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SOME REACTIONS OF PHENYLENE- AND POLYPHENYLENE-MERCURIALS

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Summary

Cleavage reactions of six phenylene- and polyphenylene-mercury heterocycles with the mercuric halides and mercuric acetate in suitable refluxing solvents readily produce 1,2-$C_6X_4(HgX)_2$; 2,2′-$C_6H_4C_6H_4(HgX)_2$ and 2,2″-$C_6H_4C_6H_4C_6H_4(HgX)_2$ ($X = Cl$, Br, I or CH_3CO_2). Addition of silver acetate to 2,2′-$C_6H_4C_6H_4(HgBr)_2$ gives 2,2′-$C_6H_4C_6H_4(HgO_2CCH_3)_2$ which reacts with concentrated hydrochloric acid to form 2,2′-$C_6H_4C_6H_4(HgCl)_2$. Treatment with sodium iodide, or in some cases simply the application of heat under vacuum, causes symmetrization of these cleavage products back to the original heterocycles in high yield. The terphenylenemercury dimer, $(C_6H_4C_6H_4C_6H_4Hg)_2$, forms solvates with a wide variety of donor and non-donor solvents. Pyrolysis of mercuric 2,3,4,5-tetrafluorobenzoate at 190°C yields 2-mercurio-3,4,5,6-tetrafluorobenzoate and 2,3,4,5-tetrafluorobenzoic acid; at 300°C the former gives tetrafluorophenylenemercury, $(C_6F_4Hg)_3$.

Introduction

The mercurials studied in this work are shown in structures I to VI; they are all very stable, both thermally and towards air. For example, in a vacuum II and III are stable to at least 400°C, while II and V can be sublimed unchanged on heating in open sample tubes held above 250°C; III resists prolonged attack by boiling

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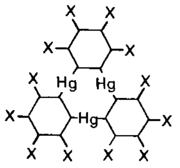
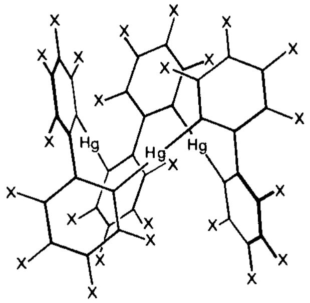
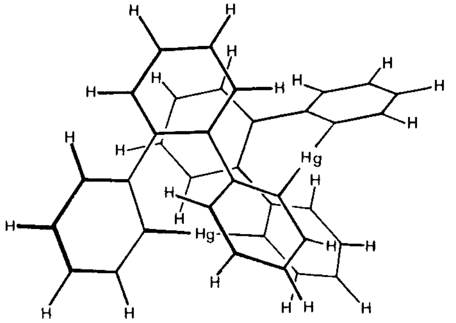


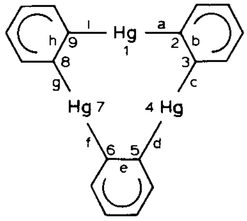
(I · X=H ;
II X=F ,
III X=Cl)



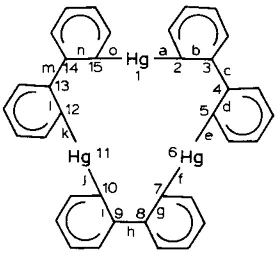
(IV . X=H ;
V : X=F)



(VI)

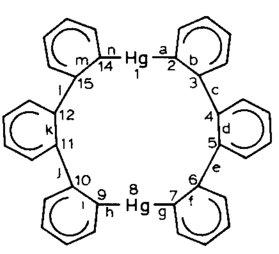


Tribenzo [*b,e,h*] [1.4.7]-trimercuronin (I)



Hexabenzo [*b,d,g,i,l,n*] [1 6.11]-trimercuracyclopentadecene

(IV)



Hexabenzo [*b,d, f, i, k, m*] [1.8] dimercuracyclotetradecene

(VI)

SCHEME 1. Structures and nomenclature of the mercurials used in this work (all the rings are aromatic although not shown as such in the diagrams for reasons of clarity).

