Spontaneous oxidation of $C_{60}Ph_5X$ (X = H, Cl) to a benzo[*b*]furanyl[60]fullerene

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On exposure to air, both $C_{60}Ph_5H$ and $C_{60}Ph_5Cl$ spontaneously oxidise with elimination of the hydrogen or chlorine attached to the cage and the *ortho* hydrogen of the adjacent phenyl group, giving a benzo[*b*]furanyl[60]fullerene; a second oxygen is located in the pentagon that is surrounded by phenyl groups.

Various fused five-membered heterocyclic derivatives of fullerenes, each prepared by [3 + 2] cycloaddition reactions, have been described. The parent heterocyclic rings (or derivatives thereof) are pyrrole,[1] pyrazole,[2] triazole,[3] isoxazole,[4] oxazole,[5] isothiazole,[6] disilolane,[7] azirine[8] and furan;[9] a bis(fullerene) derivative of furan has also been described.[10] We now report the formation of a benzo[*b*]furan derivative (Fig. 1) *via* an entirely different route, involving spontaneous oxidation.

Pure $C_{60}Ph_5H$ was prepared as described previously.[11] A sample which had been in air for *ca.* one year was found to have changed colour from bright red to orange–brown. A minor component (*ca.* 10%), soluble only in acetone, contained C=O and OH groups (IR) but could not be identified further. Analysis of the remainder by HPLC (4.6 mm × 25 cm Cosmosil Buckyprep column, 1 : 1 toluene–hexane eluent at 0.25 ml min^{-1}) showed it to consist of two new compounds of 1060 and 1136 amu (respective retention times 46.8 and 35.8 min *cf.* 29.7 min for $C_{60}Ph_5H$). The 1060 amu species (*ca.* 30%) is unsymmetrical $C_{60}Ph_4O_2$, which fragments during EI mass spectrometry to $C_{60}Ph_n$ (n = 0–4) and $C_{58}Ph_n$ (n = 0–4) species, the latter arising from 2 × CO loss.[12] The structure of the 1136 amu species (*ca.* 60%) is described below, but it can also be produced by an alternative and more rapid route, involving easier purification. In this, a benzene solution of $C_{60}Ph_5Cl$ (87 mg) was exposed to sunlight for two weeks, whence all of the reagent was consumed. Chromatography (SiO_2, CCl_4) of a CCl_4 solution of the product gave a small quantity of orange material. Elution with toluene produced the orange–red 1136 amu species (R_f = 0.57, 30 mg, 34%, needles from CCl_4). An OH-containing product co-eluted with a small amount of this, and there was a considerable amount of unidentified residue on the column which was removed with CH_2Cl_2–MeOH (9 : 1).

The EI mass spectrum (Fig. 2) of the 1136 amu species showed reproducible fragmentation involving successive loss of 16 and 14 amu species. The 16 amu fragment is clearly oxygen; the 14 amu loss was shown by ^1H NMR analysis not to be due to a methylene species. There remained the possibility that in the structure two hydrogens had been replaced by an oxygen bridge either between two *ortho* positions of adjacent phenyl groups, or between one *ortho* position and the hydrogen on the cage (in the derivation from $C_{60}Ph_5H$). The latter conjecture was proven by the ^1H NMR spectrum (Fig. 3) with 2D-COSY analysis, and by ^{13}C NMR spectroscopy. (In the derivation from $C_{60}Ph_5Cl$, the second oxygen replaces one *ortho* hydrogen and the chlorine on the cage.)

The *ortho, meta* and *para* hydrogens of four of the phenyl rings (designated A, B, C, and D) are indicated on the spectrum (Fig. 3). The spread of resonances between the positions of the rings is greater, the more downfield the signal for the *ortho*-hydrogen as noted previously for phenylated fullerenes. There

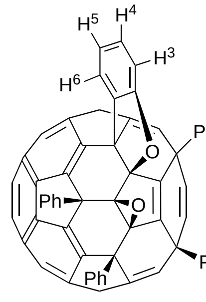

Fig. 1 The proposed structure of $C_{60}Ph_4C_6H_4O_2$; the second oxygen probably forms an epoxide across one bond of the central pentagon, thereby introducing the required asymmetry

