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[60]Fullerene Radical Cation: Reactions and Mechanism

Christina Siedschlag[a], Heinrich Luftmann[b], Christian Wolff[a] and Jochen Mattay[c]*
a) Institut für Organische Chemie der Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40,
D-24098 Kiel, Germany
b) Organisch-Chemisches Institut, Universität Münster, Corrensstr. 40,
D-48149 Münster, Germany
c) Organische Chemie I, Fakultät für Chemie, Universität Bielefeld, Postfach 100131,
D-33501 Bielefeld, Germany

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Abstract: C_{60} was irradiated in the presence of several electron transfer photosensitizers. Upon addition of H-donors such as *N,N*-dimethylformamide, 1,3-dioxolane, phenylacetaldehyde, methyl formate, *tert*-butanol, propionic acid, glycol and methoxyethanol 1-substituted 1,2-dihydro[60]fullerenes **1-3** and **5-11** and in one case a 1,2,3,4-tetrahydro[60]fullerene, **4**, were formed. A mechanistic pathway involving $C_{60}^{\bullet+}$ is proposed.

Keywords: Photoinduced electron transfer, radical cation of [60]fullerene, dihydro[60]fullerenes, mechanistic studies, fluorescence quenching experiments.

INTRODUCTION

Reduction of [60]fullerene to its radical anion is easily performed due to the high electron affinity of C_{60} [1,2]. Among the variety of methods (chemical and cathodic reduction) photoinduced electron transfer (PET) plays an important role in one-electron reduction or even oxidation [3,4,5]. Using singlet sensitizers such as the *N*-methyl acridinium ion, it has been reported that $C_{60}^{\bullet+}$ is generated in polar solvents. Generation is overwhelmingly (10fold) increased by the addition of cosensitizers such as biphenyl [3,4]. Especially Schuster et al. pioneered the new and unexpected chemistry of C_{60} radical cation [6]. Recently, the adduct formation between [60]fullerene and alcohols, ethers and aldehydes in a preparative scale has been investigated [7]. In this report we will focus on photochemical processes of [60]fullerene involving both characterization of new products including $C_{60}H_2$ and detection of the intermediate $C_{60}^{\bullet+}$ by laser flash photolysis.

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*E-mail: mattay@uni-bielefeld.de; Fax: +49-521-106-6417

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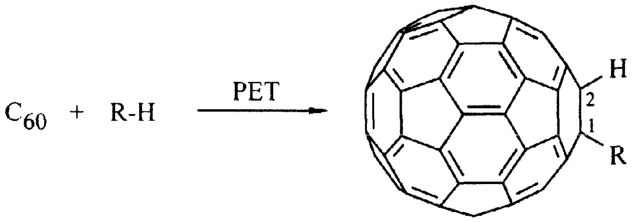
RESULTS AND DISCUSSION

Synthetic investigations

As typical procedure, mixtures of [60]fullerene, a H donor reactant and a PET sensitizer were irradiated in a suitable solvent. In earlier studies we found that 9,10-dicyanoanthracene DCA alone as sensitizer produced only traces of dihydro[60]fullerene derivatives, whereas in the presence of biphenyl as cosensitizer the efficiency was increased overwhelmingly [7]. Therefore we searched for more effective sensitizing systems as well as for other H donors as reaction partners. Comparative studies involving well-known PET sensitizers such as DCA, 1,4-dicyanonaphthalene (DCN), *N*-methylacridinium hexafluorophosphate (NMA^+) and 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) revealed the suitability of all sensitizers in the presence of biphenyl as cosensitizer with increasing velocity. We assume that the prevention of back electron transfer as an energy wasting step is crucial for product formation. Both cationic sensitizers (by using an electron shift) and cosensitizers (by taking advantage from a secondary electron transfer step) lead to an increased separation of C_{60} radical cation and the reduced sensitizer and therefore decreases the propability of back electron transfer.

In scheme 1 the general formation of 1-substituted 1,2-dihydro[60]fullerenes is shown. In principle C_{60} is inserted in a C-H bond of the reaction partner. Selected examples of our preparative studies are summarized in Table 1.



Scheme 1: Formation of dihydro[60]fullerenes under PET conditions (TPP^+ or DCA/BP, 419 nm).

In addition to our earlier results [7] we observed the formation of some unexpected products. For example, when using aldehydes as H-donor reactants the products depend on the reactivity of the intermediately formed radical. Propionaldehyde as starting material did not lead to decarbonylation because a primary alkyl radical is less stable than a benzyl radical, for example (cf. Scheme 2, **12**) [7]. In consequence, the decarbonylation during the addition of phenylacetaldehyde leading to **8** strongly suggests that this reaction involves an acyl radical. Similar observations have been made in the reactions of aldehydes to [60]fullerene in aqueous ammonia [8].

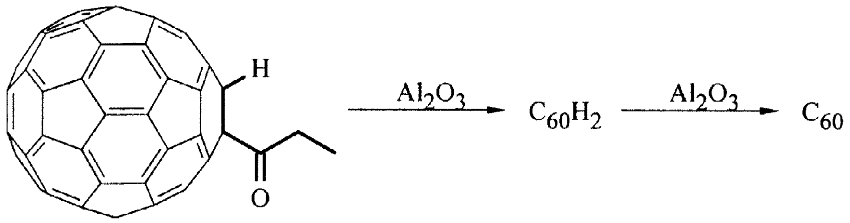
Whereas the addition of methyl formate resembles its usual radical chemistry [9] by leading to **11**, the addition of *N,N*-dimethylformamide follows a different pathway. Adduct formation results only from H abstraction at one methyl group (**10**). Interestingly the ^1H NMR spectrum of **10** showed two groups of singlets belonging to two inseparable isomers. Coalescence experiments show line broadening at 90°C but no collapse. Due to the experimental limits the coalescence point could not be determined but is supposed to be much higher than 90°C.

The reaction of [60]fullerene with 1,3-dioxolane led to somewhat unexpected products. During irradiation **5** and $C_{60}H_2$ (**6**) were produced, the former showing interesting NMR properties. Whereas the carbon multiplicities obtained by ^{13}C NMR gated decoupling measurements clearly support the structure designed in Table 1, i.e. a triplet for the dioxamethylene group, the ^1H NMR spectrum does not show the expected muliplicity of two doublets but two pseudosinglets. Nevertheless, further experiments (HSQC measurements with pulsed z-gradient) clarified that the two pseudosinglets at $\delta = 5.62$ and 5.23 belong to the same methylene group. Obviously the different contributions of the coupling constant add to zero.

