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Nitrene Additions to [60]Fullerene Do Not Generate [6,5] Aziridines

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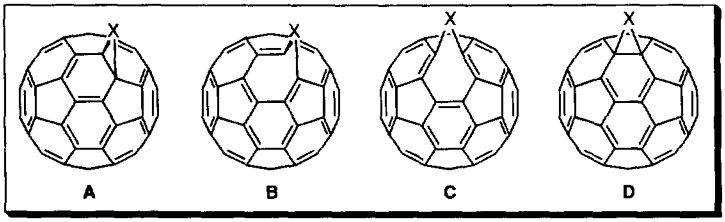
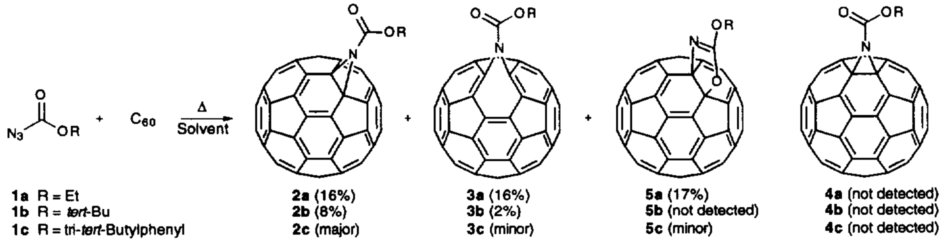
Abstract: Addition of nitrenes to C_{60} reportedly furnished the first closed [6,5] fullerene derivatives. However, detailed spectroscopic analysis has revealed that these products are open [6,5] azaannulenes rather than aziridines. Copyright © 1996 Elsevier Science Ltd

Notwithstanding the relatively brief history of fullerene science, the oxo-, methano- and aza-bridged [60]fullerenes have already stimulated intensive studies. Of the four possible types of isomeric cage structures (**A-D**), only two, the [6,6] closed derivatives **A** and [6,5] annulenes **C**, have been isolated and unambiguously characterized.[1] We reported earlier the prototypical fullerene epoxide, cyclopropane and annulene (**A**, X = O; **A** and **C**, X = CH_2) as well as the corresponding C_{70} derivatives.[2,3] Wudl et al. described the first [6,5] nitrogen-bridged azafulleroids (**C**, X = NR),[4] and two other groups have reported closed [6,6] aziridines (**A**, X = NCO_2R).[5] Oxido-bridged annulenes (**C**, X = O) remain unknown. Valence bond analysis[6] augmented by semiempirical calculations[7] provide a simple, currently accepted rationale for the selective formation of **A** and **C**: these structures do not contain destabilizing cyclopentene double bonds, whereas the isomers **B** and **D** contain three and two five-membered-ring olefins, respectively. In view of these considerations, the report by Banks et al.[8] of the first closed [6,5] derivatives, the aziridines **D** (X = NCO_2R; R = Et, *tert*-Bu, and 2,4,6-tri-*tert*-butylphenyl), was quite surprising. We have attempted to reproduce the latter work, which entailed a series of nitrene additions to C_{60}. In concurrence with the very recent observations of Hirsch and co-workers,[9] we wish to report here that the three minor products previously identified as [6,5] aziridines are in fact the isomeric aza-bridged [6,5] annulenes.



Reaction of C_{60} with ethyl azidoformate (**1a**, 2 equiv; 1,1,2,2-tetrachloroethane, reflux, 5 min) and column chromatography on silica afforded unreacted C_{60} (40% yield) and three products (Scheme 1). The first species, which eluted as a pink solution, was the expected[8] [6,6] aziridine **2a** (16% yield). Oxazoline **5a**, obtained in 17% yield from a brown eluant solution, was identified by its characteristic ^1H NMR spectrum and by its generation in the thermal rearrangement of **2a**, as reported.[5c] However, spectroscopic analysis revealed that the third compound, isolated from a purple solution (16% yield), was the [6,5] annulene **3a** rather than the aziridine **4a**. No other products were detected in significant amounts.

Scheme 1



The ^{1}H NMR spectrum of **3a** was quite similar to that of the [6,6] aziridine **2a**. The ^{13}C NMR spectrum [$CS_2/CDCl_3$ (1:1)] contained only a carbonyl resonance, ca. 30 peaks in the sp^2 region, and two sp^3 signals corresponding to the ethyl carbons. Importantly, the reported[8] resonance at 80.4 ppm was not present, a discrepancy we cannot account for. To ensure that the latter peak did not overlap with the $CDCl_3$ signals, we also measured the spectrum in CS_2 with acetone-d_6 as external lock (Figure 1). No resonances were found between 64 and 134 ppm. An earlier ^{15}N-labelling experiment by Wudl revealed a ^{13}C chemical shift of 137.06 for the bridgehead carbons in a similar aza-bridged [6,5]annulene,[4] in accord with the ^{13}C NMR spectrum and annulene structure of **3a**.

