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DODECAFLUORO-5,10-*o*-BENZENOARSANTHRENE AND DODECAFLUORO-5,10-*o*-BENZENOSTIBANTHRENE

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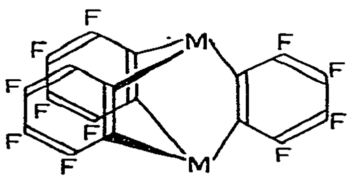
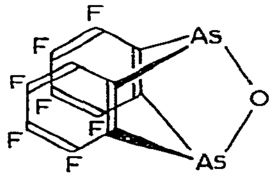
Summary

To clear some confusion in the literature, the “direct syntheses” of $As_2(C_6F_4)_3$ and of $Sb_2(C_6F_4)_3$ have been repeated and the identities of the compounds confirmed by analytical data and spectroscopic methods. Mixtures of As and Sb, when heated with 1,2-$I_2C_6F_4$, give $As_2(C_6F_4)_3$, $Sb_2(C_6F_4)_3$ and $AsSb(C_6F_4)_3$. When Sb is heated with 1,2-$I_2C_6H_4$ and 1,2-$I_2C_6F_4$, three compounds are formed: $Sb_2(C_6F_4)_3$, $Sb_2(C_6F_4)_2(C_6H_4)$ and $Sb(C_6F_4)(C_6H_4)_2$.

The syntheses of dodecafluoro-5,10-*o*-benzenoarsanthrene (I) and dodecafluoro-5,10-*o*-benzenostibanthrene (II) were described by ourselves [1] and by Cullen and Wu [2] in 1976. However, the melting points and ^{19}F NMR chemical shifts (the only data available for comparison) quoted for these compounds differed very considerably. In an effort to clear up the anomalies we repeated our work and discovered a fault in our NMR spectrometer controls which gave rise to incorrect chemical shift data. We, therefore, withdraw the ^{19}F NMR chemical shift data presented for I and II in ref. 1. The ^{19}F NMR spectrum of the arsanthrene I, dissolved in tetrahydrofuran, shows two groups of peaks of an AA′XX′ system at 122.8 and 152.6 ppm relative to internal $CFCl_3$. These shifts are in good agreement with those quoted by Cullen and Wu [2], although the latter did not state the solvent used.



(I, M = As;
II, M = Sb)



(III)

We have also been able to make I by heating arsenic powder with dodecafluorotribenzo[*b*,*e*,*h*][1,4,7]trimercuronin. (In this reaction, and in the “direct synthesis" using arsenic and 1,2-diiodotetrafluorobenzene, any oxide impurity in the arsenic gives rise to a by-product octafluoro-5,10-epoxy-5,10-dihydroarsanthrene (III) [3].) An accurate mass determination on the parent ion in the mass spectrum of I gave 593.8249; calculated for $^{12}C_{18}{}^{19}F_{12}{}^{75}As_2$, 593.8240. The melting point of I is 210—211° C (cf. 200° C; ref. 2); thus it appears that our sample of I is more or less identical to that of Cullen and Wu.

A much more serious disagreement occurs over the data for the stibanthrene II and we have therefore concentrated most of our efforts on II. Our recalculated ^{19}F chemical shifts for II are 114.5 and 153.8 ppm relative to internal $CFCl_3$ (THF solution); those of Cullen and Wu [2] are 112.8 and 150.0 ppm (unspecified solvent). The melting point of our sample of II is 258—259° C (cf. 155° C, ref. 2).

Dodecafluoro-5,10-*o*-benzenostibanthrene can be made easily and in good yield simply by heating 1,2-diiodotetrafluorobenzene and antimony powder at 250° C (see Experimental section); it can also be made by heating together $(HgC_6F_4)_3$ and Sb. An accurate mass determination on the parent peak in the mass spectrum of II gave 685.7890; calculated for $^{12}C_{18}{}^{19}F_{12}{}^{121}Sb_2$, 685.7885. Nine mass spectra recorded at intervals over the twenty minutes needed for all the sample to evaporate away from the spectrometer probe were virtually identical and hence prove the homogeneity of the sample (later used in the C, H, F analysis). The mass spectrum of II is comparatively simple, the main antimony-containing peaks being due to the ions $Sb_2(C_6F_4)_3^+$, $SbC_{12}F_8^+$, $SbC_6F_4^+$ (base peak), SbF_2^+, SbF^+ and Sb^+; the parent ion had the correct isotopic pattern for a $C_{18}Sb_2$ species. The stoichiometry of the compound is thus established as $Sb_2C_{18}F_{12}$. The ^{19}F NMR and infrared spectra are exactly as expected for a 1,2-C_6F_4 derivative; the absence of a peak at ca. 950 cm^{-1} in the infrared spectrum further confirms that the C_6F_4 rings are not directly joined together. We are thus led to the conclusion that our compound, and not that described by Cullen and Wu, is dodecafluoro-5,10-*o*-benzenostibanthrene.

