Preparation and characterisation of unsymmetrical $C_{60}Ph_4$ and symmetrical $C_{60}Ph_2$: the effect of regioselective nucleophilic attack upon $C_{60}Cl_6$

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Unsymmetrical $C_{60}Ph_4$ (1,3,11,30-tetraphenyl-1,3,11,30-tetrahydro[60]fullerene) is obtained as a minor product from the reaction of $C_{60}Cl_6$ with benzene–$FeCl_3$. The formation of either this compound or the major product ($C_{60}Ph_5Cl$) apparently depends on the position of the initial replacement of chlorine by phenyl: substitution of chlorine at the 2-position leads to $C_{60}Ph_5Cl$, whereas initial substitution of chlorine at the 1-position leads to $C_{60}Ph_4$. A small amount of symmetrical $C_{60}Ph_2$ (which mechanistic considerations indicate to be the 1,4-isomer), is also obtained and is accompanied by traces of $C_{60}Ph_3H_3$.

We have described previously the formation of some phenyl derivatives of [60]- and [70]-fullerenes, arising from electrophilic aromatic substitution of halogenated fullerenes into benzene.[1–3] The main product of reaction of $C_{60}Cl_6$ (**I**) with benzene–iron(III) chloride is $C_{60}Ph_5Cl$ (**II**).[3] We now find that byproducts of the reaction are an unsymmetrical tetraphenyl-[60]fullerene accompanied by a smaller amount of a symmetrical diphenyl[60]fullerene. We report here spectroscopic data for the compounds and propose a mechanism of their formation, based on physical organic principles. Traces of a trihydrotriphenyl[60]fullerene are also present in the reaction product.

Experimental

$C_{60}Cl_6$ (72 mg, 7.7×10^{-5} mol), prepared as described previously,[4] was dissolved in dry benzene (100 cm^3) and a catalytic amount of iron(III) chloride was added. The mixture was heated under reflux for 30 min, cooled, washed with water, dried over magnesium sulfate, and the solvent removed to give a dark-red solid. This was dissolved in CCl_4 (50 cm^3), the volume was then reduced to half, and the resultant solution left to stand at room temperature. Crystals of $C_{60}Ph_5Cl$ started to grow after 30 min, and the crystalline material was collected after 24 h, and washed with a little cold CCl_4. The filtrate and washings were combined and evaporated to dryness to give a residue which was dissolved in the minimum amount of cyclohexane. The cyclohexane solution was chromatographed on a silica-gel column. [60]Fullerene eluted first (at the solvent front) followed by a small amount of $C_{60}Ph_2$, $R_f = 0.72$ (contaminated with traces of $C_{60}Ph_3H_3$), and then brown $C_{60}Ph_4$, R_f 0.125, yield, 6.2 mg, 7.8%. $C_{60}Ph_5Cl$ and $C_{60}Ph_6$ (yet to be fully characterised) remained on the column until eluted with CCl_4.

Results and discussion

Mass spectra

The EI mass spectrum (Fig. 1, 70 eV) of the main product shows the parent ion at *m*/*z* 1028 due to $C_{60}Ph_4$, and no species of higher molecular mass. The characteristics typical of phenylated fullerenes[2,5] are evident, *viz*. the radical degradation species (odd numbers of phenyl groups) give the most intense signals. Degradation is quite pronounced, and is consistent with the general feature of fullerene derivatives namely that the fewer the addends present, the more readily they degrade back to [60]fullerene. For example, for the series of compounds $C_{70}Ph_n$ the intensity ratios $C_{70}Ph_n/C_{70}$ in the mass spectrum decrease regularly along the series, $n = 10, 8, 6, 4, 2$.[5]

