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Synthesis and Characterization of the First $C_{70}O$ Epoxides. Utilization of ^{3}He NMR in Analysis of Fullerene Derivatives

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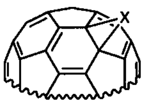
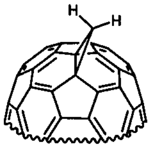
In 1991 Diederich et al. reported the isolation of the first [70]fullerene derivative, an oxide $C_{70}O$.[1] Based solely on UV and mass spectra, the compound was formulated as an annulene with the oxygen atom bridging an unspecified [6,6] ring fusion.[2] Subsequent studies of $C_{70}O$ formation via benzene/oxygen combustion,[3] ozonolysis,[4] and photooxygenation[5] have afforded no further insights into the structures of the C_{70} monooxides.

Our contributions in this area began with the synthesis and characterization of the prototypical [6,6] fullerene epoxide ($C_{60}O$, **1**)[6] and cyclopropane ($C_{61}H_2$, **2**),[7] the former in collaboration with the Exxon group. Importantly, the discovery of the cyclopropane ring in **2** led to the revision of several fullerene structures that had been misassigned as [6,6]-bridged annulenes (homofullerenes).[8] Most recently, we described the first $C_{71}H_2$ hydrocarbons, the cyclopropanes (methanofullerenes) **3** and **4** and annulenes **5** and **6**.[9] In this paper, we outline the first preparation of $C_{70}O$ species in milligram amounts and present extensive spectroscopic analyses of the resultant epoxides **7** and **8**, including ^{3}He NMR of the endohedral helium derivatives.



1 X = O
2 X = CH_2



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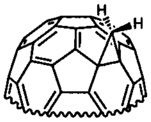

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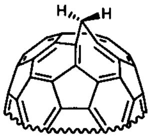

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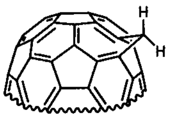

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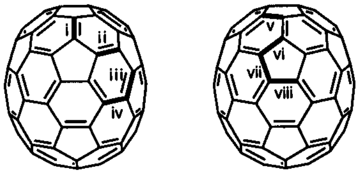

Figure 1. C_{70} bond types: [6,6] and [6,5] ring junctions (**i**−**iv** and **v**−**viii**, respectively).

Formally, the eight symmetry-nonequivalent bonds in C_{70} (Figure 1) could yield as many as eight isomeric epoxides and an equal number of oxidoannulenes. Since the discovery of "$C_{70}O$", however, all fullerene annulenes, with one exception,[10] have incorporated the bridging methylene unit at a [6,5] ring junction; oxidoannulene derivatives remain unknown. Conversely, only [6,6] cyclopropanes have been observed, complementing the epoxide structure **1**;[11] a bis-oxygenated C_{60} adduct has been formulated as a diepoxide.[12] Theoretical predictions of preferential kinetic addition to the apical [6,6] bonds of C_{70}, the sites of greatest local curvature (i.e., pyramidalization),[13] have generally been borne out.[14] We therefore envisioned that monooxygenation of C_{70} would probably furnish one or two epoxides, the oxy analogs of the $C_{71}H_2$ cyclopropanes **3** and **4**, and perhaps either or both of the oxidoannulenes corresponding to **5** and **6**.

Photooxygenation of fullerene [70] under the conditions we previously employed to prepare $C_{60}O$, with benzil or tetraphenylporphine as sensitizer, furnished only trace amounts of $C_{70}O$ (reversed-phase HPLC monitoring). Fortunately, irradiation of an oxygenated toluene solution of fullerene [70] (37 mg, 0.043 mmol) and rubrene

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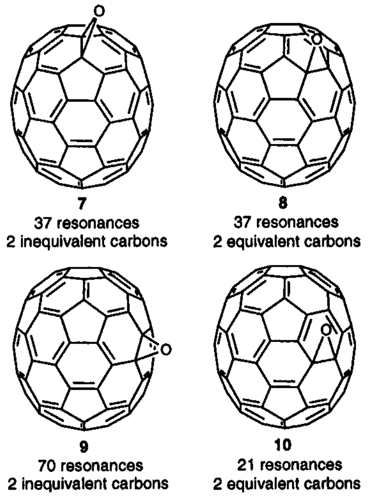

7
37 resonances
2 inequivalent carbons

8
37 resonances
2 equivalent carbons

9
70 resonances
2 inequivalent carbons

10
21 resonances
2 equivalent carbons

Figure 2. Symmetry-dependent NMR characteristics of the [6,6] $C_{70}O$ epoxides: (i) total numbers of nonequivalent skeletal carbons and (ii) equivalency of epoxide carbons.

(1.8 equiv) in toluene for 3 h did result in 14% conversion to $C_{70}O$ (based on HPLC integrations of C_{70} and $C_{70}O$), along with a minor amount (ca. 7%) of a more polar product. Higher conversion (ca. 33%) was achieved on a smaller scale (1−5 mg). Treatment of C_{70} with *m*-CPBA[6,15] [30 equiv, room temperature, PhH/CH_2Cl_2 (3:1), 3−4 days] also afforded $C_{70}O$ (35% conversion), admixed with numerous polar byproducts; a large excess of dimethyldioxirane[16] produced only traces of $C_{70}O$ amidst a large number of polar compounds.