The spectroscopic data of the products are consistent with those of other 1,2-dihydro[60]fullerenes already described in the literature [7,10]. In all cases the most characteristic NMR spectroscopic feature of the fullerene core is the strong lowfield shift executed to the directly connected hydrogen and carbon atoms.

Conversion of 1,2-dihydro[60]fullerenes

Generally the stability of the dihydro[60]fullerenes depends on the nature of the product and on treatment. Storage in solution is possible at least for days to weeks, in substance for several months under cooling. However, the stability towards column chromatography differs. For example filtration of 1-(propan-1'-one)-1,2-dihydro[60]fullerene **12** through alumina N first resulted in rapid formation of $C_{60}H_2$, whereas longer contact with the column material led to further conversion to C_{60} (Scheme 2) [11].

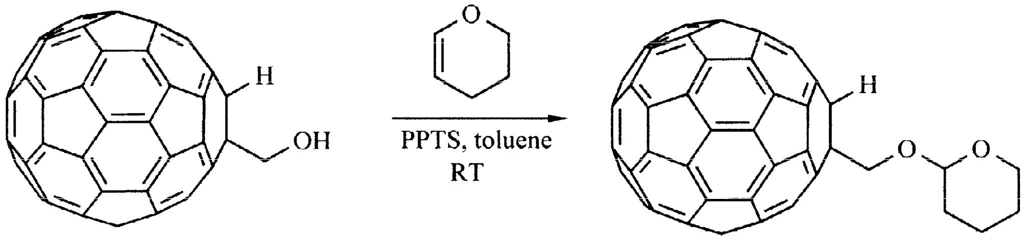


12 **6**

Scheme 2: Conversion of **12** to $C_{60}H_2$ and C_{60} on alumina N.

We assume a nucleophilic attack of hydroxy groups of the column material to the carbonyl group of **12** followed by a heterolytic cleavage under formation of propionic acid and $C_{60}H$ anion which finally is protonated leading to $C_{60}H_2$. Previous efforts to prepare $C_{60}H_2$ used reductive pathways [12,13] and to our knowledge only in one case led to a complete characterization of $C_{60}H_2$ [12c]. Unlike previous reports [13] $C_{60}H_2$ is not sensitive against oxygen but unstable under basic conditions.

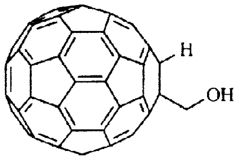
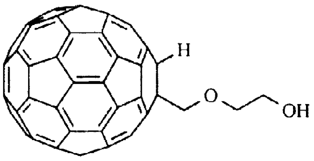
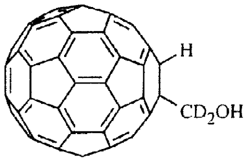
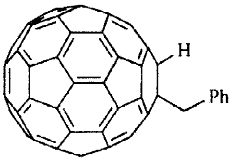
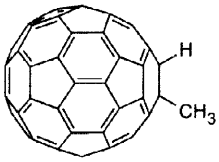
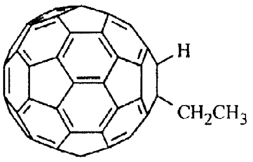
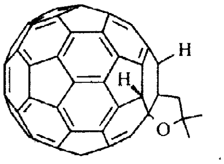
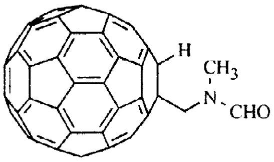
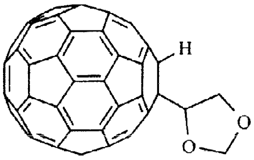
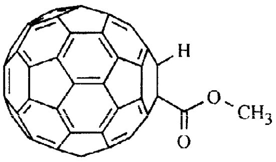
While 1,2-dihydro[60]fullerenes tend to decompose under basic conditions, the acidic catalysis was successful. 1-Hydroxymethyldihydro[60]fullerene **1** is converted to the 3,4,5,6-tetrahydro-2H-pyran (Thp)-ether **13** in a very rapid reaction when exposed to 3,4-dihydro-2*H*-pyran (DHP) and PPTS (pyridinium *p*-toluenesulfonate) (Scheme 3).



1 **13**

Scheme 3. Conversion of **1** to its THP ether (PPTS: pyridinium *p*-toluenesulfonate).

Table1. Isolated products **1-11** from PET reactions of C_{60} with various H donor reactants.

H donor: [60]fullerene product	H donor: [60]fullerene product
HO-CH_2CH_2-OH:  **1**	CH_3-O-CH_2CH_2-OH:  **7**
CD_3OD:  **2**	$PhCH_2CHO$:  **8**
t-BuOH:  **3**	CH_3CH_2COOH:  **9**
and  **4**	$(CH_3)_2NCHO$ (DMF):  **10**
1,3-Dioxolane:  **5**	$HCOOCH_3$:  **11**
and $C_{60}H_2$ **6**	

Discussion: Formation of $C_{60}^{\bullet+}$ and further reactions

Supplementary to preparative investigations we intended to elucidate the reaction mechanism. Both time-resolved laser flash photolysis studies and ESR spectroscopic investigations clearly demonstrate the formation of $C_{60}^{\bullet+}$ using PET conditions [14,15,16]. Upon addition of H-donors such as methanol the signal of $C_{60}^{\bullet+}$ is quenched as monitored both by laser flash photolysis and ESR spectroscopy [14]. The details are described elsewhere amd will be published separately [16].

Based on these studies we assume the oxidation of C_{60} followed by abstraction of a hydrogen from the H-donor as shown in Scheme 4. An alternative nucleophilic addition of the substrates to $C_{60}^{\bullet+}$ can be excluded because of the structure of the products since alkoxyfullerenes H-C_{60}-OCRR'H were not detected at all [7]. After reduction of H-C_{60}^{+} e.g. by electron transfer from the reduced sensitizer molecule H-$C_{60}^{\bullet}$ might recombine with $R^{\bullet}$ to the final product.

$$C_{60} \xrightarrow{\text{PET}} C_{60}^{\bullet+}$$

$$C_{60}^{\bullet+} + \text{RH} \longrightarrow \text{H}-C_{60}^{+} + {\bullet}\text{R}$$

$$\text{H}-C_{60}^{+} + {\bullet}\text{R} + e^{-} \longrightarrow \text{H}-C_{60}-\text{R}$$

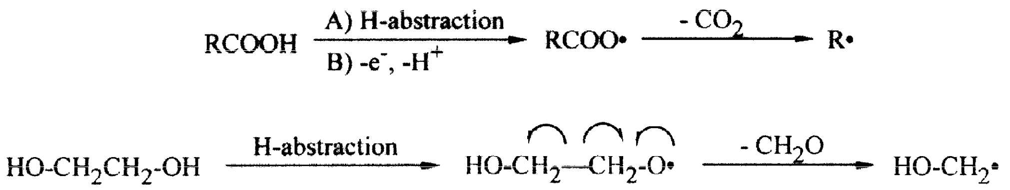
Scheme 4. Proposed mechanism of the addition of H-donors to C_{60} (PET: sensitizer, 419 nm).

