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Functionalization of [60]Fullerene by Photoinduced Electron Transfer (PET): Syntheses of 1-Substituted 1,2-Dihydro[60]fullerenes

Christina Siedschlag[a], Heinrich Luftmann[b], Christian Wolff[a] and Jochen Mattay[a]*

a) Institut für Organische Chemie der Christian-Albrechts-Universität Kiel, Olshausenstr. 40,
D-24098 Kiel, Germany, Fax: +49-431-880-7410, E-mail: mattay@oc.uni-kiel.de
b) Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Corrensstr. 40,
D-48149 Münster, Germany

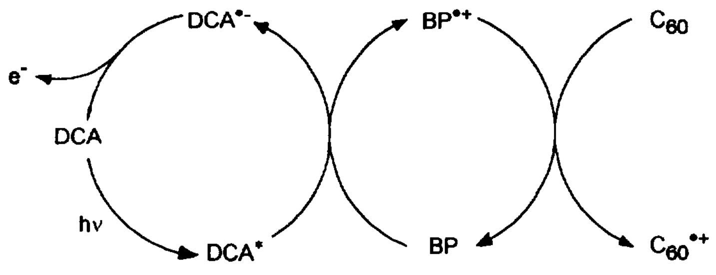
Abstract: [60]Fullerene is irradiated in the presence of the electron transfer sensitizer 9,10-dicyanoanthracene (DCA) under cosensitization with biphenyl. The generated radical cation $C_{60}^{\bullet+}$ reacts with H-donors such as *tert*-butylmethyl ether, propionaldehyde and alcohols to give 1:1-adducts, the 1-substituted 1,2-dihydro[60]fullerenes. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Whereas exohedral functionalizations of fullerenes have been performed mainly under thermal activation of the reaction partners the photochemical equivalent has gained only little interest.[1,2] This is somewhat surprising since [60]fullerene can easily be transferred into its triplet excited state either by direct excitation or by sensitization.[3] So far most of the reported photoinduced functionalizations of [60]fullerene are dealing with cycloadditons of electronically excited reactants or with photochemical conversions and rearrangements of fullerene derivatives.[2-5] We now report about our results of functionalization of [60]fullerene by means of photochemical methods especially under electron transfer conditions leading to dihydro[60]fullerenes.

FUNCTIONALIZATION OF [60]FULLERENE BY OXIDATIVE ELECTRON TRANSFER

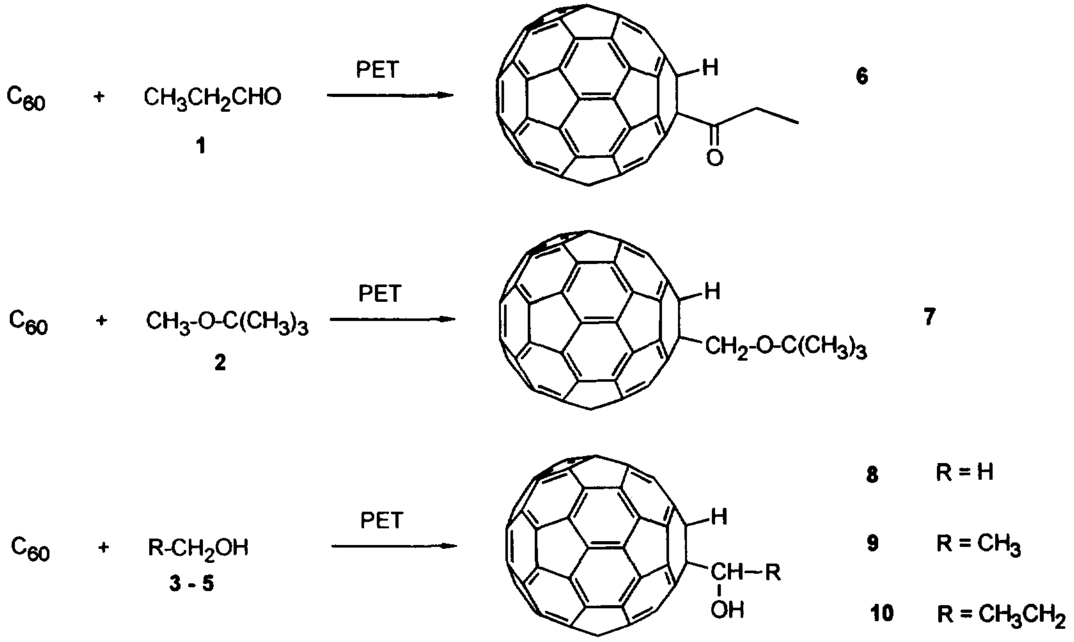
Radical ions generated by single-electron transfer from neutral compounds by means of photoinduced electron transfer (PET) are known as important intermediates in a variety of interesting chemical processes and reactions.[6-9] Whereas [60]fullerene can easily be reduced up to its hexaanion[10] and various reactions involving [60]fullerene radical anions have been reported[3,11-13] the oxidation to its radical cation has been investigated mainly by mass spectrometry and transient absorption spectroscopy.[3,14] We used 9,10-dicyanoanthracene (DCA) as electron transfer sensitizer and biphenyl (BP) as cosensitizer. The assumed mechanism of formation of $C_{60}^{\bullet+}$ by this cosensitization process is shown in scheme 1.