The $C_{70}O$ mixture (vide infra) generated by rubrene photooxygenation was isolated via reversed-phase HPLC (3 mg, 8% yield). Extensive efforts to separate the two isomers have to date been unsuccessful. The laser-desorption time-of-flight (LDToF) mass spectrum showed a parent ion at 856 amu as well as a peak for fullerene [70] (840 amu). The FTIR spectrum contained many absorptions characteristic of fullerene [70] and its derivatives. Upon treatment with PPh_3, the oxides reverted slowly but cleanly to fullerene [70] with concomitant formation of PPh_3O (50% consumption of $C_{70}O$ after 8 h at room temperature).

UV−vis spectroscopy furnished the first indication that the products were epoxides rather than oxidoannulenes. Our studies of the $C_{71}H_2$ isomers demonstrated that the UV−vis fine structure of fullerene [70] is more extensively retained in homofullerene annulenes than in methanofullerene cyclopropanes.[9] Similar correlations previously served to differentiate the spectra of fullerene [60] and its [6,5] “open” derivatives from those of $C_{60}O$ and other [6,6] “closed” systems.[6,7] Importantly, the prominent C_{70} absorption at 335 nm is clearly manifested by both the major and minor $C_{71}H_2$ annulenes (**5** and **6**) but greatly diminished for the $C_{71}H_2$ cyclopropanes (**3** and **4**) and the C_{70} oxides.

Further evidence for the formation of two epoxides and the assignments of their isomeric structures derived from ^{13}C NMR studies. Photooxygenation of fullerene [70] labeled with 12−13% ^{13}C afforded similarly enriched products. The 125-MHz ^{13}C NMR spectrum [$CS_2/CDCl_3$, $Cr(acac)_3$] contained 74 resonances, the expected number for a mixture of **7** and **8** (Figure 2). A pair of signals at 91.84 and 90.41 ppm and a two-carbon peak at 85.20 ppm were assigned to the epoxide carbons of **7** and **8**, respectively (cf., 90.2 ppm for **1**); the 1:1:2 integrated intensities revealed that the isomers were formed in approximately equal amounts. Oxidoannulenes would not be expected to resonate in the 80−100 ppm region; for example, the ^{13}C spectrum of 1,6-oxido[10]annulene[17] consists of three signals between 124 and 131 ppm. The remaining 71 peaks for the $C_{70}O$ epoxides appeared between 130 and 153 ppm. Interestingly, we noted a solvent-independent correlation linking the three chemical shifts of the epoxide carbons in **7** and **8**, measured either in $CS_2/CDCl_3$ (data given above) or in $Cl_2C_6D_4$ (δ 92.34, 90.87 for **7**, 85.70 for **8**), with the δ values for the corresponding skeletal cyclopropane carbons in **3** and **4** [64.06, 62.56 for **3**, 56.80 for **4** in $CS_2/(CD_3)_2CO$; 63.84, 62.27 for **3**, 56.39 for **4** in $Cl_2C_6D_4$; $Cr(acac)_3$ relaxant in all spectra].

Mixtures of [6,6] epoxides **7** and **10, 8** and **9,** and **9** and **10** would also give rise to three epoxide-carbon resonances upfield of the aromatic region. However, these possibilities can be excluded via further scrutiny of the ^{13}C data. Assuming full resolution, the ^{13}C spectrum of a 1:1 mixture of **7** and **8** should contain eight one-carbon resonances and 66 two-carbon resonances (74 total), in good agreement[18] with the observed pattern [9 (1C), 64 (2C), 1 (3C)]. In contrast, an **8**/**9** mixture should generate 74 one-carbon and 33 two-carbon resonances, for a total of 107, whereas a **9**/**10** mixture should yield 14 four-carbon signals in addition to 70 one-carbon and seven two-carbon peaks (91 total). A 1:1 mixture of isomers **7** and **10** would generate at most 58 carbon resonances [4 (1C), 40 (2C), 14 (4C)], whereas 74 are observed.

To obtain additional support for the epoxide structures (**7** and **8**) we turned to ^3He NMR. We previously exploited ^3He NMR analysis of endohedral helium species to differentiate and further characterize a variety of fullerene derivatives.[19] The earlier study revealed that the helium NMR chemical shifts of the cyclopropane $^3He@C_{61}H_2$ and the analogous $^3He@C_{60}O$ epoxide differ by only 0.1 ppm.[16c] We have now isolated a $^3He@C_{70}O$ mixture following photooxygenation of ^3He-doped C_{70}. In accord with the striking correlation observed for the C_{60} derivatives, the ^3He chemical shifts for the $^3He@C_{70}O$ epoxides, −27.8 and −25.8 ppm, were both within 0.3 ppm of the δ values for the corresponding $^3He@C_{71}H_2$ cyclopropanes (**3** and **4,** −28.14 and −25.56 ppm). The 1:1 ratio of $^3He@C_{70}O$ isomers demonostrated that endohedral helium had no effect on the epoxidation selectivity.

In summary, we have synthesized the $C_{70}O$ epoxides **7** and **8**, oxido analogs of the $C_{71}H_2$ cyclopropanes (**3** and **4**) previously prepared in our laboratory. The structures were elucidated via intensive spectroscopic analysis, including ^3He NMR of the endohedral helium derivatives. Current efforts are directed toward the separation of **7** and **8** as well as further study of these and related fullerene oxides, methanofullerenes, and homofullerenes.

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Supporting Information Available: Preparation, purification, and spectra of **7** and **8** (4 pages).

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