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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

XXIX *. THE SYNTHESIS OF SOME HETEROCYCLES OF Hg, S, Se, Te, As AND Sb.

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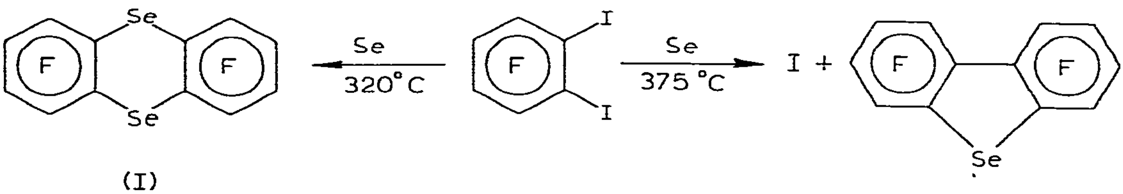
Summary

The small-scale syntheses of octafluorodibenzo-thiophen, -selenophen, -tellurophen, perfluoro-*ortho*-phenylenemercury trimer, dodecafluoro-13,14-diarsatriptycene and dodecafluoro-13,14-distibatriptycene are described. The trimer of *ortho*-phenylenemercury, $(C_6H_4Hg)_3$, has been isolated from the reaction between 1,2-diiodobenzene or 1,2-dibromobenzene and potassium amalgam in tetrahydrofuran.

The high thermal stability of many polyfluoro-aromatic derivatives of metals and metalloids greatly aids their small-scale preparation by the direct reaction between an element and the corresponding aryl iodide in a heated, sealed tube [2]. For example, we originally showed that the products formed by heating 1,2-diiodotetrafluorobenzene with selenium depend on the temperature used:



(I)

(II)

However, the thermal stability of II is such that the above reaction can be carried out at 450°C to obtain pure octafluorodibenzoselenophen in about 60% yield. Octafluorodibenzotellurophen can be prepared at the same temperature

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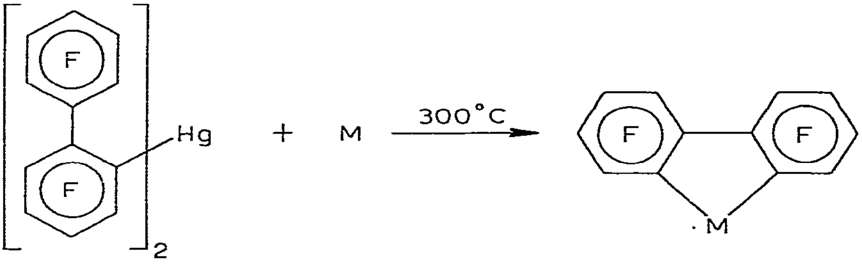
* For part XXVIII see ref. 1.

but in this case the yield is much lower (ca. 17%). Such a direct synthetic route to these compounds is particularly valuable in view of the non-availability of 1,2-dilithiotetrafluorobenzene.

One method of making the bis(pentafluorophenyl)chalcogens is to heat bis(pentafluorophenyl)mercury with sulphur, selenium or tellurium [2,3]. During attempts to extend this method to the bis(2-nonafluorobiphenyl)chalcogens it was found that at 300° C ring closure occurred:



(M = S, 55%)
(M = Se, 23%)
(M = Te, 10%)

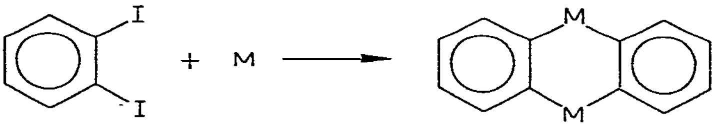
The only other identifiable solid product from these reactions was 2-hydrononafluorobiphenyl, the yield of which varied from 4—10%. Although the fate of the remaining $C_{12}F_9$ groups could not be established, the complete absence of decafluorobiphenyl ruled out a simple fluorine-migration reaction such as:

$$(2\text{-}C_{12}F_9)_2Hg + M \rightarrow C_{12}F_8M + C_{12}F_{10} + Hg$$

Similar formation of octafluorodibenzothiophen (together with 2-hydrononafluorobiphenyl) occurred when either bis(2-nonafluorobiphenyl)selenium was heated with sulphur or bis(2-nonafluorobiphenyl)sulphur was heated alone. The reaction tubes, which often showed considerable signs of charring, contained carbon dioxide, carbon oxysulphide, carbon disulphide, silicon tetrafluoride and, apparently, hexafluorodisiloxane. A reaction carried out in a stainless steel bomb gave the same products, suggesting that the silicon fluorides arose from attack of hydrogen fluoride on the glass used to construct the reaction tubes and the gas-handling systems. The source of "hydrogen" can only be water desorbed from the reaction vessel walls (all the vessels were baked out under vacuum prior to their being filled with reactants). However, only a trace of octafluorodibenzoselenophen was formed when water was deliberately added to the reactants $(C_{12}F_9)_2Hg$ and Se. The presence of carbon oxides and sulphides shows that complete disruption of some benzene rings must occur at these temperatures (300° C); the fluoroaromatics are still more stable than polychloroaromatics because direct syntheses involving C_6Cl_5I and $1,2\text{-}I_2C_6Cl_4$ at temperatures below 200° C yield hexachlorobenzene and "element chloride" as the two major products [4]. The high general stability of octafluorodibenzoselenophen can be judged from the fact that it could be recovered in yields up to 98% when heated in a sealed tube to 450° C for 7 days, heated with silver powder at 400° C for 5 days or treated with water at 150° C for 7 days.

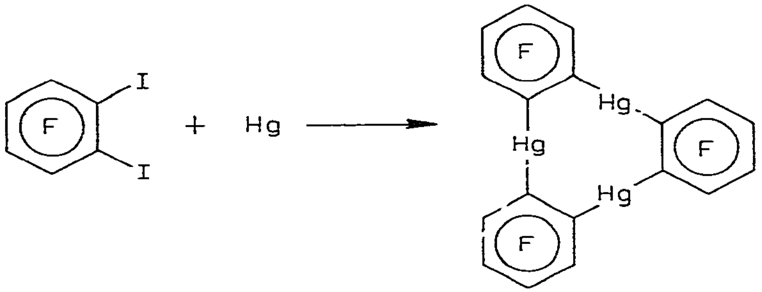
No heterocyclic derivatives were detected when tetrakis(2-nonafluorobiphenyl)germane and tetrakis(2-nonafluorobiphenyl)stannane were heated to 400° C in sealed tubes.

The successful syntheses of the heterocycles I and II described above led us to investigate the reaction of 1,2-diiodobenzene with both sulphur and selenium:



(M = S, 230°C, 48h, 17%)
(M = Se, 320°C, 48h, 26%)

When 1,2-diiodotetrafluorobenzene is heated with mercury to 200° C tetrafluoro-*ortho*-phenylenemercury trimer (III) is formed:



(III)

This mercurial has been made previously by both the decarboxylation [5] and sulphur trioxide-elimination [6] routes. Its mass spectrum, besides verifying the trimer formulation, was particularly interesting in that a group of peaks at around *m/e* 602 were found to be due to the ion $Hg_3^{+\cdot}$. The identity of the ion was proved by comparing the calculated and experimental peak heights for Hg_3^+ (see Fig. 1); furthermore, the mass of the ion at *m/e* 594, $^{198}Hg_3^{+\cdot}$; was determined as 593.9000 compared with a theoretical value of 593.9001.

Normally, perfluoro-aromatic organometallic compounds have similar structures to their hydrogen analogues but *ortho*-phenylenemercury, unlike III, is known to be a hexamer [7]. Consultation of Dreiding models showed that there are no steric reasons why a planar trimer, such as III, should not exist. For this reason we attempted the reaction between 1,2-diiodobenzene or 1,2-dibromobenzene and potassium amalgam in tetrahydrofuran in order to take a close look at "*ortho*-phenylenemercury". We obtained colourless, needle-like crystals which lost their transparency at about 330° C when viewed on the hot-stage microscope but showed no other signs of change (some sublimation took place below 330° C); the literature values for $(HgC_6H_4)_6$ are 324—326° C with decomposition [8] and 332—334° C with decomposition [9]. Analysis showed the crystals to be