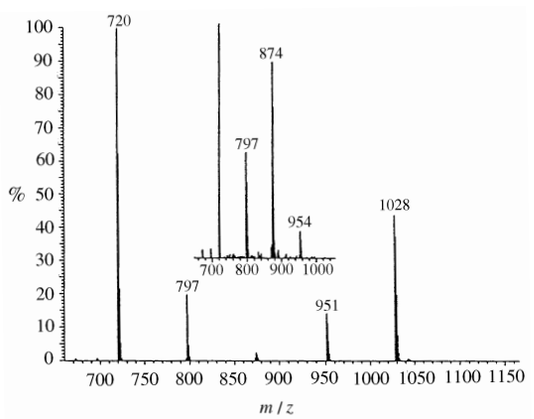


Fig. 1 EI mass spectrum (70 eV) for $C_{60}Ph_4$; inset shows spectrum for $C_{60}Ph_2$ contaminated with some $C_{60}Ph_3H_3$

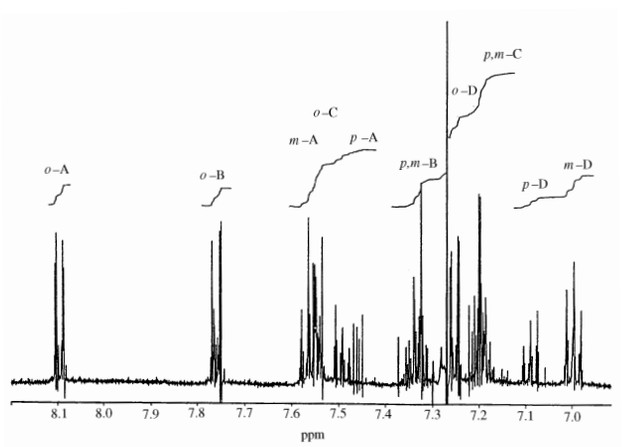


Fig. 2 ^{1}H NMR spectrum for $C_{60}Ph_4$

The mass spectrum of the minor product (70 eV, inset to Fig. 1) is commensurate with $C_{60}Ph_2$ (*m*/*z* 874), contaminated with a small amount $C_{60}Ph_3H_3$ (*m*/*z* 954). Chlorine atoms are usually lost through fragmentation during mass spectrometry, so this diphenyl compound could in principle also contain chlorine, but this is disproved by the ^{13}C NMR spectrum below.

^{1}H NMR spectra

$C_{60}Ph_4$. The spectrum (Fig. 2) shows that four phenyl groups are present and that the molecule is unsymmetrical; the peak identifiers were determined by 2D COSY analysis. The posi-

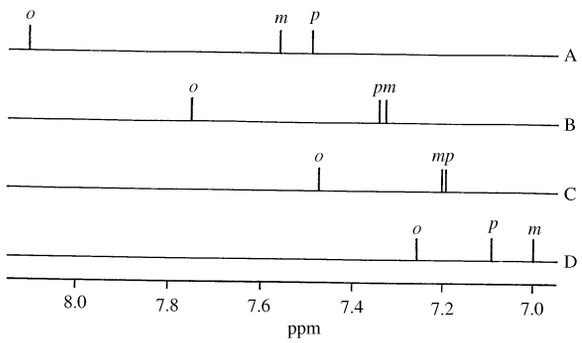


Fig. 3 Positions of the resonances for the *o*, *m*, and *p*-hydrogens of the phenyl rings in the ^{1}H NMR spectrum of $C_{60}Ph_4$, showing how increased electron withdrawal by the cage (more downfield location of the peaks) affects the relative positions for the *m* and *p*-hydrogens

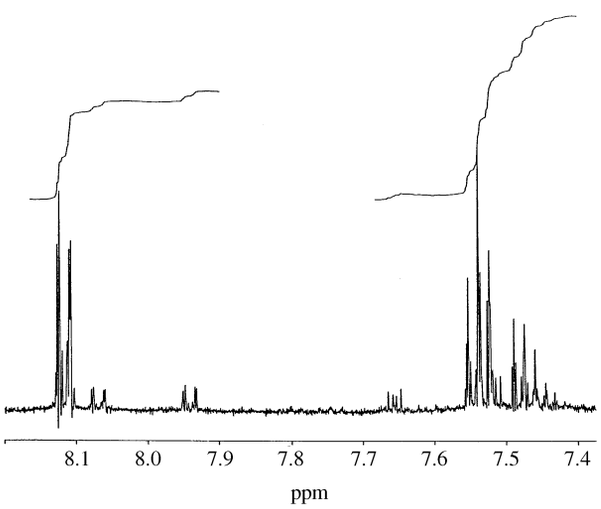


Fig. 4 ^{1}H NMR spectrum for $C_{60}Ph_2$

tions of the resonances are displayed in graphical form in Fig. 3, and show the following.

