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Oxidation of [60]Fullerene by the Methyltrioxorhenium-Hydrogen Peroxide System

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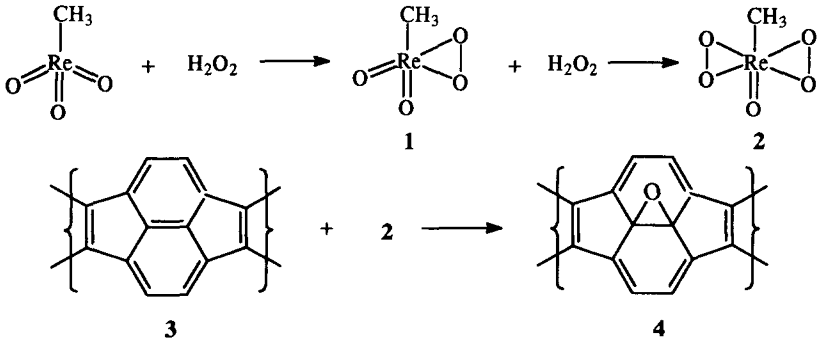
Abstract: Methyltrioxorhenium catalyzes the oxidation of C_{60} by hydrogen peroxide to give $C_{60}O$. The reaction continues to produce $C_{60}O_2$ and higher oxides. The yield of $C_{60}O$ represents a modest improvement over that given by other methods. The reaction conditions can be manipulated to give high conversions of the C_{60}. Copyright © 1996 Elsevier Science Ltd

Realization of the anticipated technical potential of fullerenes will depend to a great extent on the availability of well-characterized derivatives. Oxidation reactions are expected to play an important role in the preparation of some of these derivatives. A key oxidation derivative is the monooxide 1,2-epoxy[60]fullerene ($C_{60}O$). A number of methods have been reported for the synthesis of $C_{60}O$. Photooxidation of C_{60} in benzene, with and without added benzil, gave the oxide in modest yields.[1] Oxidation of C_{60} with dimethyldioxirane gave a low yield of $C_{60}O$ accompanied by a 1,3-dioxolane derivative.[2] A number of reports[3] have described the formation of $C_{60}O$ when C_{60} is treated with ozone. Epoxidation of C_{60} with *m*-chloroperbenzoic acid gives[4] an improved yield (30 %) of the oxide. Several P450 chemical model systems have been used[5] to oxidize C_{60} to $C_{60}O$ in moderate yield. It seemed to us that there remains a need for an additional source of $C_{60}O$ and for a process giving higher conversions of C_{60}.

We have become interested in the chemistry of the methyltrioxorhenium-hydrogen peroxide system (MTO-H_2O_2) largely because of the similarity of the chemistry of this system to that of the dioxiranes.[6] The MTO-H_2O_2 system has been used successfully to oxidize a variety of organic substrates. Of particular interest to the work described here is the use of this system to epoxidize double bonds.[7] Also of pertinence to the current work is the report[8] that this metal system is capable of oxidizing arenes.

Scheme 1



We now report that the MTO-H_2O_2 system oxidizes C_{60} **3** to $C_{60}O$ **4** in a very smooth reaction (Scheme 1) and in a yield which modestly exceeds that obtained in other methods. It has been shown[9,10] that MTO forms two adducts with hydrogen peroxide, **1** and **2** (Scheme 1).Under the conditions of our reactions we expect **2** to be the major oxidant.

We have carried out these oxidations under a variety of conditions[11] some of which are summarized in Table 1. The best yield (35.4 %, entry 5) was obtained when the MTO was at the next to highest concentration. Increasing the amount of MTO further gives a higher conversion, but with a slightly lower yield of **4** (entry 9). Likewise, adding an additional amount of UHP (Urea hydrogen Peroxide) at 12 h leads to the highest conversion, but with a reduced yield of **4** (entry 11). Allowing the MTO to prior associate with the C_{60} before adding the oxidant leads to a higher yield of **4** and a higher conversion of the C_{60} (compare entries 8 and 9). Control experiments show that using only peroxide (entry 10) or only MTO (entry 7) gives only minimal reaction.