Scheme 1: Generation of $C_{60}^{\bullet +}$ by cosensitization (hν: 419 nm, DCA: 9,10-dicyanoanthracene, BP: biphenyl).

In general solvents commonly used in PET chemistry like acetonitrile are unfavourable for dissolving [60]fullerene. In order to combine relatively high polarity of the reaction medium with good solubility of [60]fullerene the use of mixtures of *o*-dichlorobenzene, acetonitrile and the reactant (*tert*-butylmethyl ether, propionaldehyde or alcohols) turned out to be most favourable.

When applying this method [60]fullerene yields the products **6**-**10** from propanal **1**, *tert*-butylmethyl ether **2** and the alcohols **3**-**5**.[15] It should be noted that no product formation is observed in the absence of BP indicating an efficient back electron transfer from $DCA^{\bullet -}$ to $C_{60}^{\bullet +}$. Furthermore the reaction with **2** even requires the addition of $LiClO_4$ by utilizing the salt effect.[8,9] We first expected the formation of ethers analogously to Arnold's pioneering reports.[16] However, the product structures clearly support a H-abstraction process[17,18] rather than nucleophilic addition (scheme 2).



Scheme 2: Formation of dihydro[60]fullerenes from [60]fullerene under PET (cosensitization) conditions (DCA, BP, $LiClO_4$ in case of 2, 419 nm).

Spectroscopic Analysis

All products show the characteristic lowfield shift of a proton directly connected to the fullerene core (6-10: singlet at $\delta = 6.8\text{-}6.5$). The fullerenyl proton of the ketone 6 is even shifted to a lower field ($\delta = 7.8$) due to the negative anisotropic effect of the carbonyl group. The corresponding carbon shows resonances at $\delta = 57\text{-}55$. Due to their C_s symmetry 29 signals are observed. Nevertheless these data support the proposed structure of 9 and 10 with the new stereogenic centre at C-1'. All products show a shift to the lower field by ca. 20 ppm for the carbons directly connected to the fullerene core. Hirsch et al. report similar results for 1-substituted dihydro[60]fullerenes (fullerenyl proton at ca. $\delta = 6\text{-}7$, sp^3 carbons at ca. $\delta = 62\text{-}65$).[19]

The mass spectrometric analysis has been carried out using the MALDI TOF technique. All compounds show the expected molecular ion peaks. In order to compare 6 and 10 both compounds have been measured under the same conditions. As expected *m/z* 779, 781 and 721 have been observed for 6, 10 and [60]fullerene, respectively.

