Competing Pathways in the Photolytic Cycloaddition Reactions of *N*-Ethoxycarbonylazepine to [60]Fullerene: Formation of [2 + 4] and [2 + 6] Photoadducts

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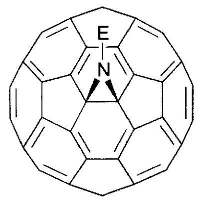
The photochemical reaction between [60]fullerene and *N*-ethoxycarbonylazepine, formed *in situ* by light-induced decomposition of ethyl azidoformate in benzene, produces two photoadducts in the ratio of 4:1 by formal [2 + 4] and[2 + 6] cycloaddition reactions as established by a series of high-field (600 MHz) NMR experiments.

Although a plethora of methods now exist for the monofunctionalisation of [60]fullerene (C_{60}) *via* thermal cycloaddition reactions,[1] photochemical derivatisation of C_{60} is still in its infancy. Reports so far include photo-epoxidation,[2] [2 + 1] photocycloaddition reaction with nitrenes derived from *N*-succinimidyl-4-azido-2,3,5,6-tetrafluorobenzoate[3] and aroylazides,[4] [2 + 2] photocycloaddition reaction with enones[5] and *N,N*-diethylpropynylamine,[6] [2 + 3] photocycloaddition reactions with 2,3-diphenyl-2*H*-azirine[7] and 1,1,2,2-tetramesityl-1,2-disilirane.[8] In all cases, functionalisation occurs at a 6,6-ring junction in C_{60}, which in the photoexcited state is a much stronger electron acceptor and serves as an ene or dienophile. We now report the first examples of photoderivatisation of C_{60} by formal [2 + 4] and [2 + 6] cycloaddition reactions with *N*-ethoxycarbonylazepine, which is generated *in situ* by photolytic decomposition of ethyl azidoformate in benzene.

We have already established that in addition to the expected formation of closed [6,6]fulleroaziridines **1** by reaction of C_{60} with singlet oxycarbonylnitrenes,[9] *e.g.* EtO_2CN:, small amounts (*ca.* 10%) of unanticipated closed 5,6-adducts **2** were obtained, apparently by trapping of triplet nitrenes in a diradical manner.[10] In an effort to investigate this conjecture further, photolytic experiments were undertaken in various solvents, and in particular benzene with divergent results. Thus, irradiation (400 W medium pressure mercury lamp, quartz reactor) of a mixture of C_{60} (1 equiv.) and ethyl azidoformate (5 equiv.) in either dichloromethane (DCM) or 1,1,2,2-tetrachloroethane led to the immediate formation of an intractable brown solid, whereas in benzene, slow consumption of C_{60} occurred to produce a 4:1 mixture of two major products (70%),† which was easily separated by flash chromatography (*n*-hexane–toluene, *n*-hexane–diethyl ether). FAB-MS analysis showed that the two products were isomeric [major (M^+ + 1) 886.08650, minor (M^+ + 1) 886.07837; $C_{69}H_{12}NO_2$ requires 886.08680] and corresponded to an adduct of C_{60} combined with benzene and photolytically generated ethoxycarbonylnitrene. Control experiments established that reaction had proceeded by capture of the nitrene by benzene to produce *N*-ethoxycarbonylazepine **3**, which then underwent further photoreaction with C_{60} by two competing pathways to form the isomeric adducts. The photogenesis of these adducts was established when azepine **3** was found to be thermally unreactive towards C_{60} upon heating in benzene under reflux for 3 h in the dark. By contrast, photolysis of **3** in the presence of C_{60} in benzene produced the same reaction mixture as obtained in the initial experiment.

The structures of the major and minor photoadducts were elucidated by a series of high-field NMR experiments, which established unequivocally that their origin resulted from formal [2 + 4] and [2 + 6] cycloaddition reactions of **3** to C_{60}, respectively. In the case of the major [2 + 4] photoadduct **4**, the one-dimensional ^1H NMR spectrum (600 MHz) showed six pairs of signals in the δ 4–8 region as follows: overlapping triplets at δ 4.21, triplets at δ 5.51 (major) and 5.64, doublets at δ 6.52 and 6.68 (major) overlapping triplets at δ 6.90, doublets at δ 7.25 (major) and 7.35, overlapping triplets at δ 7.50. In each



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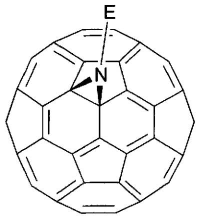

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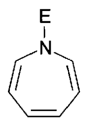

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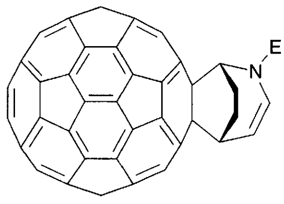
E = CO_2Et



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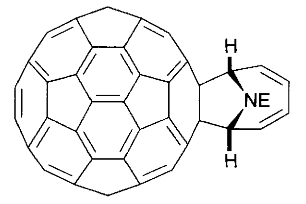

