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TRANSMETALLATION REACTIONS INVOLVING PHENYLENEMERCURIALS

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Summary

When heated with Group V and Group VI elements, the phenylenemercurials $(C_6H_4Hg)_3$, $(C_6F_4Hg)_3$ and $(C_6Cl_4Hg)_3$ form heterocycles of formulae $M_2(C_6X_4)_3$ and $M'_2(C_6X_4)_2$ where M = As, Sb, Bi and M′ = S, Se, Te. The compounds $Te_2(C_6Cl_4)_2$ and $M_2(C_6Cl_4)_3$ (M = As, Sb, Bi) were also obtained by heating the elements with 1,2-$I_2C_6Cl_4$, which was prepared by mercuration of 1,2-$H_2C_6Cl_4$ followed by iododemercuration. Octachlorothianthrene has been obtained by heating sulphur with $Te_2(C_6Cl_4)_2$, C_6Cl_6 or C_6Cl_5I, and from the reaction between 1,2-$H_2C_6Cl_4$, $AlCl_3$, and S_2Cl_2.

Introduction and discussion

Metal-exchange reactions involving simple organomercury compounds have been used in synthesis for many years [1]. Typically, a wide range of alkyls can be obtained simply by treating dialkylmercurials with the appropriate elements. Among the few reported cases of transmetallations involving the use of phenylenemercury cyclic polymers are the preparations of $Te_2(C_6H_4)_2$ (III) [2] and $Sb_2(C_6F_4)_3$ (XIV) [3] from *ortho*-phenylenemercury and its perfluoro analogue, respectively. As we had a variety of phenylenemercurials available [4], we have studied their possible use in the small-scale syntheses of heterocycles I–XVII. The method employed involved heating the chosen element with the corresponding phenylenemercurial in an evacuated sealed tube; the reaction temperatures were optimised.

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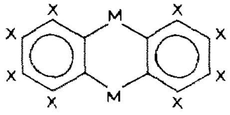
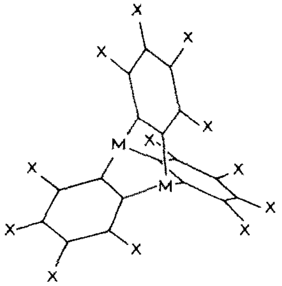


	M	X
I	S	H
II	Se	H
III	Te	H
IV	S	F
V	Se	F
VI	S	Cl
VII	Se	Cl
VIII	Te	Cl



	M	X
IX	P	H
X	As	H
XI	Sb	H
XII	Bi	H
XIII	As	F^{3}
XIV	Sb	F^{3}
XV	As	Cl
XVI	Sb	Cl
XVII	Bi	Cl

It proved possible to make compounds I and II using $(C_6H_4Hg)_3$ and either sulphur or selenium (reaction 1, X = H, M = S or Se).

$$2(C_6X_4Hg)_3 + 6M \rightarrow 3(C_6X_4M)_2 + 6Hg \qquad (1)$$

They were identified by mass spectroscopy; for example, the parent ion in the spectrum of $S_2(C_6H_4)_2$ was the base peak, and the doubly-charged ion $S_2(C_6H_4)_2{}^{2+}$ was also detectable. Two metastable peaks were observed as a result of the following reactions:

$S_2(C_6H_4)_2{}^+ \rightarrow S + S(C_6H_4)_2{}^+$ calcd. 156.7; obs. 156–158

$S(C_6H_4)_2{}^+ \rightarrow S + (C_6H_4)_2{}^+$ calcd. 125.6; obs. 124.8–126.4

Formation of these well-known compounds demonstrated the feasibility of the synthetic method.