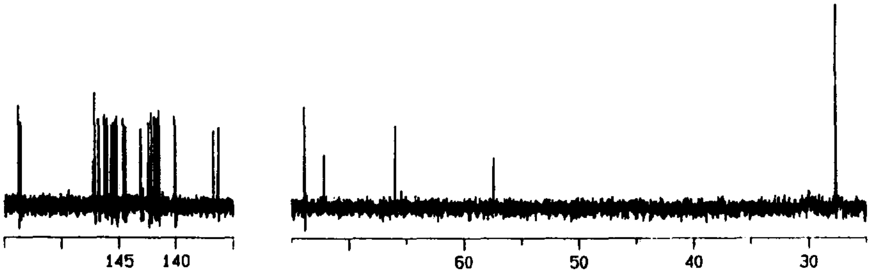


Fig. 1: ^{13}C NMR spectrum of 7 (CS_2/benzene-d_6).

SUMMARY

PET assisted additions of H-donors to [60]fullerene represent a versatile route to prepare 1-substituted 1,2-dihydro[60]fullerenes. To our knowledge analogous organodihydro[60]fullerenes have only been obtained by nucleophilic addition of organometallic compounds to [60]fullerene.[19,20] Further investigations to clarify the mechanism and the scope of this reaction are in progress.

EXPERIMENTAL

General remarks and materials

[60]Fullerene was used in *gold grade* quality (Hoechst, ≥ 99.4 %). All reactions were performed under an argon atmosphere. Carbon disulfide was used in *per analysis* quality. *O*-dichlorobenzene was of *purum* grade ≥ 98 %), toluene and acetonitrile were freshly distilled. Methanol, ethanol, *n*-propanol, *tert*-butylmethyl ether and propionaldehyde were used *per analysis* or freshly distilled. Removal of all solvents was carried out under reduced pressure. The solutions were irradiated in pyrex tubes (of 10 ml) or in photochemical reaction vessels (of 400 ml) in a RPR 100 Rayonet Photochemical Chamber Reactor with RPR-4190 Å lamps. Analytical high performance liquid chromatography (HPLC) was performed by using a C_{18}-reversed phase column (Bischoff 250 x 4 mm, Merck LiChrosorb RP18, 7µm) and toluene/acetonitrile mixtures (1 : 1 or 1 : 1.25) as eluent (UV/Vis detection at 300 nm (Kontron HPLC detector 432)), flow: 1.25 ml min^{-1}, pressure: 50 bar (Merck L-6000 pump). For preparative gel permeation chromatography a PLgel column (600 x 25 mm, PLgel, 10 µm, 100 Å), or a Jordi gel column (500 x 22 mm, Jordi gel, 10 µm, 100 Å), an Abimed-Gilson Spectrochrom detector (UV/Vis detection at 300 nm) and a Kontron HPLC pump 420 (flow: 10 ml min^{-1}, pressure: 20 bar)

were used. Column chromatography was performed on silica gel (Macherey-Nagel, 63-200 μm) or neutral alumina (Macherey-Nagel). Matrix assisted laser desorption/ionisation time-of-flight mass spectra (MALDITOF-MS) were recorded with a time-of-flight mass spectrometer Lazarus (Organisch-Chemisches Institut, Universität Münster, nitrogen laser, λ = 337 nm, matrix: 9-nitroanthracene, 4-(4'-*tert*-butylphenyl)-1,1-dicyano-3-methyl-buta-1,3-diene (DCTB), linear mode). Relative intensities are given in percentages. NMR spectra were recorded on a Bruker AM 300 spectrometer - Chemical shift data are reported relative to TMS as external standard: CS_2/acetone-d_6 (4:1): $\delta = 2.00$ (acetone) for proton and 192.34 (CS_2) for carbon and a Bruker DRX 500 - *o*-dichlorobenzene: $\delta = 6.93$ for proton and 127.19 for carbon, and CS_2/benzene-d_6 (4:1): $\delta = 7.20$ for proton (benzene) and 192.22 (CS_2) for carbon - relative to TMS as external standard. Fourier transform infrared spectra (FT IR) were recorded on a Perkin Elmer Paragon 1000 IR-spectrometer. UV/Vis spectra were performed on a Zeiss DMR 10 spectrophotometer.

