Reaction of [60]Fullerene with Diethyl Diazidomalonate: a Doubly Bridged Fulleroid

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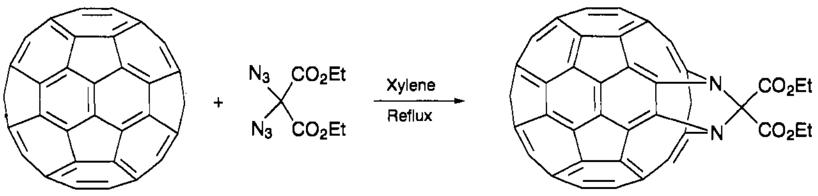
The reaction of [60]fullerene with diethyl diazidomalonate yields a 1 : 1 adduct with a doubly bridged fulleroid (homofullerene) structure **2**.

The discovery of fullerenes has engendered much excitement in the scientific community.[1] Fullerenes react with both electrophilic and nucleophilic reagents.[2–13]

Because the [60]fullerene molecule possesses a number of reactive sites, derivatization even with stoichiometric amounts of monofunctional reagents often leads to inseparable mixtures of diverse addition products (see ref. 6, for example). Because of this potential complexity, reactions of [60]fullerene with difunctional reagents have been little studied. We are aware of one report of the reaction of [60]fullerene with di-diazo compounds which provided bisfulleroids, equivalent to the addition of a mono-diazo compound to fullerene.[14] We report here the reaction of [60]fullerene with diethyl diazidomalonate **1** which gave in good yield a doubly bridged fulleroid **2**.

Compound **2** was obtained by refluxing a solution of [60]fullerene (54 mg, 0.075 mmol) and diethyl diazidomalonate **1** (25 mg, 0.10 mmol) in xylene (40 ml) for 24 h. The solution turned red. After evaporation of solvent, the residue was purified by flash column chromatography over silica gel, using cyclohexane–toluene (1 : 1) as eluent to give pure **2** in 65% yield (based on consumption of C_{60}) as an amorphous solid. HPLC analysis of **2** gave one single peak. Its FDMS exhibited a base peak at *m/z* 906 (M^+) in agreement with the expected molecular mass of **2**. Its ^{13}C NMR spectrum showed 32 peaks between δ 128 and 150 for the C_{60} moiety. In addition, there were six signals for the two carbethoxy groups at δ 164.15, 162.59, 64.71, 64.18, 14.16 and 13.97 (assignment confirmed by ^{13}C-DEPT experiment) and a signal at δ 95.38 for the $(N)_2C$ carbon atom. No resonance was found in the region 70–90 corresponding to fullerene aziridine, cyclopropane or epoxide indicative of the annulene structure of **2**. From the intensities of peaks for the C_{60} moiety, we assigned peaks at δ 144.27, 143.77, 138.41 and 128.61 each corresponding to one carbon atom, and the other 28 peaks each corresponding to two carbon atoms (Fig. 1). This suggests that compound **2** has only one plane of symmetry as far as the fullerene skeleton is concerned. On the other hand, the two carbethoxy groups are non-equivalent, from the ^{13}C and ^1H NMR spectra. The ^1H NMR of **2** showed two sets of ethoxy groups, one at δ 4.65 (q) and 1.52 (t), and the other at δ 4.55 (q) and 1.34 (t). The FTIR spectrum of **2** showed absorptions at



1 **2**

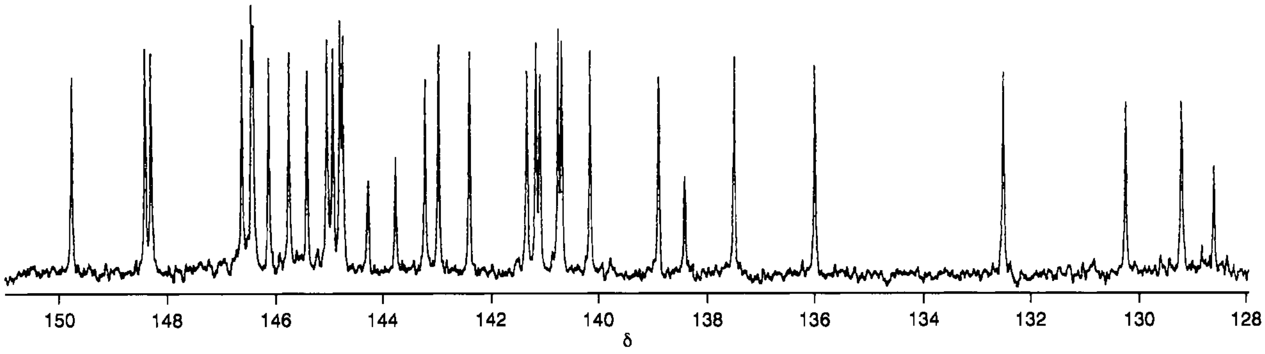
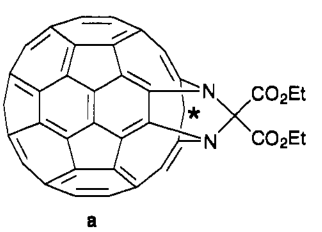
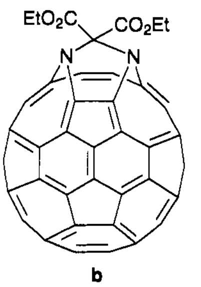


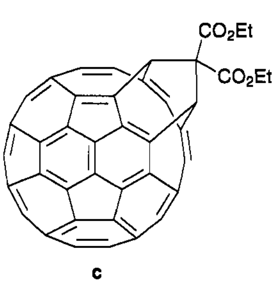
Fig. 1 Partial ^{13}C NMR spectrum of **2**



a



b



c

1755, 1121 and 1101 cm^{-1}. The UV–VIS spectrum of **2** exhibited three peaks at 229.5, 276.0 and 330.0 nm, and a shoulder at 430 nm. Compound **2** was found to be stable in air at room temperature for *ca.* four months judging from its ^{13}C NMR spectrum. It did not melt or decompose when heated to 320 °C.

Three structures **a**, **b** and **c** can be considered for compound **2**, corresponding to a double 5,6 insertion, a double 6,6 insertion and a 5,6/6,6 insertion, respectively. Structure **c** can be ruled out because the two carbethoxy groups in **c** are equivalent. While 6,6 insertion is known for carbene (or equivalent)[15] or oxygen[4] addition to [60]fullerene, addition of mono-azido compounds to [60]fullerene has been established firmly to be 5,6 insertion.[16] We, therefore, assign structure **a** to compound **2**. The preference of **a** over **b** is further supported by the very upfield location at δ 128.61 of one of the four on-axis carbons in the ^{13}C NMR of **2**. This peak is assigned to the carbon (marked by * in **a**) which is immediately adjacent to the inserted nitrogens.

Compound **2** represents a novel structure for fulleroid derivatives. Since the diaminoacetal moiety in **2** can be modified, the reaction can be considered as regioselective multifunctionalization of [60]fullerene.

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