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Preparation and Characterization of the Fullerene Diols 1,2-$C_{60}(OH)_2$, 1,2-$C_{70}(OH)_2$, and 5,6-$C_{70}(OH)_2$

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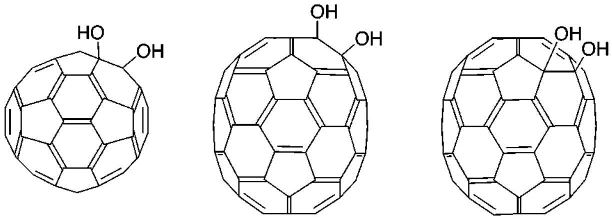
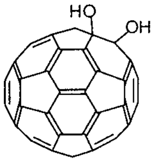
ABSTRACT



The simple fullerene diols $C_{60}(OH)_2$ and $C_{70}(OH)_2$ were prepared by addition of RuO_4 followed by acid hydrolysis. The 1,2-$C_{60}(OH)_2$ isomer was formed from C_{60}, and two isomers (1,2 and 5,6) of $C_{70}(OH)_2$ were formed in the RuO_4 hydroxylation of C_{70}. These compounds are much more soluble in THF and dioxane than the parent fullerenes. More highly hydroxylated materials are formed as well.

Polyhydroxylated fullerenes (fullerenols) have been known for some time, and these compounds have a host of interesting bioactivity properties.[1] However, these materials are typically isolated as a complex mixture of different isomers and usually are of high levels of hydroxylation (at least six hydroxyl groups, usually significantly more).[2−5]

Despite the significant and ongoing work on fullerenols, there is a conspicuous absence of a method for the preparation of the simple diols 1,2-$C_{60}(OH)_2$ (**1**), 1,2-$C_{70}(OH)_2$ (**2**), and 5,6-$C_{70}(OH)_2$ (**3**).



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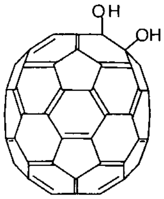

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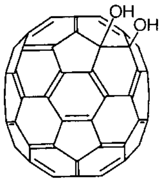

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Within the chemistry of simple alkenes, this transformation is often accomplished by osmylation, but this methodology fails in fullerenes. Osmylation of fullerenes produces stable osmate esters,[6−9] one of which has been characterized by crystallography.[7] Reaction of C_{60} with dimethyldioxirane[10] produces the acetonide of **1,** but, like the osmate, attempts at hydrolysis fail, producing (under forcing conditions) C_{60} as the sole identified product.

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Typically, RuO_4, either used in a stoichiometric amount or along with a cooxidant, cleaves double bonds to produce carboxylic acids and/or ketones. A few examples from steroid chemistry show that RuO_4 used in a stoichiometric amount could give vicinal diols selectively.[11,12]

We have found that compounds formed between fullerenes and RuO_4 can be hydrolyzed to the corresponding diols. RuO_4 is easily prepared by the reaction of $NaIO_4$ with RuO_2 hydrate and subsequent extraction into CCl_4. Because of a very low solubility of C_{60} or C_{70} in CCl_4, we chose 1,2,4-trichlorobenzene (TCB) as a main component of the reaction medium. TCB is an excellent solvent for C_{60} or C_{70} and is also relatively unreactive toward RuO_4. The addition of 2 equiv of freshly prepared RuO_4 in CCl_4 to a stirred TCB solution of fullerene (C_{60} or C_{70}) instantly produced a black precipitate. When a catalytic system was used, involving a water−1,2-dichlorobenzene two-phase system containing $RuCl_3$ and $NaIO_4$, complete decolorization of mixture occurred. The loss of color suggested significant oxidative degradation of the fullerene cage, and this was confirmed by HPLC (complex mixture) and IR (carbonyl absorptions). In the TCB system used in the current work, precipitation of the insoluble fullerene−ruthenium complex (possibly a ruthenate ester) reduces the amount of further additional degradation by RuO_4.

The precipitates obtained from the reaction of fullerenes and RuO_4 were insoluble in common solvents. However, treatment of the precipitate with dilute aqueous HCl in DMF, THF, or dioxane (along with sonication) resulted in a colored homogeneous solution. The choice of a water-miscible solvent was critical for successful hydrolysis.

