PERKIN 2

Novel base-catalysed formation of benzo[*b*]furano[60]- and -[70]fullerenes

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Reaction of $C_{60}Cl_6$ with phenol in the presence of aq. KOH and under nitrogen, produces benzo[*b*]furano-[2′,3′ : 1,2][60]fullerene arising from substitution/elimination occurring across the 1,2-positions of the hexachloro precursor. Use of either 4-fluorophenol or 4-methoxyphenol produces the corresponding fluoro- and methoxy-substituted derivatives. Reaction with an excess of phenolic reagent results in nucleophilic replacement of some of the other chloro addends in the precursor by phenoxy groups, which may also participate in oxidative ring closure. $C_{70}Cl_{10}$ reacts with phenol in the presence of aq. KOH to give benzo[*b*]furano[2′,3′ : 7,8][70]fullerene. The corresponding reaction of aniline with $C_{60}Cl_6$ produces derivatives of benzo[*b*]pyrrolo[2′,3′ : 1,2][60]fullerene, but thiophenol does not react. Removal of eclipsing steric hindrance accounts for the ready ring-closure formation of the cycloadducts across bonds containing adjacent chlorines.

A number of fullerene derivatives having a heterocyclic five-membered ring fused to the cage have been prepared, usually by [3 + 2] cycloadditions; examples include aziridino-,[1] pyrrolidino-,[2] pyrrolo-,[3] pyrazolo-,[4] isoxazolo-,[5,6] isothiazolo-,[7] thiazolo-,[6] furano-,[8] and disilolano-[60]fullerenes;[9] dihydro-oxazolo[60]fullerene has been made by rearrangement of *N*-carboaroxyaziridino[60]fullerene.[10]

Recently, we described the formation *via* spontaneous oxidation, of a cage-phenylated benzo[*b*]furano[2′,3′ : 1,2][60]fullerene (produced as an epoxide).[11] We now report the formation of the parent benzo[*b*]furano[2′,3′ : 1,2][60]fullerene and its methoxy and fluoro derivatives, by the base-catalysed reaction between $C_{60}Cl_6$ and either phenol, 4-methoxyphenol or 4-fluorophenol, respectively, accompanied in some cases by substitution without concurrent elimination; a corresponding reaction occurs between phenol and $C_{70}Cl_{10}$. The nitrogen containing analogue, benzo[*b*]pyrrolo[2′,3′ : 1,2][60]fullerene (indolo[2′,3′ : 1,2][60]fullerene) is obtained in low yield if $C_{60}Cl_6$ is reacted with aniline instead of the phenols; thiophenol did not react.

Experimental

Reaction of $C_{60}Cl_6$ with phenol

Phenol (141.5 mg, 1.5 mmol) and KOH (101 mg, 1.8 mmol, 0.5 cm^3 H_2O) were added to a solution of $C_{60}Cl_6$ (46.5 mg, 0.05 mmol) in redistilled benzene (50 cm^3). The mixture was heated under nitrogen to reflux during 4 h, whence the solution colour changed from orange to deep brown. The reaction mixture was cooled to room temperature, washed with water (3 × 50 cm^3), and the deep brown organic layer separated and dried (anhydrous $MgSO_4$). Reaction failed to occur in the absence of water.

The solvent was removed under reduced pressure, the residue washed with pentane, and the remaining brown solid redissolved in cyclohexane and passed through a silica gel chromatography column. Elution with cyclohexane yielded [60]fullerene (9.0 mg), and then with toluene which gave a light brown eluent. This was purified by HPLC using a 250 mm × 4.5 mm Cosmosil Buckyprep column, operated at 1 ml min^{-1} (1 : 1 hexane–toluene eluent). Three peaks eluted at 19.1 (major component), 15.9, and 11.1 min (**1a**–**c**), and were further purified by recycling to give the traces shown in Fig. 1; the approximate yields were 23, 6 and 3% respectively. The EI mass spectra of these components (Fig. 2) show increments of 92 amu; the components with the greater number of addends have a shorter retention time, as is customarily obtained with a Cosmosil column.

Fig. 1a–c HPLC traces for **1a**–**c**, obtained from reaction of $C_{60}Cl_6$ with phenol.

IR for **1a** (KBr): ν/cm^{-1} 1570, 1523, 1475, 1459, 1377, 1247, 1188, 1109, 987, 947, 932, 907, 767, 744, 620, 577.