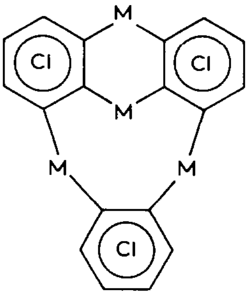
Tetrafluorophenylenemercury trimer gave IV and V in ca. 50% yields when heated with sulphur and selenium (reaction 1, X = F; M = S, Se). A "mixed" synthesis in which selenium was heated with both (C_6H_4Hg) and $(C_6F_4Hg)_3$ gave, as well as the two symmetrical products II and V, the partially-fluorinated species $Se_2(C_6H_4)(C_6F_4)$. Sulphur, selenium and tellurium reacted readily with tetrachlorophenylenemercury trimer, $(C_6Cl_4Hg)_3$, to give good yields of the perchloro-heterocycles VI, VII and VIII, respectively (reaction 1, X = Cl; M = S, Se, Te); Kharasch [5] first obtained $S_2(C_6Cl_4)_2$ as an insoluble product from the UV irradiation of C_6Cl_5SCl. However, octachlorothianthrene is slightly soluble in boiling dimethylformamide and boiling nitrobenzene, from which it rapidly separates as a colourless precipitate on cooling. A patent [6] describes the formation of VI by heating hexachlorobenzene with sulphur at 335°C for 1.5–4.5 h, but we observed no change at 350°C, and even at 400°C only partial reaction occurred during 24 h. More rapid formation of $S_2(C_6Cl_4)_2$ occurs on reaction of C_6Cl_5I with sulphur, free iodine being released. A Friedel–Crafts reaction, employing a mixture of 1,2-$H_2C_6Cl_4$, $AlCl_3$, and S_2Cl_2 warmed gently in an open tube, gave mainly $S(C_6Cl_5)_2$, but small amounts of $S_2(C_6Cl_4)_2$ were also produced; although this provides a simple route to the latter, it is difficult to separate it from bis(pentachlorophenyl)sulphur. A virtually quantitative yield of bright yellow $Te_2(C_6Cl_4)_2$ is obtained by heating tellurium powder with 1,2,3,4-tetrachloro-5,6-diiodobenzene:

$$3Te + 2o\text{-}I_2C_6Cl_4 \rightarrow \text{VIII} + TeI_4$$

These perchloro compounds have a very high all-round stability. The mercurial itself resists attack by refluxing nitric acid or aqua regia. Thermal decomposition in an evacuated sealed tube only becomes appreciable at about 450°C, and then gives mercury, hexachlorobenzene and black, insoluble residues. Water at 250°C causes loss of the tetrachlorophenyl groups as *o*-$H_2C_6Cl_4$, hence all the tubes used in these preparations were thoroughly flamed out under high vacuum before use to remove any adsorbed water. Octachlorotelluranthrene, which can be synthesised at temperatures up to 400°C, decomposes only slowly at 450°C in a sealed tube to give mainly hexachlorobenzene. Attempts to remove one of the tellurium atoms with silver at 450°C to give octachlorodibenzotellurophene resulted only in the formation of decomposition products. No reaction occurred at 400°C. Sulphur completely replaced tellurium when kept with $Te_2(C_6Cl_4)_2$ at 300°C for 48 h:

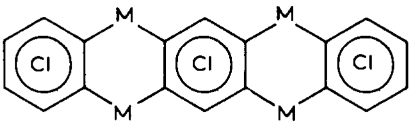
$$2S + Te_2(C_6Cl_4)_2 \rightarrow 2Te + S_2(C_6Cl_4)_2$$

Octachlorothianthrene shows high stability towards electron impact, the parent ion giving rise to the base peak in the mass spectrum. The very low solubility of compounds VI, VII and VIII precludes the use of ^{13}C NMR to substantiate the suggested structures, which are based on their elemental composition, and infrared and mass spectra. In the sulphur and selenium systems there is evidence that at high temperatures attack on the carbon–chlorine bonds occurs, to give higher molecular weight species which are so insoluble that they begin to separate from almost-boiling nitrobenzene during rapid filtration. Analysis and mass spectrometry suggest that these species have the formulae $M_4C_{18}Cl_{10}$ (M = S, Se). Thus the structure may be as in XVIII:



(XVIII a)

or



(XVIII b)

Treatment of *ortho*-phenylenemercury with antimony gives the much less thermally-stable molecule (XI) in very poor yield (eq. 2, X = H, M = Sb).

$$(C_6X_4Hg)_3 + 2M \rightarrow M_2(C_6X_4)_3 + 3Hg \tag{2}$$

The mass spectrum of XI showed a cut-off at a group of peaks around 472 m.u., the peak at 472 having an intensity of 31% relative to the base ion peak $C_{12}H_8^+$ at 152 m.u. A cross-scan computer report showed that the three peaks at 470, 472 and 474 m.u. in this cluster were directly related both to one another and to the total ion current, as expected if they represent the antimony-containing isotopomers of the

