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Electrophilic substitution of $C_{60}F_{18}$ into phenols: HF elimination between OH and a 1,3-shifted fluorine giving benzofurano[2′,3′:10,26]hexadecafluoro[60]fullerene and derivatives

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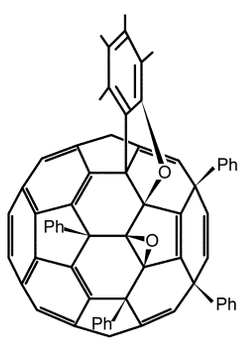
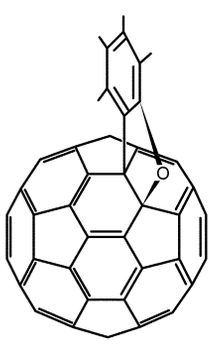
The reaction of $C_{60}F_{18}$ with phenol, 2-naphthol and quinol in the presence of ferric chloride leads to initial electrophilic substitution (aryldefluorination). This occurs at both *ortho* and *para* positions for phenol, at the *ortho* position for quinol, and at the relatively hindered but most reactive 1-position for 2-naphthol. It is followed, where sterically favourable, by HF loss either between the OH group and F (rendered adjacent as a result of a 1,3-shift) or to attack of the OH group at an adjacent double bond with loss of a β-fluorine, giving benzofurano[2′,3′:10,26]-hexadecafluoro[60]fullerene derivatives. The reaction is accompanied by some complete defluorination leading, in reaction with phenol and with 2-naphthol, to the formation of benzofurano[2′,3′:1,2][60]fullerene and naphtho[2,1:*b*]furano[*d*:1,2][60]-fullerene, respectively. The mechanism of base-catalysed reaction of phenols with $C_{60}Cl_6$ is re-evaluated.

Introduction

The electrophilicity of fullerenes is enhanced by halogenation, which increases along the series *X*full for *X* = Br < Cl < F, and their use in a number of arylations have been reported. The use of bromofullerenes is restricted by their insolubility, but some limited studies have been made using mixtures of bromine, aromatic, and ferric chloride, the bromofullerene being generated *in situ*.[1] The chlorofullerenes $C_{60}Cl_6$[2–5] and $C_{70}Cl_{10}$[6] have been used much more extensively for $FeCl_3$-catalysed arylation, whilst $C_{60}F_{18}$ has been used to make triaryl derivatives ('triumphenes') through catalysis by both $FeCl_3$ and $SbCl_5$.[7] Notable in connection with the present work has been the spontaneous oxidative conversion of $C_{60}Ph_5H$ to an epoxy tetraphenylated derivative of benzo[*b*]furano[2′,3′:1,2][60]-fullerene (**1**),[3] and the conversion of $C_{60}Cl_6$ into the parent benzofuranofullerene (**2**) and aryl derivatives by reaction with phenols in the presence of a base.[4] Formation of these derivatives was accompanied by both the complete loss of all of the chlorines, and the isolation of three products containing either one, two, or three benzofuran moieties. We consider further the mechanism of the formation of these derivatives in the light of the present results.



(**1**)



(**2**)

Experimental

The fluorofullerene $C_{60}F_{18}$ was prepared in 5.5% yield by fluorinating [60]fullerene with a mixture of MnF_3 and K_2NiF_6 at 480 °C (1 : 5.5 : 2.25 weight ratio), followed by purification by HPLC (high pressure liquid chromatography) using a 20 mm and 250 mm Cosmosil Buckyprep column with elution by toluene at a flow rate of 18 ml min^{-1}. Derivatives were prepared by evaporation (rotovap) of a toluene solution of $C_{60}F_{18}$ (3 mg) with the phenol (6 mg, xs) and $FeCl_3$ (20 mg, xs) to dryness during 30 min. The deep brown solutions were re-dissolved in toluene filtered and then separated by HPLC using a 20 mm and 250 mm Cosmosil 5 PYE column with toluene elution at 4 ml min^{-1}. Mass spectra (EI) were run at 70 eV, ^{1}H NMR and 19F NMR spectra were run at 500 and 376 MHz, respectively.