UV–Vis (CH_2Cl_2): λ/nm 206.3, 227.9, 241.0, 250.2, 279.8,

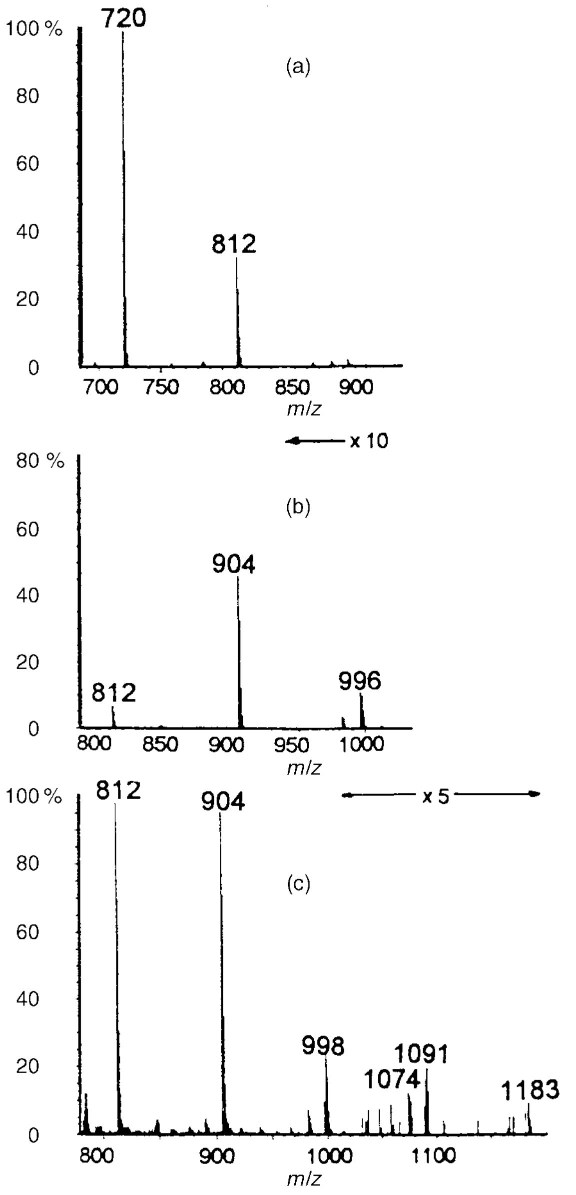


Fig. 2a–c EI mass spectra (70 eV) for **1a–c**.

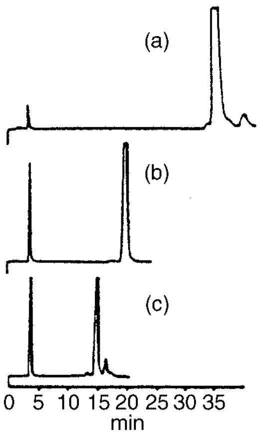


Fig. 3a–c HPLC traces for **2a–c**, obtained from reaction of $C_{60}Cl_6$ with 4-fluorophenol.

