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Photochemical [2 + 2] Cycloaddition of *N,N*-Diethylpropynylamine to C_{60}

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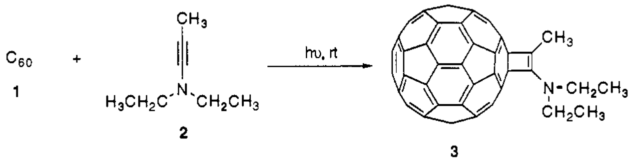
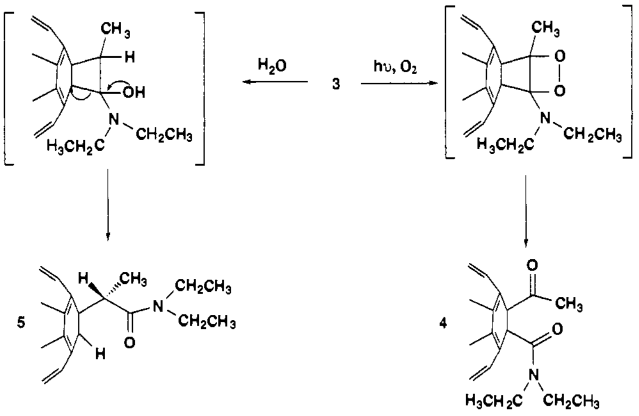
Since the discovery of fullerenes,[1] their facinating properties have attracted much attention.[2-6] Recent procedures for obtaining gram quantities of C_{60} and C_{70}[7-9] have made exploration of the chemical reactivity and functionalization of these compounds much easier. Among the derivatizations of C_{60} that have been reported, cycloadditions ([4 + 2][10-13] and [3 + 2][14]) are particularly valuable because easily separable, well-defined monoaddition adducts are obtained in most cases. We report an efficient photochemical [2 + 2] cycloaddition route to a C_{60} adduct and its subsequent reaction to give a very high yield of a difunctional dihydrofullerene in one pot.

Previous results have demonstrated that the triplet excited state of C_{60} has a reduction potential near 1.14 V vs SCE and that it is readily photoreduced by amines and other donors to C_{60} radical anion and donor radical cation.[15-18] We expected this reaction to lead to covalent adducts. Such adducts are formed with some amines in ground-state reactions.[19-22] Since dihydrofullerenes generally have their visible absorptions shifted to shorter wavelengths than the parent molecules,[23,24] excitation at the red end of the visible absorption of fullerenes should allow selective monofunctionalization. Also, multiple electron transfer should not be a problem since only one-electron reduction is possible in the excited state reactions.

Scheme I



Scheme II



An electron-rich alkyne (*N,N*-diethylpropynylamine,[25] **2**) was chosen to test the above considerations. Irradiation (>530 nm) of 0.139 mmol each of C_{60} and **2** in 80 mL of oxygen-free toluene at room temperature for 20 min afforded a single adduct (C_{60}-fused cyclobutenamine **3**) in >50% yield by HPLC. [2 + 2] cycloaddition to C_{60} has thus far been observed only with benzyne[26] and postulated in the photoinduced polymerization of solid C_{60} films.[27] While we have not yet demonstrated that the reaction goes via electron transfer, reaction in the dark under the same conditions led to a very slow reaction to **3** (<8% after 30 h at ca. 80 °C), as shown by HPLC (Scheme I).

The cyclobutenamine **3** is unique in that it has a photosensitizer (the dihydrofullerene)[28] and a photooxidizable group (the enamine) in the same molecule, and brief exposure (2 h) to air and room light cleaves the enamine double bond, cleanly producing ketoamide **4** (Scheme II) as monitored by HPLC. The oxygen- and light-sensitivity of **3** makes its isolation difficult. Compound **3** was characterized by FAB-MS (m/z = 831) and ^1H NMR and by its reactions.[29] The ^1H NMR spectrum of **3** is very similar to that of **2**, with a downfield shift due to the influence of the ring current.

Chemical transformations of **3** also demonstrate its structure. When the photoreaction of C_{60} and **2** was carried out in toluene without complete deoxygenation, ketoamide **4** was produced directly and isolated in 58% yield (92% based on recovered C_{60}!). Photooxidative cleavage of enamines is a well-known process and proceeds via an intermediate 1,2-dioxetane.[30-32] Although many 1,2-dioxetanes are relatively stable, those from enamines are extremely unstable and cleave to ketone and amide fragments

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[29] ^1H NMR for **3** (500 MHz, $CS_2/CDCl_3$): δ 3.78 (q, 4 H, J = 7.17 Hz), 2.60 (s, 3 H), 1.46 (t, 6 H, J = 7.17 Hz)

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below –40 °C in most cases. Ketoamide **4** was characterized by FAB-MS (*m/z* = 863) and ^{13}C NMR (carbonyls at 170 ppm for the amide and 204 ppm for the ketone and overall C_s symmetry for the fullerene carbons) as well as FT-IR and ^1H NMR.[33] Compound **4** shows temperature-dependent dynamic behavior in the ^1H NMR from restricted rotation around the amide bond: all four methylene hydrogens are nonequivalent at –70 °C; pairwise averaging occurs at 49 °C, where the two pairs are still broad and are apparently beginning to coalesce to a single group.

