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Ring Opening of the Heterocycle in [60]Fullereno[1,2-*d*]isoxazole*

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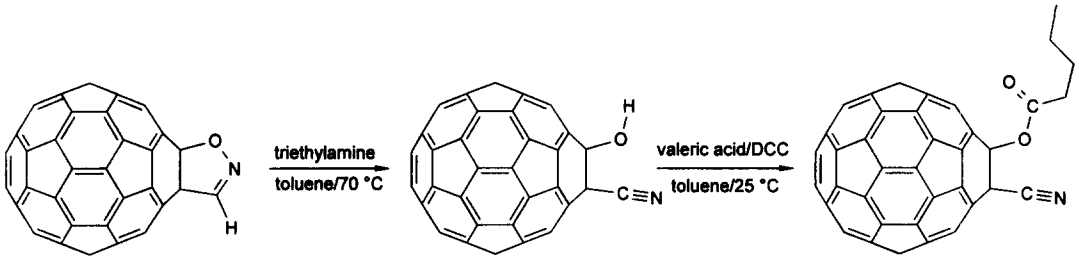
Abstract: 1-Cyano-2-hydroxy-dihydro[60]fullerene (**2**) was synthesized by N-O-bond cleavage of the isoxazoline derivative [60]fullereno[1,2-*d*]isoxazole (**1**). The esterification of valeric acid with this fullerol produced valeric acid 2-cyano-fulleryl ester (**3**). © 1997 Elsevier Science Ltd.

Recently we reported the addition of fulminic acid to [60]fullerene to produce the C3-unsubstituted isoxazoline derivative [60]fullereno[1,2*d*]isoxazole[1] (**1**), which was meanwhile also synthesized by addition of *N*-silyloxynitrone to [60]fullerene followed by treatment with *p*-toluenesulfonic acid.[2] Eleven attempts to carry out a ring opening of the heterocycle in C3-substituted fullerene-fused isoxazolines failed so far.[3] Now we present the N-O bond cleavage of compound **1** to produce 1-cyano-2-hydroxy-dihydro[60]fullerene (**2**).



1 **2** **3**

The cleavage was performed in toluene in the presence of triethylamine at elevated temperature.[4] This type of reaction was successfully employed with C3-unsubstituted isoxazolines as reported in literature.[5] The low yield of 10% (based on recovered precursor **1**) could not be increased by higher temperature, longer reaction times, higher concentration of the catalyst or addition of a different catalyzing base (pyridine, DBU, BEMP[6]). One major by-product in this reaction turned out to be C_{60}. Probably the cycloreversion of compound **1** is catalyzed by nucleophilic triethylamine via the reduced[3] fullerene **1**. The fullerol **2** is only poorly soluble ($CHCl_3$, *o*-dichlorobenzene), which makes the recording of a ^{13}C NMR spectrum impossible.

To confirm the existence of compound **2** we decided to use the fullerol in an esterification with valeric acid, using the mild and effective method employing DCC/DMAP.[7,8] The yield of ester **3** is nearly quantitative and the efficiently increased solubility makes it easy to determine the molecular structure by recording a ^{13}C NMR spectrum. The spectrum shows 30 signals arising from the fullerene core 4 with single intensity, 24

with double intensity and 2 with quadruple intensity (overlap of 2 signals with double intensity each). The two sp^3 hybridized fullerene atoms are appearing at δ 90.71 (C-OR) and δ 57.33 (C-CN). The resonances of the carbonyl, nitrile and alkyl group are detected in the expected areas.[8]

This is a new route to obtain fullerene derivatives by conversion of an easily available cycloadduct. The hydroxy and cyano group attached directly to the fullerene core allow transformations to novel isomerically pure fullerol derivatives as the fulleryl ester reported in this paper.

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* Dedicated to Prof. Günther Maier on the occasion of his 65th birthday.

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2. Ohno, M.; Yashiro, A.; Eguchi, S. *Synlett* **1996**, 815-816.
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4. 1-Cyano-2-hydroxy-dihydro[60]fullerene (**2**): In a typical run 36 mg ($4.7 \cdot 10^{-5}$ mol) of adduct **1** were dissolved in 50 ml of toluene under nitrogen. To the stirred solution were added 30 µl ($2.2 \cdot 10^{-4}$ mol) of triethylamine and the solution was heated at 70 °C for 6 h. After cooling down to room temperature the mixture was filtered through a silica-gel column, to remove unreacted adduct **1**(toluene, R_f 0.69). The product was eluted with toluene/acetonitrile 9/1 (R_f 0.50) and purified by HPLC (preparative column silica 60, toluene/acetonitrile 9/1) to produce 2 mg of a darkbrown solid. The yield was 10% (based on recovered compound **1**, 16 mg) and as a by-product 6.5 mg of C_{60} could also be isolated. FT-IR (KBr): $\tilde{\nu}$ 3353 cm^{-1} (m, OH), 2330 (w), 2245 (w, CN), 1431 (m), 1025 (m), 527 (s, fullerene); ^1H NMR (200 MHz, $CDCl_3$): δ 4.9 (br s); MS (MALDI-TOF, negative mode, matrix 9-nitroanthracene): *m/z* 763.
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8. Valeric acid 2-cyano-fulleryl ester (**3**): To a solution of 10 mg ($1.3 \cdot 10^{-5}$ mol) of the alcohol **2** in 50 ml of toluene/acetonitrile 9/1, obtained directly from the HPLC separation (see ref. 4), were added 2.8 µl ($2.6 \cdot 10^{-5}$ mol) of valeric acid, 5.4 mg ($2.6 \cdot 10^{-5}$ mol) of DCC and 0.3 mg ($2.6 \cdot 10^{-6}$ mol) of DMAP under nitrogen. The mixture was stirred at room temperature for 72 h, concentrated in vacuum and filtered through a silica-gel column (toluene, R_f 0.66) to produce a black powder in nearly quantitative yield. FT-IR (KBr): $\tilde{\nu}$ 2952 cm^{-1} (m, alkyl), 2330 (w), 2239 (w, CN), 1754 (s, CO), 1139 (m), 1096 (m), 991 (m), 526 (s, fullerene); ^1H NMR (300 MHz, $CDCl_3$): δ 3.05 (t, J = 7.5 Hz, 2H, CH_2), 2.06 (quintet, J = 7.5 Hz, 2H, CH_2), 1.66 (sextet, J = 7.5 Hz, 2H, CH_2), 1.10 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1/1): δ 174.25 (CO), 148.35 (1C), 147.81 (1C), 146.60 (2C), 146.56 (2C), 146.48 (2C), 146.24 (4C), 146.17 (2C), 145.94 (2C), 145.71 (2C), 145.44 (2C), 145.32 (2C), 145.28 (2C), 144.51 (2C), 144.46 (2C), 144.07 (2C), 143.96 (2C), 142.95 (2C), 142.72 (2C), 142.69 (2C), 142.25 (4C), 141.80 (2C), 141.43 (2C), 141.40 (2C), 140.98 (2C), 140.01 (2C), 139.70 (2C), 137.69 (2C), 136.47 (2C), 116.23 (CN), 90.72 (1C), 57.33 (1C), 34.63 (CH_2), 26.76 (CH_2), 22.51 (CH_2), 13.92 (CH_3); MS (FD, positive mode): *m/z* 847.

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