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Selective addition of H_2O to fullerene C_{60} catalyzed by Ti, Zr, and Hf catalysts

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Abstract

Selective addition of H_2O to fullerene C_{60} catalyzed by Cp_2MCl_2 (M = Ti, Zr, Hf) catalysts to yield 1-hydroxy-1,2-dihydrofullerene has been realized for the first time.

Keywords: Catalysis; Fullerene[60]; 1-Hydroxy-1,2-dihydrofullerene

As reported,[1] the known procedures for hydroxylation of fullerenes lead to a complex mixture of fullerols, separation, and identification of which are difficult. For example, the combined effect of concentrated sulfuric (H_2SO_4) and nitric (HNO_3) acids on fullerene C_{60} causes production of a mixture of fullerols containing from 14 to 15 hydroxyl groups.[2] The reaction of fullerene with aqueous NaOH solution in the presence of *tetra*-butylammonium hydroxide as catalyst gave rise to a mixture of fullerols with 24–26 hydroxyl groups.[3] The hydroxylated fullerenes are of significant practical interest due to the possibility of their use in medicine and biology,[4–7] and also in the chemistry of high-molecular compounds, for example, in the production of reticulated polymers.[8]

Taking into account that the known procedures to obtain hydroxyl-containing fullerenes do not allow the introduction of one OH group into the fullerene molecule, we have undertaken an attempt to conduct a selective addition of H_2O to fullerene C_{60} under the action of metal complex catalysts. Compounds of Ti, Zr, and Hf, which manifest high activity and selectivity in amine addition to fullerene C_{60}, were chosen as catalysts for this reaction.[9,10]

The reaction between fullerene C_{60} and H_2O ($C_{60}/H_2O = 1{:}6500$) in the presence of 20 mol % of Cp_2MCl_2 (M = Ti, Zr, Hf) catalyst at 20 °C for 24 h in toluene gave 1-hydroxy-1,2-dihydrofullerene **1**[11] in 65–75% yield (Cp_2TiCl_2 (66%), Cp_2ZrCl_2 (73%), Cp_2HfCl_2 (75%)). Increasing the temperature to 80 °C gave rise to the target product **1** in 90% yield in a shorter reaction time (1 h) (Scheme 1). The same reaction catalyzed by complexes and salts of other transition metals [$Ni(acac)_2$, $Pd(acac)_2$, $Fe(acac)_3$, $TiCl_4$, Cp_2Fe, $MnCl_2$, $CoCl_2$, $FeCl_3$, $ZrCl_4$] as well as without catalyst failed. Further increase in temperature (to 150 °C) and reaction time (to 14 h) led to complex mixtures (according to the HPLC data) of hydroxyl-containing fullerenes. Under optimized conditions (20 °C, 20 mol % Cp_2MCl_2 (M = Ti, Zr, Hf), 24 h) the reaction of fullerene C_{60} with D_2O gave 1-deuteroxy-2-deuterofullerene **2**[11] in up to 80% yield (Scheme 1).

The UV spectrum ($CHCl_3$) of compound **1** showed absorption maxima at λ 258 and 330 nm, which are characteristic of the 1,2-addition products.[12,13] The IR spectrum of **1**

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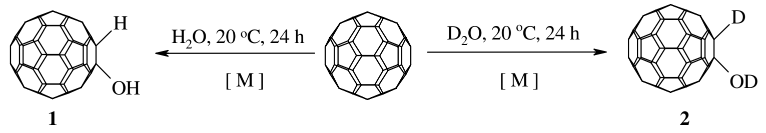
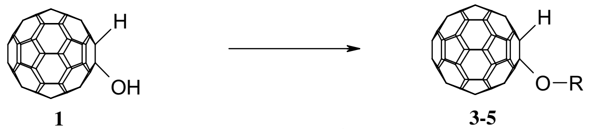


$[M] = Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2HfCl_2$.

Scheme 1.