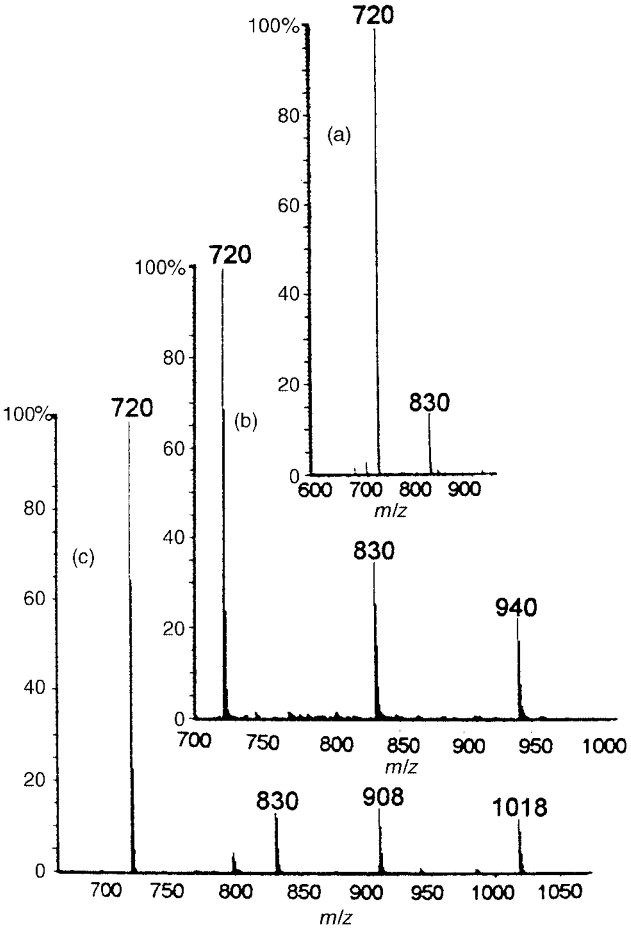


Fig. 4a–c EI mass spectra (70 eV) for **2a–c**.

287.1, 317.5 (main), 325.8 (sh); other minor shoulders were present.

The NMR spectra are described in the Discussion.

Reaction of $C_{60}Cl_6$ with 4-fluorophenol

Using the above procedure also gave three products (**2a–c**) in respective yields of 10, 27, and 5%, having HPLC retention times of 35.6, 19.0 and 14.6 min, respectively (Fig. 3). The corresponding mass spectra (Fig. 4) show 110 amu increments, the components with the greater number of addends again having the shorter retention time.

Reaction of $C_{60}Cl_6$ with 4-methoxyphenol

Use of the above procedure gave two main products **3a** and **3b**, with respective HPLC retention times of 21.9 and 19.4 min; the corresponding EI mass spectra (Fig. 5a,b) show increments of 122 amu.

Reaction of $C_{60}Cl_6$ with aniline

Despite the greater nucleophilicity of nitrogen compared to oxygen, the corresponding reaction with aniline occurred less readily, but produced ring-closed derivatives in the same way. A number of products having retention times of 15.2, 13.8, 12.2 and 10.3 min (**4a**,**b**,**c**,**d**) were isolated by HPLC. The mass spectra of **4a** and **4b** are shown in Fig. 6a and 6b, respectively, and exhibit 91 amu increments. The mass spectra of **4c** and **4d** (not shown) exhibited similar features with peaks at 811 and 902 amu being prominent.

Reaction of $C_{70}Cl_{10}$ with phenol

Since [70]fullerene is less electrophilic than [60]fullerene, reactions with nucleophiles are generally slower, hence the reaction of $C_{70}Cl_{10}$ with phenol–aq. KOH under nitrogen was slower than the corresponding reaction with $C_{60}Cl_6$. HPLC of the product gave a peak of 39 min retention time (compound **5**), the mass spectrum of which (Fig. 7) indicates the addition of one and possibly two moieties of 92 amu (*cf.* **1b**,**c**).

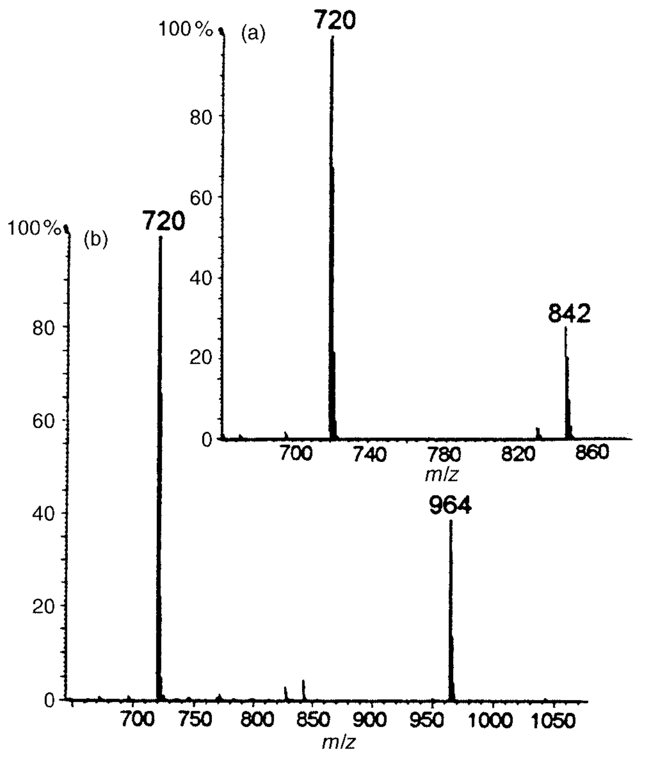


Fig. 5a,b EI mass spectra (70 eV) for **3a,b**, obtained from reaction of $C_{60}Cl_6$ with anisole.

