Aziridino[2′,3′:1,6][60]fullerene: Isolation of the First Closed [5,6]-bridged Fullerene Adduct

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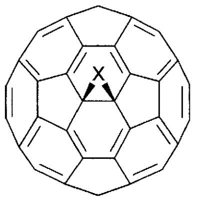
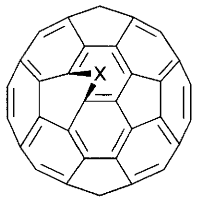
In addition to the expected formation of closed [6,6]-bridged aziridinofullerene **3** by reaction of [60]fullerene with singlet oxycarbonylnitrenes, small amounts (*ca.* 10%) of previously undetected closed [5,6]-adducts **5** have been isolated, and are thought to arise by trapping of triplet nitrenes.

In the rapid development of the chemistry of [60[fullerene, certain trends in the regiochemistry of cycloaddition reactions have become apparent.[1,2] It has been found that all [6,6]-bridged monoadducts **A**[3–9] of [60]fullerene possess a closed transannular bond, whilst all [5,6]-bridged compounds **B**[4,6,10] have an open transannular structure.[6,11] The rationale for these observations is that the structures of the two adducts reflect the electronic and structural preferences in the fullerene sphere, *e.g.* with all double bonds radiating away from pentagons and located between hexagons in a [5]radialene-like manner. There are two other structural possibilities for monoadducts of [60]fullerene; these are the [6,6]-bridged compound **C** with an open transannular structure and the [5,6]-bridged compound **D** with a closed transannular bond. So far, neither structure has been observed experimentally, the reason being given that they require the placement of double bonds in unfavourable locations, *i.e.* in pentagons and/or bridgeheads. Computational studies[6,11] on the methano fullerene (X = CH_2, CR_2) series suggest the relative stabilities for the four isomeric structures **A**–**D** to be: **A** (0 kJ mol^{-1}) > **B** (25 kJ mol^{-1}) > **D** (88 kJ mol^{-1}) with no local minima for **C**. This has led to the postulate that **D** is an intermediate in the thermal isomerisation of **B** (kinetic product) into **A** (thermodynamic product) when X = CR_2, although notably it has not been possible to effect the isomerisation when X = CH_2.[4] We now wish to report the isolation of the first examples of [5,6]-bridged derivatives of [60]fullerene with structure **D**, *i.e.* a closed transannular bond.

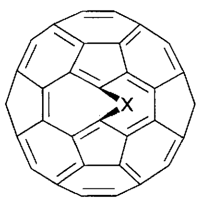
We have recently reported that reaction between [60]fullerene and an electrophilic nitrene, generated either by thermal decomposition of an azidoformate **1**[7] in boiling 1,1,2,2-tetrachloroethane (TCE, 147 °C) or by base-catalysed α-elimination of *O*-4-nitrophenylsulfonylhydroxamic acid derivatives **2**,[12]



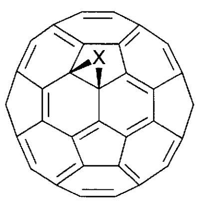
A



B

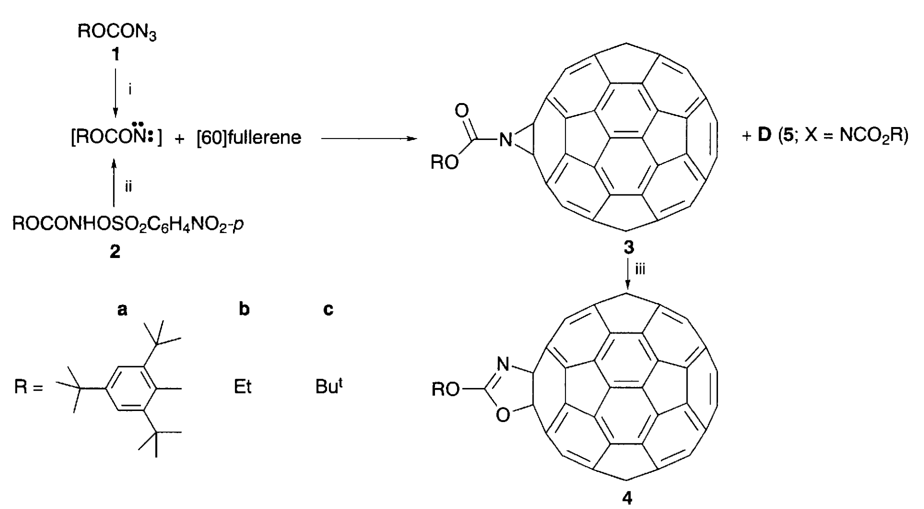


C



D

X = O[3]	
CH_2[4]	CH_2[4]
NH[5]	
CR_2[6]	CR_2[6]
NCO_2R[7,8]	NR[10]
$SiPh_2$[9]	



Scheme 1 *Reagents and conditions*: i, TCE, 147 °C; ii, $NaHCO_3$, $BzEt_3NCl$, H_2O–TCE–CH_2Cl_2, 20 °C; iii, for **3a**,**b** only: TCE, 147 °C, 12 h

offers a practicable route to *N*-substituted aziridino[2′,3′: 1,3][60]*fullerenes* **3** (Scheme 1), which upon prolonged heating in TCE rearrange to the corresponding 3-aryloxy- or 3-ethoxy-[60]fullereno[1′,2′:4,5]oxazole **4**[7,12] without loss of the [6,6]-bridging structure **A**. More recently, we have found that the heating of the *tert*-butoxycarbonyl derivative **3c** follows a separate pathway with simultaneous loss of isobutene and CO_2 to form aziridino[2′,3′:1,2][60]fullerene in 70% yield.[5]