Upon adding deuterated methanol-d_4 we observed a triplet at δ = 57.25, i.e. a dihydro[60]fullerene containing a deuterium atom connected directly to the fullerene core confirming the proposed mechanism. The functional group D is rapidly exchanged when coming in contact to column material like silica gel or AlOX during work-up procedures.

On closer examination of the products we had to state some surprising results due to the formation of unexpected radicals $R^{\bullet}$. The reaction of $C_{60}^{\bullet+}$ with glycol, propionic acid and *tert*-butanol could only be explained by loss of the hydrogen from an O-H bond, either from the neutral or from the oxidized substrate.

For example, on the addition of propionic acid we did not obtain the product of an H-abstraction at the α-C-position resulting in the formation of an fullerenic acid. Instead we isolated 1-ethyl-1,2-dihydro[60]fullerene **9** which requires an intermediate ethyl radical being formed *via* decarboxylation of propionic acid. *Libman* investigated the behaviour of aromatic acids in the PET process. When several aromatic acids were submitted to PET conditions (sensitizer: 1-cyanonaphthalene) decarboxylation products were formed. Fluorescence quenching experiments revealed quenching of the fluorescence of the sensitizer after addition of these acids which in conclusion are oxidized followed by decarboxylation (Scheme 5B, R = Ar) [17].

In order to exclude the oxidation of the H-donor substrates under our PET conditions (TPP^{+}, 419 nm) we performed additional fluorescence quenching experiments. As the fluorescene of TPP^{+} is not influenced in the presence of methanol, glycol, *tert*-butanol and propionic acid the excitited sensitizer $^{1}TPP^{+*}$ indeed is not reduced by the H-donor but by C_{60} as shown in Scheme 4. Thus the formation of the ethyl radical can only be explained by H-abstraction from the carboxyl function initiated by a C_{60}-intermediate followed by decarboxylation (Scheme 5A, R = Et).



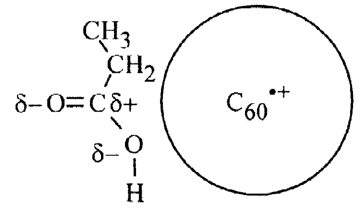
Scheme 5. Possible reaction paths to the formation of radicals from glycol and propionic acid.

As H-abstraction from propionic acid usually takes place at the α-position, the cationic character of $C_{60}^{\bullet +}$ obviously changes reaction pathways and affords H-abstraction at unusual positions. The reaction of glycol follows a similar pathway: Loss of a H-atom from the hydroxyl function followed by extrusion of formaldehyde under formation of hydroxymethyl radical $HO\text{-}CH_2\bullet$ (Scheme 5). Likewise the formation of $\bullet CH_3$ resulting from the loss of an hydrogen from the hydroxyl function of *tert*-butanol takes place (Scheme 7).

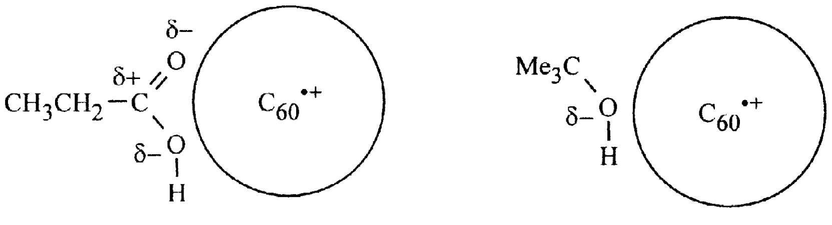
Obviously the cationic character of $C_{60}^{\bullet +}$ changes reaction pathways and affords H-abstraction at unusual positions. In Scheme 6 a possible explanation is visualized.

The bond energy of O-H is higher than that of the C-H bond (440 kJ/mol *vs.* 401 kJ/mol) [18]. Although the homolytic break of the C-H bond should therefore be favoured, the α-C-radical of propionic acid is not formed. Instead the positive charge of $C_{60}^{\bullet +}$ leads to lowering of the transition state leading to H-abstraction from the hydroxyl position of both *tert*-butanol and propionic acid (Scheme 6).

Similar results were obtained by *Gilbert et al.*. Following their investigations chloro-radicals prefer attack of the O-H-position instead of the C-H-position of both *tert*-butanol and propionic acid [19]. Likewise *Langer et al.* stated the formation of products formed both by homolytic breaking of both C-H- and O-H-bonds of *tert*-butanol in atmospheric processes [20].