TABLE 1

MASS DATA ON THE PARENT ION CLUSTER IN THE MASS SPECTRUM OF XI

Ion	Measured mass	Calculated mass
${}^{12}C_{17}{}^{13}CH_{12}{}^{123}Sb_2{}^+$	474.917	474.906
${}^{12}C_{18}H_{12}{}^{123}Sb_2{}^+$	473.906	473.902
${}^{12}C_{17}{}^{13}CH_{12}{}^{121}Sb^{123}Sb^+$	472.905	472.905
${}^{12}C_{18}H_{12}{}^{121}Sb^{123}Sb^+$	471.899	471.902
${}^{12}C_{17}{}^{13}CH_{12}{}^{121}Sb_2{}^+$	470.899	470.905
${}^{12}C_{18}H_{12}{}^{121}Sb_2{}^+$	469.900	469.901
${}^{12}C_{18}H_{11}{}^{121}Sb_2{}^+$	468.898	468.894

parent ion $Sb_2(C_6H_4)_3{}^+$. Some fragmentation of hydrogen from the parent ion was indicated by a peak at 469 m.u. (i.e. P–H) which had an intensity of 7.0% relative to 472. An accurate mass determination on all seven peaks in this cluster gave the data shown in Table 1; thus the composition $Sb_2C_{18}H_{12}$ is unambiguously established. The presence of the ions $Sb(C_6H_4)_2$ (42%) and SbC_6H_4 (52%) supports the assumption of structure XI. A very strong peak (92%) appears for $(C_6H_4)_2{}^+$ which was reported [7] to be the base ion in the spectrum of $As_2(C_6H_4)_3$ (X). The base ion in the spectrum of XI is $C_{18}H_{12}{}^+$, which probably arises from ionized triphenylene. Since this ion was not listed in the published spectrum of $As_2(C_6H_4)_3$, the purity of $Sb_2(C_6H_4)_3$ was examined by analytical thin layer chromatography. Only a single spot was observed which was well separated from that of triphenylene. An attempt to make $Sb_2(C_6H_4)_3$ from 1,2-diiodobenzene and antimony yielded small amounts of triphenylene as the only isolable product.

Finely-powdered bismuth when heated with *ortho*-phenylenemercury begins to react at 250°C to give mercury and some 1,6-dibismuthatriptycene (XII) (eq. 2, X = H; M = Bi). However, at this temperature the triptycene is thermally unstable and slowly decomposes giving tri- and hexa-phenylene, which have to be removed from XII by preparative TLC. Even with the optimum reaction time (2 h) there was too little product for elemental analysis. Heating the reaction vessel overnight reduces the yield of XII to zero. Attempts to obtain the melting point were also frustrated by decomposition; clean sublimation began at 100°C in a good vacuum (ca. 10^{-4} mmHg). The compound also seemed to be unstable to electron impact, since the parent ion was of only about 2% relative intensity to the base peak at 209 m.u. (Bi^+). The observed accurate mass of the parent ion was 646.040 (calculated for ${}^{12}C_{18}H_{12}{}^{209}Bi_2$, 646.043). Ionized biphenylene was again represented by a strong peak (96%), and triphenylene (44%) appeared as a fragment ion. The main bismuth-containing ions were $Bi_2(C_6H_4)_3{}^+$, $Bi_2(C_6H_4)_2{}^+$, $Bi_2{}^+$, $BiC_6H_4{}^+$ and Bi^+. A cross-scan report showed that all these species were related to the same compound and there was also a correlation between the parent ion and the ionized phenylenes $(C_6H_4)_3{}^+$ and $(C_6H_4)_2{}^+$. Attempts to make $As_2(C_6H_4)_3$ (X) by heating arsenic with *ortho*-phenylenemercury gave detectable amounts of product (parent ion in the mass spectrum at 378 m.u.), but since this was a known compound no attempts were made to separate it from the by-products, triphenylene and diphenylmercury.

In the 1,6-disubstituted triptycenes the strongest infrared absorption occurs at about 750 cm^{-1}. In $P_2(C_6H_4)_3$ [11] (IX) two bands appear in this region, at 735 and 760 cm^{-1}; two bands are also observed in the spectrum of $Sb_2(C_6H_4)_3$ (741 and 736

cm^{-1}) but could be barely resolved. This feature trend is repeated with $Bi_2(C_6H_4)_3$ which has only a single, but slightly broadened, peak at 740 cm^{-1}.