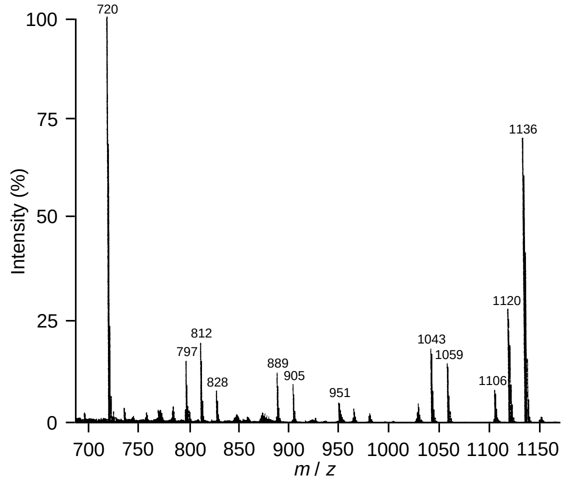

Fig. 2 EI mass spectrum (70 eV) for $C_{60}Ph_4C_6H_4O_2$

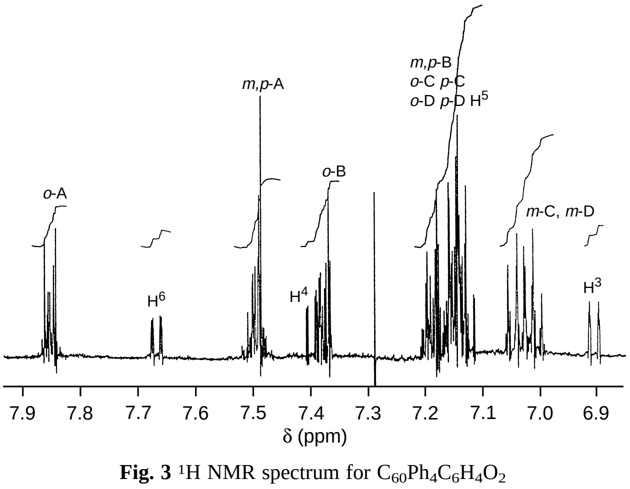

Fig. 3 ^1H NMR spectrum for $C_{60}Ph_4C_6H_4O_2$

are only four hydrogens present in the fifth ring and these appear at δ 7.66 (dd, J 7.5 and 1.3 Hz), 7.40 (dd, J 7.75 and 1.15 Hz), 7.12 (dd, J 7.40 and 1.0 Hz) and 6.90 (dt, J 8.12 and 0.8 Hz). These peaks are assigned (2D-COSY) to H^6, H^4, H^5 and H^3 respectively; the most downfield resonance is attributed to H^6, *cf.* the spectrum of 2-methylanisole.[13] Since the structure is unsymmetrical, it is probable that the remaining oxygen forms an epoxide across one of the double bonds in the pentagon at the epicentre of the phenyl groups, thereby reducing strain in this ring. One might *a priori* then expect to observe the attachment of a second oxygen across the remaining double bond in this pentagon, but this will be unfavourable due to p-orbital repulsions arising from the adjacent oxygens. This conjecture is not discounted by the indication that diepoxide formation occurs across the 1,2- and 3,4-positions of a six-membered ring (in an iridium derivative)[14] because here the greater ring size places the oxygens substantially further apart.

The 2D analysis shows that the 1,4 relationship of the four phenyl groups is D$\rightarrow$A$\rightarrow$C$\rightarrow$B, but the positions relative to the epoxide in the pentagonal ring of the cage are uncertain.

The proposed structure requires that eight resonances be observed in the sp^3 region of the ^{13}C NMR spectrum. These are found at δ_C 55.86, 55.87, 58.77, 58.80, 60.24, 74.98, 81.30,and 94.49 (all 1 C). The latter two resonances can be assigned to the epoxide carbons, since reported δ values for fullerene epoxides are δ 90.18 for $C_{60}O$,[15] and 85.78 (5,6-isomer) and 92.42, 90.99 (1,2-isomer) for $C_{70}O$;[16] the resonance at δ 74.98 probably refers to the other cage carbon that bears oxygen, and that at δ 60.24 to the carbon bearing the unique aryl group. The remaining four resonances occur as two pairs, consistent with the structure.

The structure requires 52 peaks in the sp^2 region and these are found (all 1 C except for indicated coincidences) at δ_C 152.81, 151.44, 150.86, 150.00, 148.94, 148.92, 148.89 (2 C), 148.86, 148.73, 148.68, 148.66, 148.59, 148.53, 148.45, 148.41, 148.33, 148.27, 147.97, 147.86 (3 C), 147.81, 147.80, 147.68, 147.67, 147.60, 147.58, 145.27, 144.83, 144.75, 144.66, 144.60, 144.47, 144.46, 144.44, 144.16, 144.13, 144.09, 144.03, 143.96, 143.90, 143.86, 143.77, 143.74, 143.69, 143.62, 143.44, 143.33, 143.29, 142.63, 142.42. It requires eight pairs of resonances of 2 C intensity due to the *ortho* and *meta* carbons of the four phenyl rings, and these (confirmed by proton decoupling) occur at δ_C 129.40, 129.08, 128.92, 128.51, 128.33, 128.22, 128.18 and 128.15. The fourteen remaining 1 C resonances for the other carbons of the aryl rings occur at δ_C 157.91 (*C*–O, *cf.* 159.8 for the *ipso* carbon in anisole[17]), 138.50, 138.36, 137.25, 136.73, 130.57, 128.46, 127.74, 127.71, 127.63, 125.84, 124.59, 122.47 and 110.76.

The mechanism involved in the reactions is unclear, but a rationale can be provided for the formation of the benzo[*b*]fullerene from $C_{60}Ph_5H$. The facile light-catalysed oxidation of hydrofullerenes to fullerenols[18] is a typical alkane oxidation to alkanol which proceeds *via* intermediate formation of a hydroperoxide followed by disproportionation with a second alkane molecule. For $C_{60}Ph_5H$, this disproportionation will be sterically hindered by the adjacent phenyl groups, whereas elimination of water between the hydroperoxide and the *ortho* hydrogen of the adjacent phenyl group is sterically favourable (and also reduces steric interactions between the phenyl groups). Consistent with this explanation is the fact that preformed $C_{60}Ph_5OH$ does not form the benzo[*b*]furan derivative on standing.[19] The epoxidation of one of the double bonds in the second pentagon is a typical fullerene reaction, which may here proceed *via* intermediate formation of an endoperoxide by a standard [2 + 4] cycloaddition involving singlet oxygen (readily produced by fullerenes) as dienophile.[20]

The mechanism for the formation of the same product from the chloro precursor is presently obscure, and we plan to investigate the effect of substituents in the aryl rings upon the reaction rate, in order to clarify the mechanism.

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Footnotes and References

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