Dodecafluoro-5,10-*o*-benzenostibanthrene is very stable thermally and showed no change on being heated overnight at 350° C in a sealed, evacuated tube; a slow decomposition was observed at 400° C. On the hot-stage microscope samples begin to sublime at about 160° C under atmospheric pressure and condense as colourless, needle crystals on the upper slide-cover. It also proved impossible to cleave the fluoroaromatic groups from antimony by heating II for many hours with water vapour at 300° C in a vacuum. When heated with selenium at 300° C, II gave a good yield of octafluoroselanthrene, $Se_2(C_6F_4)_2$, again demonstrating that the fluoroaromatic groups in II are not directly coupled together. In a similar reaction sulphur gave a low yield of octafluorothianthrene. No reaction occurred when II and methyl iodide were refluxed together.

When a powdered mixture of arsenic and antimony were heated at 250° C with 1,2-diiodotetrafluorobenzene the product had a mass spectrum showing three molecular ions: $Sb_2(C_6F_4)_3^+$, $As_2(C_6F_4)_3^+$ and $SbAs(C_6F_4)_3^+$. An accurate mass determination on the ion at m/e = 640 gave 639.804; calculated for $^{12}C_{18}{}^{19}F_{12}{}^{121}Sb^{75}As$, 639.806.

The hydrogen analogue of II appears not to be known. Attempts to prepare it by heating together antimony powder and 1,2-diiodobenzene repeatedly gave no isolable organoantimony compounds, although much antimony triiodide was formed. However, when antimony was heated with a mixture of 1,2-diiodobenzene and 1,2-diiodotetrafluorobenzene a product was formed which showed three molecular ions in its mass spectrum: $Sb_2(C_6F_4)_3^+$, $Sb_2(C_6F_4)_2(C_6H_4)^+$ and $Sb_2(C_6F_4)(C_6H_4)_2^+$ (interestingly, no peak corresponding to $Sb_2(C_6H_4)_3^+$ could be detected). Fragment ions of interest included $Sb(C_6F_4)(C_6H_4)^+$, $Sb(C_6H_4)_2^+$, $C_6F_4C_6H_4^+$ and $SbC_6H_4^+$.

Experimental

Reactions were carried out in sealed, evacuated tubes which had been previously dried by flaming out under vacuum.

Preparation of II

Antimony powder (1.5 g) and 1,2-diiodotetrafluorobenzene (3.0 g) were heated at 250° C overnight. After being allowed to cool, the tube was cut open and the products scraped out. After grinding to a powder, the products were extracted with three aliquots (30 ml) of boiling 60—80° petrol ether. The aliquots were mixed and cleared by boiling with charcoal; evaporation to small bulk, followed by cooling, gave crystals of dodecafluoro-5,10-*o*-benzenostibanthrene (0.99 g; 58%). The analytical sample, m.p. 258—259° C, was recrystallized from 60—80° petrol ether and dried under high vacuum. (Found: C, 31.4; H, 0.0; F, 33.0. Calcd. for $C_{18}F_{12}Sb_2$: C, 31.4; H, 0.0; F, 33.2%). The compound is soluble in all the common organic solvents but is insoluble in water.

The melting points of $P_2(C_6F_4)_3$ [1], $As_2(C_6F_4)_3$, $Sb_2(C_6F_4)_3$ and $Bi_2(C_6F_4)_3$ [2] are 160—162° C, 210—211° C, 258—259° C and >300° C dec., respectively. For compounds of similar molecular (and, presumably, crystal) structure the melting points should increase smoothly with molecular weight, as occurs in this sequence. Cullen and Wu's m.p. of 155° C for II is clearly out of line with the melting points of the other derivatives.

Reaction of II with selenium

At 250° C there was no obvious reaction between selenium and II. After 48 h at 300° C, the tube was cooled, cut open and the contents extracted with 60—80° petrol ether. The only compound to crystallize out was octafluoroselanthrene, m.p. 115—116° C (lit. [4] 117—120° C). A mass spectrum confirmed the identify of the sample.

Thermal decomposition of II

No apparent reaction occurred when the sample was heated at 350° C overnight. At 400° C the compound slowly assumed a yellow colour but after 15 h more than half the sample could be recovered (m.p. 259° C).

References

1 C.M. Woodard, G. Hughes and A.G. Massey, J. Organometal. Chem., 112 (1976) 9.

2 W.R. Cullen and A. Wu, J. Fluorine Chem., 8 (1976) 183.

3 D.S. Brown, A.G. Massey and T.K. Mistry, J. Fluorine Chem., 16 (1980) 483.

4 S.C. Cohen, M.L.N. Reddy and A.G. Massey, J. Organometal. Chem., 11 (1968) 563.