(*i*) The more downfield the resonances for the *ortho* hydrogens, the more spread out are the overall resonances for the hydrogens in that ring. A similar feature was found for $C_{70}Ph_{10}$.[2]

(*ii*) For the most upfield resonances, the *para* peaks are more downfield than the *meta* ones, whereas for the most downfield resonances, the relative *para* and *meta* positions are reversed. These features are fully consistent with the differential electron-withdrawing effects experienced by the various phenyl groups. Electron withdrawal by the cage upon the phenyl groups decreases along the series of rings designated A > B > C > D.

NOE experiements showed effects between rings A and D (1.2, 0.4%), between rings D and C (0.7%), and between rings C and B (0.4, 0.5%); there was no coupling between ring A and either of rings B or C.

$C_{60}Ph_2$. The spectrum (Fig. 4) shows only one set of resonances for the phenyl group hydrogens, showing that the molecule is symmetrical; the positions of the resonances are very similar to those of group A in $C_{60}Ph_4$. Other minor peaks are due to the presence of traces of $C_{60}Ph_3H_3$, but these have not been analysed further at this stage.

^{13}C NMR spectra

$C_{60}Ph_4$. An unsymmetrical product requires four peaks of equal intensity in the sp^3 region of the spectrum, and these are found, at δ_C 62.26 (A), 60.28 (B/C), 60.02 (B/C) and 58.69 (D), the provisional identities of the attached phenyl rings being in parentheses. In the sp^2 region there should be 56 peaks for the cage carbons, together with four for the *ipso* carbons and these are found at δ_C 159.56, 155.26, 155.24, 153.90, 153.05, 152.83, 152.51, 150.31 (2 C), 148.98, 148.57 (2 C), 148.27, 148.19, 147.92, 147.75 (2 C), 147.63, 147.58, 147.42, 147.22, 147.05, 146.73, 146.33, 146.24, 146.01, 145.90, 145.65, 145.52, 145.40, 145.21, 145.03, 144.62, 144.60, 144.55, 144.35, 144.33, 144.23, 143.80, 143.59, 143.36 (2 C), 143.26, 143.16 (2 C), 142.94, 142.89, 142.77, 142.67, 142.53, 140.73, 139.27, 138.79, 138.58, 138.53, 138.27, 138.25, 138.02, 135.90, 130.28. The signals for the other carbons of the phenyl rings are at δ_C 129.14, 128.81, 128.56 and 128.06 (*ortho*, all 2 C), 127.35, 127.18, 126.98 and 126.54 (*meta*, all 2 C), 127.98, 127.59, 127.41, 127.12 (*para*, all 1 C). We may assign the peaks in each set to rings A, B, C and D, respectively.

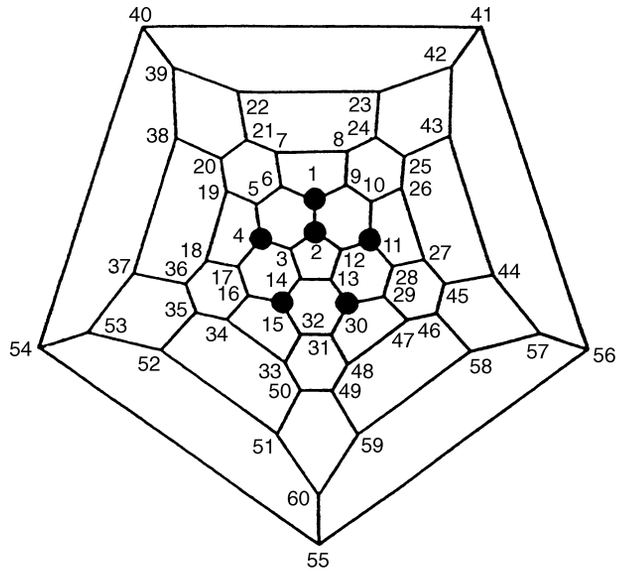


Fig. 5 Schlegel diagram for $C_{60}Cl_6$ (● = Cl) showing the numbering

These data confirm that the product consists of [60]fullerene possessing four phenyl groups with neither a plane nor a centre of symmetry.