1-(Propane-1’-one)-1,2-dihydro[60]fullerene (6)

107 mg (0.15 mmol) of [60]fullerene, 18 mg (0.08 mmol) of 9,10-dicyanoanthracene (DCA) and 4.6 g (30.0 mmol) of biphenyl were dissolved in a mixture of 140 ml of *o*-dichlorobenzene, 45 ml of acetonitrile and 22.5 ml of propionaldehyde. The solution was deoxygenated by purging with argon and irradiated in reaction vessels at 419 nm for 5 h. The solvents were evaporated *in vacuo*. Preparative gel permeation chromatography on PL gel with toluene gave 61 mg of unchanged [60]fullerene (56%) and 19 mg (16%, 37% based on consumed [60]fullerene) off 6 as dark brown solid.

MS: MALDI TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 779 (100) [M^-, calc. 778.7], 721 (17) [[60]fullerene]. ^1H NMR (500.13 MHz, ODCB-d_4): $\delta = 7.82$ (s, 1H; 2-H), 3.87 (q, ^3J(H,H) = 7.02 Hz, 2H, 2’-H), 1.73 (t, ^3J(H,H) = 7.02 Hz, 3H; 3’-H). ^{13}C NMR (125.77 MHz, ODCB-d_4): δ = 204.06, 153.33, 150.34, 147.35, 147.04, 146.95, 146.80, 146.28, 146.09, 145.96, 145.93, 145.64, 145.33, 145.11, 145.00, 144.52, 143.96, 143.05, 142.77, 142.48, 142.39, 142.17, 141.95, 141.84, 141.51, 141.41, 141.32, 140.36, 140.01, 135.00, 133.72, 78.35, 55.96, 33.85, 8.85. FT-IR (KBr): ν = 2923m, 1723s, 1508w, 1260m, 1105s, 1025w, 804w, 526s cm^{-1}. UV/Vis (in CH_2Cl_2): $\lambda_{max}>220$ (ε): 255 (157164), 320 (48140), 405sh (4343), 432 nm (3594).

1-(*tert*-Butoxymethyl)-1,2-dihydro[60]fullerene (7)

144 mg (0.20 mmol) of [60]fullerene, 47 mg (0.20 mmol) of DCA and 3.0 g (20.0 mmol) of biphenyl were dissolved in a mixture of 62.5 ml of *o*-dichlorobenzene, 25 ml of acetonitrile and 12.5 ml of *tert*-butylmethyl ether, saturated with $LiClO_4$. The solution was deoxygenated by purging with argon and irradiated in reaction vessels at 419 nm for 5.5 h. The solvents were evaporated *in vacuo*. Repeated column chromatography on silica gel (toluene/*n*-hexane 1:2) gave 35 mg of unchanged [60]fullerene, 10 mg of 7 as dark brown solid and 47 mg of a 67/33 mixture of both (HPLC), that is in total 66 mg of unchanged [60]fullerene (46%) and 26 mg (16%, 29% based on consumed [60]fullerene) of 7 .

MS: MALDI TOF (16 kV, 337 nm, matrix: 9-nitroanthracene): *m/z* ± 0.1%: 808 (23) [M^-, calc. 808.8], 720 (100) [[60]fullerene]. ^1H NMR (500.13 MHz, CS_2/benzene-d_6): $\delta = 6.60$ (s, 1H; 2-H), 5.03 (s, 2H, 1’-H), 1.55 (s, 9H, 2’’-H). ^{13}C NMR (125.77 Hz, CS_2/benzene-d_6): δ = 153.73, 153.56, 147.19, 147.03, 146.68, 146.19, 146.16, 145.97, 145.95, 145.61, 145.39, 145.22, 145.19, 145.14, 144.52, 144.39, 143.02, 142.37, 142.36, 142.11, 141.84, 141.80, 141.62, 141.44, 141.41, 140.08, 140.01, 136.71, 136.31, 73.80 (s; 1-C), 72.12 (t, ^1J(C,H) = 133.51 Hz; 1’-C), 65.96 (s, 1’’-C), 57.39 (d, ^1J (C,H) = 138.42 Hz; 2-C), 27.67 (q, ^1J(C,H) = 122.07; 2’’-C). FT-IR (KBr): ν = 2917m, 1654w, 1509w, 1458w, 1425w, 1360w, 1259w, 1182m, 1086m, 880w, 808w, 526s cm^{-1}. UV/Vis (in CH_2Cl_2): $\lambda_{max}>220$ (ε): 255 (108379), 325sh (33970), 405 (17147), 432 nm (3316).

