C_{60}^{2-} Chemistry : C_{60} Adducts bearing two Ester, Carbonyl or Alcohol Groups

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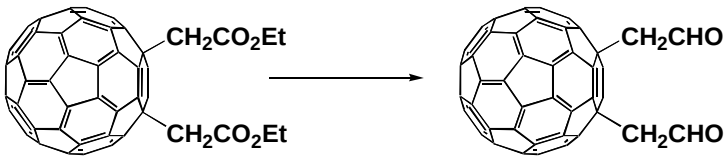
Supporting Information

Experimental

General. Solvents (dichloromethane, acetonitrile, toluene, tetrahydrofurane) were distilled under nitrogen over suitable drying agents prior to use. Carbon disulfide (Prolabo RP Normapur, 99.9%) and deuterated solvents for NMR analyses were used as received. Reagents ans starting materials were purchased from Aldrich or Acros and used as supplied.

NMR spectra were run on a Bruker Avance DRX 500 instrument working at 500.13 MHz for ^{1}H or at 125.75 MHz for ^{13}C nuclei.

Synthesis of the dialdehyde 10

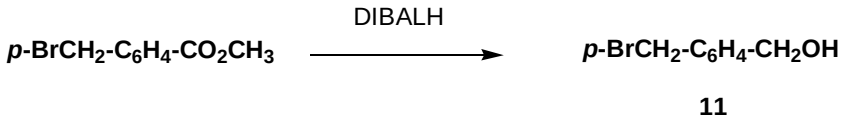


3b **10**

A solution of 0.03 mol (30 mg) diester **3b** in 50 mL toluene, under nitrogen, is cooled to –80°C, then a large excess (ca 20 eq) of DIBALH 1M in toluene is added to this solution. The reaction mixture is stirred fro two hours at –80°C, and a HCl methanol solution is then added in order to neutralize excess DIBALH. After the resultant mixture is allowed to warm

slowly to room temperature, the organic phase is washed with water until pH 7, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the dialdehyde **10** is isolated as a black solid through column chromatography over SiO_2 (eluent : toluene/ethyl acetate 90/10). Yield : 50%.

Synthesis of the alcohol *p*-$BrCH_2$-C_6H_4-CH_2OH 11



The alcohol **11** has been previously obtained through reduction of the corresponding methyl ester with AlH3 (M. Bayle-Lacoste, J. Moulines, N. Collignon, A. Boumekouez, E. de Tinguy-Moreaud and E. Neuzil, *Tetrahedron*, **1990**, *46*, 7793-7802).

The present reaction is achieved using DIBALH as the reducing reagent, according to the usual procedure described by N.M. Yoon and Y.S. Gyoung, *J. Org. Chem.*, **1985**, *50*, 2443-2450.

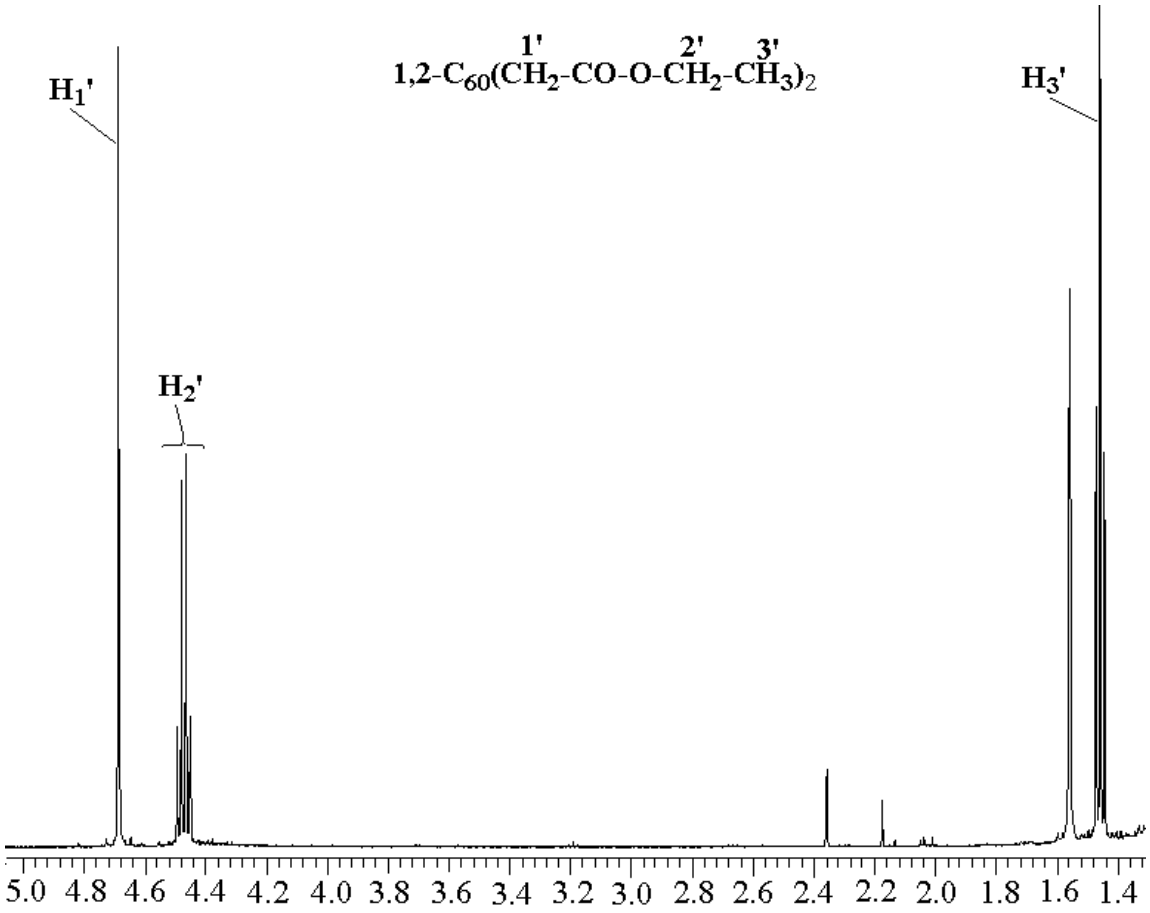
A mixture of 18.3 mmol DIBALH (18.3 mL 1M toluene solution) and 10 mL toluene is cooled to 0°C under stirring in a 250 mL round bottomed flask, under nitrogen. Then a solution of 2g (8.73 mmol) of methyl ester in 20 mL toluene is added to this medium, and the reaction mixture is stirred for 3 hours at 0°C. After addition of hydrochloric acid solution (1M) until pH 1, the organic phase is extracted, washed with water until neutrality and dried over anhydrous MgSO4. After evaporation the alcohol **11** is obtained as a white solid, and recrytallized in diethyl ether. Yield : 80%.

