 0.7 M methyl(trifluoromethyl)dioxirane (**1b**) (0.34 mmol) in TFP was added during 5 min to a solution of C_{60} (124 mg, 0.172 mmol) in 1,2-dichlorobenzene (25 mL) at 0 °C. HPLC analysis under the given conditions allowed to determine a 55% conversion of the $C_{60}O$ starting material and monooxide $C_{60}O$ (peak 2) as the main oxidation product (yield 67%). The diepoxides corresponding to peak 3 and 4 (cf. Figure 1) were also formed in yields of 10 and 15%, respectively.

Oxidation of $C_{60}O$ (3) with Methyl(trifluoromethyl)dioxirane. A sample of pure $C_{60}O$ was isolated by low-temperature column chromatography, as described above. The oxide **3** (10 mg, 0.012 mmol) in 1,2-dichlorobenzene (5 mL) at 0 °C was made to react with 0.02 mL of 0.7 M methyl(trifluoromethyl)dioxirane (**1b**) (0.014 mmol) in TFP. After 5 min, the reaction was monitored by HPLC under conditions identical to those given above. This allowed us to determine a 54% conversion of the $C_{60}O$ starting material; on the basis of the substrate reacted, the overall HPLC yield of the same diepoxide mixtures (i.e., peak 3 plus 4; cf. Figure S4, Supporting Information section) was 78%, accompanied by the above

---

(20) Menon, M.; Sunbaswamy, K. R. *Chem. Phys. Lett.* **1993**, *201*, 321.

(21) Penn, S. G.; Costa, D. A.; Balch, A. L.; Lebrilla, C. B. *Int. J. Mass Spectrosc. Ion Proc.* **1997**, *169/170*, 371.

trioxide **5a** and **5b** mixture (peak 6, yield 10%) and trioxide mixture corresponding to peak 5 (yield 12%).

Acknowledgment. Partial support of this work by the Ministry of University, Scientific and Technological Research of Italy (National Project: "Controlled Oxidation of Organic Compounds") (Rome, Italy) is gratefully acknowledged. Thanks are due to Professor P. Traldi (CNR - Laboratorio Spettrometria di Massa, Padova, Italy) for help in the setup and elucidation of MS of fullerene derivatives described herein.

Supporting Information Available: ^{13}C NMR and MS data for dioxide **4a**; UV−vis, FTIR spectra, and MALDI of the trioxides **5a**/**5b** mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9913309