Results and discussion

Reaction with phenol

Fractions were separated with the following retention times:

12.8 min. The mass spectrum showed an 812 amu parent ion, due to benzo[*b*]furano[2′,3′:1,2][60]fullerene (**2**). It was identical to that found in the base-catalysed reaction of phenols with $C_{60}Cl_6$, and as in that work, the reaction has been accompanied by loss of all of the halogens;[4] halogen loss from either $C_{60}Cl_6$, $C_{60}Br_6$, or $C_{60}Br_8$ in the presence of tetrathiafulvalene has also been reported.[8]

14.1 min. The mass spectrum (Fig. 1) shows a parent ion at 1116 amu ($C_{60}F_{16}C_6H_4O$), with regular 2 F loss down to 812 amu. This is the hexadecafluoro derivative of benzo[*b*]-furano[2′,3′:1,2][60]fullerene (**3**), showing the two fluorine atoms have been lost from the original $C_{60}F_{18}$. The characterising evidence for the structure is as follows:

^{1}H NMR spectrum. This comprised multiplets (all 1 H) at δ 7.198, 7.296, 7.533 and 7.545, assigned by 2 D NMR and decoupling experiments *either* to H^6, H^5, H^4, and H^3, respectively (as in **3a**) or the inverse order. These cannot be distinguished because the electron withdrawal by the cage and by

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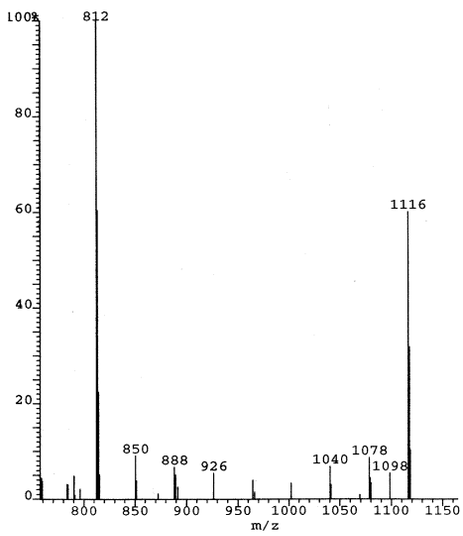


Fig. 1 EI mass spectrum (70 eV) for benzo[*b*]furano[2′,3′:10,26]hexadecafluoro[60]fullerene.

oxygen are similar, but the spectrum confirms that four hydrogens only are present in the aryl ring and that these are contiguous with each other.

^{19}F NMR spectrum. The 1 D spectrum (Fig. 2a) shows 16 lines of equal intensity at δ_F (all 1 F) −131.86 (d, *J* 22 Hz), −132.17 (d, *J* 20 Hz), −132.73 (m, *J* 7 Hz), −132.90 (m), −133.61 (m, *J* 7 Hz), −137.73 (br m), −138.36 (t, *J* 15 Hz), −138.52 (br m), −140.44 (dd, *J* 3 and 15 Hz), −140.99, (dd, *J* 6 and 27 Hz), −142.17 (dm, *J* 4 and 27 Hz), −142.43 (dm *J* 5 and 26 Hz), −142.65 (dm, *J* 5 and 28 Hz), −153.14 (m), −155.68 (m), −160.47 (m). The 2 D spectrum (not shown) reveals the following couplings: 16–2,4,5 (all 1,2); 14–1,3,8 (all 1,2); 13–11 (1,2); 12–10 (1,2); 10–6 (1,3); 9–7 (1,3); 8–5 (1,4-conj.); 8–3 (1,3); 7–6 (1,3); 6–5 and 6–3 (v. weak, *meta* across ring); 5–4 (1,3); 4–2 (1,3) 3–1 (1,3).