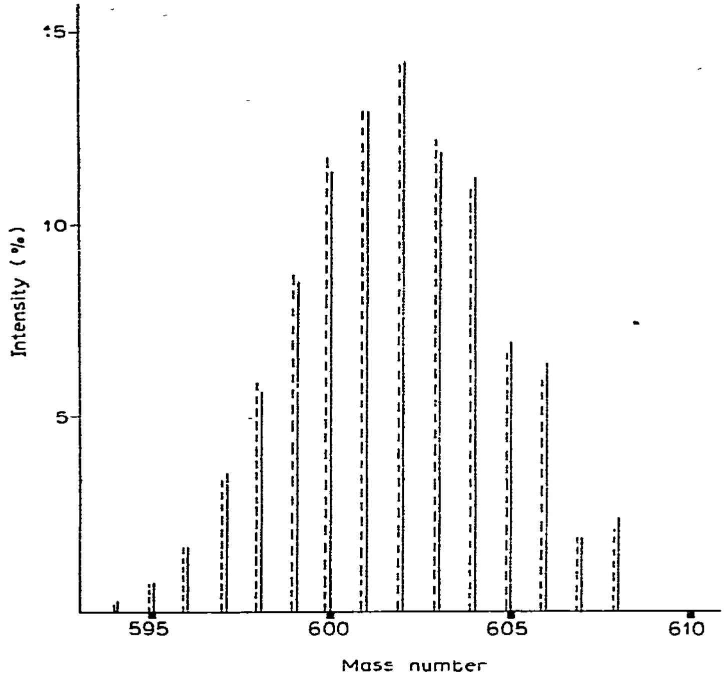


Fig. 1. Comparison of the observed (solid line) and theoretical (broken line) mass spectral intensities for the fragment ion Hg_3^+.

ortho-phenylenemercury but a mass spectrum of the analytical sample had a mass cut-off at the ion $(C_6H_4Hg)_3^+$; the excellent fit between the observed and calculated values for the peaks in the parent ion cluster, Fig. 2, leave no doubt as to the identity of the ion and also show that very little fragmentation occurs by loss of H. (A very weak ion cluster at $m/e \cong 602$ is probably due to the Hg_3^+ ion discussed above.) It appears likely that this compound is the trimer of *ortho*-phenylenemercury and hence the hydrogen analogue of III. An interesting feature of the mass spectrum was a broad meta-stable peak corresponding to the reaction:

$$(C_6H_4Hg)_3^+ \rightarrow (C_6H_4)_3^+ + \text{“(Hg)}_3\text{”}$$

m/e observed 62.8 (spans 3 mass units); *m/e* calculated 62.6.

Dreiding models indicate that $(C_6H_4Hg)_n$ polymers should be stable for values of $n = 3, 4, 6, 8 ...$, see Table 1, and it is possible that a range of such polymers is formed when *ortho*-dihalobenzenes react with sodium or potassium amalgams. (The preparative difficulties are not made any easier by the fact that the decomposition points of products are not sharp and hence are of little use as a criterion of purity.) Wittig has demonstrated that ring-coupling can occur also, to give biphenylenemercury tetramer $(C_6H_4C_6H_4Hg)_4$ (IV) and triphenylenemercury dimer $(C_6H_4C_6H_4C_6H_4Hg)_2$. Table 1 shows that certain “mixed” one ring-two ring systems are possible and, in particular, $C_6H_4HgC_6H_4HgC_6H_4C_6H_4Hg$ (V). Impure samples of *ortho*-phenylenemercury trimer have a group of peaks around *m/e* 906 which represent the ion $C_{24}H_{16}Hg_3^+$. We suggest that this is the parent

