

THE PREPARATION AND CHARACTERIZATION OF THE FULLERENE DIOLS 1,2-C₆₀(OH)₂, 1,2-C₇₀(OH)₂, AND 5,6-C₇₀(OH)₂

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Introduction

Polyhydroxylated fullerenes (fullerenols) have been known for some time, and these compounds have a host of interesting properties bioactivity.¹ However, these materials are typically isolated as a complex mixture of different isomers and usually are of high levels of hydroxylation (at least 6 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-C₆₀(OH)₂ (**1**), 1,2-C₇₀(OH)₂ (**2**) and 5,6-C₇₀(OH)₂ (**3**) (Figure 1).

Results and Discussion

We have found that compounds formed between fullerenes and RuO₄ can be hydrolyzed to the corresponding diols. RuO₄ is easily prepared by the reaction of NaIO₄ with RuO₂ hydrate and subsequent extraction into CCl₄. Due to a very low solubility of C₆₀ or C₇₀ in CCl₄ we chose 1,2,4-trichlorobenzene (TCB) as a main component of the reaction medium. TCB is an excellent solvent for C₆₀ or C₇₀ and is also relatively unreactive towards RuO₄. The addition of 2 equivalents of freshly prepared RuO₄ in CCl₄ to a stirred TCB solution of fullerene (C₆₀ or C₇₀) instantly produced a black precipitate. Precipitation of the insoluble fullerene-ruthenium complex (possibly a ruthenate ester) reduces the amount of further additional degradation by RuO₄.

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. Most of the water-immiscible solvents (such as toluene or diethyl ether) produced much lower yields of the desired fullerene diols.

IR analysis of the crude fullerene-RuO₄ hydrolysis product mixtures showed two significant features: hydroxyl groups

(3250 cm⁻¹ for C₆₀ and 3340 cm⁻¹ for C₇₀) as well as carbonyl groups (1725 cm⁻¹ for C₆₀ and 1715 cm⁻¹ for C₇₀) band 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 C₆₀ series (Figure 2) and two major products in the 3:1 ratio in the C₇₀ series (Figure 3). 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.

The absorption spectra (Figure 4) of **1** (obtained in 11% yield after chromatographic purification) closely matches the spectrum of 1,2-C₆₀H₂. Comparison of absorption spectra the C₇₀(OH)₂ isomers with those of C₇₀(C₆H₄) species we have isolated previously^{6,7} indicates that hydroxylation occurs primarily at the 1,2 position (10.5 %), with the minor isomer being the 5,6 isomer (3.2 %).

There are few monohydroxylated fullerenes in the literature for comparison. In the epoxyfullerenol C₆₀Me₅O₂OH, the ¹³C resonance of the hydroxyl carbon appears at 75.11 ppm, while the ¹³C resonances for the epoxide carbons range from 72.35 to 86.60 ppm.⁸ In the equatorially-modified fullereneol C₇₀Ph₉OH, the hydroxylated carbon has a ¹³C resonance at 84.07 ppm.⁹

Conclusions

We have developed a method for the preparation of the fullerene diols **1** - **3**. The procedure is successful due to the precipitation of a RuO₄-fullerene species (so additional, uncontrolled degradation is minimized) and to the successful hydrolysis. The latter step is unsuccessful in the similar OsO₄ system. These diols may present entry into a new family of fullerene derivatives.

Experimental Procedures

General. Fullerenes C₆₀ and C₇₀ were obtained from MER Corp. A solution of RuO₄ in CCl₄ was prepared as follows: A separatory funnel in a well ventilated area was used for generation of RuO₄• RuO₂ hydrate (338 mg, 2 mmol, assuming dihydrate) was suspended in a mixture of water (30 mL) and CCl₄ (30 mL). Sodium periodate (2.14 g, 10 mmol) was added at once and the mixture was shaken vigorously until solid disappeared. The yellow CCl₄ layer was separated and the water layer was extracted with 20 mL of CCl₄. The combined CCl₄ layers were dried over anhydrous MgSO₄ for 20 min. then filtered through a layer of anhydrous sodium sulfate into an addition funnel.

1,2-C₆₀(OH)₂ (1). C₆₀ (720mg, 1 mmol) was dissolved in 1,2,4-trichlorobenzene (200 mL). To this solution was added dropwise (30 min.) a freshly-prepared solution of RuO₄ (2 mmol) in carbon tetrachloride (50 mL). The resulting black suspension was stirred for 3 h, then suction filtered through a 0.2 μ nylon filter membrane. The filtrate contained 162 mg (0.225 mmol) of unreacted C₆₀. The filter cake was resuspended in toluene and centrifuged. This was repeated three times. The resulting pellet was dried in air to give 1.05 g of a black powder that was insoluble in common solvents. The solid was suspended in water/dioxane (1:25, 280 mL) containing 2 mL conc. aq. HCl and sonicated for 30 min. at 40°C. The clear solution was stirred while 300 mL of toluene was added over 5 min. The aqueous layer was separated and the organic solution was dried over anhydrous sodium sulfate for 10 hrs, filtered and evaporated to dryness. The resulting brown solid (574 mg) was redissolved in toluene/dioxane (80:20) mixture and purified using column chromatography on Florisil (40 g) eluting with toluene/dioxane (80:20 to 50:50) solvent system. Fractions containing C₆₀(OH)₂ were combined and concentrated. Crude 1,2-C₆₀(OH)₂ (137 mg) was further purified by HPLC on a semipreparative PBB Cosmosil column (toluene/THF = 90:10) to give 64 mg (8.5%, 11% based on reacted C₆₀). ¹³C NMR (CS₂/dioxane-d₈) δ (relative intensity) 84.94, 136.85, 140.18, 142.34, 142.55, 142.93, 143.30, 143.38, 145.55, 145.90, 145.99, 146.30, 146.64, 146.93, 147.17, 149.30, 152.90; IR (KBr) ν 3285 cm⁻¹; FAB MS (negative ion, *m*-nitrobenzyl alcohol) *m/z* (%) 754 (M⁺,40), 736 (67), 720 (100).