The spectra of $C_{60}F_{18}$ and derivatives invariably show, grouped close together in the −(157–170 ppm) region, three upfield multiplets that are strongly coupled to the three adjacent fluorines, one of which (the ones on the periphery) in each case appears well downfield in the −(128–134 ppm) region. The normal upfield position of these multiplets is due not only to the adjacency of the sp^3 carbons, but also to electron release from the lone pairs of the adjacent fluorines.[9]

Of the remaining twelve fluorines, the six equivalent ones that are furthest away from the central benzenoid ring invariably appear in the −(141–151 ppm) region, whilst the six equivalent ones adjacent to this ring appear in the −(136–138 ppm) region. The pattern in the present case is very different:

(i) The three upfield peaks are no longer grouped together. No. 14 (see Fig. 2a) is well downfield relative to the customary position, showing that the normal motif for $C_{60}F_{18}$ has evidently been disrupted, and on the side of the structure (see structure 3a, Fig. 2) containing peak no. 14.

(ii) Peak 15 is no longer a complex multiplet showing that it has lost an adjacent fluorine, and this results also in a downfield shift of the peak. The replacing substituent must be an aryl group, known to produce downfield shifts.[7]

(iii) There are only five peaks in the −(141–151 ppm) region, instead of six, so one fluorine has been lost from this region

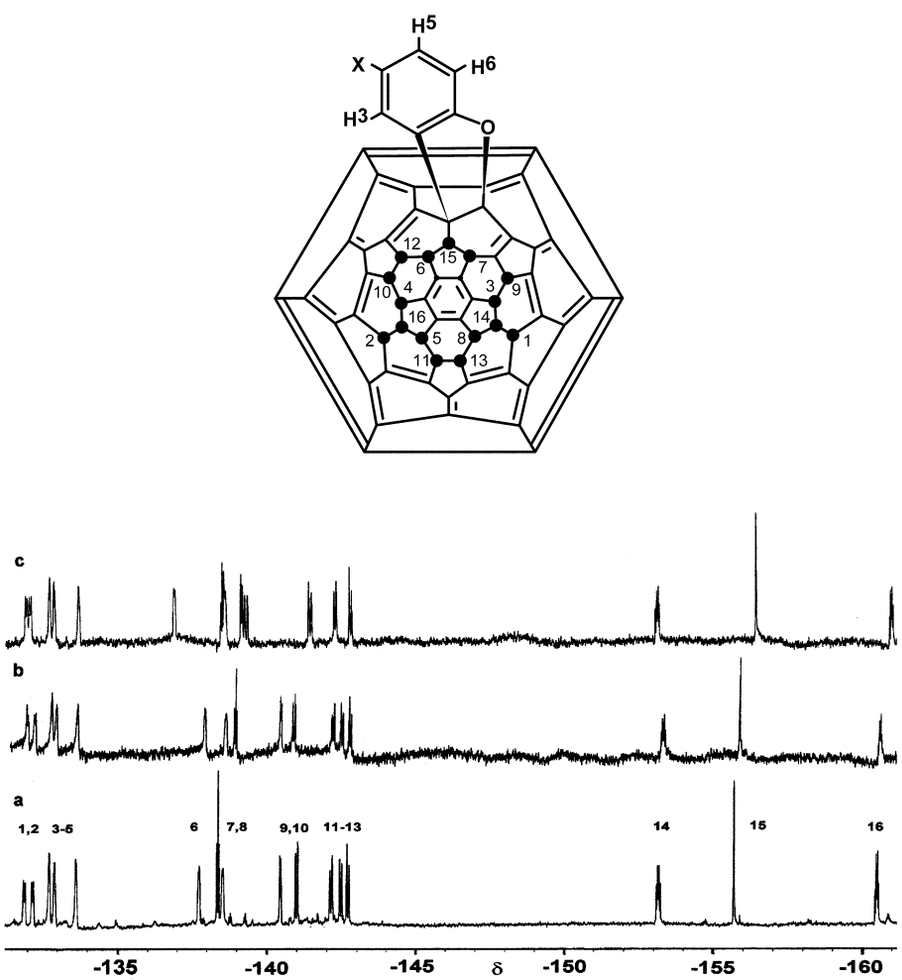
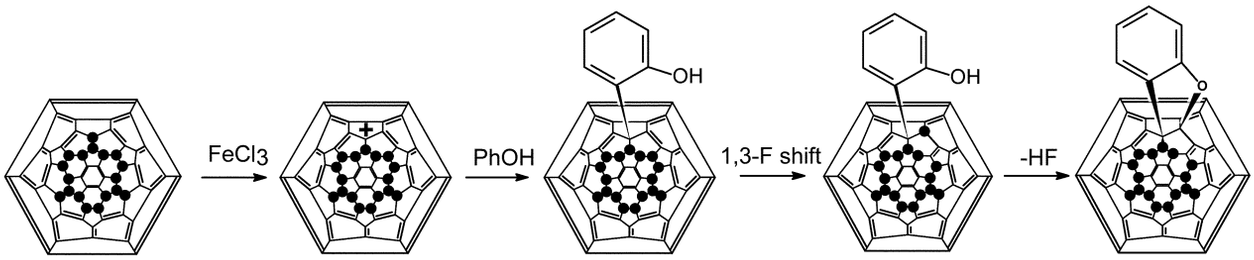