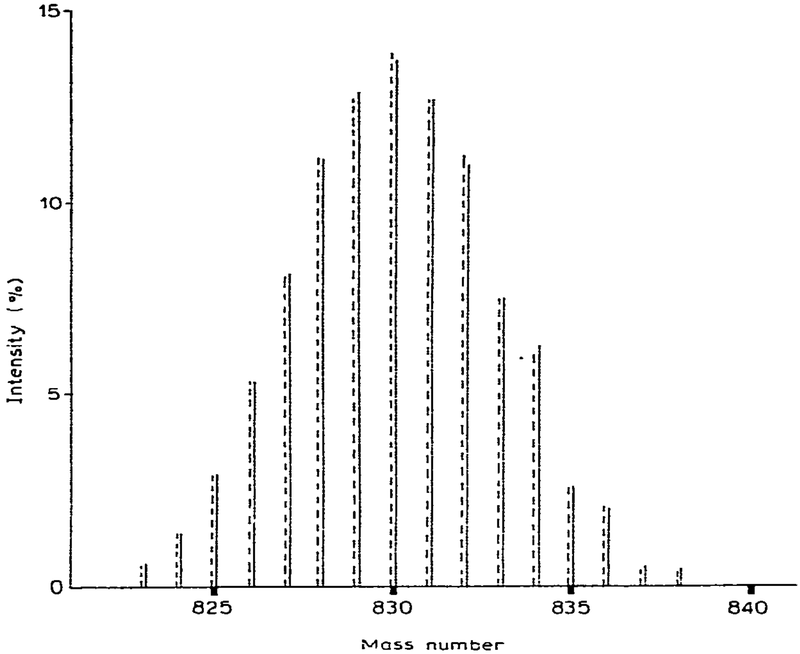


Fig. 2. Comparison of the observed (solid line) and theoretical (broken line) mass spectral intensities for the parent ion, $C_{18}H_{12}Hg_3^{+}$, of *o*-phenylenemercury trimer.

ion cluster of V. In some spectra very weak peaks also appear at around *m/e* 985 and could be due to the ion $\overline{C_6H_4C_6H_4HgC_6H_4HgC_6H_4C_6H_4Hg}^{+}$. An interesting point to notice in connection with these mixed species is that the first published infrared spectrum [5] of $(C_6F_4Hg)_3$ had a peak at 940 cm^{-1}, the region normally associated with the inter-ring C—C bond of 2,2'-C_6F_4—C_6F_4 derivatives; Deacon [6] has since pointed out that this peak in $(C_6F_4Hg)_3$ is due to an impurity. Perhaps the original sample contained a small amount of the perfluoro-analogue of a mixed species such as V, although Sartori [10] assumes the 940 cm^{-1} band to have been due to a C—Cl vibration (the chlorine remaining from the perchloro starting material).

The perfluoro-analogue of Wittig's biphenylenemercury tetramer (IV), although originally thought to be a tetramer, has a mass spectrum corresponding to the trimer, with no detectable ions heavier than $(C_{12}F_8Hg)_3^{+}$. Three different samples of this compound have now given identical mass spectra and we assume that our original molecular weight determination, using vapour phase osmometry, was in error, possibly due to the compound's low solubility. The fairly intense group of peaks due to the ion $(C_{12}F_8Hg)_2^{+}$ in the mass spectrum of $(C_{12}F_8Hg)_3$, is unlikely to be due to the parent ion of perfluorobiphenylenemercury dimer as impurity because this dimer is probably incapable of existence (Table 1).

When 1,2-diiodotetrafluorobenzene and either arsenic or antimony are heated together in an evacuated, sealed tube the colourless compounds dodecafluoro-13,14-diarsatriptycene and dodecafluoro-13,14-distibatriptycene are formed,

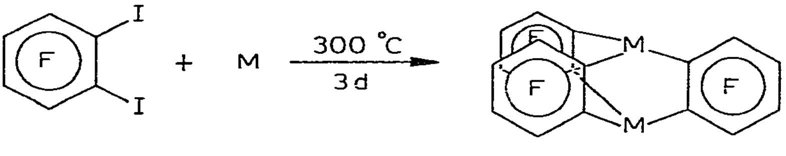
TABLE 1

PREDICTED STABILITY OF *ORTHO*-PHENYLENEMERCURY DERIVATIVES USING DREIDING MODELS [a]