Much more stable triptycene-like derivatives, (XV–XVII), were produced by reactions of As, Sb and Bi with tetrachlorophenylenemercury trimer (eq. 2, $X = Cl$; $M = As, Sb, Bi$). We have previously described the synthesis of $Sb_2(C_6Cl_4)_3$ (XVI) from antimony and 1,2,3,4-tetrachloro-5,6-diiodobenzene [8]. In the present work XV and XVII were obtained by analogous syntheses (eq. 3, $M = As, Bi$):

$$3C_6Cl_4I_2 + 4M \rightarrow M_2(C_6Cl_4)_3 + 2MI_3 \qquad (3)$$

The three triptycenes XV–XVII are very insoluble in all organic solvents but are just sufficiently soluble in boiling dimethylformamide or nitrobenzene to be extracted slowly. Owing to the high boiling points of these solvents, some trouble was encountered with the oxidation of the excess of arsenic to As_2O_3, which tended to contaminate the product $As_2(C_6Cl_4)_3$. In addition, prolonged boiling of nitrobenzene solutions of $Bi_2(C_6Cl_4)_3$ gave some metallic bismuth owing to slight thermal decomposition.

1,2,3,4-Tetrachloro-5,6-diiodobenzene used in the present and earlier syntheses [4,8], has previously been isolated in modest yield by fractional crystallization of the products arising from iododemercuration of involatile residues produced on pyrolysis of mercuric 2,3,4,5-tetrachlorbenzenesulphonate dihydrate [9]. In the present study, it was obtained far more conveniently, and in better yield, by dimercuration of 1,2,3,4-tetrachlorobenzene followed by iododemercuration:

$$o\text{-}H_2C_6Cl_4 \xrightarrow[230\,°C]{Hg(O_2CCF_3)_2} o\text{-}(CF_3CO_2Hg)_2C_6Cl_4 \xrightarrow[DMF]{I_3^-} o\text{-}I_2C_6Cl_4$$

Experimental

Except where stated, the reactions were carried out in Pyrex tubes which had been rigorously dried by baking in vacuum before being charged with reactants, re-evacuated, and sealed using a gas torch. The preparation of the mercurials used in these syntheses has been described previously [4]. Mass and infrared spectra, and microanalyses were obtained as described in ref. 13.

Reaction of sulphur with ortho-phenylenemercury trimer

$(HgC_6H_4)_3$ (500 mg) was heated at 250°C with an excess of sulphur for 14 h. The tube was coated with a black substance presumed to be HgS formed by reaction of the extruded mercury with sulphur. The $S_2(C_6H_4)_2$ product was extracted with 40–60°C petroleum ether (yield 125 mg) and analysed by mass spectrometry (molecular ion, 216 m.u.; $C_{12}H_8S_2$ calcd. mol. wt. 216). Selenium instead of sulphur gave $Se_2(C_6H_4)_2$ in similar yields (parent ion cluster in the mass spectrum occurred at around 310 m.u.).

A similar reaction between 300 mg of $(C_6F_4Hg)_3$ and 200 mg of sulphur at 300°C for 2 d gave, on extraction of the products with diethyl ether followed by vacuum distillation, octafluorothianthrene (45%), m.p. 103–104°C (lit. 10 102.4–104°C). Parent ion in mass spectrum: 360 ($C_{12}F_8S_2$ calcd. mol. wt. 360); the infrared spectrum was identical with that of an authentic sample. Octafluoroselanthrene was similarly obtained in 55% yield. A mixed reaction in which selenium was heated to 300°C with both $(C_6H_4Hg)_3$ and $(C_6F_4Hg)_3$ gave a product by extraction with diethyl ether which had a mass spectrum showing all three of the ions $Se_2(C_6H_4)_2{}^+$, $Se_2(C_6F_4)_2{}^+$ and $Se_2(C_6H_4)(C_6F_4)^+$.

Reaction of sulphur with tetrachlorophenylenemercury trimer

No reaction occurred when the mercurial and sulphur were refluxed in either dimethylformamide or nitrobenzene. In sealed tubes at 300°C, $(HgC_6Cl_4)_3$ (2.0 g) and an excess of sulphur reacted rapidly within 30 min. Extraction with boiling nitrobenzene or DMF gave white octachlorothianthrene (30–40%). The infrared spectrum was identical to the product obtained by heating excess sulphur with $Te_2(C_6Cl_4)_2$ to 300°C for 48 h where extraction of the products with boiling nitrobenzene gave $S_2(C_6Cl_4)_2$ in essentially 100% yield based on the tellurium starting material (Found: C, 29.6; H, 0.0. $C_{12}Cl_8S_2$ calcd.: C, 29.3; H, 0.0%).