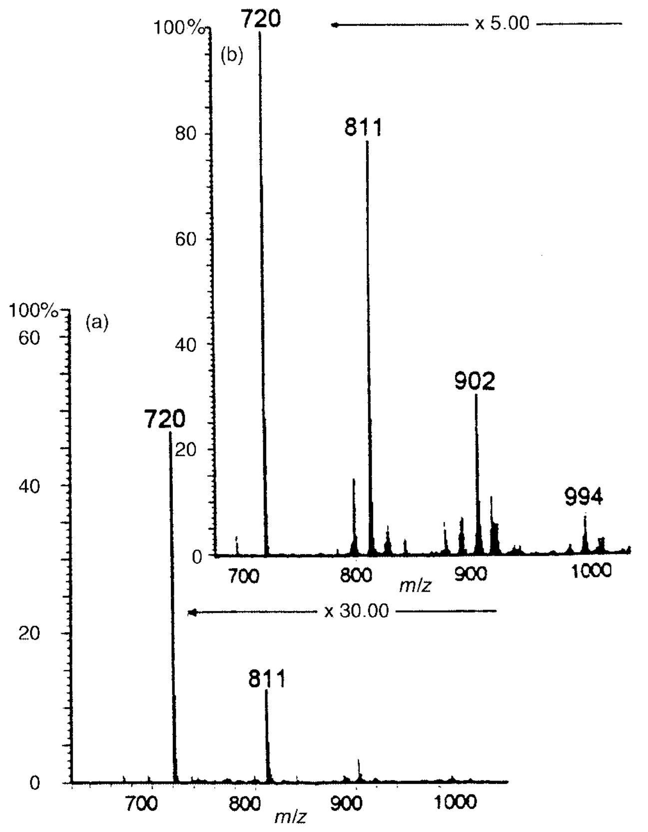


Fig. 6a,b EI mass spectra (70 eV) for **4a,b**, obtained from reaction of $C_{60}Cl_6$ with aniline.

Discussion

A feature of these results is that the mass spectra are in some cases misleading. EI mass spectra cannot normally be obtained for alkoxyfullerenes because fragmentation occurs to give the parent fullerene. Fullerenols behave similarly. Fragmentation also occurs with some of the compounds described here, but an accompanying reaction involves elimination within the mass spectrometer giving cyclisation. Cyclisation to give similar cycloaddends, prior to mass spectrometric analysis, also occurs where elimination of H and Cl is possible, as described below.

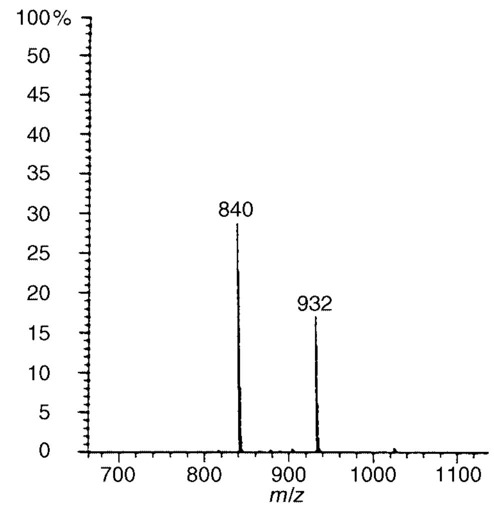


Fig. 7 EI mass spectrum (70 eV) for **5**, obtained from reaction of $C_{70}Cl_{10}$ with phenol.