The structure of cyclobutenamine **3** was further secured by its hydrolysis to amide **5**,[34] catalyzed by SiO_2. Hydrolysis did not give the cyclobutanone and diethylamine. Instead, amide **5** is produced; the dihydrofullerene ring is apparently such a strong electron acceptor that it is a better leaving group than diethylamine. This is in agreement with the high acidity ($pK_a \approx 5.7$) of dihydrofullerenes reported by Fagan and Wudl.[35,36] The ^{13}C NMR spectrum of **5** shows an amide carbonyl at 172.6 ppm. The area for the aromatic region integrates as 58 carbons, for the aliphatic region eight carbons; a DEPT experiment located three CH_3 peaks at 16.05, 16.02, and 14.08 ppm, two CH_2s at 43.51 and 41.64 ppm, two CHs at 56.29 and 47.03 ppm, and one quaternary carbon at 68.25 ppm. In the ^1H NMR spectrum of **5**, the hydrogen attached to the fullerene appears as a singlet at 7.62 ppm, far downfield of normal allylic hydrogens. Groups attached to the fullerene ring experience large downfield shifts; in $C_{60}H_2$, the hydrogens appear at 5.07 ppm.[35,37] Two methylene hydrogens appear as AB multiplets at 3.76 and 3.51 ppm (J_{AB} = 14.3 Hz), respectively. FT-IR revealed a strong amide band at 1638 cm^{-1} as well as fullerene bands. UV–vis spectra of **4** and **5** show the same loss of C_{60} fine structure between 500 and 650 nm and new bands at 700 and 430 nm.[33,34] These two bands are highly characteristic for 6,6 dihydrofullerene adducts.[7,38]

These preliminary studies demonstrate a potentially versatile, high-yield photochemical functionalization of C_{60}. The moderately stable cyclobutenamine **3** undergoes interesting chemical changes that lead to useful functionalized dihydrofullerenes that should be easily converted to a wide variety of derivatives. The mechanism of the photochemical [2 + 2] cycloaddition of C_{60} with electron-rich compounds is under investigation.

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Supplementary Material Available: ^1H NMR spectra of **3**, **4**, and **5**; ^{13}C NMR spectra for **4** and **5**; and FT-IR spectra for **4** and **5** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(33) Representative physical data for **4**: ^1H NMR (500 MHz, $CS_2/CDCl_3$, –70 °C) δ 5.00 (q, 1 H, *J* = 7.62 Hz), 3.96 (q, 1 H, *J* = 6.83 Hz), 3.65 (q, 1 H, *J* = 7.12 Hz), 3.30 (q, 1 H, *J* = 7.05 Hz), 3.18 (s, 3 H), 1.43 (t, 3 H, *J* = 6.96 Hz), 1.32 (t, 3 H, *J* = 6.91 Hz); at 25 °C, δ 4.28 (br s, 2 H), 3.68 (br s, 2 H), 3.17 (s, 3 H), 1.45 (t, 3 H, *J* = 6.98 Hz), 1.38 (t, 3 H, *J* = 6.94 Hz); ^{13}C NMR (90 MHz, $CS_2/CDCl_3$) δ 203.58, 170.21, 151.67, 147.19, 147.10, 146.18, 146.09, 145.90, 145.87, 145.53 (br), 145.32, 145.26, 145.17, 145.07, 144.68 (br), 144.20, 142.99, 142.21, 141.92, 141.84, 141.72, 141.60, 141.29, 141.25, 139.87, 139.29, 136.08 (br), 135.44, 81.17, 75.83, 43.30, 43.05, 30.80, 13.86, 12.21. FT-IR (KBr) cm^{-1} 2920 (w), 1717 (s), 1707 (s), 1626 (s), 1424 (s), 1350 (m), 1260 (s), 1170 (s), 1096 (m), 814 (m), 669 (m), 554 (w), 527 (s); UV–vis λ_{max} (ε) (CH_2Cl_2) 702 (330), 433 (2980), 314 (36 300), 268 (66 900), 249 (73 500), and 240 (68 100).

(34) Representative physical data for **5**: ^1H NMR (500 MHz, CS_2/acetone-d_6) δ 7.62 (s, 1 H), 4.50 (q, 1 H, *J* = 6.85 Hz), 3.76 (m, 2 H, NCH_2), 3.51 (m, 2 H, J_{AB} = 14.3 Hz, *J* = 6.88 Hz, NCH_2), 2.35 (d, 3 H, *J* = 6.88 Hz), 1.39 (t, 3 H, *J* = 7.07 Hz), 1.32 (t, 3 H, *J* = 7.03 Hz); ^{13}C NMR (90 MHz, CS_2/acetone-d_6) δ 172.57, 156.32 (2 C), 155.75 (2 C), 155.43, 155.33, 148.10, 147.99 (2 C), 147.72, 146.97 (2 C), 146.94, 146.88 (2 C), 146.82 (3 C), 146.71 (4 C), 146.53, 146.44, 146.01 (2 C), 145.89 (2 C), 145.85 (2 C), 145.74, 145.53, 145.36, 145.08, 144.97, 143.76, 143.12, 143.05 (2 C), 142.97, 142.65, 142.49, 142.32, 142.14 (2 C), 142.11 (2 C), 142.09 (3 C), 141.99, 140.86, 140.48, 140.40, 137.60, 137.46, 136.95, 136.57, 68.25, 56.29 (CH), 47.03 (CH), 43.51 (CH_2), 41.64 (CH_2), 16.05 (CH_3), 16.02 (CH_3), 14.08 (CH_3). FT-IR (KBr) cm^{-1} 1638 (s), 1560 (w), 1508 (w), 1460 (m), 1428 (m), 1383 (m), 1246 (m), 1215 (m), 1103 (w), 669 (s), 575 (m), 526 (s); UV–vis λ_{max} (ε) (CH_2Cl_2) 710 (350), 432 (3310), 322 (30 000), 264 (68 300), 256 (66 200), 248 (68 300).

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