$C_{60}Ph_2$. In the sp^3 region of the spectrum there is only one peak at δ_C 61.81, which confirms the symmetry of the product, and that no chlorines remain in the structure. The position of the resonance is also similar to that of group A in $C_{60}Ph_4$ (*cf.* the ^{1}H NMR spectra above). The remaining 58 sp^2 carbons require 31 peaks (27 × 2C and 4 × 1C) for a compound of C_s symmetry, and these are found: δ_C 156.62, 150.93, 148.74, 148.51, 147.21, 147.07, 146.98, 146.92, 145.65, 145.34 (1 C), 145.19, 145.18, 144.95 (1 C), 144.81, 144.46, 144.42, 144.34, 144.30, 144.08 (*ca.* 3 C, due probably to an underlying impurity peak), 143.93, 143.29, 143.26, 143.23, 142.72, 142.61, 142.35, 142.16 (1 H), 141.16 (1 H), 140.36, 138.92, 137.51.

IR spectra

$C_{60}Ph_4$. There are six main bands at ν/cm^{-1} 1493, 1446, 735, 694, 544.0 and 530 and less intense ones at ν/cm^{-1} 1384, 1032, 917, 581, 577, 556 and 539.

$C_{60}Ph_2$. The bands appear at ν/cm^{-1} 1154, 1492 (m), 1459, 1445, 1384, 1032, 745, 736, 705, 693 (m), 595, 587, 558, 542 and 534.

The structures of $C_{60}Ph_4$ and $C_{60}Ph_2$

In deducing the structure of $C_{60}Ph_4$ we assume that the phenyl groups occupy some of the sites previously occupied by chlorine in $C_{60}Cl_6$ (Fig. 5), and none of the other sites; this is reasonable given the relationships between the structures of $C_{60}Ph_5Cl$ and $C_{60}Cl_6$,[3,4] $C_{70}Ph_{10}$ and $C_{70}Cl_{10}$.[2] [This assumption has implications regarding the mechanism of nucleophilic substitution on the cage. Previously, we have argued that nucleophilic substitution of fluorine probably occurs *via* an addition–elimination mechanism (whence the incoming group occupies

a different position from the departing one), S_N2 being impossible and S_N1 improbable.[6] For $C_{60}Cl_6$ a form of the latter mechanism (frontside attack only) may be involved since chlorine (aided by the Lewis acid catalyst) is a better leaving group than fluorine, and the absence of numerous strongly electron-withdrawing groups would make the cage here better able to accommodate a positive charge in the intermediate.]

If four of the original sites remain occupied, and the product is unsymmetrical, three structures [Fig. 6(*a*–*c*)] are possible. For structure **6a** a reasonable formation mechanism may be postulated, and moreover it has only one destabilising[7] double bond in a pentagon. However, **6a** can be ruled out by the presence of adjacent phenyl groups which would suffer restricted rotation, as found in $C_{70}Ph_{10}$, where such adjacency occurs.[2] The ^{1}H NMR spectrum shows no evidence for such restriction. It might be argued that if the adjacent phenyl groups were constrained such that their planes were parallel, then no difference in the resonances for the pairs of *ortho* hydrogens would be apparent in the spectrum (likewise for the pairs of *meta* hydrogens) *provided* that there was a plane of symmetry orthogonal to the planes of the phenyl groups. However, such symmetry is destroyed by the presence of the other two phenyl groups. Structure **6a** may therefore be discarded.

