Bis-Functionalisation of C_{60} *via* Thermal Rearrangement of an Isolable Fulleroaziridine Bearing a 'Solubilising' Supermesityl Ester Moiety

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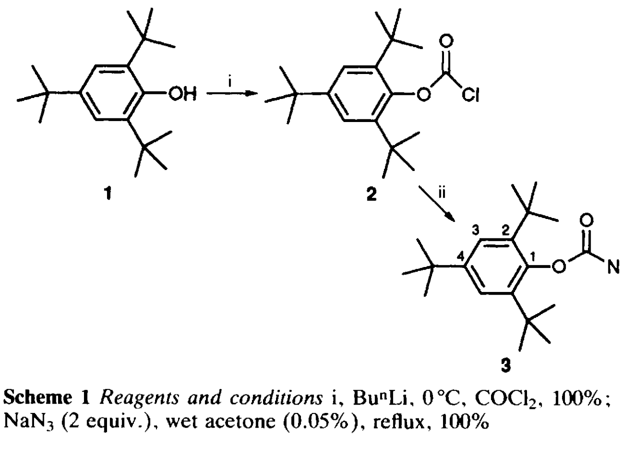
Heating of C_{60} with the novel azidoformate **3** bearing a highly solubilising supermesityl group affords the first example of a nitrogen-bridged fullerene **4** with a σ-homoaromatic closed 6,6-aziridine structure, which by further heating can be induced to undergo rearrangement on the fullerene surface to form as the sole product, the closed isomeric oxazole derivative **5** with O and N vicinally bound to the fullerene framework at a 6,6-ring juncture

The preparation of synthetically useful mono-adducts of C_{60} is currently one of the prime objectives in the rapidly expanding area of fullerene chemistry. So far considerable success has been achieved in the building of three-,[1] four-,[2] five-[3] and six-membered ring systems[4] onto C_{60} and high-field ^{13}C NMR spectroscopy is proving to be a powerful probe in elucidating their structure.[1a,5,6] In theory, mono-adducts of C_{60} may possess one of four possible structures depending upon whether attachment occurs between two hexagons (6,6-ring junction) or a pentagon and a hexagon (5,6-ring junction), and also whether addition results in an open fulleroid or a closed fullerene structure. Pertinently, symmetrical addition to a 6,6-junction leads to adducts, *e.g.* $C_{60}O$, with C_{2v} symmetry[1b] and unsymmetric addition to the 6,6,-junction (or symmetric addition to the 5,6-junction) exhibits C_s symmetry; unsymmetric addition to a 5,6-junction reduces symmetry to C_1. We now report the isolation of the first example of a nitrogen-bridged fulleroaziridine **4** with a σ-homoaromatic closed 6,6 structure from the reaction of C_{60} with an azidoformate **3** at elevated temperature, and secondly its clean and propitious rearrangement on the fullerene surface upon further heating to the *vic*-functionalised fullerene **5** having different hetero-atoms (O and N) at the 6,6-ring fusion.

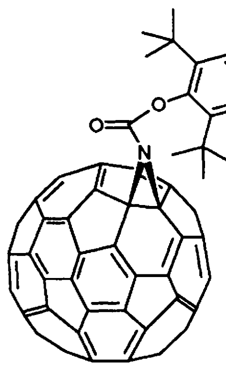
We designed the azidoformate **3** in order to provide a nitrene of sufficient electrophilicity (*vide infra*) to bring about reaction with 'electron deficient' C_{60} and improve the solubility of the fullerene adduct by utilising the inherent lipophilicity of the 2,4,6-tri-*tert*-butylphenyl (supermesityl) group. Thus phosgenation of the lithium salt of anhydrous 2,4,6-tri-*tert*-butylphenol **1** led to chloroformate **2**† in quantitative yield from which azidoformate **3**‡ was obtained by heating with sodium azide in wet acetone overnight (Scheme 1).

When a boiling solution of C_{60} (1 equiv.) in 1,1,2,2-tetrachloroethane (TCE) (147 °C) was treated with a dilute solution of azidoformate **3** (2 equiv.) in TCE over 1 min, nitrogen evolution occurred immediately and the colour of the solution changed from purple to dark brown. The reaction mixture was heated for a further 5 min and then poured onto crushed ice to give a reaction product in 70% yield which was easily separated into two components (9:1) by preparative HPLC using a FullerenSep® RP-HPLC column.[7] FAB-MS analysis showed that both components were mono-adducts of C_{60} and **3**, and formed by loss of nitrogen, the major product being characterised as the fulleroaziridine **4** [(M + 1) 1024.22767, $C_{79}H_{30}NO_2$ requires 1024.22764] with a closed structure on the following spectroscopic evidence.