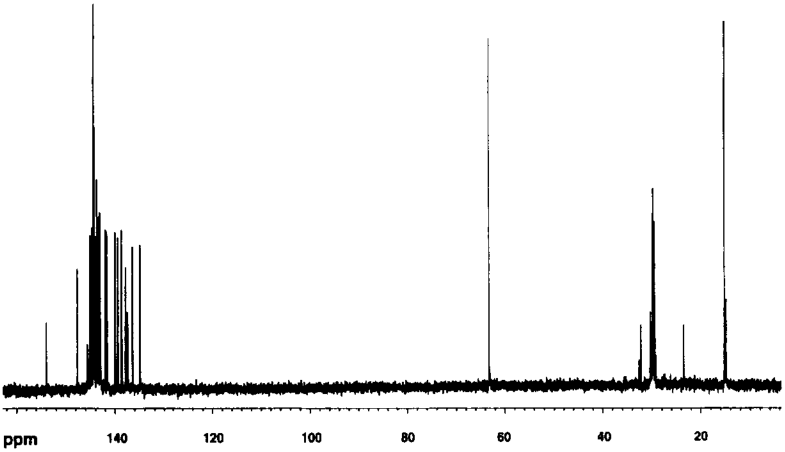


Figure 1. ^{13}C NMR spectrum of **3a** in CS_2/acetone-d_6.

Under the conditions described above for **1a**, the reaction of *tert*-butyl azidoformate (**1b**) with C_{60} proved to be exceedingly slow. Thus, we treated C_{60} with excess **1b** (15 equiv) in 1,2-dichlorobenzene at 170 °C for 10 min and obtained two products (Scheme 1). For [6,6] aziridine **2b**, the major product (8% yield) as reported earlier,[5d] the methyl carbons resonated at 28.00 ppm. The sp^2 region of the ^{13}C NMR spectrum consisted of 15 peaks for the fullerene cage and a carbonyl signal, indicative of C_{2v} symmetry. Two additional singlets at 81.2 and 84.2 ppm were assigned to the *tert*-butyl quaternary carbon and the sp^3 carbons of the aziridine ring, respectively (Figure 2); Banks et al.[5d,8] reported only one peak, at 83.3 ppm. A resonance at 29.7 ppm, assigned by Banks to the *tert*-butyl quaternary carbon, did not appear in our spectrum and apparently should be attributed to an impurity.[10] We also note that the published[4d] assignment for this signal is inconsistent with the ^{13}C chemical shifts for several Boc-protected amines.[11] The ^{13}C NMR spectrum of the minor product (2% yield) contained 30 resonances in the sp^2 region, indicative of C_s symmetry, along with sp^3 *tert*-butyl peaks at 17.92 (CH_3) and 83.15 (quaternary C). As before, no aziridine carbons were present.

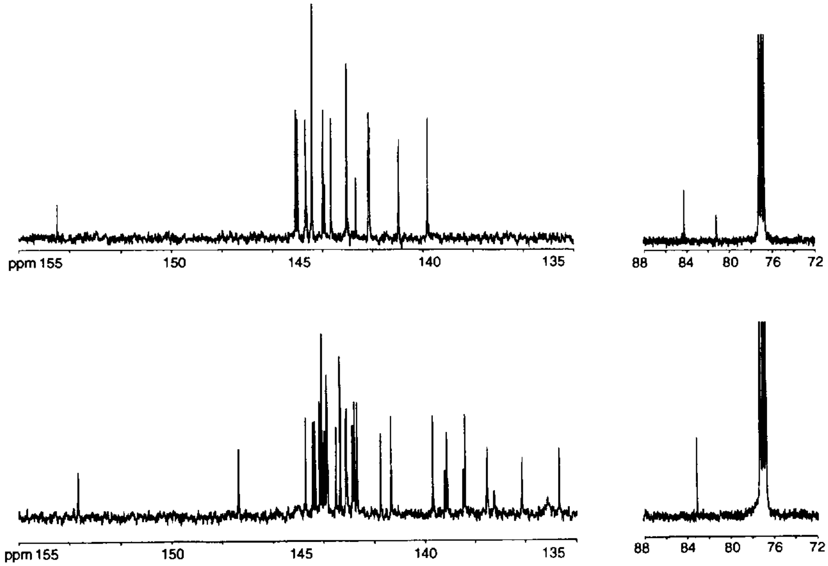


Figure 2. ^{13}C NMR spectra in $CS_2/CDCl_3$ of (top) aziridine **2b**; (bottom) annulene **3b**.

