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# Trifluorohemifullerene : Gas Phase Argon Ion Fragmentation of Hexafluorotribenzotriphenylene

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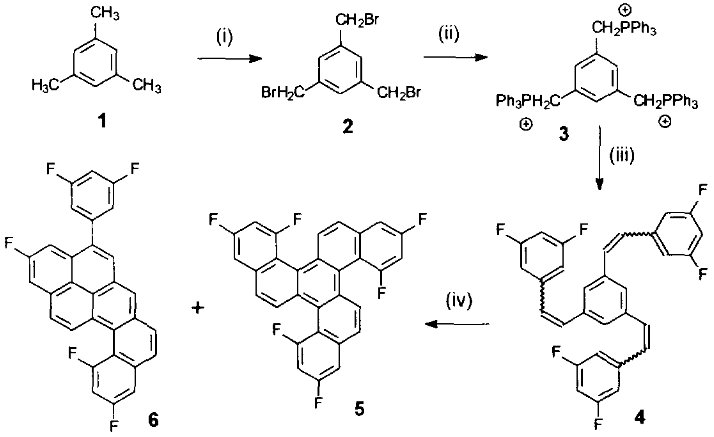
***Abstract*** Gas phase argon ion fragmentation of hexafluorotribenzotriphenylene generates a key fullerene fragment trifluorohemifullerene Copyright © 1996 Elsevier Science Ltd

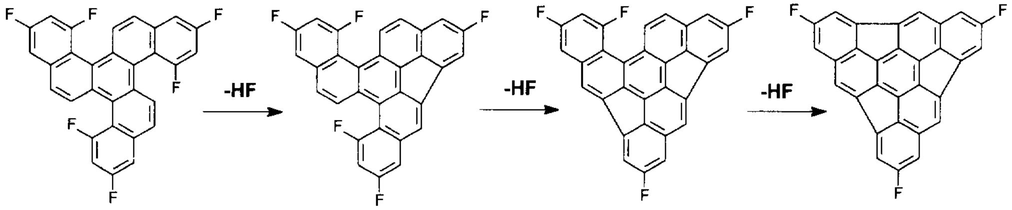
Fullerene fragments collectively known as 'Buckybowls' have appeal as a new intellectual curiosity and present a formidable synthetic challenge either by contemporary synthesis or by pyrolytic methods.[1] Disconnection of Buckminsterfullerene into two enantiotopic halves gives the $C_{30}$ fragment known as Hemifullerene or Semibuckminsterfullerene[2] which we have studied as a potential precursor to the $C_{60}$ nucleus[3] and $C_{60}$ endohedral complexes and as a novel $\pi$-complexing agent for metal ions.[4] Further to our model studies on the pyrolysis of halogenated benzo[c]phenanthrenes to give benzo[ghi]fluoranthenes,[5] a key sub-structure in hemifullerene **9**, we now report our attemps to prepare hemifullerene via the intermediate hexafluorotribenzotriphenylene **5**.

Treatment of trisphosphonium salt **3**,[6] prepared from mesitylene **1**, with 3,5-difluorobenzaldehyde in isopropanol with cesium carbonate gave the tris-stilbene **4** as a mixture of cis and trans isomers. Photocyclisation in benzene ($10^{-4}$M) under nitrogen gave a mixture of products which were difficult to separate and fully characterise owing to the complexity of the nmr spectra. However mass spectral analysis of the mixture showed the presence of the desired compound **5** (m/z 486) along with the anticipated isomer **6**(m/z 468) formed by a competing photocyclisation reaction. The fragmentation pattern was of particular interest



(i) NBS/AIBN/$CCl_4$/Δ 4hr 51%
(ii) $PPh_3$/DMF/Δ 1hr 95%
(iii) 3,5-Difluorobenzaldehyde/$Cs_2CO_3$/$^iPrOH$/RT 3hr 58%
(iv)hν/$I_2$/ benzene/propylene oxide/$N_2$/2hr 54%

owing to the presence of peaks of decreasing intensity at m/z 466, 446 and 426 due to the loss of hydrogen fluoride(20) and presumably a consequence of a series of ring couplings illustrated below as the fragment spontaneously closes up into the hemifullerene core. A more detailed mass spectral analysis was performed using a triple quadrupole mass spectrometer to increase the daughter ion intensity and to show if the molecular ion m/z 468 is a fragment from the molecular ion m/z 486. The molecular ion m/z 486 of hexafluorotribenzotriphenylene **5** was selected in the first quadrupole, bombarded with argon ion gas and scanned with the third quadrupole to detect the daughter ions created. The spectra showed a weak peak at m/z 466 **7** (15%) and peaks at m/z 446 **8** (100%) and 426 **9** (35%). The 468 peak was not observed confirming this to be a separate component in the original mixture. No fragmentations were observed from m/z 426 **9** suggesting that each loss of HF(20) is associated with a ring coupling reaction.



**5** m/z 486 **7** m/z 466 (15%) **8** m/z 446 (100%) **9** m/z 426 (35%)

The mass spectrum of tribenzotriphenylene shows a strong molecular ion but no fragments due to loss of hydrogen suggesting that spontaneous ring couplings into buckybowl fragments does not occur. Presumably hexafluorotribenzotriphenylene **5** is more reactive and more prone to fold into trifluorohemifullerene **9** because of increased molecular strain and because the positively charged molecular ion may be more reactive owing to the electron withdrawing effect of the fluorine substituents. This study lends credence to our view that larger fluorinated polycyclics, albeit as an intellectual curiosity, may spontaneously fold into fullerenes by electron impact or argon ion fragmentation. Relevant to this is our previous report of the synthesis of the first and as yet only potential unimolecular polycyclic aromatic hydrocarbon precursor to $C_{60}$.[7] We are continuing our studies on the pyrolysis of fluorinated polycyclic precursors to give fullerene fragments and fullerenes.

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