IR analysis of the crude fullerene−RuO_4 hydrolysis product mixtures showed two significant features: hydroxyl group (3250 cm^{-1} for C_{60} and 3340 cm^{-1} for C_{70}) as well as carbonyl group (1725 cm^{-1} for C_{60} and 1715 cm^{-1} for C_{70}) bands from highly oxidized material. The formation of this highly oxidized material is presumably responsible for the modest yields of **1**, **2**, and **3**.

Analysis of the crude hydrolysis mixtures by HPLC revealed that one major product is present in the C_{60} series (Figure 1) and two major products in a 3:1 ratio in the C_{70} series (Figure 2). These major products were isolated by a preliminary filtration through Florisil or silica gel and subsequent HPLC purification using a semipreparative Cosmosil 5-PBB column.[13]

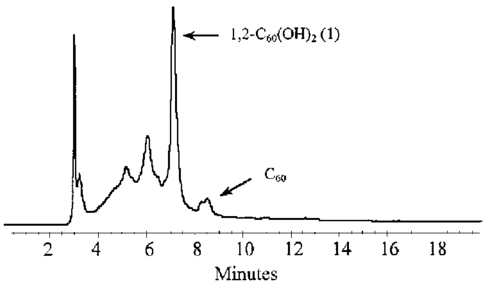

Figure 1. HPLC analysis of the crude C_{60}−RuO_4 hydrolysis mixture. Conditions: Cosmosil 5-PBB column, 1 mL/min 90:10 toluene/THF, monitored at 310 nm.

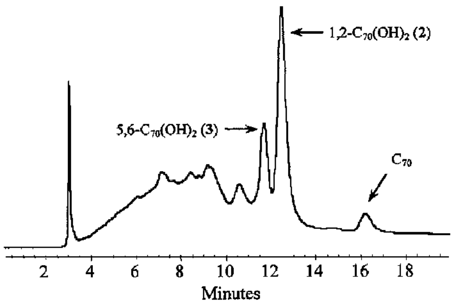

Figure 2. HPLC analysis of the crude C_{70}−RuO_4 hydrolysis mixture. Conditions: Cosmosil 5-PBB column, 1 mL/min 90:10 toluene/THF, monitored at 310 nm.

The fullerene diols are unstable in DMF and THF, decomposing significantly in minutes in DMF and in hours in THF. It was also observed that the diols are sensitive to base. However, dilute aqueous acid/dioxane solutions of the fullerene diols **1**−**3** are stable even for several days at room temperature. It was our general observation that C_{60} diols are less stable that C_{70} diols.

The absorption spectra (Figure 3) of **1** (obtained in 11% yield after chromatographic purification) closely matches the spectrum of 1,2-$C_{60}H_2$. Comparison of absorption spectra of the $C_{70}(OH)_2$ isomers with those of $C_{70}(C_6H_4)$ species we have isolated previously[14,15] indicates that hydroxylation occurs primarily at the 1,2 position (10.5%), with the minor isomer being the 5,6 isomer (3.2%).

The structural assignments were further supported by ^{13}C NMR spectroscopy in a mixed CS_2/dioxane solvent system, IR, and FAB MS spectroscopy. No commonly used NMR solvent that did not have resonances superimposed on the resonances of **1**−**3** was able to dissolve more than 1 mg/mL of the fullerene diols. We found that up to 20 mg/mL concentrations of **1**−**3** could be achieved in ca. 1:1 CS_2/dioxane-d_8. This concentration is significantly higher than the concentrations achieved in either pure CS_2 or pure dioxane. A similar observation was made for a toluene/dioxane solvent system, but overlapping ^{13}C resonances were a significant problem.