^{1}H NMR data ($CDCl_3$) : d 1.82 (broad s, 1H, OH), 4.5 (s, 2H, C*H*$_2$Br), 4.68 (s, 2H, C*H*$_2$OH), 7.32-7.41 (d.d, 4H).

^{1}H NMR Spectra

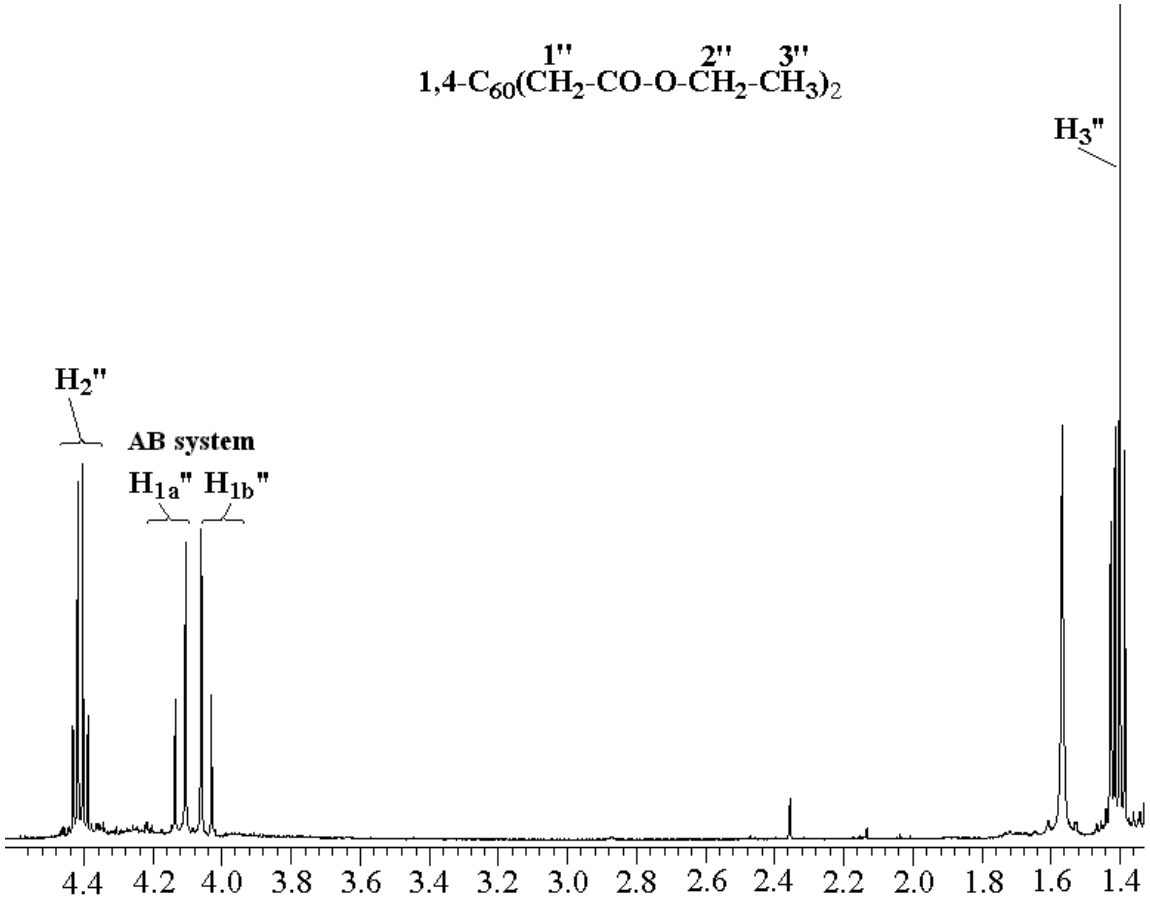
$C_{60}(CH_2\text{-}CO_2C_2H_5)_2$:1,2-isomer **3a**

Solvent : $CDCl_3$



$C_{60}(CH_2\text{-}CO_2C_2H_5)_2$:1,4-isomer **3b**

Solvent: $CDCl_3$



$C_{60}(CH_2\text{-}CHO)_2$ 10

Solvent : CS_2/C_6D_6