Heating sulphur with hexachlorobenzene at 400°C for 48 h gave only a low yield of $S_2(C_6Cl_4)_2$ (Found: C, 29.75; H, 0.2; S, 13.1. $C_{12}Cl_8S_2$ calcd.: C, 29.3; H, 0.0; S, 13.1%). The presence of sulphur chlorides among the products was amply confirmed by smell! The infrared spectra of all three samples of $S_2(C_6Cl_4)_2$ were identical; the mass spectrum of the thianthrene showed a cut-off at around 492 m.u. representing the parent ion cluster of $S_2C_{12}Cl_8{}^+$.

Other syntheses of $S_2(C_6Cl_4)_2$

An excess of sulphur was treated with C_6Cl_5I at 350°C for 14 h when copious amounts of iodine were formed. The iodine and excess sulphur were extracted with boiling carbon tetrachloride and the thianthrene removed (15–20% yield) by boiling nitrobenzene.

A pink, insoluble residue remained which was exhaustively extracted with boiling nitrobenzene, DMF and pyridine before being analysed [Found, total 99.3%: C, 30.9; H, 0.0; Cl, 49.1; S, 19.3; $C_{72}Cl_{39}S_{17}$ calcd.: C, 31.0; Cl, 49.5; S, 19.5%; $C_{72}Cl_{38}S_{17}$ calcd.: C, 31.4; Cl, 48.9; S, 19.8%]. Unfortunately this highly polymeric compound is so insoluble and involatile that it is impossible to attempt the usual spectroscopic techniques. The needle crystals from the evaporation of the carbon tetrachloride solution were identified as hexachlorobenzene by infrared spectroscopy.

When a mixture of $1,2\text{-}H_2C_6Cl_4$, $AlCl_3$ and S_2Cl_2 was warmed to 50–60°C in an open beaker, a brisk evolution of HCl occurred. The solid was triturated twice with acetone, decanted and the residue extracted with boiling DMF. The first two extractions gave pure bis(pentachlorophenyl)sulphur, $(C_6Cl_5)_2S$ [Found: C, 26.9; H, 0.0; Cl, 67.1; S, 6.0%. $C_{12}Cl_{10}S$ calcd.: C, 27.1; H, 0.0; Cl, 66.8; S, 6.05%] and the third a mixture of $S_2(C_6Cl_4)_2$ and $(C_6Cl_5)_2S$ (infrared identificatioin).

In some of the reactions between sulphur and $(HgC_6Cl_4)_3$ carried out above 300°C a second component was obtained from nitrobenzene which analysed for "$S_4C_{18}Cl_{10}$" [Found: C, 30.7; 31.3; H, 0.0; N, 0.0,; Cl, 48.6; 48.8; 48.9; S, 18.1%; $C_{18}Cl_{10}S_4$ calcd.: C, 30.9; Cl, 50.8; S, 18.3%]. Many other polychloroaromatic compounds have given low chlorine figures, so this compound may be typical in being difficult to analyse accurately for chlorine.

Reactions of Se and Te with $(HgC_6Cl_4)_3$ and with $o\text{-}I_2C_6Cl_4$

Mixtures of Se or Te (in excess) with $(HgC_6Cl_4)_3$ were heated at 320°C (Se) or up to 400°C (Te). The products $M_2(C_6Cl_4)_2$ (M = Se or Te), being insoluble in common organic solvents, were extracted using boiling nitrobenzene, washed copiously with acetone and dried overnight at 85 °C in an oven (yields 60–70%). [Found: C, 24.4; 24.6; H, 0.0; $C_{12}Cl_8Se_2$ calcd.: C, 24.6; H, 0.0%. Found: C, 21.0; H, 0.0; Cl, 41.2%; $C_{12}Cl_8Te_2$ calcd.: C, 21.1; H, 0.0; Cl, 41.5%]. A highly insoluble selenium by-product was obtained in some experiments and this showed a mass cut-off in its mass spectrum corresponding to the ion $Se_4C_{18}Cl_{10}^+$ (cf. to the above sulphur derivative).