1-Hydroxymethyl-1,2-dihydro[60]fullerene (8)

315 mg (0.44 mmol) of [60]fullerene, 98.0 mg (0.43 mmol) of (DCA) and 0.66 g (4.3 mmol) of biphenyl were dissolved in a mixture of 250 ml of 1,2-dichlorobenzene and 125 ml of methanol. The solution was deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 60 h. The solvents were evaporated *in vacuo* and purification of the residue by column chromatography on alumina N with toluene followed by acetonitrile and toluene/acetonitrile/ethanol 2:2:1 gave 187 mg (59%) of unconverted [60]fullerene (1st fraction) and 85 mg (26%, 64% based on consumed [60]fullerene) of **8** (2nd fraction) as brown black powder.

MS: MALDI TOF (16 kV, 337 nm, matrix: 9-nitroanthracene): *m/z* ± 0.1%: 752 (100) [M$^+$, calc. 752.7], 720 (34) [[60]fullerene]. ^{1}H NMR (300.13 MHz, CS_2/acetone-d_6): δ = 6.74 (s, 1H; 2-H), 5.31 (d, ^3J(H,H) = 5.93 Hz, 2H, 1'-H), 4.79 (t, ^3J(H,H) = 6.00 Hz, 1H; O<u>H</u>). ^{13}C NMR (75.47 MHz, CS_2/Acetone-d_6): δ = 153.89, 153.59, 147.24, 147.17, 147.10, 146.89, 146.28, 146.22, 146.07, 146.03, 145.68, 145.45, 145.31, 145.29, 145.22, 144.59, 144.42, 143.08, 142.95 ([60]fullerene), 142.46, 142.44, 142.25, 141.94, 141.87, 141.68, 141.55, 141.50, 140.17, 140.11, 136.88, 136.34, 73.07 (t, ^1J(C,H) = 144.90 Hz, 1'-C), 68.33 (s, 1-C), 57.23 (d, ^1J(C,H) = 138.32 Hz, 2-C). FT-IR (KBr): ν = 3447br.s (OH), 2922w, 1718w, 1636w, 1508m, 1498m, 1459w, 1425w, 1181w, 1044w, 526s cm^{-1}. UV/Vis (in CH_2Cl_2): λ_{max}>220 (ε): 255 (102367), 325 (30108), 405 (3914), 431 nm (3011).

1-(1'-Hydroxyethyl)-1,2-dihydro[60]fullerene (9)

203 mg (0.28 mmol) of [60]fullerene, 32 mg (0.14 mmol) of DCA and 4.2 g (27 mmol) of biphenyl were dissolved in a mixture of 250 ml of *o*-dichlorobenzene, 70 ml of acetonitrile and 70 ml of ethanol. The solution was deoxygenated by freeze and pump and irradiated in a reaction vessel at 419 nm for 14 h. The solvents were evaporated *in vacuo* and the residue was dissolved in toluene. Preparative gel permeation chromatography on Jordi gel with toluene gave 68 mg of unchanged [60]fullerene (33%) and 48 mg (23%, 34% based on consumed [60]fullerene) off 9 as dark brown solid.