concentrated nitric acid or aqua regia and sublimes in high vacuum only when heated strongly with a gas torch. Notwithstanding their proven stability we have been able to show that these heterocycles react readily with a number of reagents on moderate heating: typically, bromine and iodine cleave perfluorobiphenylenemercury (V) to give the corresponding 2,2'-dihalogenooctafluorobiphenyls and cleavage products are formed with mercuric salts. Only one isolated example of such cleavage is known [1], although Wittig has also described [2] the reaction of his supposed hexameric phenylenemercury, $(C_6H_4Hg)_6$, with mercuric chloride. This 'hexamer' is, in fact, the trimer I [3].

Discussion

The mercuric halides (HgY_2; Y = Cl, Br, I) react virtually quantitatively with I, II, III, IV and VI on being refluxed in a high boiling solvent such as mesitylene (a) or nitrobenzene (b):

$$(C_6X_4Hg)_3 + 3HgY_2 \rightarrow 3[1,2\text{-}C_6X_4(HgY)_2] \qquad (1)$$

(X = H, F, Y = Cl, Br, I; solvent (a);

X = Cl, Y = Cl, Br, ≠ I; solvent (b))

$$(C_6H_4C_6H_4Hg)_3 + 3HgY_2 \xrightarrow{(a)} 3[2,2'\text{-}C_6H_4C_6H_4(HgY)_2] \qquad (2)$$
$$(Y = Cl, Br, I)$$

$$(C_6H_4C_6H_4C_6H_4Hg)_2 + 2HgY_2 \xrightarrow{(a)} 2[2,2''\text{-}C_6H_4C_6H_4C_6H_4(HgY)_2] \qquad (3)$$
$$(Y = Cl, Br, I)$$

Mercurous chloride can also be used, when free mercury is precipitated:

$$(C_6H_4C_6H_4Hg)_3 + 3Hg_2Cl_2 \xrightarrow{(a)} 3Hg + 3[2,2'\text{-}C_6H_4C_6H_4(HgCl)_2]$$

$$(C_6Cl_4Hg)_3 + 3Hg_2Cl_2 \xrightarrow{(b)} 3Hg + 3[1,2\text{-}C_6Cl_4(HgCl)_2]$$

but mercuric oxide, mercury(II) tetrathiocyanatocobaltate(II), mercuric nitrate, mercuric sulphate and mercurous sulphate did not react with IV on being heated for some hours in boiling mesitylene. The choice of solvent is obviously critical in many of these reactions since IV does not react with mercuric halides in either boiling toluene or the xylenes (probably because the temperature is too low). Moreover, mercuric acetate reacts smoothly with IV in refluxing methanol but not in refluxing mesitylene (eq. 2; Y = CH_3COO). The same product is formed, but in lower yield, by simply boiling the mercurial IV in glacial acetic acid:

$$(C_6H_4C_6H_4Hg)_3 + 4CH_3CO_2H \rightarrow$$
$$2,2'\text{-}C_6H_4C_6H_4(HgO_2CCH_3)_2 + Hg(O_2CCH_3)_2 + (C_6H_5)_2 \qquad (4)$$

By contrast the halogenomercurio compounds $2,2'\text{-}C_6H_4C_6H_4(HgX)_2$ can be recovered unchanged after being refluxed with glacial acetic acid for some hours, but are converted into VII on treatment with the stoichiometric amount of silver acetate in an appropriate solvent system:

$$\begin{array}{lll} 2,2'\text{-}C_6H_4C_6H_4(HgX)_2 + 2AgO_2CCH_3 & \rightarrow 2,2'\text{-}C_6H_4C_6H_4(HgO_2CCH_3)_2 + AgX \\ \quad(\text{in DMF}) \qquad\quad (\text{in } 5\%\ CH_3CO_2H) & \qquad\qquad\qquad (\text{VII}) \\ \quad(X = Cl, Br) & \end{array}$$

