Formation of $C_{60}Ph_{12}$ by Electrophilic Aromatic Substitution

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A product of molecular formula $C_{60}Ph_{12}$ is obained by heating benzene, bromine and C_{60} in the presence of iron(III) chloride; other phenylated and oxygenated derivatives are also present.

The formation of adducts between C_{60} and benzene, by allowing these reagents to stand overnight in the presence of iron(III) chloride and bromine, was recently described.[1] Mass spectroscopic analysis of the reaction mixture showed peaks at *m/z* 798, 874, 952, 1028, 1106 and 1186; this was interpreted as arising from the addition of up to six *benzene* molecules to the cage. The mechanism by which the benzene rings become attached to the cage was unclear, but the adducts were thought to involve covalent binding. Other aromatics, *e.g.* toluene and *p*-xylene, formed adducts in the presence of iron(III) chloride alone.

Having a particular interest in the attachment of aromatic rings to C_{60}, we repeated the experiment involving benzene, but heated the reagents for 2–3 h in the hope of increasing the yield. The benzene solution was then poured into water, separated, washed with water and sodium hydrogencarbonate and then dried (Na_2SO_4). UV/VIS spectroscopy of the solid obtained after benzene removal showed the usual bands[2] for C_{60} together with a broad band at approximately 485 nm. The solid, dissolved in hexane, was purified by column chromatography (neutral alumina). The C_{60} eluted first, followed by a pinkish–yellow fraction for which mass spectroscopic analysis [fast atom bombardment (FAB) conditions, *m*-NBA (*m*-nitrobenzyl alcohol)] gave different results from those described in the literature.[1] Peaks were observed at *m/z* 1105, 1182, 1259, 1336, 1413, 1490, 1567 and 1644, with relative

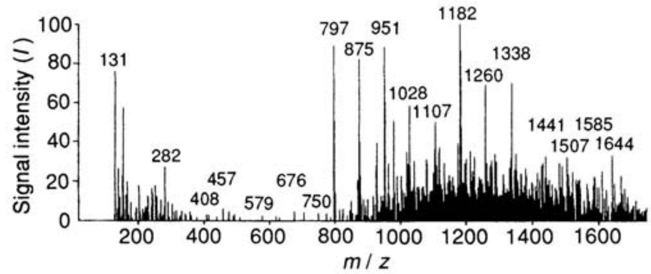

Fig. 1

intensities of 2:11:2:11:1:3:1:2. These mass differences (77 u) are clearly consistent with the presence of between five and twelve phenyl rings being attached to the C_{60} cage. The most abundant ions are those corresponding to the presence of an even number of phenyl rings, suggesting that the phenyl groups are attached in pairs (*i.e.* across bonds of high order).

Further mass spectrometric analysis (FAB conditions) for metastable ions that lose 77 u (one phenyl group) gave peaks at *m/z* 797, 875, 951, 1028, 1107, 1183, 1260, 1338 and 1644; a typical spectrum is shown in Fig. 1. [The peak masses differ by 76, 77 or 78 u but slight variations (± 1 u) were obtained from different spectra, due probably to calibration drift, the scans being run at very low resolution.] Our results show that up to twelve phenyl groups are attached to the fullerene cage. The product also appears to be a mixture of derivatives as addition of chloroform causes part of it to dissolve, the residue being soluble in acetone.

A second batch of material was prepared as described above, but with heating for 24 h. The product was partially separated by column chromatography (neutral alumina) with elution in turn by hexane, carbon tetrachloride and dichloromethane. The residue, after evaporating the carbon tetrachloride eluate to dryness, was separated into acetone- and chloroform-soluble fractions. Laser-desorption mass spectrometry of the latter fraction and the dichloromethane eluate, under both positive and negative ion conditions, gave fragmentation (more significant under the former conditions), with ready elimination of a single phenyl group, so that peaks with odd numbers of phenyl groups dominated. The eluted dichloromethane-soluble fraction showed evidence of the presence of up to 16-phenyl groups, although there was a sharp cut off in concentration (deduced from the intensities of the peaks arising from loss of 77 u) at $C_{60}Ph_{12}$. The chloroform-soluble fraction consisted mainly of $C_{60}Ph_8$. ^1H NMR spectra of these fractions showed a number of peaks in the aromatic region (δ 6.80–7.90).

The positive ion mass spectra also showed peaks 24 u lower than the peaks assigned to Ph_nC_{60}, a common feature of the mass spectrometry of fullerenes, and generally attributed to cage contraction. More significantly, peaks were observed at 16 and 32 u higher than the peaks assigned to Ph_nC_{60}, a result more apparent under the less destructive negative ion conditions. Up to two oxygen atoms are evidently attached to the cage, and it seems unlikely that this attachment occurs during the mass spectrometry process, because the ratio of the peak heights for the oxygenated derivatives compared with each main peak is greater in the acetone extract. This indicates that the oxygenated material is concentrated in this fraction. $C_{60}O$ (and possibly $C_{60}O_2$) has been detected in cluster beam studies involving laser vaporisation of carbon, when oxygen is added to the helium carrier gas,[3] and oxygen derivatives of C_{60}[4] and C_{70} has been reported.[5] Our material could arise from nucleophilic replacement of Br by OH during the work-up process, followed by elimination either of water from adjacent OH groups or of HBr from adjacent Br and OH groups, giving an epoxide structure spanning one of the high order C–C bonds. (These are the bonds between a pair of pentagonal rings.[6])

The significance of the overall results is twofold. Firstly, we believe these derivatives are formed by electrophilic substitution of benzene in which C_{60} provides the electrophilic species. Initial bromine addition produces an alkyl dibromide that in the presence of the Friedel–Crafts catalyst substitutes benzene in the normal way. (Reaction of polychlorinated C_{60} with benzene under more drastic Friedel–Crafts conditions has been reported very recently to give rise also to polyphenylated C_{60}.[7]) Substitution of two C_{60} moieties into benzene is unlikely because of steric hindrance and the electron withdrawing nature of the C_{60} cage (it reacts with nucleophiles).[8,9] 24 bromine atoms add very readily to C_{60} at room temperature,[8] a similar result being reported in a very recent communication.[9] (Another report[7] states that only 2–4 bromines are added but the IR spectrum given is almost identical with that for more highly brominated material.[8]) Our observation that not more than 16 phenyl groups are attached to C_{60} might reflect the instability of either the polybrominated material (which loses bromine on heating)[7,8] or the polyphenylated material (which appears to decompose partly on standing).

Secondly, our results provide further evidence that six bonds are commonly involved in additions of C_{60}; for example, six diphenylcarbon moieties ($Ph_2C=$) (from diphenyldiazomethane) have recently been shown to add to C_{60},[10] as have six $(Et_3P)_2Pt$ groups.[11] Two combinations of six bonds can be considered as the addition sites in C_{60}, but the one that involves octahedral addition appears more likely,[12] and has been confirmed for the addition of platinum. The possibility that addition of bulky groups such as phenyl may involve non-adjacent sites in order to avoid eclipsing interactions, must also be considered.

We thank Dr M. J. C. Smith of BP Research for the laser-desorption mass spectrometry, and VG Instruments for a preliminary spectrum. We also thank BP and ICI for financial support.

Received, 15th January 1992; Com. 2/00224H

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