MS: MALDI TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 766 (100) [M$^+$, calc. 766.7], 720 (21) [[60]fullerene]. ^{1}H NMR (500M.13 Hz, ODCB-d_4): δ = 6.60 (s, 1H; 2-H), 5.36 (q, ^3J(H,H) = 6.09 Hz, 1H, 1'-H), 2.88 (br.s, 1H; O<u>H</u>), 2.20 (d, ^3J(H,H) = 6.29 Hz, 3H; 2'-H). ^{13}C NMR (125.77 MHz, ODCB-d_4): δ = 154.24, 153.83, 153.67, 152.79, 147.28, 147.26, 147.11, 147.09, 146.74, 146.29, 146.26, 146.20, 146.07, 146.04, 146.01, 145.67, 145.40, 145.38, 145.29, 145.20, 145.18, 144.60, 144.55, 144.34, 143.03, 142.81, 142.43, 142.39, 142.33, 142.31, 141.95, 141.92, 141.88, 141.87, 141.57, 141.51, 141.50, 141.49, 141.43, 140.15, 140.13, 140.01, 139.82, 136.93, 136.80, 136.22, 136.07, 76.44 (d, ^1J(C,H) = 147.88 Hz; 1'-C), 72.06 (s; 1-C), 55.73 (d, ^1J(C,H) = 137.74; 2-C), 20.24 (q, ^1J(C,H) = 126.73 Hz). FT-IR (KBr): ν = 3446 br.s (OH), 2922w, 1508m, 526s cm^{-1}. UV/Vis (in CH_2Cl_2): λ_{max}>220 (ε): 255 (99085), 325 (21363), 432 nm (2583).

1-(1'-Hydroxypropyl)-1,2-dihydro[60]fullerene (10)

200 mg (0.28 mmol) of [60]fullerene, 63 mg (0.28 mmol) of DCA and 8.6 g (56 mmol) of biphenyl were dissolved in a mixture of 250 ml of *o*-dichlorobenzene, 70 ml of acetonitrile and 70 ml of *n*-propanol. The solution was deoxygenated by freeze and pump and irradiated in a reaction vessel at 419 nm for 18 h. The solvents were evaporated in vacuo and the residue was dissolved in toluene. Preparative gel permeation chromatography on Jordi gel with toluene gave 96 mg of unchanged [60]fullerene (48%) and 53 mg (24%, 47% based on consumed [60]fullerene) off 10 as dark brown solid.

MS: MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 781 (100) [M$^-$, calc. 780.7], 721 (45) [[60]fullerene]. ^{1}H NMR (500.13 MHz, ODCB-d_4): δ = 6.58 (s, 1H; 2-H), 5.03 (dd, ^{3}J(H,H) = 10.58 Hz, ^{3}J(H,H) = 2.10 Hz, 1H; 1'-H), 2.94 (bs, 1H, OH), 2.69 (dqd, ^3J(H,H) = 2.23 Hz, ^3J(H,H) = 7.17 Hz, ^2J(H,H) = 13.89 Hz, 1H; 2'-H_a), 2.50 (ddq, ^3J(H,H) = 7.13 Hz, ^3J(H,H) = 10.59 Hz, ^2J(H,H) = 13.89, 1H; 2'-H_b), 1.48 (t, ^3J(H,H) = 7.29 Hz, 3H, 3'-H). ^{13}C NMR (125.77 MHz, ODCB-d_4): δ =154.30, 153.86, 153.83, 152.88, 147.28, 147.26, 147.08, 146.74, 146.26, 146.24, 146.18, 146.18, 146.05, 146.03, 146.00, 145.68, 145.66, 145.37, 145.34, 145.27, 145.19, 145.16, 144.58, 144.55, 144.33, 144.31, 143.03, 142.79, 142.41, 142.38, 142.32, 142.27, 141.93, 141.89, 141.87, 141.85, 141.60, 141.55, 141.49, 141.46, 141.42, 140.15, 140.12, 139.97, 139.80, 137.59, 136.85, 136.80, 136.23, 136.05, 82.01, 71.97, 56.10, 27.25, 11.56. **FT-IR** (KBr): ν = 3421 br.s (OH), 2921m, 1654w, 1458w, 526s cm^{-1}. **UV/Vis** (in CH_2Cl_2): λ_{max}>220 (ε): 255 (75610), 325 (25656), 435 nm (3287).

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