Concentrated hydrochloric acid converts the acetate VII into the chloride:

$$\begin{array}{r} 2,2'\text{-}C_6H_4C_6H_4(HgO_2CCH_3)_2 + 2HCl(aq) \rightarrow 2,2'\text{-}C_6H_4C_6H_4(HgCl)_2 + 2CH_3CO_2H \\ (\text{VIII}) \end{array}$$

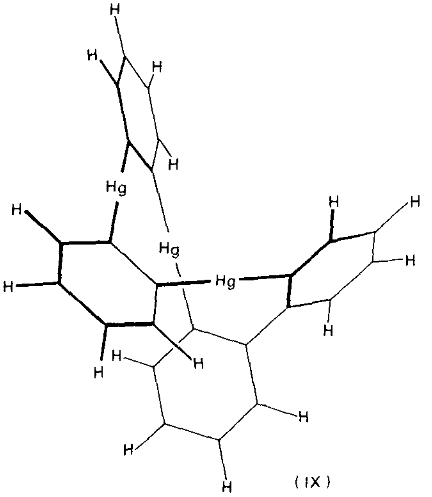
Attempts to make VIII directly by adding an excess of mercuric chloride to 2,2'-dilithiobiphenyl in the presence of tetramethylethylenediamine, TMEDA, failed. The main product was the complex $HgCl_2 \cdot$ TMEDA together with small amounts of IV and 2-chloromercuriobiphenyl.

Symmetrization of mono-organomercurials by reducing or complexing agents to give diorganomercurials is well known [4]. Similar reactions of the above bis(halogenomercurio)- and bis(acetatomercurio)-arenes could potentially yield the parent heterocycles I–VI. These reactions could be of major synthetic importance where routes other than reactions 1–3 can be devised for the bis(halogenomercurio)arenes, or are already known; for example, *o*-$(XHg)_2C_6F_4$ ($X = Cl, CH_3CO_2, CF_3CO_2$) [1] or especially when the normal syntheses of the heterocycles give very low yields (e.g. $(C_6H_4Hg)_3$) [5]. In view of the differing degree of oligomerisation claimed or established in some of the mercury heterocycles [3,5,6], this degree of association in the symmetrization products is of particular interest. Initial reactions involving 2,2'-$C_6H_4C_6H_4(HgY)_2$, where Y = Cl, Br or I, and sodium iodide in alcohol showed that symmetrization to the heterocyclics did, indeed, occur and in very high yields. The apparently amorphous, precipitated products had identical infrared spectra with that of biphenylenemercury trimer, IV, except for one minor feature, viz. a band of medium intensity at about 770 cm^{-1} was a relatively broad singlet instead of the doublet (774 and 769 cm^{-1}) normally observed for this trimer. Crystallization of the product from toluene gave this doublet; undoubtably this splitting is due to crystal lattice effects.

Thermal symmetrization was noted when attempts were made to sublime 2,2'-$C_6H_4C_6H_4(HgBr)_2$ and 2,2'-$C_6H_4C_6H_4(HgI)_2$ under vacuum (ca. 10^{-4} mmHg). For example, when the iodide was slowly heated, red HgI_2 began to appear on the cold finger of the sublimation apparatus at about 150°C. After 1 h at 200°C all the iodine in the compound had been lost as mercuric iodide leaving a residue of pure biphenylenemercury trimer. Again no splitting of the 770 cm^{-1} peak was apparent in the infrared spectrum until the samples had been recrystallized. No symmetrization occurred on heating a sample of 2,2'-$C_6H_4C_6H_4(HgBr)_2$ in an open tube at 200°C.

Symmetrization of 1,2-$C_6H_4(HgY)_2$ and 1,2-$C_6F_4(HgY)_2$ with sodium iodide likewise occurred smoothly to give only the known trimeric species I and II. The attempted thermal symmetrization of 1,2-$C_6H_4(HgBr)_2$ in a vacuum sublimer at 220°C failed and the reactant was recovered.