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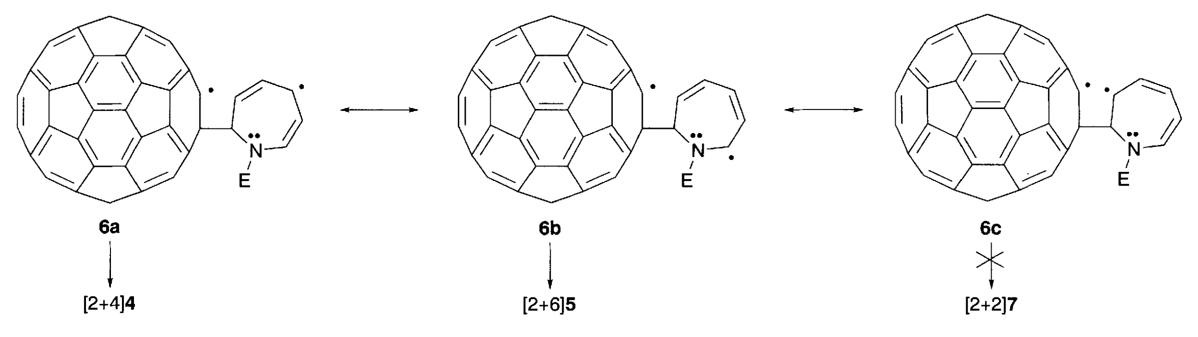

case saturation of one of the members of a resolved pair resulted in saturation transfer to the other, indicating exchange between two conformers or isomers. A two-dimensional HMQC[11] carbon–proton correlation experiment showed that the protons resonating at δ 4.21 (two), 6.52 and 6.68 are bonded to sp^3-hybridised carbon atoms at δ 44.7/44.9, 58.2 and 58.8, respectively; the remaining protons being bonded to alkene carbon atoms. Proton spin-decoupling experiments confirmed that the protons constitute a linear spin system in which two alkene units are separated by an sp^3-hybridised carbon atom. Above 60 °C the pairs of proton signals coalesced to show sharp doublets or triplets as expected. The ^{13}C NMR spectrum (62.5 MHz) also exhibited signals at δ 71.5 and 69.7, which were assigned to sp^3 carbon atoms of the fullerene sphere, along with 35 (out of 60) resolved lines in the δ 135–155 region for the fullerene sphere. Resonances due to the alkene portion of **4** were observed at δ 139.0, 127.0, 124.5 and 108.7 whilst the *N*-ethoxycarbonyl moiety had resonances at δ 14.3, 62.6 and 153.7; both of these sets of signals occurred as major/minor pairs. The FT-IR spectrum (KBr) exhibited bands at 1704 (C=O), 1647 (C=C), 1323, 1254, 725 and 526 (fullerene) cm^{-1}. The UV–VIS spectrum (DCM) of **4** exhibited a maximum at 309 nm accompanied by shoulders at 415 and 435 nm.

For the minor [2 + 6] photoadduct **5**, more elaborate NMR experiments were required to determine its structure. Thus, in addition to the methyl (δ 1.48), and diastereotopic methylene (δ 4.41 and 4.44) resonances, the one-dimensional ^{1}H NMR spectrum (600 MHz) showed a two-proton multiplet centred at δ 6.31, similar in appearance to one portion of an $[AX]_2$ spectrum, a one-proton doublet at δ 6.36 showing a further long-range coupling, and a complex pattern, integrating for three protons, in the range δ 6.40–6.48. A saturation difference experiment with irradiation at δ 6.36 revealed a similar doublet at δ 6.43. A two-dimensional HMQC[11] carbon–proton correlation experiment showed that these two protons are bonded to sp^3-hybridised carbon atoms at δ 67.5 and 67.7, respectively, the remaining four protons being bonded to alkene carbon atoms at δ 137.1, 136.6, 125.4 and 125.1. Examination of the two-dimensional proton DQFCOSY[12] spectrum located the remaining two protons at δ 6.42 and 6.46 and confirmed the shift of the other four protons. The three-bond coupling cross peaks showed that the protons constitute a linear spin system which terminates with protons bonded to sp^3-hybridised carbon atoms. The exchange of the terminal protons arises from the rotation about the N–CO_2Et bond which is slow on the NMR time-scale at the temperature (25 °C) at which the spectra were obtained. Hence the symmetry expected in a fast exchange situation, which occurs at a temperature higher than could be made on this sample, is not observed. Owing to its C_i symmetry, the ^{13}C NMR spectrum (62.5 MHz) of photoadduct **5** showed two fullerene carbon sp^3 resonances at δ 81.5 and 80.4, along with 43 (of 60) resolved peaks between δ 134.2 and 153.6, the *N*-ethoxycarbonyl moiety also showed resonances at δ 14.6, 61.91 and 153.1. The FT-IR spectrum (KBr) displayed major absorbances at 1705 (C=O), 1509, 1316, 1262, 717 and 525 (fullerene) cm^{-1}. The UV–VIS spectrum (DCM) of **5** showed maxima at 303 and 426 nm. The sharp but weak feature at 426 nm is characteristic of 6,6-substituted fullerenes.[2,4,6,8,9]

From a mechanistic viewpoint, an explanation for the previously unobserved modes of photo-induced addition to azepine **3** is that the process involves reaction with the photoexcited (triplet) state[13] of C_{60}. The involvement of diradical intermediates such as **6a–c** can be visualised in which delocalisation as indicated accounts for the preferred formation of photoadduct **4** over photoadduct **5**. We failed to detect the formation of [2 + 2] photoadduct **7**, presumably owing to a combination of two factors. Firstly, of the three diradical intermediates **6a–c** proposed, the one that would result in a [2 + 2] photoadduct, *i.e.* **6c**, is the least stable, and secondly, formation of a four-membered ring is energetically less favourable than the larger rings formed in the observed alternative products, **4** and **5**.

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Footnote

† Analysis of the crude reaction mixture by HPLC (FullereneSep®, 2 ml min^{-1}, 7% ethyl acetate–*n*-hexane, 258 nm)[14] also established the concomitant formation of small amounts of [6,6]fulleroaziridine **1** (3%); when the C_{60} : ethyl azidoformate ratio was changed to 1 : 60, [5,6]fulleroaziridine **2** (*ca.* 1%) was also detected.

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