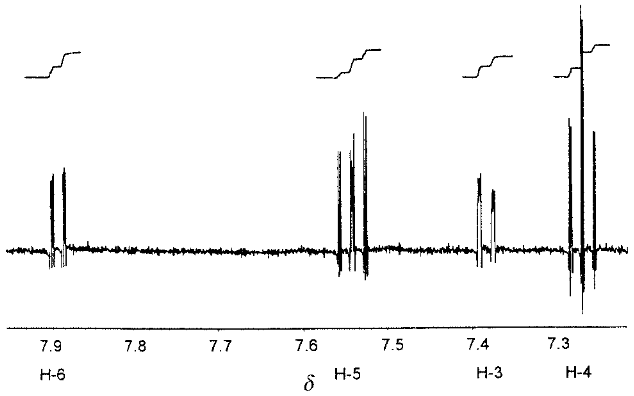
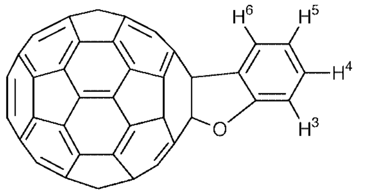
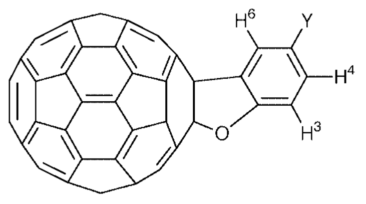


Fig. 8 ^{1}H NMR spectrum for **1a**, $C_{60}C_6H_4O$.



A

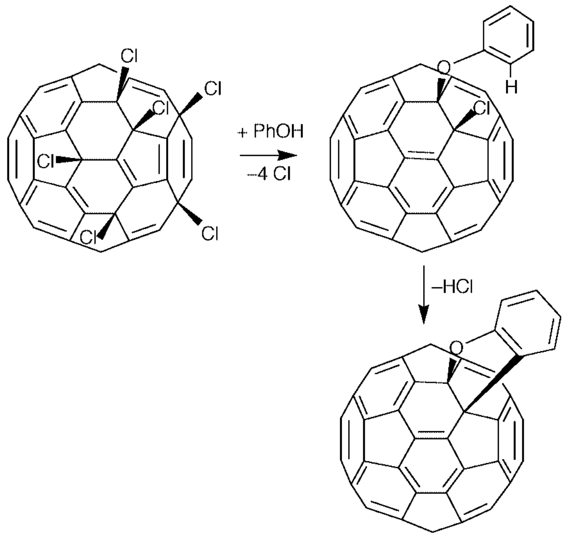


B (Y = F, OMe)

Compounds 1a–c

The mass spectrum for **1a** (Fig. 2a) shows that C_6H_4O (92 amu) has added to the cage, a result which is consistent only with structure **A**. The presence of four aryl hydrogens was confirmed by the ^{1}H NMR spectrum (Fig. 8, CS–acetone-d_6), the resonances being assigned as follows: δ 7.89 (dd, J 7.5, 1.4 and 0.5 Hz, H-6); 7.54 (dt, J 8.15 and 1.4 Hz, H-5); 7.38 (dd, J 8.45, 1.0 and 0.5 Hz, H-3); 7.27 (dt, J 7.5 and 1.05 Hz, H-4). The adjacency of H-6 and H-5 was determined by decoupling. The most downfield resonance is attributed to H-6 since it points towards the cage, such adjacency having been shown previously to produce a downfield shift of the C-*H* resonance.[12] The ^{13}C NMR spectrum [CS_2/acetone-d_6] of **1a** consists of two lines at δ 59.55 and 102.72 due to the sp^3-hybridised cage carbons and 29 lines due to the sp^2-hybridised cage carbons (one 1 C line could not be clearly distinguished from the base line) showing the molecule to be C_s-symmetric. They appear (all 2 C except where indicated) at δ 150.72, 147.37 (1 C), 146.29, 146.21, 146.15, 146.04, 145.93, 145.51, 145.49, 145.28, 145.18, 145.17, 145.05, 145.01, 144.44, 144.37, 142.93, 142.74, 142.73, 142.69, 142.33, 142.29, 142.15, 141.81, 141.80, 140.82, 139.81, 137.44, 135.75. The six aryl-carbon lines are at δ 157.55 (*ipso* to O, *cf.* 159.8 for the *ipso* carbon in anisole[13]), 130.93, 126.27, 125.73, 122.73, and 112.20.

The method of formation of **1a** is believed to involve initial nucleophilic substitution of chlorine by phenoxy at C-1, resulting in close proximity between the *ortho* hydrogen of the phenyl ring and the chlorine at C-2. This facilitates elimination of HCl between the chlorine and the *ortho* hydrogen of the phenyloxy ring (Scheme 1). Concurrently or consecutively, the other four chlorines (1,4 to each other) are eliminated, a process favoured by removal of both double bonds from the central pentagonal ring.