Since these symmetrization reactions occur readily, and in good yield, we considered the possibility of 'cross symmetrizations'. Treatment of a mixture of



(IX)

2,2′-$C_6H_4C_6H_4(HgCl)_2$ and 1,2-$C_6H_4(HgCl)_2$ with sodium iodide in aqueous alcohol gave a white precipitate with infrared absorptions indicative of I and IV. However, a mass spectrum of the mixture revealed the presence of a third component having a molecular ion $Hg_3(C_6H_4)_4^+$. A study of Dreiding models showed that this may be the mixed species $\overline{-C_6H_4HgC_6H_4HgC_6H_4C_6H_4Hg-}$ which apparently would suffer no steric strain if it had the structure shown in IX.

Models also show that in the terphenylenemercury series only the dimer is free of strain and hence is presumably the only species capable of existence. Not surprisingly, symmetrization reactions of 2,2″-$C_6H_4C_6H_4C_6H_4(HgY)_2$ using sodium iodide in ethanol gave high yields of the dimer VI. A relatively unusual property for a hydrogen-substituted mercurial is shown by terphenylenemercury dimer: it crystallizes from every solvent tried, except diethyl ether, as a solvate. Although some 'adducts' are known for R_2Hg derivatives, the sheer number and range of stoichiometries of the IV-solvates is surprising. The ratio of dimer/solvent varies with the solvent used and, as shown in Table 1, this ratio seems to be closely associated with the size of the occluded molecule. Large molecules form solvates with a ratio of 1/0.5 whilst the smallest can apparently pack two molecules per dimer within the crystal; intermediate-sized solvent molecules show ratios of either 1/1 or 1/1.5. An X-ray crystal study has been started on these solvates and, initially, has shown that the assumed dimeric structure of unsolvated VI is indeed correct [8].

An alternative route to the perfluorophenylenemercury trimer II has been established from observations that pyrolysis of mercuric 2,3,4,5-tetrafluorobenzoate, at 190°C under vacuum, yields 2-mercurio-3,4,5,6-tetrafluorobenzoate (X) and 2,3,4,5-tetrafluorobenzoic acid.

This product has previously been made in trimeric form by heating mercuric 2,3,4,5-tetrafluorophthalate (XI) at 220°C, and is considered to be an intermediate in the decarboxylation synthesis of II [7] from decomposition of the tetrafluorophthalate at 300°C. We have shown that X does in fact yield II at 300°C, and

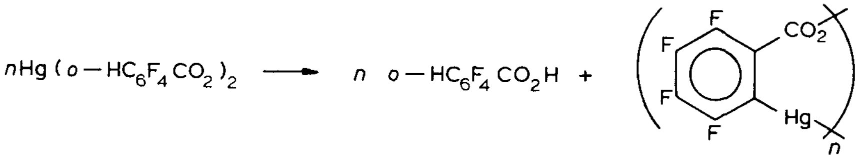
TABLE 1

ANALYTICAL DATA FOR SOLVATES OF TERPHENYLENEMERCURY DIMER (TD)

Solvent	TD/solvent ratio	Analyses (Found (calc) (%))		
		C	H	N (or Cl)
cyclohexane	1/0.5	52.0; 52.2	3.3; 3.2	
		(52.0)	(3.4)	
cyclohexanone	1/0.5	51.9	3.3	
		(51.7)	(3.2)	
mesitylene	1/0.5	53.15; 52.7; 53.3	3.4; 3.3; 3.1	
		(53 0)	(3.3)	
p-xylene	1/0.5	53.3	3.0	
		(52.7)	(3.2)	
m-xylene	1/1	55.6; 54.6	3.6; 3.5	
		(54.9)	(3.5)	
o-xylene	1/1	54.9	3.5	
		(55.05)	(3.55)	
toluene	1/1	54.4	3.4	
		(54.2)	(3.4)	
ethylbenzene	1/1	55 25	3.5	
		(54 9)	(3.5)	
chlorobenzene	1/1	52.6	3.2	3.9
		(52.0)	(3.2)	(3.7)
dimethylformamide	1/1	50.3	3.5	1.6
		(50.3)	(3.4)	(1.5)
diethylformamide	1/1	51.0	3.6	1.5
		(51.35)	(3.7)	(1.5)
2-picoline	1/1	53.2	3.3	1.4
		(53.1)	(3.3)	(1.5)
pyridine	1/1.5	54.2; 53.2; 54.1	3.2; 3.3; 3.1	2.2; 1.9; 2.2
		(53.5)	(3.2)	(2.15)
acetone	1/1.5	analysed gravimetrically [a]; weight loss observed 8.9% (calc 9.2%)		
chloroform	1/2 0	analysed gravimetrically [a]; weight loss observed 21.5; 21.9; 21.9 (calc 21 8%)		
ether	no solvate	analysed gravitmetrically [a]; weight loss observed 0.05% (calc 0 0%)		