Treatment of C_{60} with 2,4,6-tri-*tert*-butylphenyl azidoformate (**1c**, ca. 5 equiv; $Cl_2CHCHCl_2$, reflux, 10 min; Scheme 1) likewise furnished [6,6] aziridine **2c**[5a] as the major product, accompanied by oxazoline **5c**.[4a] We encountered some difficulty in assigning the relative ^{13}C peak intensities for the second minor product, but the spectrum was generally consistent with the [6,5] azaannulene structure **3c**. Importantly, the absence of resonances assignable to aziridine carbons excluded the previously proposed structure **4c**. The reported[8] resonance at 104.2 ppm, assigned to the aziridine ring carbons but not present in our spectrum, might reflect the presence of hexachloroethane or another impurity.

The UV-visible spectra of the aziridines and annulenes described herein provide further support for the structure assignments. For example, aziridine **2b** displays absorptions characteristic of [6,6] closed structures at 420.8 nm (Figure 3). In contrast, the spectrum of azaannulene **3b** resembles those of C_{60} and its open [6,5] annulene derivatives, all of which lack the 430-500 nm band. These observations parallel our earlier findings for C_{60}, the $C_{60}O$ [6,6] epoxide, and the parent $C_{61}H_2$ annulene and cyclopropane, as well as the $C_{71}H_2$ annulenes and cyclopropanes and $C_{70}O$ epoxides previously characterized in our laboratory.[2b,e]

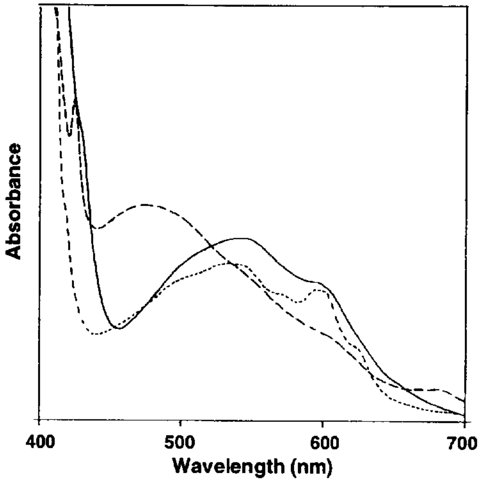


Figure 3. UV-visible spectra of C_{60} (- - -), aziridine **2b** (– – –) and annulene **3b** (——) in toluene.

In summary, detailed spectroscopic analysis demonstrates that the [6,5] aziridines reportedly[8] formed in nitrene additions to [60]fullerene should be reformulated as the isomeric [6,5] aza-bridged annulenes.

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Experimental

Reaction of 1a with [60]Fullerene. Under Ar at reflux (147 °C) a purple solution of C_{60} (65 mg, 0.090 mmol) in 1,1,2,2-tetrachloroethane (130 mL) was treated with ethyl azidoformate (**1a**, 20 mg, 0.18 mmol, 1 M in 1,1,2,2-tetrachloroethane) dropwise over 1 min. The resultant mixture was stirred 5 min further, cooled to room temperature, and concentrated in vacuo. Column chromatography (1:9 hexanes/toluene) furnished unreacted C_{60} (26 mg, 40% yield) followed by (gradient elution, 1:9 → 1:1 hexane/toluene) a pink solution of aziridine **2a** (12 mg, 16% yield), a purple solution of annulene **3a** (12 mg, 16% yield), and a brown solution of oxazalone **5a** (13 mg, 17% yield).

2a: FT-IR (KBr) 2918, 1744, 1428, 1407, 1228, 526 cm^{-1}; UV-vis (*n*-hexane) λ_{max} 208.8, 255.2, 323.2, 408.4, 420.8 nm; ^1H NMR [500 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 1.52 (t, J = 7.1 Hz, 3 H), 4.55 (q, J = 7.1 Hz, 2 H); ^{13}C NMR [125 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 14.62 (CH_3), 64.18 (CH_2), 80.82 (2 C), 139.89 (4 C), 140.94 (4 C), 142.07 (4 C), 142.09 (4 C), 142.62 (2 C), 143.00 (4 C), 143.04 (4 C), 143.60 (8 C), 143.84 (4 C), 144.31 (2 C), 144.38 (4 C), 144.62 (2 C), 144.69 (4 C), 144.97 (4 C), 145.05 (4 C), 155.67 (C=O).

5a: ^1H NMR (500 MHz, $CDCl_3$) δ 1.71 (t, J = 7.1 Hz, 3 H), 4.84 (q, J = 7.1 Hz, 2 H).