	Compound	Comments
	Stable mercurials	
1	$(C_6H_4Hg)_3$	this work; perfluoro analogue also known [5,6]
2	$(C_6H_4Hg)_4$	
3	$(C_6H_4Hg)_6$	ref. 7, 8, 9
4	$(C_6H_4Hg)_8$	non-rigid
5	$(C_6H_4)_8Hg$	non-rigid
6	$(C_6H_4C_6H_4Hg)_3$	perfluoro analogue known; this work
7	$(C_6H_4C_6H_4Hg)_4$	ref. 8
8	$(C_6H_4C_6H_4C_6H_4Hg)_2$	ref. 8; two structural isomers possible, one being non-rigid
9	$\overline{C_6H_4Hg(C_6H_4)_5Hg}$	formula "isomer" of 8
10	$\overline{C_6H_4C_6H_4Hg(C_6H_4Hg})_4$	
11	$\overline{C_6H_4C_6H_4HgC_6H_4HgC_6H_4Hg}$	detected; this work
12	$\overline{C_6H_4C_6H_4HgC_6H_4C_6H_4HgC_6H_4Hg}$	detected; this work
13	$\overline{C_6H_4C_6H_4HgC_6H_4C_6H_4HgC_6H_4HgC_6H_4Hg}$	two isomers possible depending on the relative positions of the single C_6H_4 rings
14	$\overline{C_6H_4C_6H_4C_6H_4C_6H_4HgC_6H_4Hg}$	
15	$\overline{C_6H_4C_6H_4C_6H_4C_6H_4Hg(C_6H_4C_6H_4Hg}$)	non-rigid
16	$(\overline{C_6H_4)_4Hg(C_6H_4)_4Hg}$	non-rigid
	Unstable mercurials	
17	$(C_6H_4Hg)_5$	C—Hg—C bonds only slightly bent; possible borderline stability
18	$\overline{C_6H_4C_6H_4HgC_6H_4C_6H_4Hg}$	Hg ··· Hg separation too small
19	$\overline{C_6H_4C_6H_4C_6H_4Hg}$	C—Hg—C angle < 180°
20	$\overline{C_6H_4C_6H_4HgC_6H_4Hg}$	C—Hg—C angle < 180°
21	$\overline{C_6H_4C_6H_4C_6H_4HgC_6H_4Hg}$	ditto
22	$(C_6H_4)_4Hg$	ditto
23	$\overline{C_6H_4C_6H_4C_6H_4HgC_6H_4C_6H_4Hg}$	C—Hg—C angle < 180°; Hg ··· Hg distance only about 2.7 Å
24	$(C_6H_4)_5Hg$	C—Hg—C angle < 180°; two H atoms approach to within 0.6 Å
25	$(C_6H_4)_6Hg$	two pairs of H atoms approach to within 0.6 Å

[a] Criteria used were that the C—Hg—C angles had to be 180° and the Hg ··· Hg interactions ⩾ 3.5 Å.

respectively:



(VI): M = As, m.p. 210–211°C;

(VII): M = Sb, m.p. 258–259°C

The molecular weights of VI and VII were established using mass spectrometry; the presence of two antimony isotopes helped to prove the identity of the parent ion of VII as $Sb_2C_{18}F_{12}^{+\cdot}$. The mass spectrum of the arsenic derivative showed three metastable transitions involving arsenic:

$As_2(C_6F_4)_3^+ \rightarrow As(C_6F_4)^+ + As(C_6F_4)_2$
594 233 M^* (found: 83.7; calcd.: 83.7)

$As(C_6F_4)_2^+ \rightarrow C_{12}F_8^+ + As$
371 296 M^* (found: 236.2; calcd.: 236.2)

$As(C_6F_4)_2^+ \rightarrow C_{12}F_6^+ + AsF_2$
371 258 M^* (found: 179.5; calcd.: 179.4)

Such a loss of AsF_2, and the presence of AsF^+, AsF_2^+, SbF^+ and SbF_2^+ ions in these mass spectra, is not unexpected of fluoroaromatic compounds [2]. Neither compound exhibited a peak in their infrared spectrum at around 950 cm^{-1} which is taken as evidence that ring-coupling has not occurred during preparation. The corresponding reaction between 1,2-diidobenzene and arsenic gave the known 13,14-diarsatriptycene, m.p. 296—298°C (lit. [11] value 295—296°C).

Heating 1,2-diiodotetrafluorobenzene with germanium resulted in the formation of low yields of the known [12] bis(octafluorobiphenylene)germane, but with tin the reaction was more complex; the main product appeared to be the colourless $Sn_2(C_6F_4)_4I_4$, together with small amounts of $Sn_2(C_6F_4)_6I_4$ but we have been unable to deduce their structures. Unlike the germanium case, no ring-coupling would appear to have occurred during the preparation of these tin derivatives as evidenced by the lack of a band at about 950 cm^{-1} in their infrared spectrum.