Fig. 2 ^{19}F NMR spectra of the benzofurano derivatives from reaction of (a) phenol, (b) quinol, and (c) 2-naphthol with $C_{60}F_{18}$. (**3a**,**b** X = H[4], OH; ● = F, where numbering identifies the peaks for **3a** in the ^{19}F NMR spectrum, Fig. 2a).



Scheme 1 Conjectured mechanism for $FeCl_3$-catalysed formation of **3a** (for an alternative see text).

making a total of two altogether. These conclusions together with the observed couplings allows structure **3a** to be deduced, and its mechanism of formation. Following the well-established Lewis acid-catalysed loss of one of the outer fluorines,[7] the resultant cation substitutes into either the *para* or *ortho* positions of phenol, both being very reactive towards electrophilic substitution. The steric hindrance resulting from the latter substitution can be relieved by ring-closing loss of HF. However, this cannot involve fluorine no. 15 because the resultant benzofuran moiety would be sandwiched between fluorines 6 and 7, which is sterically unfeasible. A suitable fluorine can only become available through a 1,3-shift, (a process having recently been unambiguously characterised in a $C_{60}F_{36}$ isomer)[10] and then HF is eliminated (Scheme 1), giving a product having no symmetry plane. An alternative (which cannot be distinguished) is that the OH group attacks the adjacent double bond and following electron pair migration, the β-fluorine is displaced. Either mechanism differs from that which applies to the base-catalysed reaction involving $C_{60}Cl_6$ (see Introduction) where the initial attack is by the phenoxide ion.

20 min. This gave a parent ion of 1194 amu in the mass spectrum, consistent with a derivative formed between $C_{60}F_{16}$, a Ph and a C_6H_4OH group (1024 + 77 + 93 amu). No further details of structure or formation mode could be deduced.

24 min. The parent ion of 1136 amu in the mass spectrum, is consistent with substitution of the intermediate cation into the *para* position of phenol, giving **4**, which is sterically unable to eliminate HF.

Reaction with hydroquinone

HPLC separation gave only one main peak of 16.3 min retention time. The mass spectrum (Fig. 3) showed a parent ion at 1132 amu, consistent with 4-hydroxybenzo[*b*]furano-[2′,3′:10,26]hexadecafluoro[60]fullerene, structure **3b**.

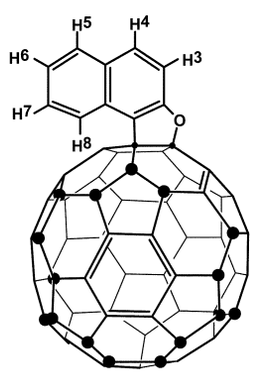
^{1}H NMR spectrum. This gave peaks at δ 7.066 (1 H, d, *J* 17 Hz, H^1), 7.05 (1 H, dd, *J* 17 and 5.5 Hz, H^2), 6.98 (1 H, m, H^4), the multiplicity of the latter peak arising from long-range coupling with the neighbouring fluorine no. 6. The resonance for the OH peak on the aryl ring, identified by spin saturation with water, appeared at δ 4.97. The data are fully consistent with structure **3b**.