unfavoured transition state

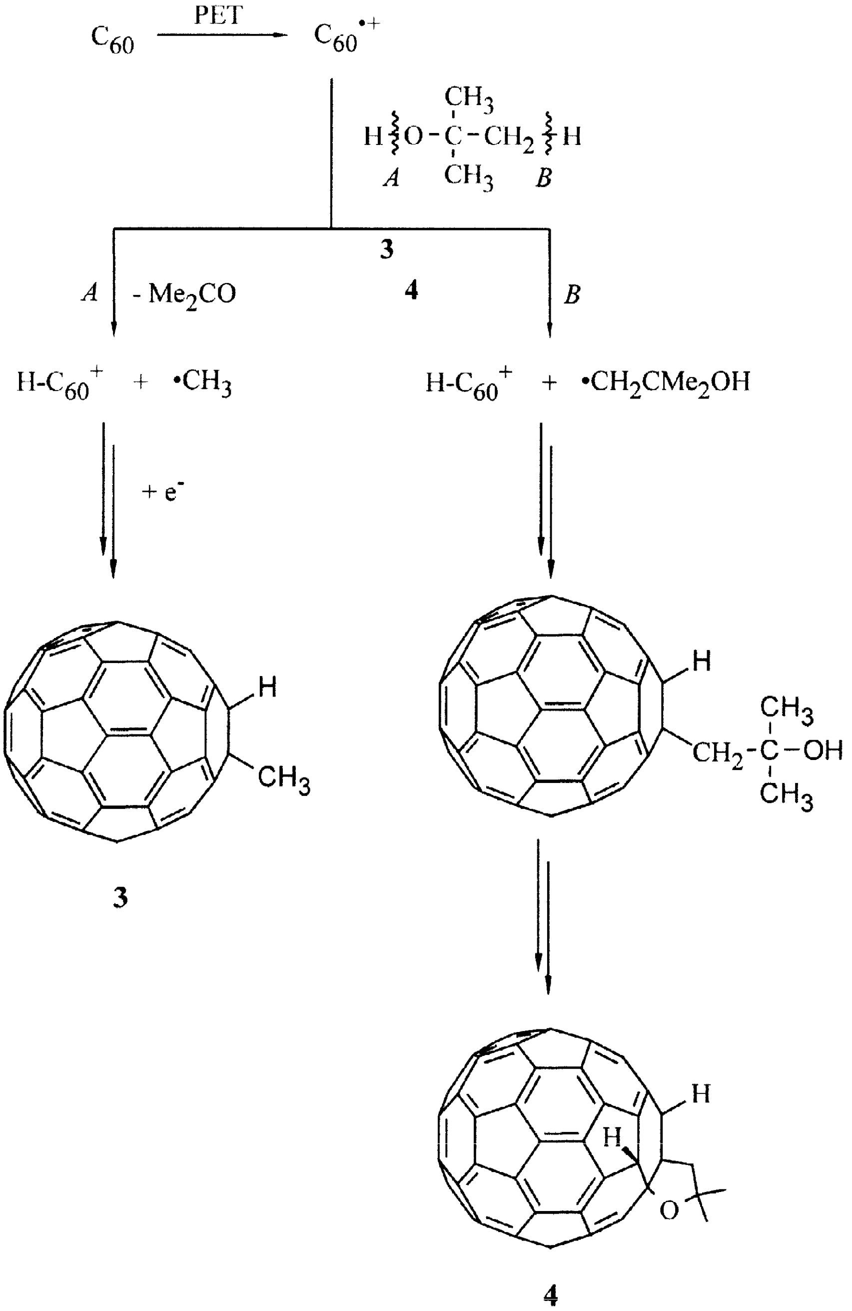


favoured transition states

Scheme 6. Possible transition states during the H-abstraction by $C_{60}^{\bullet +}$.

Following this argumentation the products of the reaction of *tert*-butanol and C_{60} under PET-conditions can easily be explained (Scheme 7). Homolytic bond breaking at the O-H-position leads to formation of the dihydro[60]fullerene **3**, abstraction at the C-H-position leads to isolation of a tetrahydro[60]fullerene **4**.

From this point of view our first assumption has to be modified. Upon reaction of alcohols and C_{60} under PET-conditions hydroxylated dihydro[60]fullerenes are isolated. We first considered the α-C-centered hydroxyalkyl radicals being formed by direct abstraction of a hydrogen from the C-H-bond. Instead, we clearly showed that α-C-centered hydroxyalkyl radicals can be formed in a bimolecular process from O-centered radicals as second step in a pseudo-[1,2]-shift manner [20]. Analogously the product of the reaction with methoxyethanol can be explained. The primarily generated O-centered radical is transformed into the C-centered radical *via* a [1,5]-H-shift in a six membered transition state [21]. Whether simple alcohols react with $C_{60}^{\bullet+}$ by direct H-abstraction from the α-position or via O-centered radicals in a two-step mechanism cannot finally be decided. Both reaction paths may operate.



Scheme 7. Reaction of *tert*-butanol and C_{60} under PET conditions.

The investigations reveal the strong electrophilic character of $C_{60}^{\bullet+}$. It does not show the typical properties of neither a cation nor a radical cation. Its radical characteristic does not ressemble that of a C-centered radical but those of an electrophilic radical preferring bond-breaking of O-H bonds instead of C-H bonds.

CONCLUSION

PET-assisted addition of H-donors to [60]fullerene has been proved to be a versatile route for the functionalization of [60]fullerene. The formation of the radical cation of $C_{60}^{\bullet+}$ as central intermediate has been proven by ns laser flash photolysis [14] and ESR experiments [16]. Decay experiments of $C_{60}^{\bullet+}$ by the addition of alcohols support the proposed mechanism of H-abstraction as first step. The involved radicals products reveal $C_{60}^{\bullet+}$ reacting as an electrophilic radical.

EXPERIMENTAL

General remarks and materials

C_{60} was used in *gold grade* quality (Hoechst, ≥ 99.4 %). TPP^+ (2,4,6-triphenylpyrylium tetrafluoroborate) was recristallized from acetone before use. 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. *N,N*-dimethylformamide, 1,3-dioxolane, phenylacetaldehyde, methyl formate, methoxyethanol, propionic acid, *tert*-butanol 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 liquid phase (UV/Vis detection at 300 nm Kontron HPLC detector 432), flow: 1.25 ml min^{-1} (Merck L-6000 pump). For preparative gel permeation chromatography HPLC a PLgel column (600 x 25 mm, PLgel, 10 μm, 100 Å), for preparative HPLC a Buckyclutcher column (Regis, precolumn 50x10.0mm, column 250x21.1mm, Buckyclutcher 1, 10μm, 100Å), an Abimed-Gilson Spectrochrom detector (UV/Vis detection at 300 nm) and a Kontron HPLC pump 420 (flow: 10 ml min^{-1}) were used. Column chromatography was performed on silica gel (Macherey-Nagel, 63-200 μm and 40-60μm) or neutral alumina (Macherey-Nagel). After isolation the products were purified by dissolving in CS_2, precipitating with pentane, centrifugation and decanting to remove the pentane-soluble components. It was finally dried under vacuum. Matrix assisted laser desorption time-of-flight mass spectra (MALDITOF-MS) were recorded with a time-of-flight mass spectrometer Lazarus I-III (Organisch-Chemisches Institut, Universität Münster, nitrogen laser, λ = 337 nm, matrix: 4-(4'-*tert*-butylphenyl)-1,1-dicyano-3-methyl-buta-1,3-diene (DCTB), 2,5-dihyrdroxybenzoic acid (DHB), linear mode). Relative intensities are given in percentages. NMR spectra were recorded on Bruker AM 300 and DRX 500 spectrometers - Chemical shift data are reported relative to TMS as external standard: Bruker AM 300: CS_2/acetone-d_6: $\delta = 2.00$ (acetone) for proton and 192.34 (CS_2) for carbon; CS_2/benzene-d_6: $\delta = 7.20$ for proton (benzene) and 192.23 (CS_2) for carbon; Bruker DRX 500: *o*-dichlorobenzene: $\delta = 6.93$ for proton and 127.19 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.