C₇₀(OH)₂ (2 and 3). C₇₀ was reacted with RuO₄ according to the procedure described above for C₆₀(OH)₂. Starting from 420 mg (0.5 mmol), 143 mg of unreacted C₇₀ was recovered after initial reaction with RuO₄. Also, Florisil was replaced by silica gel in the process of preliminary purification. Two isomers of C₇₀(OH)₂ were isolated using

the work-up procedure described above: 45 mg (10.5%, 16% based on reacted C₇₀) of (1,2) isomer together with 14 mg (3.2%, 4.8% based on reacted C₇₀) of (5,6) isomer.

1,2-C₇₀(OH)₂ (2): ¹³C NMR (CS₂/dioxane-d₈) δ (relative intensity) 80.36, 81.60, 132.07, 132.09, 132.75, 133.38, 134.15, 138.00, 141.09, 141.54, 144.01, 144.16, 144.26, 144.49, 146.30, 146.68, 147.28, 147.29, 147.96, 147.98, 148.06, 148.41, 149.13, 149.74, 149.90, 150.06, 150.09, 150.47, 150.83, 151.31, 151.79, 151.82, 152.03, 152.11, 154.98, 157.37, 157.38. IR (KBr) ν 3280 cm⁻¹; FAB MS (negative ion, *m*-nitrobenzyl alcohol) *m/z* (%) 874 (M⁺,55), 856 (100), 840 (100).

5,6-C₇₀(OH)₂ (3): ¹³C NMR (CS₂/dioxane-d₈) δ (relative intensity) 78.03, 126.93, 129.33, 130.97, 133.01, 133.20, 141.44, 143.44, 143.55, 144.53, 144.69, 145.04, 145.52, 145.63, 146.01, 146.09, 146.60, 146.80, 146.86, 147.27, 147.57, 147.64, 147.75, 148.66, 149.46, 149.61, 149.64, 149.90, 150.10, 150.62, 150.79, 151.30, 151.31, 152.28, 152.48, 155.61, 166.67. IR (KBr) ν 3285 cm⁻¹; FAB MS (negative ion, *m*-nitrobenzyl alcohol) *m/z* (%) 891 (11), 874 (M⁺,32), 856 (80), 840 (100).

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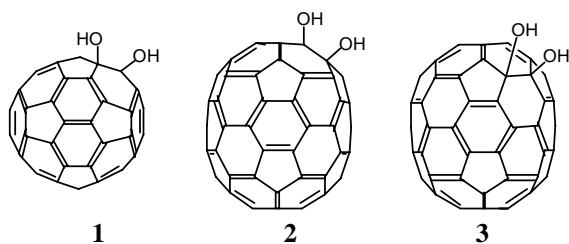


Figure 1, The structures of 1,2- $C_{60}(OH)_2$ (**1**), 1,2- $C_{70}(OH)_2$ (**2**) and 5,6- $C_{70}(OH)_2$ (**3**).



Figure 2. 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 3. 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.

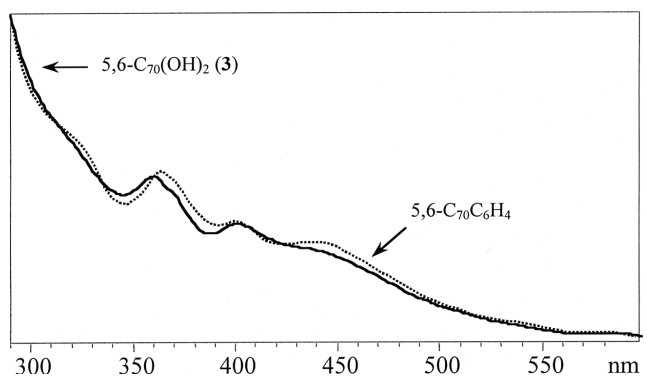
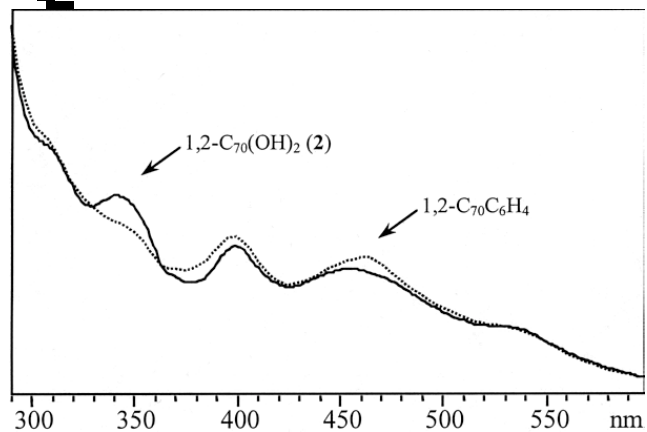


Figure 4. Absorption spectra of 1,2- $C_{60}(OH)_2$ (1), 1,2- $C_{70}(OH)_2$ (2) and 5,6- $C_{70}(OH)_2$ (3) measured in 90% toluene/10% THF.