Experimental

The fluoroaromatic starting metrials were purchased from Bristol Organics, and we thank Professor P. Sartori of the Institut für Anorganische Chemie der Technischen Hochschule, Aachen for a sample of $(C_6F_4Hg)_3$. All the sealed-tube reactions were carried out using 1—1.5 g of the corresponding fluoroaromatic compound; gaseous products were identified using a combination of infrared and mass spectroscopy.

Reactions involving bis(2-nonafluorobiphenyl)mercury

Bis(2-nonafluorobiphenyl)mercury was prepared as described previously [13] by treating mercuric chloride with 2-lithiononafluorobiphenyl in ether. Decomposition at 400°C for 18 h gave 2,2′-bis(pentafluorophenyl)octafluorobiphenyl, m.p. 167—169°C (lit. [13] 167—168°C) as the only isolable material (6%); silver powder at 250°C gave the same product in 37% yield. It had been hoped that one or other of these reactions would give perfluorobiphenylenemercury.

Heating bis(2-nonafluorobiphenyl)mercury with sulphur at 300°C for 2 d gave octafluorodibenzothiophen in 55% yield. M.p. 108—109°C (lit. [14] 108.5—109.5°C). Gaseous products included sulphur dioxide, hydrogen sulphide, carbon dioxide, carbon oxysulphide, carbon disulphide and silicon tetrafluoride; the only other identified solid product was mercuric sulphide.

Heating bis(2-nonafluorobiphenyl)mercury with selenium at 300°C for 3 d gave octafluorodibenzoselenophen in 25% yield. M.p. 118—119°C (lit. [14] 118.5—120.5°C).

Heating bis(2-nonafluorobiphenyl)mercury with tellurium at 300°C for 4 d gave octafluorodibenzotellurophen in 10% yield. M.p. 114—116°C (lit. [14] 116—119°C). The involatile residue contained mercuric selenide, identified by X-ray powder photography.

In all these sealed tube reactions 2-hydrononafluorobiphenyl was obtained as a side-product, but no HgF_2 or Hg_2F_2 could be detected using X-ray powder photography.

When bis(2-nonafluorobiphenyl)mercury and selenium were heated together at 300°C in a stainless-steel Hoke bomb, octafluorodibenzoselenophen (22%), bis(2-nonafluorobiphenyl)selenium (9%) and 2-hydrononafluorobiphenyl (19%) were the isolated solid products. Gaseous by-products, identified by infrared and mass spectroscopy, were carbon dioxide, silicon tetrafluoride and hexafluorodisiloxane; we assume that the silicon fluorides arose from attack on the glass gas handling system by hydrogen fluoride formed in the bomb.

2-Hydrononafluorobiphenyl (24%) and octafluorodibenzoselenophen (trace) were formed when bis(2-nonafluorobiphenyl)mercury, selenium and water were heated at 270°C for 3 d in a sealed, evacuated tube.

Preparation of bis(2-nonafluorobiphenyl)chalcogens

Sulphur dichloride, selenium tetrachloride or tellurium tetrachloride were treated with 2-lithiononafluorobiphenyl in ether at —78°C and the mixture allowed to warm up to room temperature. After 2 h the solvent was removed under reduced pressure and the product sublimed under vacuum onto a cold finger held at —78°C.

Bis(2-nonafluorobiphenyl)sulphur: (70%) m.p. 155—157°C (Found: C, 43.9; F, 50.9; Mol. wt. (mass spectrum) 662. $C_{24}F_{18}S$ calcd.: C, 43.5; F, 51.6%; Mol. wt. 662). Bis(2-nonafluorobiphenyl)selenium: (63%) m.p. 133—135°C (Found: C, 42.1; F, 47.2, Mol. wt. (mass spectrum) 710. $C_{24}F_{18}Se$ calcd.: C, 41.6; F, 48.2%; Mol. wt. 710 for $C_{24}F_{18}{}^{80}Se$).

Bis(2-nonafluorobiphenyl)tellurium: (32%) m.p. 111—113°C; identified by the isotopic pattern of the peaks in the parent ion at around *m/e* 758. 2,2′-Bis(pentafluorophenyl)octafluorobiphenyl was a by-product in the latter reaction.