Reaction of *tert*-butanol and C_{60} using PET conditions

324 mg (0.450 mmol) of C_{60} and 178 mg (0.450 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) were dissolved in a mixture of 250 ml *o*-dichlorobenzene, 70 ml of acetonitrile and 70 ml of *tert*-butanol. The solution was deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 4 h. The solvents were evaporated *in vacuo*. Purification of the residue was carried out by filtration on silica gel (toluene) followed by preparative gel permeation chromatography (Plgel, toluene), HPLC on a buckyclutcher column (toluene) and final gel permeation chromatography (Plgel, toluene). In this way 121 mg (37%) of unchanged C_{60}, 62 mg (19%, 30% based on consumed C_{60}) **3** and 8 mg (2%, 4% based on consumed C_{60}) **4** are obtained als black brown powder.

1-Methyl-1,2-dihydro[60]fullerene (3): **^{1}H NMR** (500 MHz, $CS_2/CDCl_3$): δ = 6.39 (s, 1H, 2-H), 3.26 (s, 3H, 1'-H). **^{13}C NMR** (126 MHz, $CS_2/CDCl_3$): δ = 156.60, 153.28, 147.19, 147.08, 146.70, 146.17, 146.11, 145.99, 145.95, 145.62, 145.58, 145.30, 145.20, 145.15, 145.14, 144.45, 144.39, 143.04, 142.83. 142.34, 141.94, 141.81, 141.79, 141.74, 141.47, 141.45, 140.24, 139.98, 136.24, 135.11 (30 C_{60} sp^2 signals), 61.23 (d, ^1J = 137.37 Hz, C-2), 59.93 (s, C-1), 34.97 (q, ^1J = 130.29 Hz, C-1'). **FT-IR** (KBr): ν = 2908w, 1459m, 1442m, 1524m, 1257w, 1211w, 1185w, 807w, 760w, 580w, 561w, 551w, 525s, 512m cm^{-1}. **UV/Vis** (CH_2Cl_2): $\lambda_{max} > 220$ (ε): 255 (67776), 325 (22396), 405 (4297), 431 nm (3561). **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 737 (100) [$M^{\cdot}$, calc. 736.7].

2,2-Dimethyl-1,2,3,4-tetrahydro[60]fullereno[2,3-b]tetrahydrofuran (4): **^{1}H NMR** (500 MHz, CS_2/C_6D_6): δ = 6.04 (s, 1H, 4-H), 6.18 (s, 1H, 1-H), 3.24 (d, ^2J= 12.6 Hz, 1H, $C\underline{H}_2$), (d, ^2J= 12.6 Hz, 1H, $C\underline{H}_2$), 2.11 (s, 3H, $C\underline{H}_3$), 1.70 (s, 3H, $C\underline{H}_3$). **^{13}C NMR** (126 MHz, CS_2/C_6D_6): δ = 151.26, 149.81, 149.13, 149.01, 148.98, 148.50, 148.24, 148.03, 147.56, 146.92, 146.84, 146.81, 146.74, 146.72, 146.37, 146.35, 146.26, 145.54, 145.50, 145.26, 145.00, 144.87, 144.76, 144.62, 144.60, 144.51, 144.49, 144.23, 144.19, 144.15, 144.10, 144.05, 143.92, 143.82, 143.54, 143.44, 143.29, 143.11, 143.01, 142.86, 142.54, 142.40, 142.22, 142.17, 141.87, 141.59, 141.15, 140.72, 138.59, 137.90, 136.02, 135.94, 134.29 (53 C_{60} sp^2–Signale), 95.41 (C-2), 85.13 ($\underline{C}(CH_3)_2$), 64.47 (C-3), 61.54 ($\underline{C}H_2$), 60.20 (C-4), 59.57 (C-1), 29.97 ($\underline{C}H_3$). **FT-IR** (KBr): $\tilde{\nu}$ = 2918m, 1458m, 1365w, 1017m, 996m, 806w, 564w, 528m, 521s cm^{-1}. **UV/Vis** (CH_2Cl_2): $\lambda_{max} > 220$ (ε): 255 (88488), 430 nm (5431) cm $^{-1}$. **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 795 (100) [$M^{\cdot}$, calc. 794.8].

Reaction of 1,3-dioxolane and C_{60} using PET conditions

144 mg (0.200 mmol) of C_{60}, 46 mg (0.20 mmol) of 9,10-dicyanoanthracene (DCA) and 4.70 g (30.5 mmol) of biphenyl were dissolved in a mixture of 170 ml of *o*-dichlorobenzene, 84 ml of acetonitrile and 35 ml of 1,3-dioxolane. The solution was deoxygenated by purging with argon and irradiated in reaction vessels at 419 nm for 3 h. The solvents were evaporated *in vacuo*. Chromatography of the residue on alumina N first gave a mixture of C_{60} and $C_{60}H_2$ (toluene) followed by eluation of 9 mg (5%, 8% based on consumed C_{60}) **5** (toluene/acetonitrile = 10:1). Further purification of C_{60} and $C_{60}H_2$ by separation on a preparative bucky-clutcher column (toluene/cyclohexane = 3:1) gave 19 mg (13%, 20% based on consumed C_{60}) $C_{60}H_2$ and 49 mg (34%) of unconverted C_{60}.