3: R= Ac (Ac_2O, Py, 110 °C, 8 h, 95%)
4: R= PhCO (PhCOCl, Py, 110 °C, 8 h, 92%)
5: R= Me_3Si (Me_3SiCl, Py, 20 °C, 24 h, 98%)

Scheme 2.

contained absorption bands at 3400 (br, OH), 2930 (C_{60}–H), 1445, 1375 and 1080 cm^{-1}. In the ^{13}C NMR spectrum of **1**, sp^3-hybridized carbon atoms of the fullerene sphere were characterized by resonances at 57.02 and 75.62 ppm, whereas 27 signals attributed to the sp^2-hybridized carbon atoms of fullerene were observed in the field of 137–158 ppm. The mass-spectrum (MALDI TOF) of adduct **1** showed the presence of a molecular ion $[M]^+$, *m/z* 738 and fragmentation ion [M−H] *m/z* 737 confirming the addition of one water molecule to fullerene C_{60}.

To obtain further proof of the structure of 1-hydroxy-1,2-dihydrofullerene we performed transformations characteristic for alcohols. Treatment of **1** in dry pyridine with acetic anhydride or benzoyl chloride at 110 °C for 8 h led quantitatively to 1-acetoxy-1,2-dihydrofullerene **3**[14] or 1-benzoyloxy-1,2-dihydrofullerene **4**,[14] respectively. The reaction of trimethylchlorosilane with 1-hydroxy-1,2-dihydrofullerene at 20 °C for 24 h resulted in the formation of 1-trimethylsilyloxy-1,2-dihydrofullerene **5**[15] with >90% yield (see Scheme 2).

The IR spectra of compounds **3**–**5** showed that the band at 3400 cm^{-1}, attributed to the hydroxyl group of initial **1** had disappeared. Simultaneously, characteristic carbonyl group absorptions appeared at 1780, 1740, and 1680 cm^{-1} for **3** and at 1730 cm^{-1} for **4**.

In conclusion, we have demonstrated the first example of the synthesis of 1-hydroxy-1,2-dihydrofullerene from fullerene C_{60} and H_2O in the presence of Cp_2MCl_2 (M = Ti, Zr, Hf) catalyst. This procedure opens new prospects for the synthesis of fullerene hydroxyl-derivatives.

Acknowledgments

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11. Synthesis of compounds **1** and **2**: A 50 mL glass reactor was charged with a freshly prepared solution of 0.01 mmol of fullerene[60] in 10 mL of toluene, 55 mmol H_2O (or D_2O) and 0.002 mmol of Cp_2MCl_2 catalyst (M = Ti, Zr, Hf), and the mixture was stirred for 1 h at 80 °C. The reaction products were separated from unreacted C_{60} by preparative HPLC. 1-Hydroxy-1,2-dihydrofullerene (**1**). IR (KBr) ν (cm^{-1}) 520, 740, 1080, 1375, 1445, 2930, 3400; UV ($CHCl_3$) λ (nm) 258, 330; ^1H NMR ($CDCl_3$, CS_2) δ 1.32 s (1H, C_{60}–H), 3.36 s (1H, OH); ^{13}C NMR ($CDCl_3$, CS_2) δ 57.02, 75.62, 137.79, 138.03, 138.08, 138.23, 140.21, 140.43, 142.16, 142.26, 142.35, 142.40, 142.94, 143.00, 143.39, 144.78, 144.96, 145.67, 145.74, 145.79, 146.15, 146.37, 146.47, 146.60, 146.68, 146.69, 147.48, 155.72, 157.46; MALDI TOF, *m/z* 738 (M), 737 (M−H), 720 (base peak). 1-Deuteroxy-2-deuterofullerene (**2**). IR (KBr) ν (cm^{-1}) 520, 740, 1080, 1375, 1445, 2260, 3400; UV ($CHCl_3$) λ (nm) 256; ^{13}C NMR ($CDCl_3$, CS_2) δ 56.19, 74.98, 137.00, 137.15, 137.23, 137.31, 137.59, 139.57, 139.79, 141.52, 141.63, 141.72, 141.77, 141.80, 142.31, 142.37, 144.15, 144.33, 145.04, 145.10, 145.16, 145.53, 145.74, 145.83, 145.97, 146.06, 146.85, 155.11, 156.96.
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14. Synthesis of compounds **3** and **4**: A 17-mL metal finger-like high-pressure reactor was charged with a freshly prepared solution of 0.03 mmol of 1-hydroxy-1,2-dihydrofullerene (**1**) in 20 mL of dried pyridine, 3 mmol of acetic anhydride **3** (or benzoyl chloride **4**) and 0.0015 mmol of 2-(*N*,*N*-dimethylamino)pyridine (DMAP) under an argon atmosphere, and the mixture was stirred for 8 h at 110 °C. 1-Acetoxy-1,2-dihydrofullerene (**3**). IR (KBr) ν (cm^{-1}) 520, 710, 1080, 1400, 1445, 1680, 1740, 1780, 2920; UV ($CHCl_3$) λ (nm) 257; ^1H NMR ($CDCl_3$, CS_2) δ 1.34 s (1H, C_{60}–H), 2.18 s (3H, CH_3); ^{13}C NMR

