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Cycloaddition of 1,8-Dehydronaphthalene to [60]Fullerene in Benzene Solution. A New Functionalization of C_{60} by in situ Generated 6b,10a-Dihydrofluoranthene [1-3]

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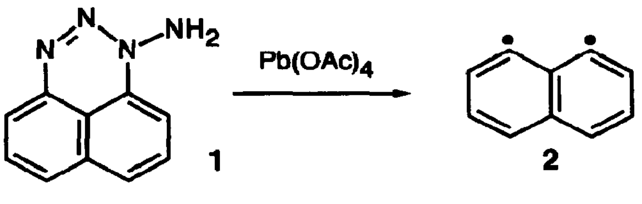
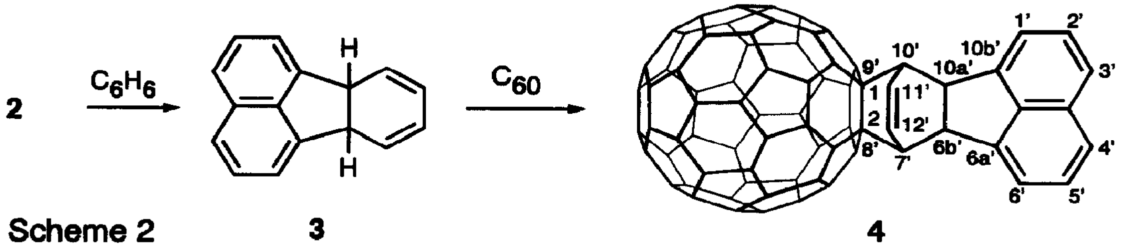
Abstract: The reaction of C_{60} with in situ generated 6b,10a-dihydrofluoranthene **3** affords the stable [4+2]cycloadduct 1,2-(7,10-etheno-6b,7,8,9,10,10a-hexahydrofluorantheno)-[60]fullerene **4**. A similar incorporation of the solvent is observed in the reaction of 1,8-dehydronaphthalene **2** with C_{60} in toluene.

Among the methods of exohedral derivatizations of [60]fullerene cycloadditions play an important role [7]. Because of the electrophilic character of C_{60} often 1,3-dipolar cycloadditions and Diels-Alder reactions have been applied to generate well-defined and easily separable monoadducts [8,9]. We now report the Diels-Alder reaction of 6b,10a-dihydrofluoranthene **3** with C_{60} [2,3]. **3** is formed in situ from 1,8-dehydronaphthalene **2** and benzene. Our initial interest was to generate **2** from the amino triazine **1** [10] followed by a cycloaddition to C_{60} to form the naphthalene adduct **5**.



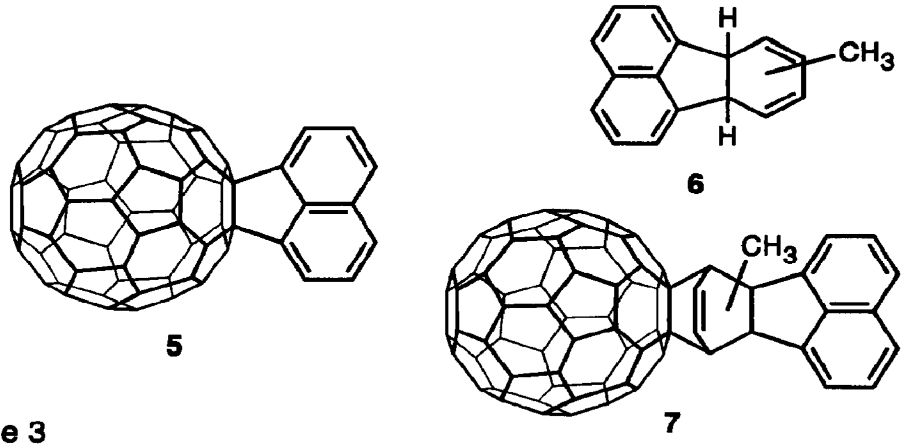
Scheme 1

When using toluene or benzene as solvent an effective reaction occurred at 40 °C leading to the disappearance of 1 and the formation of several new products. Mass spectral analysis by the field desorption (FD) technique indicates the formation of mono and higher adducts, however including the reaction of the solvent molecules with the intermediate 1,8-dehydronaphthalene **2** to **3**. In order to simplify the addition we performed the reaction in benzene up to ca. 40% conversion of C_{60}. Chromatographic analysis on a RP-18 column (HPLC) shows the formation of a main product (2nd fraction) beside several minor products (1st fraction) and unconverted C_{60} (3rd fraction). The main product was isolated in 27% yield by semipreparative HPLC and identified as 1,2-(7,10-etheno-6b,7,8,9,10,10a-hexahydrofluorantheno)-[60]fullerene 4 by standard spectroscopic methods.