1,3-Dioxolan-4-yl-1,2-dihydro[60]fullerene (5): **^{1}H NMR** (500 MHz, o-$C_6D_4Cl_2/(CD_3)_2CO$): δ = 6.50 (s, 1H, 2-H), 5.62 (s, 1H, 2'-H), 5.61 (dd, ^3J= 7.1 Hz, 4.9 Hz, 1H, 4'-H), 5.23 (s, 1H, 2'-H), 5.12 (dd, ^3J= 4.9 Hz, 9.1 Hz, 1H, 5'-H), 4.61 (dd, ^3J= 7.1 Hz, 9.1 Hz, 1H, 5'-H). **^{13}C NMR** (126 MHz, o-$C_6D_4Cl_2$): δ = 153.39, 153.32, 152.39, 151.79, 147.06, 146.89, 146.81, 146.69, 146.44, 146.06, 145.99, 145.84, 145.79, 145.44, 145.41, 145.27, 145.18, 145.05, 144.97, 144.35, 144.29, 144.10, 144.03, 143.84, 142.80, 142.74, 142.56 (C_{60}), 142.16, 141.99, 141.66, 141.60, 141.37, 141.32, 141.26, 141.17, 141.13, 139.90, 139.81, 139.73, 139.51, 136.82, 136.29, 136.06, 135.69 (43 C_{60} sp^2 signals), 96.83 (t, ^2J = 166.4, C-2'), 83.20 (d, ^2J = 162.3, C-4'), 67.96 (s, C-1), 67.51 (t, ^2J = 149.3, C-5'), 55.68 (d, ^2J = 137.8, C-2). **FT-IR** (KBr): $\tilde{\nu}$ = 2920s, 2849m, 1718w, 1456w, 1261m, 1082m, 1022m, 802m, 526m cm^{-1}. **UV/Vis** (CH_2Cl_2): λ_{max} > 220 (ε) = 258 (66985), 328 (21572)sh, 430 nm (3690)sh. **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DHB): *m/z* ± 0.1%: 796 (100) [M$^+$, calc. 794.5], 721 (100) [C_{60}].

1,2-Dihydro[60]fullerene $C_{60}H_2$ (6): **^{1}H NMR** (500 MHz, *o*-$C_6D_4Cl_2$): δ = 6.64 (s, 1H, 1-H). **^{13}C NMR** (126 MHz, *o*-$C_6D_4Cl_2$): δ = 152.28, 147.58, 147.17, 146.17, 146.11, 145.89, 145.30, 145.23, 144.52, 143.10, 142.79 (C_{60}), 142.33, 141.76, 141.74, 141.40, 140.16, 136.14 (16 C_{60} sp^2 signals), 53.10 (C-1). **FT-IR** (KBr): $\tilde{\nu}$ = 2917m, 2845w, 2119w, 1459m, 1425m, 1179m, 859w, 576m, 565w, 550w, 525s cm^{-1}. **UV/Vis** (CH_2Cl_2): λ_{max} > 220 (ε) = 258 (44866), 327 (13249), 405 (1656) sh, 435 nm (1204). **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 724 (87) [$^{13}C^{12}C_{59}H_2$], 723 (100) [M$^-$, calc. 722.7], 722 (93) [$^{13}C^{12}C_{59}$], 721 (68) [$^{12}C_{60}$].

Reaction of 1-(propan-1'-one)-1,2-dihydro[60]fullerene (12) by filtration on alumina

1,2-Dihydro[60]fullerene $C_{60}H_2$. 216 mg (0.30 mmol) of C_{60}, 64 mg (0.28 mmol) of 9,10-dicyanoanthracene (DCA) and 9.6 g (60.0 mmol) of biphenyl were dissolved in a mixture of 140 ml of *o*-dichlorobenzene, 50 ml of acetonitrile and 50 ml of propionaldehyde. The solution was deoxygenated by purging with argon and irradiated in reaction vessels at 419 nm for 7 h. The solvents were evaporated *in vacuo*. Rapid filtration of the residue on alumina N with toluene as eluent followed by preparative gel chromatography on PL gel with toluene gave 58 mg (27%) of unconverted C_{60} and 23 mg (10%, 14% based on consumed C_{60}) of $C_{60}H_2$.

Reaction of methoxyethanol and C_{60} using PET conditions

230 mg (0.319 mmol) of C_{60} and 56 mg (0.14 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP$^+$) were dissolved in 250 ml of 1,2-dichlorobenzene and 125 ml of methoxyethanol. The solution was deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 4 h. The solvents were evapurated *in vacuo*. Chromatography on silica gel first gave 99 mg (43%) of unchanged C_{60} (toluene) followed by a mixture of **7** and polar products (toluene/ethanol = 10:1). Further purification by preparative gel chromatography (Plgel, toluene) and preparative HPLC on a buckyclutcher column (toluene/Essigester = 10:1) gave 31 mg (12%, 21% based on consumed C_{60}) of **7** as black brown powder.

1-Hydroxyethoxymethyl-1,2-dihydro[60]fullerene (7): **^{1}H NMR** (500 MHz, *o*-$C_6D_4Cl_2$): δ = 6.54 (s, 1H, 2-H), 5.09, (s, 2H, 1'-H), 4.13-4.11 (m, 2H, 3'-H), 4.03-4.04 (m, 2H, 4'-H), 2.34 (s, 1H, O$\underline{H}$). **^{13}C NMR** (126 MHz, *o*-$C_6D_4Cl_2$): δ = 153.44, 153.31, 147.29, 147.14, 147.08, 146.71, 146.28, 146.22, 146.07, 146.02, 145.69, 145.46, 145.29, 145.23, 145.20, 144.58, 144.38, 143.03, 142.41, 142.39, 142.19, 141.91, 141.84, 141.67, 141.49, 141.47, 140.09, 136.79, 136.19 (29 C_{60} sp^2 signals), 80.99 (t, ^1J = 145.7 Hz, C-1'), 73.95 (t, ^1J = 141.5 Hz, C-3'), 66.31 (s, C-1), 62.16 (t, ^1J = 142.4 Hz, C-4'), 57.47 (d, ^1J = 138.7 Hz, C-2). **FT-IR** (KBr): $\tilde{\nu}$ = 3423br (OH), 2448w, 1459w, 1425w, 1345w, 1181w, 1119m, 1056m, 807w, 762w, 526s cm^{-1}. **UV/Vis** (CH_2Cl_2): λ_{max} > 220 (ε) = 255 (57847), 325 (17666), 405 (2511)sh, 432 nm (2078). **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 796 (100) [M$^+$, calc. 796.7].

Reaction of phenylacetaldehyde and C_{60} using PET conditions

288 mg (0.400 mmol) of [60]fullerene and 81 mg (0.20 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) were dissolved in a mixture of 280 ml *o*-dichlorobenzene, 90 ml of acetonitrile and 45 ml of phenylacetaldehyde. The solution was deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 3 h. The solvents were evaporated *in vacuo*. The residue was dissolved in toluene and filtrated on silica gel (cyclohexane/toluene 1:1). Preparative HPLC on a buckyclutcher column (cyclohexane/toluene 2:1) followed by preparative gel chromatography on PL gel (toluene) gave 50 mg (17%) of unconverted [60]-fullerene and 12 mg (3.7%, 4.5% based on consumed [60]fullerene) of **8** as brown black powder.