The ^{13}C NMR spectrum (90 MHz, $CDCl_3$–CS_2) of highly soluble **4** was found to be relatively simple, consisting of four lines at δ 31.0, 31.4, 34.2 and 35.2 corresponding to two *o-tert*-butyl and one *p-tert*-butyl groups, along with five lines at δ 152.8, 147.1, 141.1, 123.1 and 146.2 due to C=O and C^{1-4} of the supermesityl ligand. The region between δ 139.8 and 144.3 contained 13 lines of intensity 4 and three lines of intensity 2. A further line of intensity 2 was observed at δ 85.6. This data suggests that the mono-adduct **4** possesses C_{2v} symmetry which would be consistent with the incorporation of an aziridine ring at a 6,6-junction of C_{60} with fast pyramidal inversion at nitrogen.[8] The resonance at δ 85.6 in the sp^3 region lies between those found for the cyclopropane (meth-



Scheme 1 *Reagents and conditions* i, Bu^nLi, 0 °C, $COCl_2$, 100%; ii, NaN_3 (2 equiv.), wet acetone (0.05%), reflux, 100%



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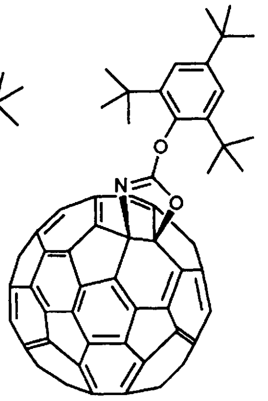

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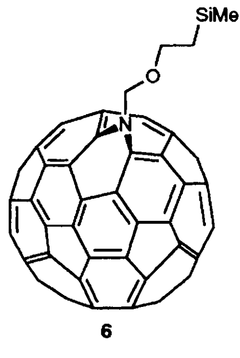

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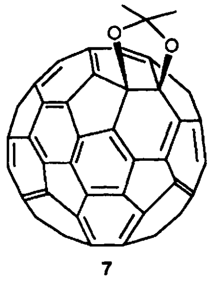

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anofullerene) derivative[1a] (δ 80) and the corresponding epoxide $C_{60}O$ (δ 90)[1b] and was assigned to the bridgehead sp^3 carbon atoms in the fullerene cage. This finding is in sharp contrast to a report[9] which appeared during the course of this work in which the heating of an equimolar mixture of [(trimethylsilyl)ethoxy]methyl azide and C_{60} in chlorobenzene (bp 132 °C) overnight produced an azafulleroid **6** with an open 5,6-structure as identified from the ^{13}C NMR resonance at δ 137.06 for the bridging sp^2 carbon atoms. A possible explanation for this divergence in behaviour may lie in the mode of formation of **4** *vis-à-vis* **6**. In the latter case it is proposed[10] that the azafulleroid is formed *via* 1,3-dipolar addition and subsequent elimination of nitrogen from the resultant triazoline adduct. In our case reaction is more likely to occur *via* nitrene addition since analysis of the crude reaction mixture revealed the presence of other nitrene-derived products, including an isocyanate and a benzoxazolone, both of which are formed by attack on the aromatic ring of the supermesityl grouping.[11]

The ^1H NMR spectrum of the fulleroaziridine **4** was unremarkable, consisting of three singlets at δ 1.55 (9H), 1.65 (18H) and 7.47 (2H), and the FTIR (KBr) of **4** had diagnostic bands at 1752 and 526 cm^{-1}. The UV-VIS spectrum of a pink-red solution of **4** in CH_2Cl_2 exhibited λ_{max} at 226 nm ($\varepsilon = 3.86 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$), 256 (4.83×10^4) and 323 (1.24×10^4) together with two weak but sharp features at 408 and 421 nm. The feature at 421 nm is reported to be highly diagnostic for closed 6,6-bridged fullerene derivatives[1b,6] and both these weak features are observed in the spectrum of $C_{60}O$[1b] (*vide supra*). The longer wavelength spectrum between 450 and 700 nm is much less structured when compared with that of C_{60} and its maximum is hypsochromically shifted from 550 to 474 nm.