^{19}F NMR spectrum. The 1 D spectrum (Fig. 2b) shows 16 lines of equal intensity at δ_F (all 1 F) −132.05 (d, *J* 21 Hz), −132.31 (d, *J* 20 Hz), −132.86 (m, *J* 7 Hz), −133.02 (m), −133.73 (m, *J* 7 Hz), −137.98 (m), −138.68 (m), −139.00 (t, *J* 16 Hz), −140.50 (d, *J* 16 Hz), −140.94, (dd, *J* 6 and 27 Hz), −142.30 (dm, *J* 4 and 27 Hz), −142.56 (dm *J* 5 and 27 Hz), −142.84 (dm, *J* 5 and 28 Hz), −153.31 (m), −155.84 (m), −160.61 (m). The pattern here is almost identical to that in Fig. 2a for the product of reaction with phenol, the only significant difference is the small upfield shift of the peak assigned to fluorine no. 7. This could conceivably arise from a long range interaction with the lone pairs on the furano oxygen, which will be affected by the OH substituent in the aryl ring.

Reaction with 2-naphthol

HPLC separation gave two main peaks with the following retention times:

13.0 min. The mass spectrum showed a parent ion at 862 amu, peak attributable to naphtho[2,1:*b*]furano[*d*:1,2][60]fullerene, the result of defluorination of the initially formed hexadecafluoro cycloadduct (**5**).



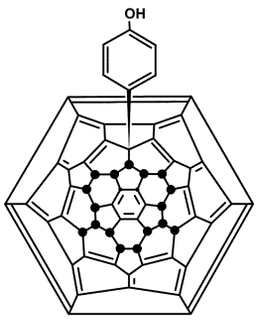
(**5**)

14.7 min. The parent ion of 1166 amu in the mass spectrum (Fig. 4), which also shows the fragmentation ion resulting from loss of all of the fluorines, is consistent with structure **5** for which the spectroscopic evidence is as follows:

^{1}H NMR spectrum. This comprises six lines at δ 8.439 (1 H, m, H^8), 8.077 (1 H, d, *J* 8.8 Hz, H^3), 7.982 (1 H, d, *J* 8.0 Hz, H^5), 7.743 (1 H, t, *J* 8.5 Hz, H^7), 7.539 (1 H, t, *J* 8.4 Hz, H^6), 7.384 (1 H, d, *J* 8.9 Hz, H^6). The multiplet for H^8 is due to coupling with the adjacent fluorine on the cage (no. 6), which is broadened in consequence. The data are all fully consistent with structure **5**, and this is proved further by selective decoupling of various resonances (not shown).

^{19}F NMR spectrum. The spectrum (Fig 2c) shows strong similarity to Figs. 2a and 2b, the only significant differences being that peaks no. 7 and 15 have moved upfield by about 0.2 ppm whilst peaks no. 9 and 10 have moved downfield by a similar amount. The sixteen equal-intensity lines appeared at δ_F (all 1 F) −132.31 (d, *J* 22 Hz), −132.45 (d, *J* 20 Hz), −133.08 (m, *J* 7 Hz), −132.23 (m), −134.04 (m, *J* 7 Hz), −137.24 (br m), −138.85 (t, *J* 15 Hz), −138.94 (br m), −139.49 (d, *J* 15 Hz), −139.69, (dm, *J* 27 Hz), −141.81 (dm, *J* 27 Hz), −142.65 (dm *J* 26 Hz), −143.17 (dm, *J* 27 Hz), −153.43 (dt, *J* 13 and 21 Hz), −156.73 (m), −161.32 (dt, *J* 13 and 21 Hz).

Structure **5** is consistent with our understanding of electrophilic aromatic substitution of 2-naphthol in that substitution takes place at the very reactive 1-position. In principle this gives a hindered product, the hindrance being relieved by the subsequent HF elimination. 1-Naphthol appears not to



(**4**)

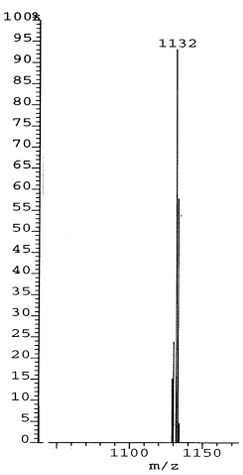


Fig. 3 EI mass spectrum (70 eV) for 4-hydroxybenzo[*b*]furano-[2′,3′:10,26]hexadecafluoro[60]fullerene.