1-Benzyl-1,2-dihydro[60]fullerene (8): **^{1}H NMR** (500 MHz, $CS_2/(CD_3)_2CO$): δ = 7.78-7.80 (m, 2H, 2''-H, 6''-H), 7.44-7.48 (m, 2H, 3''-H, 5''-H), 7.36-7.39 (m, 1H, 4''-H), 6.74 (s, 1H, 2-H), 4.80 (s, 2H, 1'-H). **^{13}C NMR** (126 MHz, $CS_2/(CD_3)_2CO$): δ = 155.23, 153.97, 147.15, 146.99, 146.80, 146.22, 146.12, 146.08, 145.94, 145.87, 145.55, 145.20, 145.13, 145.09, 145.07, 144.45, 144.31, 142.95, 142.27, 141.95, 141.77, 141.72, 141.66, 141.37, 141.30, 139.92, 139.63, 136.11, 135.88 (29 C_{60} sp^2 signals), 135.56 (C-1''), 131.24 (C-2'', C-6''), 128.53 (C-3'', C-5''), 127.54 (C-4''), 65.76 (C-1), 59.02 (C-2), 52.68 (C-1'). **FT-IR** (KBr): $\tilde{\nu}$ = 1425m, 1179w, 806w, 742w, 696m, 573w, 525s cm^{-1}. **UV/Vis** (CH_2Cl_2): $\lambda_{max} > 220$ (ε) = 255 (123952), 325 (39285)sh, 405 (5927), 432 nm (4911). **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 813 (100) [M^+, calc. 812.8].

Reaction of propionic acid and C_{60} using PET conditions

216 mg (0.300) of C_{60} and 125 mg (0.315 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+)were dissolved in a mixture of 250 ml of *o*-dichlorobenzene, 70 ml of acetonitrile und 70 ml of propionic acid. The solution is deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 1.5 h. The solvent was evaporated *in vacuo*, the residue dissolved in toluene and filtrated on silica gel. Preparative gelpermeation chromatography (Plgel, toluene) gave 89 mg (41%) of unconverted C_{60} and 37 mg (16%, 28% based on consumed C_{60}) of 9 as brown black powder.

1-Ethyl-1,2-dihydro[60]fullerene (9): **^{1}H NMR** (500 MHz, *o*-$C_6D_4Cl_2$): δ = 6.12 (s, 1H, 2-H), 3.25 (q, ^3J = 7.4 Hz, 2H, 1'-H), 1.39 (t, ^3J = 7.4 Hz, 3H, 2'-H). **^{13}C NMR** (126 MHz, *o*-$C_6D_4Cl_2$): δ = 155.85, 153.75, 147.27, 147.13, 147.00, 146.34, 146.23, 146.17, 146.04, 145.99, 145.70, 145.23, 145.20, 144.54, 144.44, 143.03, 142.36, 142.10, 141.87, 141.84, 141.44, 140.03, 139.96, 136.37, 135.89 (25 C_{60} sp^2 signals), 65.55 (C-1), 59.16 (C-2), 40.10 (C-1'), 11.14 (C-2'). **FT-IR** (KBr): $\tilde{\nu}$ = 2912w, 1500m, 1448w, 1424w, 1376w, 1179w, 802w, 571w, 525s, 512m cm^{-1}. **UV/Vis** (CH_2Cl_2): $\lambda_{max} > 220$ (ε) = 255 (135126), 325 (42339), 405 (6006), 432 nm (5005). **MS:** MALDI TOF (16.2 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 751 (100) [M^-, calc. 750.7].

Reaction of dimethylformamide and C_{60} using PET conditions

231 mg (0.320 mmol) of [60]fullerene and 59 mg (0.150 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP^+) were dissolved in a mixture of 280 ml *o*-dichlorobenzene, 90 ml of acetonitrile and 90 ml of dimethyl formamide. The solution was deoxygenated by purging with argon and irradiated in a reaction vessel at 419 nm for 2.5 h. The solvents were evaporated *in vacuo* and the residue dissolved in toluene. Column chromatography on silica gel (0.06 - 0.20 µm) with toluene followed by chloroforme gave 79 mg (34%) of unconverted [60]fullerene and 97 mg (38%, 58% based on consumed [60]fullerene) of **10** as brown black powder.

N-Formyl-N-methylaminomethyl-1,2-dihydro[60]fullerene (10): **^{1}H NMR** (500 MHz, *o*-$C_6D_4Cl_2$): δ = 8.47 (B, s, 1H, C$\underline{H}$O), 8.22 (A, s, 1H, C$\underline{H}$O), 6.45 (A, s, 1H, 2-H), 5.84 (B, s, 1H, 2-H), 4.90 (A, s, 2H, 1'-H), 4.72 (B, s, 2H, 1'-H), 3.10 (B, s, 3H, N-C$\underline{\text{H}}_3$), 3.06 (A, s, 3H, N-C$\underline{\text{H}}_3$). **^{13}C NMR** (126 MHz, *o*-$C_6D_4Cl_2$): δ = 164.24 (A; C=O), 163.45 (B; C=O), 153.47, 153.44, 152.40, 152.22, 147.27, 147.11, 147.08, 146.80, 146.54, 146.23, 146.19, 146.15, 146.06, 146.03, 145.99, 145.60, 145.45, 145.37, 145.24, 145.22, 145.16, 144.55, 144.48, 144.25, 144.18, 144.08, 143.02, 142.97, 142.78, 142.42, 142.37, 142.35, 142.09, 141.94, 141.89, 141.74, 141.72, 141.53, 141.49, 141.45, 140.12, 140.02, 139.94, 136.23, 136.12, 135.83 (46 C_{60} sp^2 signals), 66.44 (B, s, C-1), 66.14 (A, s, C-1), 63.24 (B, t, ^1J = 143.4 Hz, C-1'), 58.18 (A, t, ^1J = 144 Hz, C-1'), 57.84 (B, d, ^1J = 136.0 Hz, C-2), 57.68 (A, d, ^1J = 138.0 Hz, C-2), 37.45 (A, q, ^1J = 139 Hz, N-$\underline{\text{C}}$H$_3$), 33.91 (B, q, ^1J = 139 Hz, N-$\underline{\text{C}}$H$_3$). **FT-IR** (KBr): $\tilde{\nu}$ = 1676s (C=O), 1426w, 1388w, 1183w, 1070w, 746w, 691w, 574w, 526s cm^{-1}. **UV/Vis** (CH_2Cl_2): λ_{max} > 220 (ε) = 255 (76729), 325 (23813)sh, 432 nm (2646). **MS:** MALDI-TOF (16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 793 (100) [M$^-$, calc. 793.7], 720 (26) [C_{60}].