[a] Weight loss measured at constant 85°C for 100–200 mg samples weighed to six places on a micro-balance.

hence that pyrolysis of mercuric 2,3,4,5-tetrafluorobenzoate at this temperature is a potential source of II. The identity of X in the present work was confirmed by iodomercuration to give 2,3,4,5-tetrafluoro-6-iodobenzoic acid.



(X)

Experimental

The preparation of phenylenemercury trimer [5,6], perfluorophenylenemercury trimer [7], biphenylenemercury trimer [5,9], terphenylenemercury dimer [10] and 2,3,4,5,-tetrafluorobenzoic acid [11] have been described previously. Bis(2-chlorophenyl)mercury was prepared by treating mercuric chloride with two moles of 2-chlorophenyllithium [13], stabilized by TMEDA, at −90°C and allowing the mixture to warm slowly to room temperature; yield 80%. The analytical sample was recrystallized from chloroform, m.p. 138–140°C (lit. 14 146–147°C); (Found: C, 33.7; H, 1.9; Cl, 16.6. $C_{12}H_8Cl_2Hg$ calc: C, 34.0; H, 1.9; Cl, 16.8%). Reactions involving organolithium reagents required a dry, oxygen-free atmosphere. Reactions under vacuum were carried out at the stated temperatures in evacuated (ca. 10^{-4} mmHg) pyrex tubes which were sealed at the upper of two constrictions. After reaction, the cooled tubes were scratched at the remaining constriction, wrapped in a towel, and snapped open. (Hot-spotting with a glass rod at the scratched constriction can sometimes lead to explosions). Products were scraped or washed out and recrystallized from suitable solvents. Analyses were performed by the Micro-analytical Laboratory of Manchester University; mass spectra were obtained by Mr. P.D. Cook of Queen Mary College, London. Infrared spectra were recorded on a Perkin–Elmer 457 grating spectrometer.

(a) The biphenylenemercury trimer system

(i) Reaction of biphenylenemercury trimer with mercuric chloride

The mercurial (461.4 mg, 0.436 mmol) and mercuric chloride (359.8 mg, 1.325 mmol) were heated for 15 min in boiling mesitylene (50 ml). The solvent was evaporated to ca. 10 ml when 2,2'-$C_{12}H_8(HgCl)_2$, m.p. 252°C, crystallized out on cooling to room temperature (yield ca. 100%). An analytical sample was recrystallized from chloroform as needle-like crystals (Found: C, 23.15; H, 1.1; Cl, 11.2; $C_{12}H_8Hg_2Cl_2$ calc: C, 23.1; H, 1.3; Cl, 11.4%) IR spectrum (Nujol mull): 1282w, 1239w, 1156w, 1030, 1024m (doublet); 948w, 937w, 878w, 770m, 764m, 754s, 746s, 731sh, 728s, 663w, 616m, 550m, 532w, 441s, 432m, 359w, 330vs (doublet) and 315s cm^{-1}.