The bis(2-nonafluorobiphenyl)chalcogens were isolated also from the direct reaction between 2-iodononafluorobiphenyl and the appropriate chalcogen at 240—260°C in sealed tubes: $C_{24}F_{18}S$ (65% after 1 d); $C_{24}F_{18}Se$ (65% after 2 d); $C_{24}F_{18}Te$ (35% after 4 d; 2,2′-bis(pentafluorophenyl)octafluorobiphenyl, 7%, obtained as a side product).

Reactions of bis(2-nonafluorobiphenyl)chalcogens

A mixture of bis(2-nonafluorobiphenyl)sulphur and silver powder, when heated at 250°C for 48 h, gave unchanged starting material (25%) and octafluorodibenzothiophen (30%), m.p. 107—108°C.

Bis(2-nonafluorobiphenyl)selenium and sulphur at 300°C in a sealed tube gave a 25% yield of octafluorodibenzothiophen.

Preparation of tetrafluorophenylenemercury trimer

1,2-Diiodotetrafluorobenzene and mercury were heated at 300°C for 2 d in a sealed tube to give tetrafluorophenylenemercury trimer in 16% yield. The analytical sample was purified by sublimation at 300°C in an open sample tube held in a furnace. Dec. point, 337°C (lit. [5] 340°C) (Found: C, 20.5; F, 21.2. $C_{18}F_{12}Hg_3$ calcd.: C, 20.7; F, 21.8%). The parent ion in the mass spectrum was observed at around *m/e* 1046, and the pattern of peaks due to the various mercury and carbon isotopes matched virtually identically to that calculated for $C_{18}Hg_3$. Carbon dioxide, silicon tetrafluoride and hexafluorodisiloxane were identified as gaseous products using a combination of infrared and mass spectroscopy.

When the trimer and selenium powder were heated together at 300°C a 52% yield of octafluoroselenanthrene was obtained; the identity of the product was checked by comparing its infrared spectrum with that of an authentic sample [14]. Under similar conditions the trimer and sulphur gave octafluorodibenzothiophen in a 48% yield.

Reactions of 1,2-diiodotetrafluorobenzene with arsenic and antimony

The reactions were carried out at 300°C in sealed tubes and the products purified by vacuum sublimation. Dodecafluoro-13,14-diarsatriptycene (13%) m.p. 205—206°C (Found: C, 35.4, $C_{18}F_{12}As_2$ calcd.: C, 36.4%). The parent ion in the mass spectrum occurred at *m/e* 594; strong peaks were observed for the ions $AsC_{18}F_{10}^+$ (i.e. $P-AsF_2$); $C_{18}F_{12}^+$; $As(C_6F_4)_2^+$; $C_{12}F_8^+$; $C_{12}F_6^+$; $AsC_6F_4^+$ and AsF_2^+. Principal infrared peaks (nujol mull) were, in cm^{-1}, 1296 m, 1260 m, 1101 s, 1026 s, 830 m, 771 m, 730 m, 389 m and in particular no peaks occurred between 830 and 1026 cm^{-1}.

Dodecafluoro-13,14-distibatriptycene (12%) m.p. 245—246°C (Found: C, 30.6. $C_{18}F_{12}Sb_2$ calcd.: C, 31.4%). The parent ion cluster in the mass spectrum appeared around *m/e* 688, the pattern of peaks being that expected for carbon and antimony isotopes in a $C_{18}Sb_2^+$ ion. Other prominent peaks in the mass spectrum were due to the ions $Sb(C_6F_4)_2^+$, $SbC_6F_4^+$, SbF_2^+, SbF^+ and Sb^+. The principal infrared absorption peaks (nujol mull) were, in cm^{-1}, 1428 m, 1260 m, 1254 m, 1091 s, 1010 s, 806 m, 753 m, 720 m, 367 m; in particular, there were no peaks between 806 and 1010 cm^{-1}.