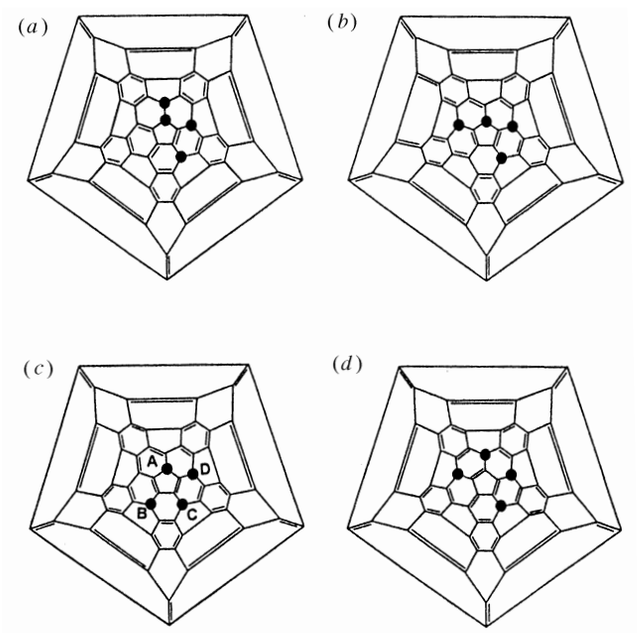


Fig. 6 Schlegel diagrams for possible structures for $C_{60}Ph_4$ (● = Ph)

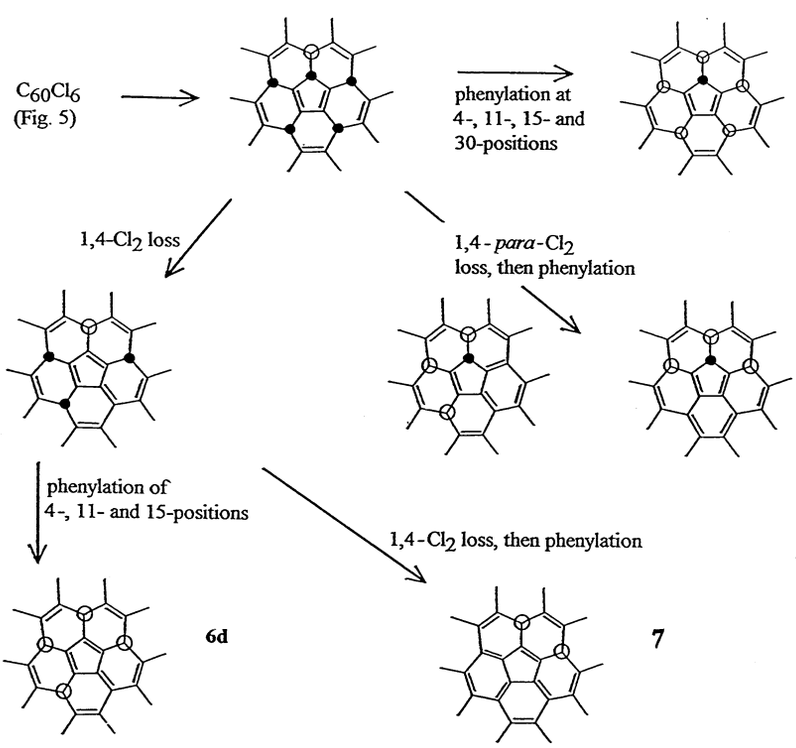
Of the two remaining structures, **6b** has eight double bonds in pentagons (including four in pentagons that do not possess any strain-relieving sp^3-hybridised carbons) whereas **6c** has four (two in pentagons without sp^3 carbons). These facts disfavour **6b**, and moreover, no reasonable mechanism for its formation appears possible. By contrast, it is possible to propose satisfactory mechanisms leading to formation of (chiral) **6c**, and the accompanying major product $C_{60}Ph_5Cl$; accordingly we assign on **6c** the phenyl groups based on the NOE experiments.

