

Short Communication

Dihydrofuro-Fused Fullerene C₆₀ Derivatives: Side-Chain Reactions and Characterization

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Buckminsterfullerene C₆₀ may undergo a large variety of chemical reactions and form adducts, which might be interesting for material science¹ and biological² applications. The development of applications of fullerenes in a number of disciplines has been limited by the lack of suitable fullerene derivatives.^{3,4} This paper describes the preparation of a reactive fullerene derivative (dihydrofuro-fused C₆₀ acid chloride) that may be used to generate many functionalized fullerenes.

Few fullerene side-chain modifications have been reported until now.^{5,6} Although the derivatization presented here is not often applied to obtain modified fullerenes, it allows increased solubility and reactivity. The influence by C₆₀ on the reactivity of other functional groups in the molecule may also be observed.

In this contribution a method is presented that allows the synthesis of the dihydrofuro-fused C₆₀ carboxylic acid **2** and acid chloride **3** starting from the appropriate *tert*-butyl ester **1** (Fig. 1). C₆₀ dihydrofuro-fused *tert*-butyl ester **1** was synthesized in a formal oxidative [3+2] cycloaddition reaction starting from C₆₀ and *tert*-butyl acetoacetate.⁷ Subsequently, **1** was used as the starting material for further ester group transformations. The

ester **1** is a physically and thermally stable compound, a main requirement for further chemical transformation in the side-chain.

Conversion of **1** into carboxylic acid **2** can be achieved by treatment of a chloroform solution of **1** with trifluoroacetic acid (CF₃COOH) at room temperature. An insoluble, black compound **2** was isolated after vacuum evaporation of the solvent. A suspension of **2** in dry toluene was treated with an excess of thionyl chloride (SOCl₂) in presence of a catalytic amount of *N,N*-dimethylformamide (DMF) for 3 h at 100 °C. Excess SOCl₂ and DMF were removed by vacuum evaporation and the corresponding dihydrofuro-fused acid chloride **3** was isolated and dried under vacuum.

IR characterization of compounds **2** and **3** resulted in the following.

IR ν/cm^{-1} (KBr): (**2**) 3436, 1675, 1631, 1430, 1374, 1218, 1035, 850, 828, 564, 554; (**3**) 1724, 1698, 1612, 1428, 1299, 975, 930, 882, 741, 580, 550.

The two compounds **2** and **3** were also characterized by FAB+MS. The mass spectrum of **2** reflected the molar mass with a low intensity, while no molar mass was observed in **3**. This is due to the high reactivity of the compounds caused by the high temperatures.

The structure of all three compounds were confirmed by solid state ¹³C NMR spectroscopy. C₆₀ carboxylic acid and acid chloride⁵ could not be characterised by usual liquid state ¹³C NMR because of the low solubility of the compounds. ¹³C NMR spectra of the three compounds are presented in Fig. 2. The repetition time of 30 s in the experiment was chosen to yield almost complete relaxation of C₅₈.⁸ The cross relaxation time of 1.5 ms leads to efficient enhancement of ¹³C intensities within a few bonds to protons. The intensity variations

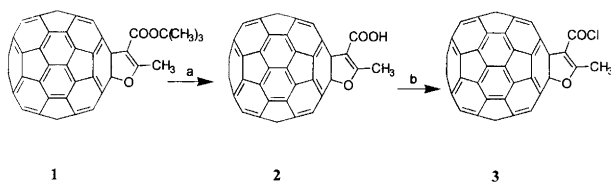


Fig. 1. Reagents and conditions: (a) CF₃COOH, CHCl₃, room temperature (95–97%); (b) SOCl₂, DMF, CH₃C₆H₅, 3 h, 100 °C (75–85%).

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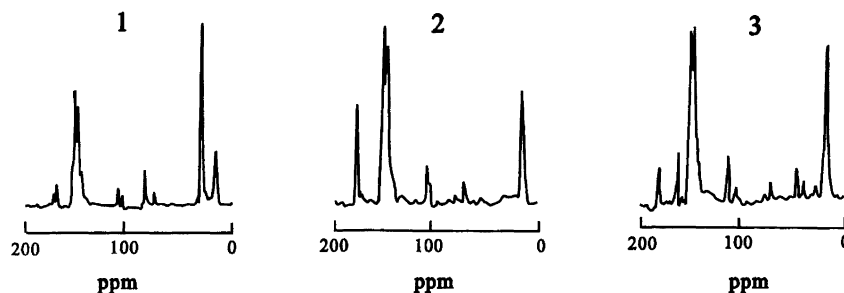


Fig. 2. ^{13}C TOSS NMR spectra of the compounds **1**, **2** and **3**. The spectra were acquired with a Bruker MSL300 spectrometer at room temperature with a constant magnetic field of 7 T. The experimental parameters were as follows: 90° pulses $5\ \mu\text{s}$; spectral width 40 kHz; dead time delay $30\ \mu\text{s}$; recycle delay 30 s; cross-polarization time 1.5 ms. Spectra were sampled in 4 K data points. The investigation was carried out using a Bruker MAS HPWP73A probehead at a spinning rate equal to 4 kHz.

are, therefore, significantly influenced by cross-relaxation.

The lines in the solid state NMR spectra are broader than for liquids, but it is possible to identify the structures of **1**, **2** and **3**. The lines were assigned as follows: (**1**) δ 10–20 ($-\text{CH}_3$), 25–35 [$-(\text{CH}_3)_3$], 70–73 ($-\text{C}_{58}-\text{C}=\text{C}$), 78–83 [$-\text{OC}(\text{CH}_3)$], 101–104 ($-\text{C}_{58}-\text{C}-\text{O}$), 104–108 ($>\text{C}=\text{C}<$), 133–150 ($\text{C}_{58}<$), 160–163 ($\text{O}-\text{C}=\text{C}$), 164–168 ($-\text{COO}$); (**2**) δ 10–20 ($-\text{CH}_3$), 70–73 ($-\text{C}_{58}-\text{C}=\text{C}$), 100–108 ($-\text{C}_{58}-\text{C}-\text{O}$, $>\text{C}=\text{C}<$), 133–150 ($\text{C}_{58}<$), 160–168 ($\text{O}-\text{C}=\text{C}$, $-\text{COO}$); (**3**) δ 10–20 ($-\text{CH}_3$), 70–73 ($-\text{C}_{58}-\text{C}=\text{C}$), 101–104 ($-\text{C}_{58}-\text{C}-\text{O}$), 108–112 ($>\text{C}=\text{C}<$), 133–150 ($\text{C}_{58}<$), 160–168 ($\text{O}-\text{C}=\text{C}$, $-\text{CO}$). The solvent DMF (δ 38, 45, 155) was present in **3**. Structures of the compounds are not only supported by the chemical shifts δ , but also by signal intensities. In general, the ^{13}C intensities are proportional to number of ^{13}C equivalent nuclei and, additionally, are enhanced by interaction with nearby protons.⁹ Thus, for example, low ($-\text{CO}$) signal intensity of **3** in comparison with compound **2** reflects absence of the carboxylic proton in **3**.

The $-\text{COCl}$ group in **3** may be used to form a number of derivatives by esterification or amidation. The stability of the C_{60} core link under these conditions make **3** an attractive intermediate in potential syntheses of C_{60} derivatives.

In summary, we report new side-chain transformation

products of a dihydrofuro-fused C_{60} *tert*-butyl ester derivative, which can be used for a large variety of further side-chain transformations. Solid state ^{13}C NMR spectroscopy is shown to be a useful technique for the characterization of compounds with low solubility.

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