Under similar conditions 1,2-diiodobenzene reacted with arsenic to give 13,14-diarsatriptycene m.p. 296—298°C (lit. [11] 295—296°C); the parent ion occurred at *m/e* 378 is the mass spectrum and a metastable peak was observed for the reaction:

$$C_{18}H_{12}As_2^+ \rightarrow C_{12}H_8As^+ + C_6H_4As;\ M^* \text{ (found: 136.7; calcd.: 136.3)}$$

An attempt to make an arsa-stibatriptycene by heating arsenic and antimony with 1,2-diiodotetrafluorobenzene at 300°C for 3 d gave only dodecafluoro-13,14-diarsatriptycene.

X-ray powder diffraction studies showed that dodecafluoro-13,14-diarsa- and distaba- triptycene were isostructural. The ^{19}F NMR spectra of the two compounds exhibited an $AA'XX'$ pattern with the following chemical shifts (relative to CCl_3F, ±1 ppm):

$(C_6F_4)_3As_2$ $F_3, F_6 = 136.9$ ppm; $F_4, F_5 = 165.9$ ppm

$(C_6F_4)_3Sb_2$ F_3, F_6 = 128.3 ppm; F_4, F_5 = 166.4 ppm

cf. $(C_6F_4)_3Hg_3$. F_3, F_6 = 128.2 ppm; F_4, F_5 = 167.3 ppm

Reaction of 1,2-diiodotetrafluorobenzene with selenium and tellurium

1,2-Diiodotetrafluorobenzene was heated at 450° C in a sealed tube for 3 d with selenium powder; vacuum sublimation at 90—100° C (10^{-3} mmHg) gave octafluorodibenzoselenophen in 62% yield. Identified by m.p. 119—120° C (lit. [14] 118.5—120.5° C), infrared and mass spectroscopy.

When tellurium powder was used in place of selenium the product was octafluorodibenzotellurophen (17%) m.p. 115—116° C (lit. [14] 116—119° C).

Reaction of 1,2-diiodotetrafluorobenzene with lead, bismuth and phosphorus

When 1,2-diiodotetrafluorobenzene was treated with either lead or bismuth for 3 d at 300° C, a mixture of perfluorobiphenylene (2—3%), perfluorotriphenylene (13—16%) and perfluorotetraphenylene (2—5%) was obtained.

Red phosphorus and 1,2-diiodotetrafluorobenzene on being heated to 250° C for 3 d gave a 15% yield of dodecafluoro-13,14-diphosphatriptycene, m.p. 160—162°. The parent ion in the mass spectrum occurred at m/e 506; a strong metastable peak was detectable for the reaction:

$C_{18}F_{12}P_2^+ \rightarrow C_{18}F_{10}P^+ + PF_2$; M^* (found: 386.1; calcd.: 386.2)

Preparation of ortho-phenylenemercury

1,2-Diiodobenzene (or 1,2-dibromobenzene) was shaken with potassium amalgam in tetrahydrofuran at room temperature for 2 h. The solvent was removed under reduced pressure and the mercurial extracted using dimethylformamide. Purification was accomplished by either recrystallisation from dimethylformamide or by sublimation under vacuum. The compound appeared to have no melting point, but at 330° C the needle-like crystals lost their transparency; above about 260° C there was a slow sublimation to the upper slide-cover of the hot-stage microscope. (Found: C, 26.1; H, 1.5. $C_{18}H_{12}Hg_3$ calcd.: C, 26.0; H, 1.45%.) The identity of the parent ion in the mass spectrum was proved by the excellent fit obtained between the observed and calculated peak intensities of the ion cluster (see Fig. 2); it is obvious from Fig. 2 that very little fragmentation by loss of H occurs from the ion. Other peaks in the mass spectrum corresponded to the ions Hg_3^+, $Hg_2(C_6H_4)_2^+$, Hg_2^+, $Hg(C_6H_4)_2^+$, $[Hg_2(C_6H_4)_3]^{++}$, $HgC_6H_4^+$, $C_{18}H_{12}^+$, C Hg^{++}, Hg^+. A trace of triphenylene was the only other compound which was isolated.

Thermal decomposition of bis(2-iodotetrafluorophenyl)sulphur

When bis(2-iodotetrafluorophenyl)sulphur was heated in a sealed tube to 350° C for 3 d the products were octafluorodibenzothiophen (18%), silicon tetrafluoride, carbon disulphide and carbon oxysulphide.

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