Alternative assignments of the resonances could in principle be the sequence BCDA rather than ADCB. One set of resonances is significantly more downfield than those in either $C_{60}Ph_5Cl$ or $C_{60}Ph_5H$,[3] a result consistent with phenyl group A being attached to the strained cyclopentadiene ring. On the other hand as noted above, one set of resonances in both proton and carbon NMR appear at almost the same position as in $C_{60}Ph_2$ which we deduce below to be the 1,4-isomer. This could imply that group A is located at position B (as in the 1,4-isomer); however the notably downfield location of the resonances in $C_{60}Ph_2$ may simply reflect the fewer number of sp^3 carbons in the cage and hence greater electron withdrawal.

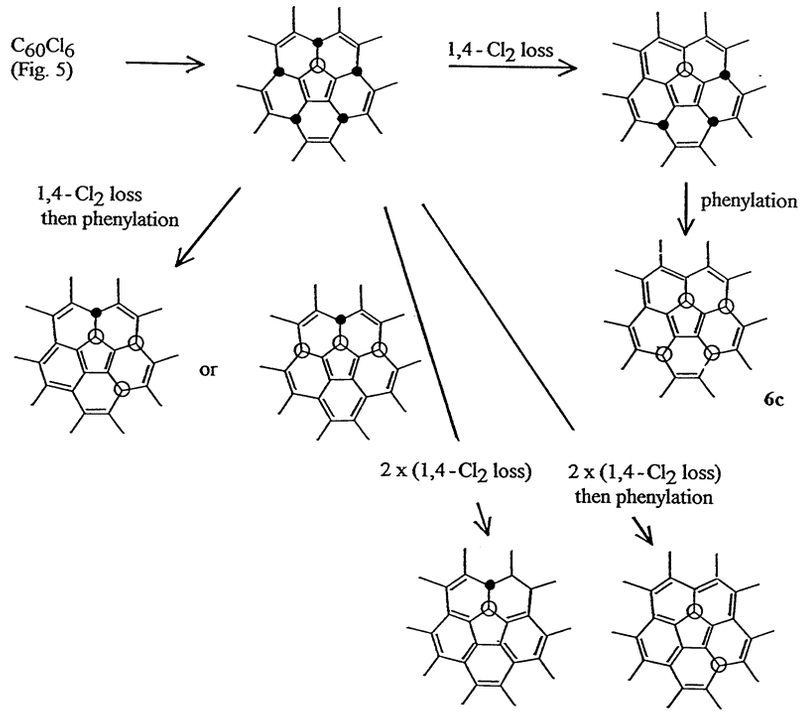
Mechanism of product formation

We propose below the mechanism of formation of the products and, based on these proposals, indicate some other components that might be observed under favourable circumstances. In Schemes 1–4, ● = chlorine, ○ = phenyl. The following premises are central to our deductions:

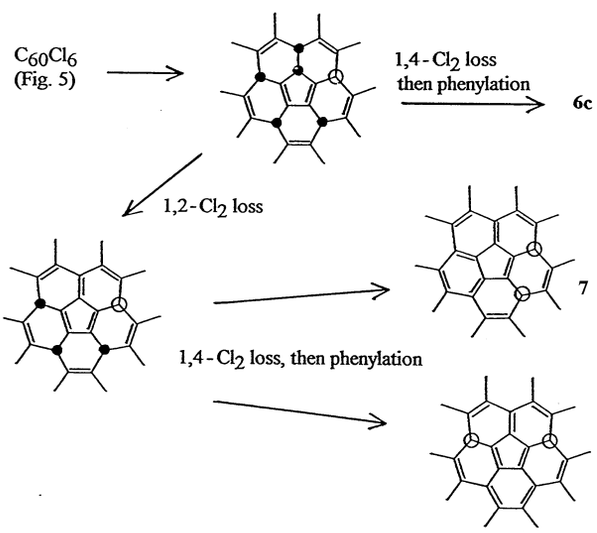
1. Chlorinated (and brominated) fullerenes readily lose their halogens during EI mass spectrometry or on heating, and since



Scheme 1 Initial phenylation at position 1 (● = Cl, ○ = Ph). Bold numerals in this scheme and Schemes 2–4 indicate structures in Figs. 5–7.



