Formation of triumphene, $C_{60}F_{15}Ph_3$: first member of a new trefoil-shaped class of phenylated [60]fullerenes

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Reaction of $C_{60}F_{18}$ with benzene/$FeCl_3$ during two weeks at room temperature produces the phenylated trefoil-shaped derivative $C_{60}F_{15}Ph_3$; higher reaction temperatures produce $C_{60}Ph_{18}$ from replacement of all fluorines by phenyl groups.

Arylated fullerenes may ultimately constitute the largest class of fullerene derivatives. Many have been made and some fully characterised, *e.g.* $C_{60}Ar_5X$, (X = H, Cl),[1–3] $C_{60}Ph_5OH$ (two isomers),[4] $C_{60}Ph_n$ (n = 2, 4),[5] $C_{70}Ph_n$ (n = 2, 4, 6, 8, 10),[6] $C_{70}Ph_9OH$,[7] $C_{70}Ph_8(OH)_2$,[4] $C_{60}PhH$ and $C_{70}PhH$,[8] a benzo-[*b*]furo[60]fullerene[9] and an isoquinolino[60]fullerene.[10] A number of other derivatives have been identified but so far by mass spectrometry only.[11,12] Most have been made by Friedel–Crafts reactions of fullerenes or halogenofullerenes with the aromatics. They are reasonably soluble and stable, especially towards EI mass spectrometry, and some are luminescent.[6] In $C_{60}Cl_6$, the least accessible chlorine was not readily replaced.[1,2]

Recently we described the formation and characterisation of $C_{60}F_{18}$, a polar crown-shaped molecule, shown in Fig. 1.[13] Fluorofullerenes are very susceptible towards nucleophilic substitution,[14] and fluoroalkanes are the most reactive of the halogenoalkanes in Friedel–Crafts alkylation of aromatics.[15] We now describe the successful isolation and characterisation of the first derivative that results from replacement of fluorine by phenyl, and which shows a unique arylation pattern.

Two samples of $C_{60}F_{18}$ (5 mg) were each added to solutions of anhydrous $FeCl_3$ (*ca.* 5 mg) dissolved in anhydrous benzene (2 ml). One solution was set aside for two weeks, the other was heated to *ca.* 70 °C for 1 h. The mixtures were evaporated to dryness and the resultant solids extracted with CCl_4 (to separate unreacted catalyst). Removal of this solvent under vacuum gave deposits that were dissolved in 1 : 1 hexane–toluene and purified by HPLC using a 4.6 mm × 25 cm Cosmosil Buckyprep column, with a flow rate of 1 ml min^{-1}. From both samples a main fraction of $C_{60}F_{15}Ph_3$ eluted at 49.6 min, and from the heated sample, minor fractions eluted at 14.3 and 17.7 min, these being $C_{60}F_{15}Ph_5$ and $C_{60}F_{15}Ph_7$, respectively. Comparison with the retention time of $C_{60}F_{18}$ (*ca.* 45 min with elution by toluene) shows that replacement of F by Ph reduces the retention time. As in the case of phenylated [60]fullerenes,[12] the retention time is reduced by increasing the phenylation level.

The mass spectrum of the crude extract showed also the presence of $C_{60}Ph_{18}$, but attempted separation resulted in degradation, with a broad peak indicated to be $C_{60}Ph_{18}O(OH)_2$, 2142 amu, eluting at 9.3 min (1 : 1 hexane–toluene, 0.5 ml min^{-1}).

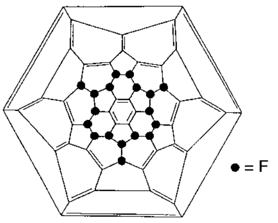

Fig. 1 Schlegel diagram for $C_{60}F_{18}$

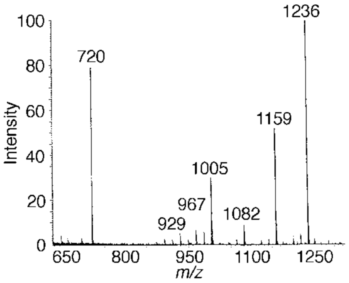

Fig. 2 EI mass spectrum (70 eV) for $C_{60}F_{15}Ph_3$

The mass spectrum (Fig. 2) shows the $C_{60}F_{15}Ph_3$ parent ion at 1236 amu, with peaks at 1159, 1082 and 1005 amu due to successive loss of phenyl groups. The structure of $C_{60}F_{18}$ suggests that the three fluorines which have been replaced by phenyl are the most accessible ones giving a product of C_{3v} symmetry. This is confirmed by the ^1H NMR spectrum (Fig. 3) which shows only one set each of the *o*-, *m*- and *p*-hydrogens of the phenyl groups; a spectrum run at −60 °C is identical, proving that the phenyl groups rotate freely and are thus not in a hindered environment.

The structure is further confirmed by the ^{19}F NMR spectrum (Fig. 4) which shows three peaks in a 1 : 2 : 2 intensity ratio at δ −137.22, −138.36 and −145.0, with respective half-height peak widths are *ca.* 12, 12 and 8 Hz respectively. Comparison with the ^{19}F NMR spectrum for $C_{60}F_{18}$ (four peaks in a 2 : 2 : 1 : 1 intensity ratio) shows that it is one of the latter (due to three equivalent fluorine atoms) that is replaced. The 2D-COSY spectrum (inset to Fig. 4), shows that the single intensity fluorine is directly coupled to one of the (adjacent) double intensity peaks. Thus it is the most accessible fluorine that has been replaced, the ease of replacement of the chlorines in $C_{60}Cl_6$.