Scheme 1 Conjectured mechanism leading to the formation of benzo-[*b*]furano[2′,3′:1,2][60]fullerene (**1a**) from phenol and $C_{60}Cl_6$; this substitution/elimination is accompanied by loss of the other four chlorines.

The yields of **1b** and **1c** were too small to allow for structural assignment by NMR spectroscopy. The mass spectrum of **1b** indicates the presence of a second cycloaddend of 92 amu. [This could conceivably arise only through elimination of HCl from chlorine and the *ortho*-hydrogen of phenoxy (either the C-4/15 or C-11/30 pair) situated *para* across a hexagonal ring.] We believe however (and this is supported by the data for the fluoro derivative described below), that elimination occurs during mass spectrometry, so that **1b** has actually two phenoxy groups (93 amu) attached at two of the sites originally occupied by chlorines, the other pair of chlorines having been eliminated. This would require a species of 998 amu and the small peak observed at 996 amu supports the conjecture that three addends are actually present. For **1c**, four phenoxy groups should be present, giving five addends overall, and the mass spectrum provides support for this, as well as confirming the presence of the 998 amu species.

Compounds 2a–c

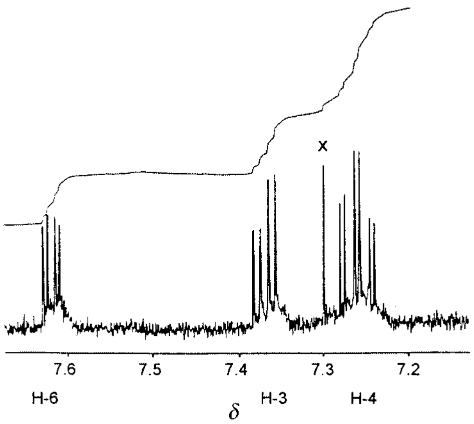


Fig. 9 ^1H NMR spectrum for **2a**, $C_{60}C_6H_3FO$.

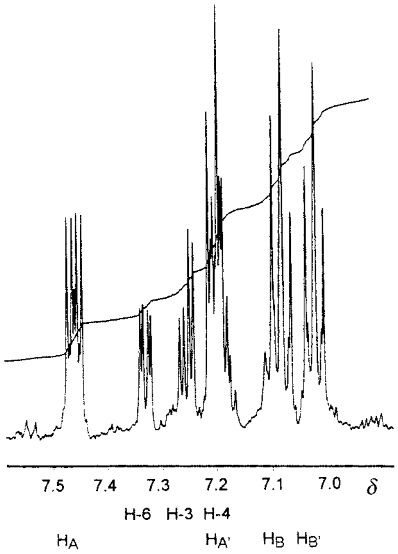


Fig. 10 ^1H NMR spectrum for **2b**, $(4\text{-}FC_6H_4O)_2C_{60}C_6H_3FO$.

The mass spectrum for **2a** (Fig. 4) shows that FC_6H_3O (110 amu) has added to the cage, consistent with structure **B** (Y = F). The ^1H NMR spectrum [CS–acetone-d_6] (Fig. 9) showed three resonances, assigned as follows: δ 7.62 (dd, *J* 7.51 and 2.1 Hz, H-6); 7.37 (dd, *J* 8.7 and 4.1 Hz, H-3); 7.26 (dt, *J* 8.7 and 2.1 Hz, H-4). Although there was insufficient material for obtaining a ^{13}C NMR spectrum, it is reasonable to assume that the structure has C_s symmetry as does the phenoxy mono-adduct. The ^{19}F NMR spectrum consists of a single peak at δ_F −119.15 ppm.

The mass spectrum for **2b** suggests that this product has just two cycloaddends on the cage, but this is incorrect as was proved in three ways. First, the ^1H NMR spectrum (Fig. 10) shows that there are two kinds of addends on the cage. One is a cycloaddend as in the case of **2a**, and gives rise to three sets of peaks in a 1 : 1 : 1 ratio, corresponding to those seen in Fig. 9 at δ 7.33 (1 H, dd, *J* 2.5 and 7.3 Hz, H-6), 7.255 (1 H, dd, 8.7 and 4.1 Hz, H-3), *ca.* 7.20 (1 H, unresolved due to peak coincidences, H-4). (The peaks are less downfield than those for **2a** because of the greater number of sp^3 carbons on the cage, these being less electron withdrawing than the sp^2 carbons which they replace.) The other type of addend gives rise to two sets of peaks at δ 7.46 (2 H, dd, *J* 8.9 and 4.6 Hz), *ca.* 7.18 (2 H, unresolved due to peak coincidences), 7.08 (2 H, t, *J*, 8.5 Hz), 7.02 (2 H, t, *J* 8.5 Hz). These are each in a 2 : 1 ratio relative to those in the cycloaddend and are thus due to two non-identical 4-fluorophenoxy groups attached to the cage. Given that fluorine is more electronegative than oxygen, the peak pairs (themselves identified by nOe) are assigned as shown in Fig. 10, revealed by the coupling of the H_A peaks to fluorine, confirmed also by the ^{19}F coupling constants in the