(CDCl$_3$, CS$_2$) δ 21.73, 56.77, 75.31, 134.60, 135.60, 136.32, 136.75, 136.90, 137.29, 137.44, 137.53, 137.71, 137.81, 138.06, 139.84, 140.06, 140.88, 141.62, 141.80, 141.89, 141.99, 142.15, 142.59, 144.42, 144.59, 145.31, 145.42, 145.83, 146.01, 146.11, 146.24, 146.34, 147.13, 155.43, 157.17, 178.63. 1-Benzenecarbonyloxy-1,2-dihydrofullerene (**4**). IR (KBr) ν (cm^{-1}) 520, 690, 780, 1080, 1390, 1440, 1580, 1730, 2920; UV (CHCl$_3$) λ (nm) 256; ^{1}H NMR (CDCl$_3$, CS$_2$) δ 1.37 s (1H, C$_{60}$–H), 7.40–8.10 m (5H, Ph); ^{13}C NMR (CDCl$_3$, CS$_2$) δ 59.36, 75.26, 128.14, 128.22, 128.94, 137.33, 137.37, 137.79, 139.78, 139.99, 141.73, 141.83, 141.93, 141.97, 142.01, 142.52, 142.57, 142.90, 142.96, 142.99, 144.36, 144.53, 144.86, 145.25, 145.30, 145.31, 145.36, 145.75, 145.95, 146.04, 146.17, 146.27, 147.06, 148.78, 155.34, 157.09, 178.72.

15. Synthesis of compound **5**: A 50 mL glass reactor was charged with a freshly prepared solution of 0.03 mmol of 1-hydroxy-1,2-dihydrofullerene (**1**) in 20 mL of dried pyridine, 3 mmol of chloro(trimethyl)silane and 0.0015 mmol of DMAP under an argon atmosphere, and the mixture was stirred for 24 h at ~20 °C. 1-Trimethylsilyloxy-1,2-dihydrofullerene (**5**). IR (KBr) ν (cm^{-1}) 510, 730, 1380, 1450, 2930; UV (CHCl$_3$) λ (nm) 257; ^{1}H NMR (CDCl$_3$, CS$_2$) δ 0.07 s (9H, CH$_3$), 1.25 s (1H, C$_{60}$–H); ^{13}C NMR (CDCl$_3$, CS$_2$) δ 0.99, 57.07, 75.26, 128.67, 130.46, 137.39, 137.82, 137.95, 139.80, 140.02, 141.75, 141.86, 141.95, 142.03, 142.55, 142.60, 143.01, 144.38, 144.56, 145.27, 145.34, 145.38, 145.78, 145.97, 146.06, 146.20, 146.29, 147.09, 155.38, 157.12.