Scheme 2 Initital phenylation at position 2 (● = Cl, ○ = Ph)



Scheme 3 Initital phenylation at position 4 (● = Cl, ○ = Ph)

the halogens must be evolved as Hal_2 species, either a 1,2- or a 1,4-elimination is involved. Chlorine can be lost in this way during the heating involved in phenylation.

2. In the case of $C_{60}Ph_5Cl$, which has an isolated chlorine atom, the chlorine is retained during mass spectrometry.[3] A lone chlorine is therefore very reluctant to leave (it would have to do so as chlorobenzene, the chlorine atom and a phenyl group being on adjacent carbons).

3. In $C_{60}Cl_6$ there are four distinct chlorine positions, and in principle, any one of these may be attacked first. Electronic considerations dictate that attack at the 1- and 2-positions will be preferred, and of these the 1-position is sterically more accessible.

4. Products involving adjacency of phenyl groups are less likely to be formed.

5. In the following discussion, the terms '1,4-elimination' *etc.* have their usual mechanistic meaning; standard IUPAC numbering is used in the description of phenylated products.[8]

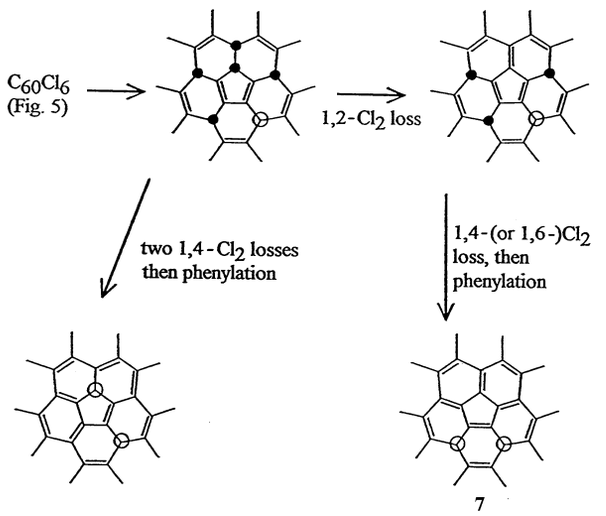
The four scenarios are as follows.

Initial phenyl substitution at the 1-position (Scheme 1). If the chlorine at the 1-position is replaced first, then although the C(2)–Cl bond is weakened due to increased eclipsing strain, the chlorine at position 2 is 'trapped' since it cannot eliminate in either a 1,2-(*ortho*) or 1,4-(*para*) process involving any other chlorine. Replacement of the other chlorines by phenyls then leads ultimately to $C_{60}Ph_5Cl$. The 2-chlorine could however conceivably participate in a steric strain-driven '1,4-elimination' involving chlorine at the 15-position (or 30-position which is equivalent). Replacement of the remaining chlorines by phenyl groups would produce a symmetrical $C_{60}Ph_4$ compound (structure **6d**). Alternative 1,4-eliminations of other chlorines can occur leading to a variety of possible products, including the symmetrical 1,4-diphenyl-1,4-dihydro[60]fullerene **7** (which notably has only one double bond in a pentagon and is likely therefore to be particularly stable).

Initial phenyl substitution at the 2-position (Scheme 2). If the chlorine at the 2-position is replaced first, then lengthening of the C(1)–Cl bond due to strain will favour eliminations of the 1-chlorine. This chlorine can only leave in a 1,4-(*para*) elimination involving the chlorine at position 4 (or 11 which is equivalent). Replacement of the remaining chlorines by phenyl groups then leads to structure **6c**. Alternative 1,4-chlorine losses followed by phenyl substitution lead to two different $C_{60}Ph_3Cl$ structures, but both these have adjacent phenyl groups. Alternatively, two consecutive 1,4-chlorine eliminations, followed by replacement of chlorine by phenyl can lead to $C_{60}PhCl$ and an unsymmetrical 1,14-diphenyl[60]fullerene.