The structure of $C_{60}F_{15}Ph_3$, which has encouraged us to name it as ‘triumphene’, is therefore as shown in Fig. 5. The simplicity of preparation suggests that it will be possible to make a large range of other aryl derivatives, the limiting step being only the low availability at present of $C_{60}F_{18}$.

Previously, one of us suggested that nucleophilic replacement of fluorine (in the absence of a catalyst) occurs *via* addition-elimination, because S_N1 substitution (giving a cation on the strongly electron-withdrawing cage) seemed improbable, and S_N2 substitution is impossible.[14] However, if $C_{60}F_{15}Ph_3$

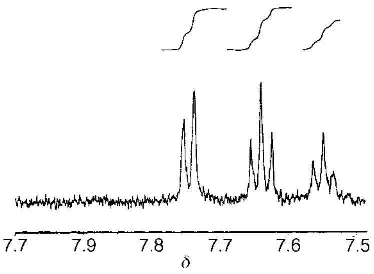

Fig. 3 ^1H NMR spectrum for $C_{60}F_{15}Ph_3$

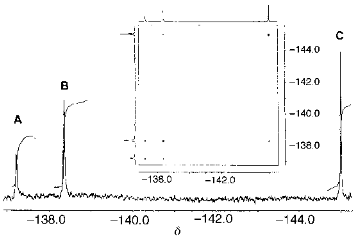

Fig. 4 ^{19}F NMR spectrum for $C_{60}F_{15}Ph_3$ with 2D-COSY spectrum inset. The peak labels correspond to the fluorine atoms identified as in Fig. 5.

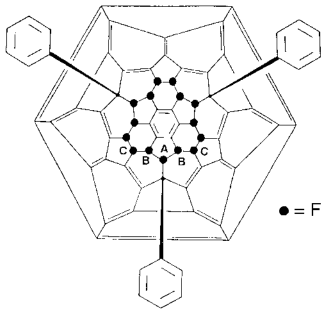

Fig. 5 Schlegel diagram of the structure of $C_{60}F_{15}Ph_3$

was formed by addition-elimination, it could not have C_{3v} symmetry since the phenyl groups would necessarily lie off the symmetry plane of the original $C_{60}F_{18}$. The present work therefore provides unambiguous evidence for direct fluorine replacement in nucleophilic substitution of fluorofullerenes, and is here facilitated by the presence of the Friedel–Crafts catalyst. This reinforces our conclusions concerning replacement of chlorine by phenyl in $C_{60}Cl_6$.[2] Moreover, the reaction of $C_{60}Ph_5Cl$ with $AlCl_3$ produces a free isolable carbocation,[16] and it is clear now that in the presence of these catalysts, substitution in halogenofullerenes takes place *via* an S_N1 mechanism, though necessarily involving frontside attack only.

We have insufficient $C_{60}F_{15}Ph_7$ and $C_{60}F_{15}Ph_5$ at present for full characterisation, but the addition of phenyl groups in pairs suggests that they add across a 6,6-double bond, *e.g.* that which lies on the symmetry plane (the bond across which oxygen adds to give $C_{60}F_{18}O$).[16] One could expect that with longer reaction times, $C_{60}F_{15}Ph_9$ may be observed as a further derivative.

Remarkably, we observed the presence of more volatile $C_{60}Ph_{18}$ (2108 amu) in an early acquisition of the mass spectrum of the crude material (Fig. 6); the mass spectrum shows also the doubly charged $M^+/2$ ions. The spectrum is notable in being less contaminated by the lower phenylated components that we have seen with other phenylation methods.

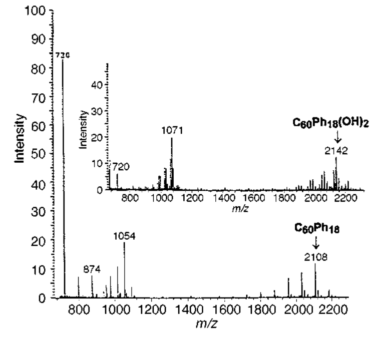

Fig. 6 EI mass spectrum for $C_{60}Ph_{18}$; inset is the mass spectrum for $C_{60}Ph_{18}(OH)_2$ showing also traces of the epoxide derivative

Despite the anticipated steric hindrance, the addition pattern in $C_{60}Ph_{18}$ is likely to be the same as in the fluoro precursor. The mass spectrum shows the presence of a nineteenth phenyl group at much lower intensity. This is due to further phenylation of the cage (well-known to occur with fullerenes and benzene in the presence of Friedel–Crafts catalysts)[11] and indicated in this work by the formation of $C_{60}F_{15}Ph_7$ *etc.* However, the markedly lower intensity of $C_{60}Ph_{19}$ compared to that of $C_{60}Ph_{18}$ provides very strong circumstantial evidence that the eighteen phenyl groups are indeed located at the sites previously occupied by fluorine, giving rise to a fascinating structure of extreme aromaticity.

We have been unable to obtain substitution of F by Ph in $C_{60}F_{36}$ (or in $C_{60}F_{48}$) under the conditions described above.

We attempted also to purify the $C_{60}Ph_{18}$ by HPLC but were unsuccessful because it appeared to oxidise to a diol, $C_{60}Ph_{18}(OH)_2$, and the epoxide derivative, as shown by peaks of 2142 and 2158 amu in the mass spectrum (inset to Fig. 6). Oxygenated derivatives of phenylated fullerenes are prone to form readily.[12]

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Notes and References

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