In the course of these studies, HPLC analysis (Fullerenesep®,[13] 2 ml min^{-1} 7% ethyl acetate–*n*-hexane, 258 nm) of the crude reaction mixtures established that the [6,6]-bridged aziridinofullerenes **3** were accompanied in each case by a minor product in the ratio *ca.* 8:1, irrespective of the mode of formation. By combining the outcome of several reaction mixtures with careful flash chromatography on silica (*n*-hexane–toluene), we have now managed to isolate and characterise these minor products as being isomeric with the closed [6,6]-bridged major products **3**. Thus, molecular ions were found by FAB-MS at the following values: **5a** (M^+ + 1) 1024.22345, $C_{79}H_{30}NO_2$ requires 1024.22354; **5b** (M^+ + 1) 808.03577, $C_{63}H_6NO_2$ requires 808.03985; **5c** (M^+ + 1) 836.06967, $C_{65}H_{10}NO_2$ requires 836.07115. Further support for structural isomerism came from the close similarity of the respective ^1H NMR spectra. Comparison of the FT-IR spectra also verified the integrity of the oxycarbonylaziridine moiety with carbonyl bands at 1749.6 cm^{-1} for **5a** (*cf.* 1752.3, **3a**), 1731.6 for **5b** (1743.0, **3b**) and 1731.8 for **5c** (1738.0, **3c**). Likewise, the ^{13}C NMR spectra for **5a–c** showed carbonyl resonances at δ 152.01 (*cf.* 152.8, **3a**), 153.97 (155.5, **3b**) and 153.04 (154.4, **3c**), respectively, and in each case resonances owing to the R group at values very close to those recorded for the [6,6]-bridged aziridinofullerenes **3** were observed.

With the foregoing evidence in hand, the intriguing question remained as to the nature of the bonding in the minor isomers **5**. By analysis of the ^{13}C NMR spectroscopic data for the fullerene skeletons, in each case we are drawn to the conclusion that the site of substitution must be at a closed [5,6]-ring junction, *i.e.* compounds **5** are of the hitherto unobserved structural type **D** (X = NCO_2R). Thus, the spectra of **5** consisted of 32 lines for the fullerene carbon atoms in the expected ratio for a compound with C_s symmetry (28 lines of intensity 2, 4 lines of intensity 1),[1] *cf.* corresponding spectra of the closed [6,6]-bridged major product **3** which consisted of only 17 lines for the fullerene sphere as predicted for C_{2v} symmetry.[5,7,12] Of the 32 lines for **5**, 31 were observed between δ 146 and 132 (27 lines of intensity 2, 4 lines of intensity 1) as well as a single and diagnostically significant line, assigned to the two equivalent sp^3 carbon atoms attached to the aziridine nitrogen, at δ 104.2 for **5a**, (*cf.* 85.6, **3a**), 80.4 for **5b**, (80.5, **3b**) and 82.6 for **5c**, (83.3, **3c**). In this connection, it is also worth noting that these values are distinctly different to that reported for the open [5,6]-bridged compound **B** (X = $NCH_2OCH_2CH_2SiMe_3$) for which the sp^2 carbon atoms attached to the nitrogen function resonate at δ 137.06.[10]

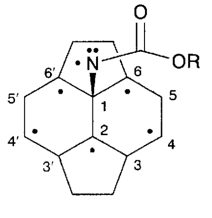


Fig. 1 Part structure of [60]fullerene denoting the delocalised position of the unpaired electron following addition of triplet nitrene (ROCOṄ:)

The UV–VIS spectra (*n*-hexane) of minor isomers **5** all showed similar features to [60]fullerene and the closed [6,6]-bridged isomers **3** in the region of 200–400 with absorbances occurring at λ_{max} *ca.* 210 nm ($\varepsilon = 5 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$), 256 (4×10^4) and 325 (9×10^3). However, they lacked the distinctive fine structure observed in [60]fullerene and closed [6,6]-bridged compounds in the region *ca.* 405–425 nm.[3,5,7,12,14] In addition, relative to the closed [6,6]-bridged compounds **3** the closed [5,6]-isomers **5** showed a slight red shift (3–5 nm).

At this stage, little is known about the mechanistic origin of the minor closed [5,6]-isomers **5**. The formation of the major closed [6,6]-isomers can be rationalised in terms of trapping by [60]fullerene of a singlet nitrene and it is proposed that the minor isomeric products **5** may result from intersystem crossover with the nitrene acting in a triplet diradical manner (Fig. 1). Thus, after the initial radical addition reaction has occurred at position 1, the unpaired electron is mostly located on two fused hexagons with the highest spin densities at positions 2, 4 and 6.[15] Radical recombination at position 4 seems unlikely, whereas recombination at position 2 gives rise to the closed [6,6]-isomers **3**; recombination at position 6 would lead to the observed formation of closed [5,6]-isomers **5**.

We are continuing our investigations into these intriguing isomers.

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