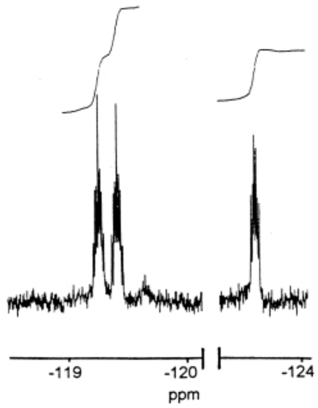


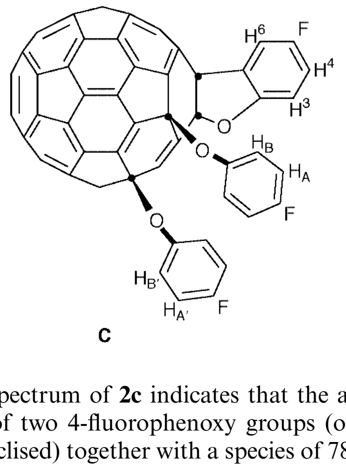
Fig. 11 ^{19}F NMR spectrum for **2b**, $(4\text{-}FC_6H_4O)_2C_{60}C_6H_3FO$.

^{19}F NMR spectrum (Fig. 11); possible sites of attachment are considered below.

The ^{13}C NMR spectrum shows four lines in the sp^3 region, at δ_C 110.64, 81.89, 79.27 and 65.24, due to the location sites (two) of the cycloaddend and one each of the 4-fluorophenoxy groups. The structure requires 56 lines in the sp^2 region, and 55 are identifiable (six lines are coincident) at δ_C (all 1 C except where indicated): 150.90, 150.85, 150.63, 150.29, 149.86, 149.84, 149.59, 149.42, 148.88, 148.68, 148.58, 148.14, 147.86, 147.37 (2 C), 147.23, 146.94, 146.92, 146.40, 146.26, 146.17, 146.12 (2 C), 145.57, 145.48, 145.42 (2 C), 145.33, 145.00, 144.98, 144.85, 144.77, 144.74, 144.71 (2 C), 144.49, 144.38, 144.08, 144.02, 143.76 (2 C), 143.68, 143.42, 142.97, 142.44, 142.21 (2 C), 141.10, 139.87, 139.02, 138.89, 138.43, 137.35, 134.83, 134.76.

The ^{19}F NMR spectrum (Fig. 11) shows three lines in a 1 : 1 : 1 ratio at δ_F −119.25, −119.41 (both symmetrical multiplets, J 4.6 Hz) and −123.61 (unsymmetrical multiplet). The former pair are thus due to the 4-fluorophenoxy addends, and the latter to the cycloaddend.

The two 4-fluorophenoxy addends may reasonably be assumed to be attached to either of the 4- and 15-carbons or at the 4- and 30-carbons (sites occupied originally by chlorine). (The mirror image equivalents involve attachment to the 11- and 30-carbons and the 11- and 15-carbons, respectively.) They cannot be attached at either of the 4/11- or 15/30-carbon pairs since in each case they would show just a single addend in the NMR spectra, due to the resultant C_s symmetry of the molecule. One of the two possible structural isomers, having the 4-fluorophenoxy groups attached to the 4- and 15- (or 11- and 30-)carbons (the cycloaddend spans the 1,2-bond), is shown in **C**.



C

The mass spectrum of **2c** indicates that the addends on the cage consist of two 4-fluorophenoxy groups (one or more of which have cyclised) together with a species of 78 amu, presumably Ph and H. The reaction is carried out in benzene as solvent, and it appears that *despite the absence of any Lewis acid catalyst*, cage-Cl bond polarisation is sufficient to provide a strongly electrophilic species, resulting in concurrent electrophilic substitution into benzene.