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(13) **Sample procedure:** To a stirred solution of C_{60} (1 mmol) in 1,2,4-trichlorobenzene (200 mL) was added a freshly prepared solution of RuO_4 (2 mmol) in 50 mL of CCl_4. The resulting black precipitate was separated by filtration, washed with toluene, and dried. This material was suspended in 280 mL of H_2O−dioxane (1:25), 2 mL of concentrated HCl was added, and the mixture was sonicated at 40 °C for 30 min. Toluene (300 mL) was added, and the organic layer was separated, dried over Na_2SO_4, and concentrated. Filtration through Fluorisil and subsequent HPLC on a semipreparative Cosmosil 5-PBB column yielded 64 mg (8.5%) of pure 1,2-$C_{60}(OH)_2$.

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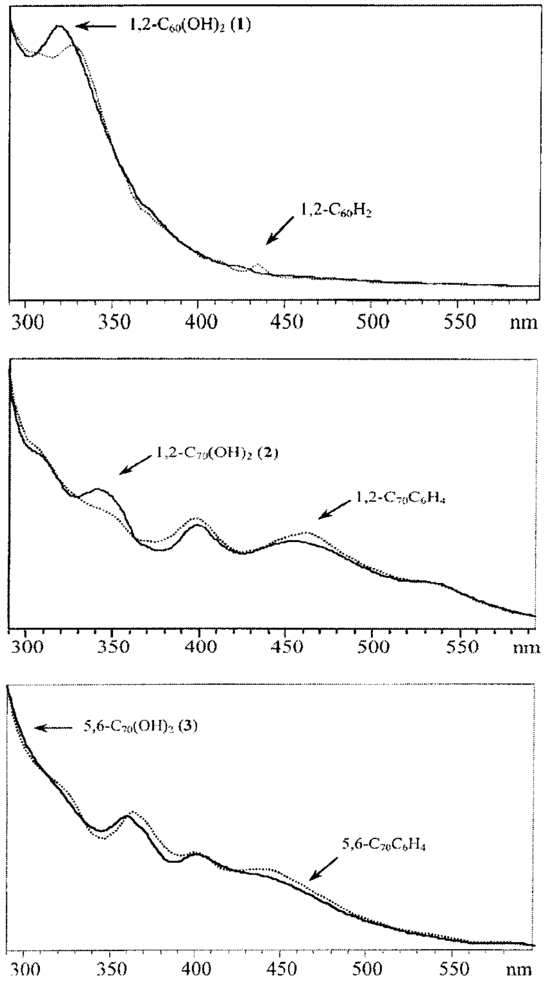

Figure 3. Absorption spectra of 1,2-$C_{60}(OH)_2$ (**1**), 1,2-$C_{70}(OH)_2$ (**2**), and 5,6-$C_{70}(OH)_2$ (**3**) measured in 90% toluene/10% THF.

The symmetry of each compound was established by the total line count in the ^{13}C spectra and the presence of the requisite number of resonances for HO-bearing carbons. The chemical shifts of the hydroxylated carbons (84.90 ppm in **1**, 81.60 and 80.36 ppm for **2**, 78.03 ppm for **3**) are generally upfield from the chemical shifts reported for fullerene epoxides 1,2-$C_{60}O$[16] and $C_{70}O$ (91.84 and 90.41 ppm for 1,2-$C_{70}O$ and 85.20 ppm for 5,6-$C_{70}O$).[17] The oxygen-bearing fullerene carbons of the acetonide of **1** appear at 96.15 ppm,[10] again further downfield than the oxygen-bearing carbons in **1**−**3**. There are few monohydroxylated fullerenes in the literature for comparison. In the epoxyfullerenol $C_{60}Me_5O_2$-OH, the ^{13}C resonance of the hydroxyl carbon appears at 75.11 ppm, while the ^{13}C resonances for the epoxide carbons range from 72.35 to 86.60 ppm.[18] In the equatorially modified fullerenol $C_{70}Ph_9OH$, the hydroxylated carbon has a ^{13}C resonance at 84.07 ppm.[19]

We have developed a method for the preparation of fullerene diols **1**−**3**. The procedure is successful due to the precipitation of a RuO_4−fullerene species (so additional, uncontrolled degradation is minimized) and to the successful hydrolysis. The latter step is unsuccessful in the similar OsO_4 system. These diols may present entry into a new family of fullerene derivatives.

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Supporting Information Available: Experimental procedures and ^{13}C NMR for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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