Initial phenyl substitution at the 4-position (Scheme 3). Replacement of the 4-chlorine by phenyl followed by 1,4-chlorine loss also leads to the tetraphenyl compound **6c** as shown. Consecutive 1,2- and 1,4-chlorine losses (either order) can lead to the 1,4-diphenyl isomer **7**, and also the 1,15-diphenyl isomer (also symmetrical, but containing four double bonds in pentagons, none of which have strain-compensating sp^3-hybridised carbons, so making the structure rather unstable).

Initial phenyl substitution at the 15-position (Scheme 4). Replacement of the 15-chlorine followed by 1,2-elimination and then either a 1,4- or 1,6-chlorine loss and phenylation



Scheme 4 Initital phenylation at position 15 (● = Cl, ○ = Ph)

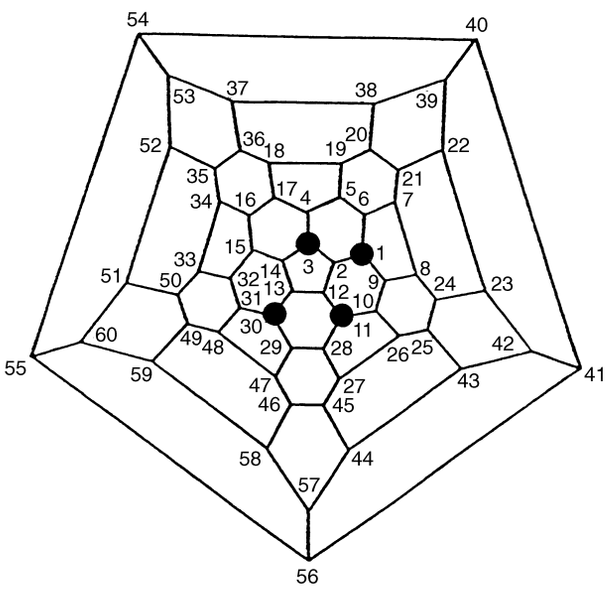


Fig. 7 Schlegel diagram for $C_{60}Ph_4$ (● = Ph) showing the numbering

would (in either case) again produce the symmetrical 1,4-diphenyl-1,4-dihydro[60]fullerene (**7**). Alternatively, two consecutive 1,4-chlorine eliminations can give the 1,14-diphenyl isomer.

In summary, two mechanisms produce the unsymmetrical tetraphenyl derivative **6c**, three produce the symmetrical 1,4-diphenyl derivative, and three predict that the symmetrical tetraphenyl derivative **6d** should also be isolable. It may be relevant therefore that reaction of $^3He@C_{60}Cl_6$ with benzene and iron(III) chloride indicated the presence of two other products (apart from $C_{60}Ph_5Cl$), as revealed by ^3He NMR spectroscopy.[9]

Nomenclature

It will become increasingly apparent as more derivatives of fullerenes are made, that due to the fullerene structures, application of the standard lowest locant rule may make it difficult to appreciate the derivatisation that has occurred. It is likely that increased use of Schlegel diagrams will be necessary. Figs. 5 and 7 illustrate the problem. The precursor for the present studies is $C_{60}Cl_6$ and the numbering of the addends according to the lowest locant rule is 1, 2, 4, 11, 15, 30 (Fig. 5). However, lowest locant numbering for the tetraphenyl derivative is 1, 3, 11, 30 (groups D, A, C and B, respectively). Thus it is not apparent from a consideration of the numbering without the diagram, that positions 1, 3, 11 and 30 of the derivative, are derived respectively from positions 11, 2, 30 and 15 in the precursor (Fig. 7).

Furthermore, the tetraphenyl derivative is chiral, and the enantiomer shown should therefore be defined as ^{f}C according to the commendable system proposed by Diederich and coworkers.[10] In this the descriptors are ^{f}C and ^{f}A according to whether the lowest locants in the contiguous numbering system are encountered in a clockwise or anticlockwise fashion, respectively.

Acknowledgements

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