The exact molecular mass of the minor adduct [(M + 1) 1024.22767] established its identity to be an isomer of **4** (*vide supra*). In light of our earlier studies into the thermal rearrangement of aziridine moieties[12] we reasoned that this isomeric form might contain an oxazole ring such as that depicted in **5**, the origin of which lies in a thermal transformation of fulleroaziridine **4** *via* a mechanism involving a diradical species. A control experiment confirmed that heating of a pure sample of fulleroaziridine **4** in boiling TCE over a period of 5 h resulted in the irreversible quantitative formation of **5**. A kinetic study of the rearrangement under the same conditions showed the process to be first order ($k = 1.3 \times 10^{-2}\ s^{-1}$). Further proof of the oxazole structure came from the FTIR (KBr) spectrum which showed that the strong C=O stretching absorption at 1753 cm^{-1} in **4** had been replaced by a less intense C=N absorption band at 1666 cm^{-1}.

The question remained as to the position of bridging in **5**. The ^{13}C NMR spectrum (150 MHz) of the adduct consisted of 39 signals of which nine corresponded to the appended ligand which resonated at δ 148.4 (C=N), along with peaks at δ 31.4, 31.7, 34.5, and 35.6 (*o*- and *p*-*tert*-butyl groups) and δ 147.5, 141.4, 123.4, and 147.4 (C^{1-4} of the supermesityl ligand). The most diagnostic of the remaining peaks ascribed to the C_{60} skeleton were found in the sp^3 region at δ 97.5 (1C, br) for the *N*-bound carbon and 88.6 (1C, s) for the *O*-bound carbon. The rest of the spectrum was observed between δ 135 and 148 and consisted of one line of intensity 4, one line of intensity 3, 22 sharp lines of intensity 2, three broad lines of intensity 2, and one sharp line of intensity 1. Allowing for coincidental resonances at δ 144.3 (intensity 4 which corresponds to 2 × 2C) and at δ 141.9 (intensity 3 which corresponds to 1 × 2C and 1 × 1C), there is a total of 28 lines of intensity 2 and four lines of intensity 1 which would indicate C_s symmetry with the point of attachment of the supermesityl ligand across a 6,6-junction with O and N vicinally bound to the fullerene framework. The UV-VIS spectrum of **5** (yellow solution in CH_2Cl_2) exhibited λ_{max} at 227 nm ($\varepsilon = 9.82 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$), 255 (1.13×10^5) and 316 (4.03×10^4), but lacked the distinctive sharp features at 408 and 421 nm found in the spectrum observed for fulleroaziridine **4**. Interestingly the spectrum of **5** in the longer wavelength region closely resembles the spectrum reported for the 1,3-dioxolane 6,6-bridged fullerene **7**[3a] formed from the reaction of C_{60} with 1,2-dimethyloxirane.

In conclusion, we have shown despite earlier evidence[9] that C_{60} can undergo reaction with an azide to yield an isolable 1,2-nitrogen bridged fullerene with a ring-closed structure, and that this fulleroaziridine **4** by virtue of its attached supermesityl ester grouping displays not only exceptional solubility in common organic solvents (chlorinated hydrocarbons, ethers and ethyl acetate) unlike C_{60}, but also highlights the potential of carrying out chemical transformations on the fullerene core by rearranging quantitatively to a fullerene 4,5-substituted oxazole **5** on heating.

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Footnotes

† *Selected data for* **2**: FAB-MS (M^+) 324.18850, $C_{19}H_{29}ClO_2$ requires 324.18559; ^1H NMR (60 MHz, $CDCl_3$), δ 1.3 (s, 9H, *p*-Bu^t), 1.4 (s, 18H, 2 × *o*-Bu^t), 7.4 (s, 2H, 2 × *m*-H); ^{13}C NMR (90.5 MHz, $CDCl_3$), δ 150.8 (C=O), 148.6 (O–C^1), 146.9 (C^4), 140.7 (C^2), 123.6 (C^3–H), 35.4 (*o*-quat. C), 34.8 (*p*-quat. C), 31.4 (*o*- and *p*-*tert*-butyl CH_3); FTIR ν_{max} 1787 (C=O), 1117 (C–O) cm^{-1}.

‡ *Selected data for* **3**: FAB-MS (M^+ + 1) 332.23180, $C_{19}H_{30}N_3O_2$ requires 332.23379; ^1H NMR (60 MHz, $CDCl_3$), δ 1.3 (s, 9H, *p*-Bu^t), 1.4 (s, 18H, 2 × *o*-Bu^t), 7.4 (s, 2H, 2 × *m*-H); ^{13}C NMR (90.5 MHz, $CDCl_3$), δ 157.3 (C=O), 148.0 (C^1, C^4), 141.1 (C^2), 123.4 (C^3,-H), 35.5 (*o*-quart. C), 34.7 (*p*-quart. C), 31.4 (*o*- and *p*-*tert*-butyl CH_3); FTIR ν_{max} 2187m, 2135s, 2119m (N_3), 1788m, 1744 (C=O), 1230 (C–O) cm^{-1}.

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