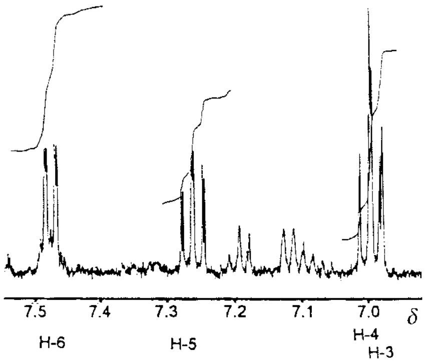


Fig. 12 ^{1}H NMR spectrum for **5**, $C_{70}C_6H_4O$.

Compounds 3a,b

Compound **3a** is evidently the cycloaddend derivative **B** (Y = OMe). Compound **3b** appears from the mass spectrum to have two such cycloaddends, but in view of the result obtained with the corresponding fluorophenol, it is likely that ring closure occurs during mass spectrometry. Insufficient material was available for more detailed analysis. Crude material showed the presence of up to five ring-closed addends (842, 964, 1086, 1208 and 1330 amu), and therefore it seems likely that oxidative ring closure again occurs during mass spectrometry.

Compound 4a–d

Although the mass spectrum of **4a** (Fig. 6a) indicates that it contains mainly a single ring-closed addend (811 amu), the ^{1}H NMR spectrum shows that additional C_6H_4NH groups are attached to the cage. The mass spectra of either of **4b**,**c**,**d** show the presence of two or more ring-closed addends (*e.g.* Fig. 6b) and it is likely that other C_6H_4NH groups are present, but insufficient materials were available to obtain a ^{1}H NMR spectrum.

Compound 5

The ^{1}H NMR spectrum (CS–acetone-d_6) of **5**, the derivative made from decachloro[70]fullerene[14] and phenol, is shown in Fig. 12, the four aryl hydrogen assignments being: δ 7.48 (dd, J 7.4 and 1.4 Hz, H-6); 7.26 (dt, J 7.5 and 1.4 Hz, H-5); 7.00 (dt, J 7.5 and 1.1 Hz, H-4); 6.98 (dd, J 7.5 and *ca.* 1.3 Hz, H-3). The upfield positions of the resonances relative to those of the corresponding [60][fullerene derivative (Fig. 8) are significant. First, this is consistent with the less electron-withdrawing nature of [70]fullerene, and we have noted similar results, for example, in hydrogenation[15] and cycloaddition.[16] Secondly the shift differences for H-6 and H-3, which are closest to the cages, are greater (*ca.* 0.41 ppm) compared to those for H-5 and H-4 (*ca.* 0.27 ppm) which are further away and thus less affected by differences in the electron-withdrawing properties of the cages.

We may reasonably assume that cycloaddition takes place across the 7,8-bond which has adjacent chlorine addends (for numbering see ref. 17). Concurrently with this, the other eight chlorines are eliminated in the manner found with hexachloro[60]fullerene. (The ^{1}H NMR spectrum indicates that the cycloadduct may be associated with a small amount of material arising presumably, in the first step, from nucleophilic substitution of one or two of the chlorines by phenoxy groups.)

Mechanism of the reaction

Notable features of the results are as follows:

(a) The ease of reaction (as judged by the rapidity of the colour change of the $C_{60}Cl_6$ solution during heating) was as follows: $C_6H_5NH_2 > 4\text{-}MeOC_6H_4OH > 4\text{-}FC_6H_4OH > C_6H_5\text{-}OH$, consistent with nucleophilicity of these reagents being an important factor in the mechanism.

(b) No reaction occurs in the absence of a trace of water, attributable to the need to convert the phenols into the more nucleophilic phenoxides, and which requires the KOH to be in solution.

(c) Cycloaddition occurs across the bond possessing a pair of adjacent chlorines, and the driving force for this reaction is removal of the eclipsing interactions between them. The *ortho* hydrogen of the aryloxy group and the chlorine on the ring in the intermediate following the initial addition are in close proximity, which further promotes the subsequent elimination of HCl.

(d) More than one aryloxy group becomes attached to the cage, and these groups also readily convert during mass spectrometry, into a cycloaddend through loss of a hydrogen, the above proximity effect being pertinent here also.

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