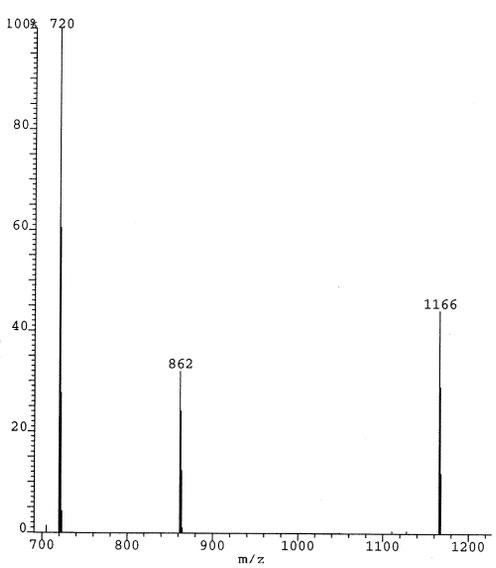
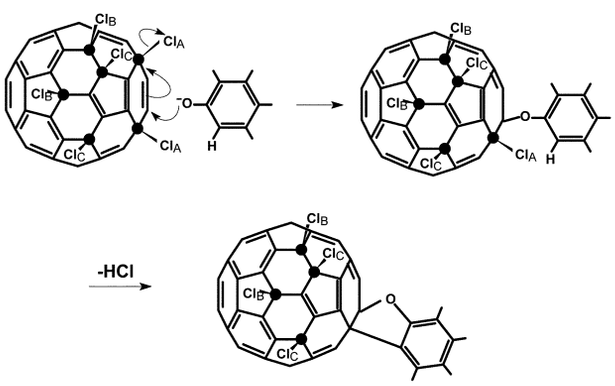


Fig. 4 EI mass spectrum (70 eV) for naphtho[2,1:*b*]furano[*d*:10,26]-hexadecafluoro[60]fullerene

form a ring-closed product in the same way, understandable to some extent from the rate coefficients for hydrogen exchange (an unhindered electrophilic aromatic substitution) for the corresponding methoxy derivatives (models for the hydroxy derivatives for which data are not available). For 1-methoxynaphthalene rate coefficients (10^2k, s^{-1} for exchange in TFA at 70 °C) are 53 (2-position) and 9.5,[11] so that in the absence of steric hindrance the 2-position is favoured and remains so even when reacting with bulky $C_{60}F_{18}$; we have not found any product resulting from substitution at the 4-position.

Further evaluation of the results of base-catalysed formation of benzofuranofullerenes

In previous work on the KOH-catalysed reaction of phenols with $C_{60}Cl_6$, products were obtained showing the addition of up to three aryloxide moieties, and a mechanism was proposed for this.[4] Following the unambiguous proof of the S_n2' mechanism for nucleophilic substitution in fullerenes,[12] we now provide a revised mechanism for reaction of $C_{60}Cl_6$ with KOH. This requires pairs of chlorines to be in a 1,4-relationship, and in $C_{60}Cl_6$ there are three such pairs, designated Cl_A, Cl_B and Cl_C (Scheme 2). The mechanism is shown for elimination of the Cl_A pair, and can similarly occur for elimination of the other two pairs. The difference from that provisionally proposed earlier,[4] is that only three aryloxy groups should attach to the cage, as found in practise, and the alternative location of the benzofurano moieties relative to those of the departing chlorines. As in the previous work, the location of the polyaddends cannot be determined, and for the monoaddition product (benzo[*b*]-furano[2′,3′:1,2][60]fullerene) it is of course not possible to determine the location relative to the departing chlorines, since all of these are lost.



Scheme 2 Conjectured mechanism for the first step of the base-catalysed reaction of phenols with $C_{60}Cl_6$.

Acknowledgements

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