Table 1. Oxidation of C_{60} with H_2O_2-Methyltrioxorhenium[a]

Entry	C_{60} mg,(mmol)	UHP g, (mmol)	MTO mg, (mmol)	Yield of $C_{60}O$(%)[b]	Conversion (%)
1	5 (0.0069)	0.01306 (0.1388)	1.0 (0.004)	31.28	38.00
2	5 (0.0069)	0.01306 (0.1388)	0.2 (0.0008)	8.45	12.69
3	5 (0.0069)	0.01306 (0.1388)	0.5 (0.002)	24.59	36.49
4[c]	5 (0.0069)	0.1 mL (0.1388)	0.5 (0.002)	10.30	28.66
5	5 (0.0069)	0.1306 (0.1388)	4.0 (0.016)	35.40	42.72
6[d]	5 (0.0069)	0.01306 (0.1388)	1.7 (0.007)	27.69	41.68
7[d]	5 (0.0069)	_	1.7 (0.007)	1.00	1.00
8	5 (0.0069)	0.01306 (1.388)	34.7 (0.139)	22.63	35.95
9	5 (0.0069)	0.1306[e] (1.388)	34.7 (0.139)	34.51	61.89
10	5 (0.0069)	0.01306 (1.388)	_	0.63	1.49
11	5 (0.0069)	0.1306 (1.388)	34.7 (0.139)	33.54[f]	60.11[f]
				28.67[g]	66.76[g]

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[a] RT, 24h; Solvent - Benzene 10 mL. [b] Assayed by HPLC. [c] 0.1 mL H_2O_2 in ethanol used. [d] 5 mL Benzene used. [e] Oxidant added after 1h. [f] At 12h. [g] Additional UHP (1.38 mmol) added after 12h.

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11. Sample procedure: C_{60} (Fluka, 5 mg, 0.0069 mmol) was dissolved in 10 mL of benzene along with methyltrioxorhenium (1 mg, 0.004 mmol) and the solution stirred for 1 h at room temperature. Urea hydrogen peroxide.[7e,12] (UHP, 13 mg, 0.139 mmol) was then added and stirring continued for an additional 12 h. The reaction mixture was filtered through filter paper to remove insoluble material. The filtrate was further filtered through Whatman 13 mm ZC Syringe filters prior to HPLC analysis.[13] The ^{13}C NMR spectrum of the HPLC isolated **4** is similar to that previously reported.[2,5] The small differences may be due to the use of a different internal lock standard. The MALDI-TOF (matrix dihydroxybenzoic acid) and ESI mass spectra of isolated **4** show a peak at *m/z* 736 as well as a peak at m/*z* 720 arising from loss of an oxygen atom from **4.** HPLC isolated samples of $C_{60}O_2$ and $C_{60}O_3$ were also characterized by ESI mass spectroscopy giving peaks at *m/z* of 752 and 768, respectively. The HPLC chromatogram is similar to that published earlier.[3c,e] In general longer reaction times give increasing amounts of the higher oxides. Under the conditions used for entry 9 of Table 1 18.3 and 6.2 % of the di- and tri-oxides were obtained, respectively. The conditions of entry 11 (modified as shown in footnote g) gave 17.27 and 18.24 % of the di- and trioxides, respectively.
12. The use of UHP in organic solvents avoids some of the disadvantages of using water as a solvent. (a) Marcantoni, E.; Petrini, M.; Polimanti, O. *Tetrahedron Lett.* **1995**, *36*, 3561-3562. (b) Adam, W.; Mitchell, C.M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 533-535. Adam, W.; Kumar, R.; Reddy, T.I.; Renz, M. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 880-882. (c) Murray, R.W.; Iyanar, K.; Chen, J.; Wearing, J.T. *J. Org. Chem.*, in press.
13. HPLC conditions. Analytical: Alltech Rsil C_{18} 10 μ column, 4.6 x 250 mm; eluent: toluene:acetonitrile (1:1 v/v), flow rate 3 mL/min, pressure 100 atm with UV detection at 357 nm. Preparative: Alltech Kromasil C_{18} 5 μ column, 10x250 mm, eluent: toluene:acetonitrile (1:1 v/v), flow rate 10 mL/min, pressure 250 atm with UV detection at 357 nm.

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