Reaction of methyl formate and C_{60} using PET conditions

225 mg (0.312 mmol) of [60]fullerene and 110 mg (0.278 mmol) of 2,4,6-triphenylpyrylium tetrafluoroborate (TPP$^+$) were dissolved in a mixture of 280 ml *o*-dichlorobenzene, 90 ml of acetonitrile and 90 ml of methyl formate. The solution was deoxygenated by purging with argon an irradiated in a reaction vessel at 419 nm for 3 h. The solvents were evaporated *in vacuo*. Repeated purification of the residue by flash chromatography on SiO_2 with cyclohexane/toluene 1:1 gave 72 mg (32%) of unconverted [60]fullerene and 21 mg (8%, 12% based on consumed [60]fullerene) of **11** as brown black powder.

1-(Methoxycarbonyl)-1,2-dihydro[60]fullerene (11): **^{1}H NMR** (500 MHz, *o*-$C_6D_4Cl_2$): δ = 7.46 (s, 1H, 2-H), 4.16 (s, 3H, C$\underline{\text{H}}_3$). **^{13}C NMR** (126 MHz, *o*-$C_6D_4Cl_2$): δ = 171.85 (C=O), 152.07, 149.95, 147.48, 147.20, 146.93, 146.82, 146.29, 146.09, 145.97, 145.95, 145.63, 145.45, 145.29, 145.12, 144.46, 144.09, 143.00, 142.77, 142.44, 142.39, 142.11, 141.94, 141.89, 141.50, 141.41, 141.27, 140.37, 139.88, 135.79, 135.28 (30 C_{60} sp^2 signals), 69.60 (s, C-1), 57.04 (d, ^1J = 139.40 Hz, C-2), 54.72 (q, ^1J = 148.35 Hz, *C*H$_3$). **FT-IR** (KBr): $\tilde{\nu}$ = 2940w, 1737s, 1426m, 1223m, 1209s, 1180m, 1011w, 806w, 764w, 698w, 526s cm^{-1}. **UV/Vis** (CH_2Cl_2): λ_{max} > 220 (ε) = 255 (66829), 326 (20111), 405 (2764), 433 nm (2170). **MS** (MALDI-TOF, 16 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 782 (100) [M$^+$, calc. 780.7].

Reaction of 1-hydroxymethyl-1,2-dihydro[60]fullerene (1) with DHP

A solution of 336 mg (0.466 mmol) of C_{60} and 96 mg (0.24 mmol) of TPP$^+$ (2,4,6-triphenylpyrylium tetrafluoroborate) in 250 ml of *o*-dichlorobenzene and 125 ml methanol is purged with argon for 3 h in a reaction vessel and irradiated with light of 419 nm wavelength for 80 min. The solvent is evaporated *in vacuo* dissolved in toluene and filtrated on alumina N. At first C_{60} is eluated (toluene), the second fraction (toluene/acetonitrile/ethanol 10:1:1) consists of 1-hydroxymethyl-1,2-dihydro[60]fullerene (**1**). This solution is concentrated to 150 ml and 110.5 mg (0.440 mmol) of pyridinium-*p*-toluenesulfonate (PPTS) and 35 ml of dihydropyran are added. After 90 min of stirring at room temperature the reaction is completed. The solution is filtrated over silica gel (toluene). After preparative GPC (PLgel, toluene) 190 mg (56%) of C_{60} and 65 mg (17%, 38% ref. to consumed C_{60}) of **13** are isolated as black brown powder.

1,2-Dihydro-1-([3',4',5',6'-tetrahydro-2'H-pyran-2'-yl]oxymethyl)[60]fullerene (13): **^{1}H NMR** (500 MHz, CS_2/C_6D_6): δ = 6.62 (s, 1H, 2-H), 5.40 (d, ^2J = 9.00 Hz, 1H, 1'-H), 5.13 (t, ^3J = 3.49 Hz, 1H, 1''-H), 4.99 (d, ^2J = 9.01 Hz, 1H, 1'-H), 4.12-4.07 (m, 1H, 3''-H), 3.70-3.65 (m, 1H, 3''-H), 2.01-2.10 (m, 1H), 1.99-1.87 (m, 2H), 1.71-1.59 (m, 3H) (4''-H, 5''-H, 6''-H). **^{13}C NMR** (126 MHz, CS_2/ C_6D_6): δ = 153.48, 153.40, 153.34, 153.14, 147.20, 147.55, 146, 99, 146.98, 146.69, 146.61, 146.22, 146.18, 146.01, 145.97, 145.61, 145.60, 145.45, 145.43, 145.25, 145.23, 145,22, 145.15, 144.52, 144.37, 144.35, 143.03, 142.40, 142.38, 142.11, 142.10, 141.86, 141.82, 141.61, 141.59, 141.47, 141.46, 141.45, 141.42, 140.13, 140.12, 140.03, 136.67, 136.59, 136.27, 136.16 (45 C_{60} sp^2-signals), 98.96 (d, ^1J = 160.90 Hz, C-1''), 76.59 (t, ^1J = 144.27 Hz, C-1'), 65.70 (s, C-1), 62.17 (t, ^1J = 142.92 Hz, C-3''), 57.44 (d, ^1J = 133.83 Hz, C-2), 30.82 (t, ^1J = 125.29 Hz, C-6''), 25.93 (t, ^1J = 126.85 Hz, C-4''), 19.81 (t, ^1J = 125.69 Hz, C-5''). **FT-IR** (KBr): $\tilde{\nu}$ = 1425w, 1180w, 1121m, 1072w, 1062w, 1030s, 973m, 902m, 572w, 525s cm^{-1}. **UV/Vis** (CH_2Cl_2): $\lambda_{max} > 220$ (ε) = 255 (143269), 325 (46827), 405 (7108), 432 nm (5714). **MS:** MALDI-TOF (16.2 kV, 337 nm, matrix: DCTB): *m/z* ± 0.1%: 836 (100) [M^-, calc. 836.2].

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