When an excess of tellurium powder and *o*-diiodotetrachlorobenzene were heated at 300 °C a black liquid (TeI_4?) was formed, from which large needle-like crystals of $Te_2(C_6Cl_4)_2$ separated on cooling. Boiling DMF (50 ml) removed virtually all the TeI_4; the residue was extracted with a further four 25 ml aliquots of DMF which were combined and boiled down to give sulphur-yellow, needle crystals on cooling. Yields 70–80%, m.p. > 320 °C [Found: C, 21.0; Cl, 39.3, 41.3%]. The compound was insoluble in such typical solvents as H_2O, $CHCl_3$, $(CH_3)_2CO$, C_6H_{14}, C_2H_5OH and CCl_4 but was slightly soluble in boiling toluene, DMF, nitrobenzene and pyridine. Although well-formed crystals could be seen in reaction mixtures from heating Se and *o*-$I_2C_6Cl_4$, surprisingly no identifiable products could be isolated.

Reaction of Sb with $(C_6H_4Hg)_3$

The two compounds were carefully ground together with a mortar to form an intimate mixture and then heated to 260 °C for 6 h. The products, which contained free mercury, were extracted with boiling 60–80 °C petroleum ether to give colourless crystals of a hexane hemisolvate (yield ca. 1%) [Found: C, 48.9; 49.35; H, 3.45, 3.6%; $C_{21}H_{18}Sb_2$ calcd.: C, 48.9; H, 3.6%]. At 85 °C overnight, the hexane was driven off to leave $Sb_2(C_6H_4)_3$ [Found: C, 45.3; 45.5; 45.3; H, 3.5; 3.2; 3.3%; $C_{12}H_8Sb_2$ calcd.: C, 45.8; H, 2.6%]. For the mass spectral data see Table 1, and Discussion section. The yield was not improved when the reaction was carried out as described [2] for the preparation of $Te_2(C_6H_4)_2$.

Attempts to make a "mixed" triptycene, by heating together excess antimony and tris(2-chlorophenyl)arsenic, $As_2(C_6ClH_4)_3$, at 260 °C overnight, failed. Only the starting arsenical could be isolated; m.p. 156 °C (lit. 14 156–157 °C) [Found: C, 53.1; H, 3.0; Cl, 25.3; $C_{18}H_{12}Cl_3As$ calcd.: C, 52.8; H, 2.9; Cl, 26.0%].

Finely powdered bismuth, intimately mixed with $(C_6H_4Hg)_3$, was heated to 250 °C when $Bi_2(C_6H_4)_3$ was formed; however, it is thermally unstable at the reaction temperature and the heating time had to be limited to about 2 h. The products were extracted from the reaction residues using 60–80 °C petroleum ether and subjected to preparative TLC on silica using petroleum ether/diethyl ether solvent mixtures. Three main bands were collected and shown to contain $Bi_2(C_6H_4)_3$, triphenylene (228 m.u.) and hexaphenylene (456 m.u.) by mass spectrometry.

Reaction of As, Sb, and Bi with $(C_6Cl_4Hg)_3$ and with o-$I_2C_6Cl_4$

No reaction between these elements and the mercurial appears to occur below about 300 °C. The syntheses were carried out on intimate mixtures of excess element and mercurial; the products were extracted with either DMF or nitrobenzene in yields of ca. 10% (As) and 60–70% (Sb, Bi). In the direct syntheses using *o*-$I_2C_6Cl_4$ at 260 °C, the element iodides obtained as by-products were removed by two aliquots of DMF before the remaining products were extracted with boiling nitrobenzene; thus some loss of the triptycenes occurred in the DMF fractions (which were discarded). In both methods some oxidation of the excess arsenic to As_2O_3 occurred on boiling with nitrobenzene and this was removed by treatment with dilute sodium hydroxide followed by copious washing of the crystals with distilled water. [Found: C, 26.5; H, 0.0%; $C_{18}Cl_{12}As_2$ calcd.: C, 27.3; H, 0.0%].

The antimony triptycene gave hemi-solvates, on recrystallization from a range of solvents, which were stable on vacuum-drying at room temperature.