3a: FT-IR (KBr) 2919, 1734, 1508, 1438, 1397, 1293, 1242, 1096, 1036, 526 cm^{-1}; UV-vis (*n*-hexane) λ_{max} 209.6, 259.2, 328.8, 408.4 nm; ^1H NMR [500 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 1.47 (t, J = 7.1 Hz, 3 H), 4.50 (q, J = 7.1

Hz, 2 H); ^{13}C NMR (125 MHz, CS_2 with acetone-d_6 as external lock solvent) δ 15.20 (CH_3), 63.26 (CH_2), 134.91 (2 C), 136.43 (2 C), 137.50 (2 C), 137.84 (2 C), 138.64 (2 C), 138.71 (1 C), 139.37 (2 C), 139.48 (1 C), 139.96 (2 C), 141.62 (2 C), 141.97 (2 C), 142.95 (2 C), 143.06 (2 C), 143.13 (2 C), 143.35 (2 C), 143.39 (2 C), 143.61 (4 C), 143.79 (2 C), 144.14 (6 C), 144.32 (8 C), 144.40 (2 C), 144.58 (2 C), 144.68 (2 C), 145.01 (2 C), 147.62 (2 C), 153.91 (C=O).

Reaction of 1b with [60]Fullerene. Under Ar at reflux (147 °C) a purple solution of C_{60} (200 mg, 0.278 mmol) in 1,2-dichlorobenzene (100 mL) was treated with *tert*-butyl azidoformate (**1b**, 60 mg, 4.2 mmol, 1 M in 1,2-dichlorobenzene) dropwise over 30 s and stirred for an additional 10 min. The resultant reddish brown mixture was cooled to room temperature and then concentrated in vacuo. Column chromatography (1:9 hexanes/toluene) gave unreacted C_{60} followed by (gradient elution, 9:1 → 7:3 hexane/toluene) a pink solution of **2b** and a purple solution of **3b**. HPLC analysis indicated that both fractions contained residual C_{60}. Further purification of these fractions by column chromatography (1:9 hexanes/toluene) provided unreacted C_{60} followed by (gradient elution, 9:1 → 7:3 hexane/toluene) pure **2b** (19 mg, 8% yield) and **3b** (5.0 mg, 2% yield).

2b: FT-IR (KBr) 2918, 1740, 1367, 1246, 1146, 526 cm^{-1}; UV-vis (*n*-hexane) λ_{max} 210.0, 255.26 323.2, 408.2, 420.8 nm; ^1H NMR [500 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 1.69 (s, CH_3); ^{13}C NMR [125 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 28.00 (3 C, CH_3), 81.23, [1 C, $C(CH_3)_3$], 84.25 (2 C), 139.79 (4 C), 140.95 (4 C), 142.12 (4 C), 142.16 (4 C), 142.67 (2 C), 143.03 (8 C), 143.64 (4 C), 143.90 (2 C), 143.98 (4 C), 144.40 (8 C), 144.62 (2 C), 144.67 (4 C), 144.98 (4 C), 145.06 (4 C), 154.48 (C=O).

3b: FT-IR (KBr) 2918, 1734, 1230, 1153, 527 cm^{-1}; UV-vis (*n*-hexane) λ_{max} 209.6, 259.6, 328.4 nm; ^1H NMR [500 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 1.65 (s, CH_3); ^{13}C NMR [125 MHz, $CS_2/CDCl_3$, 1:1 (v/v)] δ 28.15 (3 C, CH_3), 83.15 [1 C, $C(CH_3)_3$], 134.67 (2 C), 136.14 (2 C), 137.25 (2 C), 137.52 (2 C), 138.39 (2 C), 138.46 (1 C), 139.11 (2 C), 139.22 (1 C), 139.68 (2 C), 141.34 (2 C), 141.76 (2 C), 142.67 (2 C), 142.78 (2 C), 142.85 (2 C), 143.08 (2 C), 143.12 (2 C), 143.34 (4 C), 143.51 (2 C), 143.85 (4 C), 143.87 (2 C), 143.95 (2 C), 144.05 (8 C), 144.14 (2 C), 144.32 (2 C), 144.41 (2 C), 144.71 (2 C), 147.36 (2 C), 153.65 (C=O).

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10. We have frequently encountered an impurity in commercial $CDCl_3$ which resonates at 29.6 ppm.
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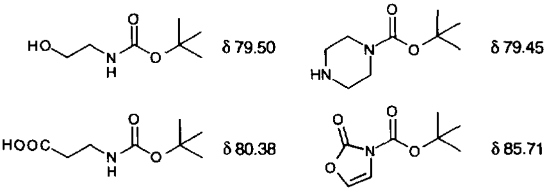

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