Scheme 2

The FD+ mass spectrum indicates that 4 is an 1:1 adduct. The proton decoupled ^{13}C-NMR spectrum shows only 38 signals indicating C_S symmetry of the molecule. Three signals are observed in the aliphatic region of the ^{13}C-NMR spectrum, including the sp^3 hybridized carbons of C_{60} appearing at 71.06 ppm. A total of 35 signals out of the 37 expected signals for the fullerene and aromatic/alkenyl carbons are observed in the sp^2 region. The signals at 4.71, 5.37, 6.76 in the ^{1}H-NMR spectrum display on a spin decoupling experiment an AA'MM'XX' splitting for the six non aromatic protons, the six aromatic protons appear at 7.56 and 7.68 ppm. The spectrum was simulated with the measured coupling constants using the program PANIC [11] which confirms the assigned structure of 4. The weak long-wavelength absorption at 710 nm in the UV-Vis spectrum is diagnostic for the dihydrofullerene structure [12]. The IR bands at 527, 576, 1182 and 1428 cm^{-1} are attributed to the fullerene moiety [13].



Scheme 3

As reported by Kahr et al. [14] we have no indication for the formation of 1,2-dihydro(7',10'-etheno-6b',7',8',9',10',10a'-hexahydrofluorantheno)-[60]fullerene **5**. Obviously **2** reacts with the solvent [10] before it cycloadds to C_{60}. In toluene similar monoadducts **7** are formed in 29% yield [2]. Due to the nonselective formation of the toluene cycloadducts **6** we observe at least three regioisomers of **7** on the basis of NMR spectroscopy. The use of other solvents to avoid this reaction is currently under investigation. The results reported here do not represent a single case. We also observed incorporation of benzene and toluene in the reactions of nitrenes with C_{60} [15].

The present reaction confirms the dienophilic character of C_{60} and demonstrates the usefulness of [4+2] cycloadditions for C_{60} functionalization.

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1,2-(7,10-etheno-6b,7,8,9,10,10a-hexahydrofluorantheno)-[60]fullerene **4**. 100 mg (0.54 mmol) of 1-aminonaphtho[1,8-de]triazine **1** in 40 ml of benzene was added in drops to a stirred solution of 96 mg (0.13 mmol) of C_{60} (Hoechst goldgrade, $C_{60} > 99.4\%$) and 380 mg (0.86 mmol) of lead tetraacetate in benzene (170 ml). Nitrogen was immediately evolved and stirring was continued for 75 min. Lead salts were separated by column filtration (toluene, neutral alumina) and the solvent was distilled off under reduced pressure. The adduct **5** was finally separated by HPLC (column: 250 x 20 mm, Merck LiChrosorb RP-18 7 μm, eluent: toluene/acetonitrile 1.75:1, detection wavelength: 310 nm) in 27% (33 mg) yield (64% based on reacted C_{60}).

FD+-MS (m/e (%)): 924 (74; M^+), 720 (100; $C_{60}^+ = M^+ - C_{16}H_{12}$), 204 (44; $C_{16}H_{12}^+$). ^{1}H-NMR (360 MHz, CS_2/(D_6)acetone 10:1, υ/υ): 4.71 (s, 2 H), 5.37 (m, 2 H), 6.76 (m, 2 H), 7.56 (m, 4 H), 7.68 (m, 2 H). ^{13}C-NMR (90.5 MHz; CS_2/(D_6)acetone 10:1, υ/υ): 49.69, 49.91, 71.06, 119.89, 123.89, 128.95, 132.28, 133.91, 137.18, 137.91, 140.65, 140.81, 141.62, 142.24, 142.35, 142.53, 142.57, 142.73, 143.02, 143.16, 143.20, 143.67, 143.78, 145.28, 145.30, 146.04, 146.08, 146.14, 146.33, 146.73, 146.80, 146.82, 147.00, 147.15, 147.38, 148.12, 156.44, 157.06. FT-IR (KBr): 3053w, 2922s, 2850m, 1735, 1716, 1699, 1684m, 1653s, 1634s, 1617s, 1558w, 1540w, 1505w 1457m, 1428m, 1364w, 1324w, 1260w, 1182w, 1029s, br, 827m, 778ss, 744m, 691w, 668s, 599m, 576m, 563m, 527ss. UV/Vis (λ_{max} (ε) in toluene): 311 (47000), 415 (sh, 5100), 438 (sh, 3600), 710 (400-450).

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