[Found: C, 25.65; H, 0.4; N, 0.9; Cl, 45.2%; $Sb_2(C_6Cl_4)_3 \cdot 0.5$ pyridine calcd.: C, 26.6; H, 0.3; N, 0.8; Cl, 46.0%]

[Found: C, 25.7; 26.65; H, 0.4, 0.4; N, 0.7, 0.7; Cl, 44.25%; $Sb_2(C_6Cl_4)_3 \cdot 0.5$ DMF calcd.: C, 25.4; H, 0.4; N, 0.8; Cl, 46.2%]

[Found: C, 26.55; H, 0.7; N, 0.8; C, 43.4%; $Sb_2(C_6Cl_4)_3 \cdot 0.5$ diethyl formamide calcd.: C, 26.3; H, 0.6; N, 0.75, Cl, 45.5%]

[Found: C, 26.9; H, 0.3; N, 0.75; Cl, 45.1%; $Sb_2(C_6Cl_4)_3 \cdot 0.5$ nitrobenzene calcd.: C, 26.6; H, 0.3; N, 0.7; Cl, 45.0%]

The bismuth triptycene also seemed to hold tenaciously to solvents though not in apparently stoichiometric amounts. A sample recrystallized from nitrobenzene, washed with acetone and dried overnight at room temperature, gave [Found: C, 21.1; 21.3; H, 0.02; 0.1; N, 0.35; 0.2; Cl, 37.7%; $Bi_2(C_6Cl_4)_3 \cdot 0.5$ nitrobenzene calcd.: C, 22.5; H, 0.2; N, 0.6; Cl, 37.9%]. After washing with acetone and drying at 75°C for 72 h the solvent was lost [Found: C, 20.6; H, 0.0; N, 0.0; Cl, 40.0%; $C_{18}Cl_{12}Bi_2$ calcd.: C, 20.6; H, 0.0; N, 0.0; Cl, 40.5%]

Synthesis of 1,2,3,4-tetrachloro-5,6-diiodobenzene

1,2,3,4-Tetrachlorobenzene (10 mmol) was added to a melt of mercuric trifluoroacetate (60 mmol) [for preparation and handling see ref. 15] maintained at 230°C. Vigorous evolution of trifluoroacetic acid occurred and the reaction mixture solidified in about 2 min. Heating was maintained for 10 min to complete the reaction. On cooling, 50 ml of DMF was added and the residue slowly dissolved on shaking. This was added to a solution of iodine (40 mmol) in DMF (100 ml), and the reaction mixture was stirred at 100°C for 30 min, the iodine colour being discharged. Aqueous potassium bromide (200 ml, 10% w/v) was added to the cooled solution giving a precipitate of the title compound; which was dried over silica gel and recrystallized from toluene/petroleum ether (100–120°C) giving pale yellow crystals, m.p. 230–234°C (lit. 9 227–231°C). The infrared spectrum agreed with that reported [9].

Infrared spectra in Nujol mulls (± 2 cm^{-1})

$Sb_2(C_6H_4)_3$: 1423m, 1415sh, 1249m, 1244wsh, 1158w, 1072m, 1019w, 936w, 869w, 741s, 736s, 678w, 416m, 360s, 297sh, 291m, 267 wsh, 258m, 250sh, 245sh.

$Bi_2(C_6H_4)_3$, dilute mull only: 1246w, 1003w, 758wsh, 740s, 696w, 410w, 318w.

$S_2(C_6Cl_4)_2$: 1338sb, 1325s, 1290mb, 1106m, 878m, 788vw, 732m, 701w, 694w, 684m, 634m, 579vw, 431m, 388w.

$Se_2(C_6Cl_4)_2$: 1335s, 1329ssh, 1285m, 1272m, 1089m, 861w, 845mb, 701w, 672m, 669msh, 621m, 618msh, 580w, 360w.

$Te_2(C_6Cl_4)_2$: 1339w, 1314msh, 1304s, 1301msh, 1276s, 1254m, 1149w, 1139w, 1070m, 1065vwsh, 848m, 826s, 702w, 653m, 589m, 338msh, 332m.

$As_2(C_6Cl_4)_3$: 1326s, 1319msh, 1306s, 1294s, 1280wsh, 1166w, 1150s, 1074s, 849m, 831m, 698w, 654m, 610w, 586vw, 369m, 264mb.

$Sb_2(C_6Cl_4)_3 \cdot 0.5$ nitrobenzene: 1526w, 1344m, 1317ssh, 1311s, 1296m, 1282s, 1264wsh, 1175wb, 1143m, 1126m, 1062m, 847wsh, 840m, 816s, 788w, 700m, 679w, 638m, 586wsh, 580w, 339m.
$Bi_2(C_6Cl_4)_3$: 1311m, 1300s, 1285w, 1271sb, 1246wsh, 1168wb, 1142wsh, 1129m, 1104w, 1049m, 831m, 803s, 629m, 579vw, 322w.

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