(ii) Reaction of biphenylenemercury trimer with mercuric bromide

The bromide 2,2'-$C_{12}H_8(HgBr)_2$ was made in an exactly analogous way to the chloride (yield, ca. 100%) the analytical sample was recrystallized from chloroform and dried at 80°C; m.p. 198°C (Found: C, 20.4, 20.9; H, 0.95, 0.95; Br, 23.1, 22.4 for two separately-prepared samples; $C_{12}H_8Hg_2Br_2$ calc: C, 20.2; H, 1.1; Br, 22.4%). IR spectrum: 1570w, 1156w, 1108vw, 1042m, 998s, 939vw, 767m, 762m, 753m, 745vs, 729s, 722s, 661w, 614w, 549w, 446vw, 431w, cm^{-1}.

(iii) Reaction of biphenylenemercury trimer with mercuric iodide

To the mercurial (349.4 mg, 0.3303 mmol) in boiling mesitylene (40 ml), mercuric iodide (450.7 mg, 0.9919 mmol) was slowly added. The red colour of the HgI_2 was discharged on contact with the solution. Boiling was continued for a further 15 min; on cooling the whole reaction mixture solidified. After extracting the mesitylene with two aliquots of boiling 40–60°C petroleum ether the remaining solid was recrystallized from chloroform (yield, ca. 100%) m.p. 197°C (lit 6. 198°C). (Found:

C, 17.7; H, 0.9; $C_{12}H_8Hg_2I_2$ calc: C, 17.85; H, 1.0%. Attempts to determine the iodine content failed due to the formation of HgI_2 which sublimed away from the heated reaction zone [12]). The infrared spectrum was identical to that described previously [6].

(iv) Reaction of biphenylenemercury trimer with mercurous chloride

When 1 mol of mercurial was refluxed with 3 mol of mercurous chloride in mesitylene, the mixture slowly turned black due to the separation of free mercury. Filtration and evaporation of the solvent to small volume gave 2,2′-$C_{12}H_8(HgCl)_2$, identified by m.p. (250–252°C), mixed melting point and comparison of its infrared spectrum with an authentic sample. (Found: C, 22.3; H, 1.2%). Attempted extraction of the black residue with pyridine gave a pyridine-mercuric chloride complex, m.p. 187–189°C (Found: C, 12.2; H, 0.9; Cl, 21.9; N, 2.8; $(HgCl_2)_3py_2$ calc: C, 12.3; H, 1.0; Cl, 21.9; N, 2.9%), probably formed by symmetrization of some undissolved 2,2′-$C_{12}H_8(HgCl)_2$.

(v) Reaction of biphenylenemercury trimer with mercuric oxide

No reaction was observed when the mercurial and red oxide (mole ratio 1/3) were refluxed for several hours in mesitylene. The components were recovered unchanged as shown by infrared identification of the trimer and the colour of the oxide.

(vi) Reaction of biphenylenemercury trimer with mercuric acetate

Stoichiometric amounts of the reactants were refluxed in boiling mesitylene for 30 min after which the solvent was partially evaporated; only unchanged biphenylenemercury trimer separated out on cooling or on further evaporation of the filtrate.

To biphenylenemercury suspended in boiling methanol was added mercuric acetate in small amounts until all the trimer had dissolved; a little more trimer was then added until some remained undissolved. Filtration and evaporation to small volume gave needle-shaped crystals of 2,2′-$C_{12}H_8(HgO_2CCH_3)_2$, which were washed quickly with cold, glacial acetic acid and then copious amounts of distilled water before being dried at 80°C (yield ca. 100%), m.p. 225–226°C (Found: C, 27.9, 28.1; H, 2.0, 1.9% for separate samples; $C_{16}H_{14}O_4Hg_2$ calcd.: C, 28.6; H, 2.1%). IR spectrum: 1613msh; 1580vs vb; 1362vs; 1328vs; 1316vs; 1040vw; 1029w; 1010mb; 924vw; 776m; 751s; 733m; 689s; 661vw; 652vw; 616sh; 608w; 445m; 290mb; 276sh, cm^{-1}.

(vii) Reaction of biphenylenemercury trimer with glacial acetic acid

A small amount of trimer was boiled in acetic acid for 1.5 h. The solution was filtered and the acid removed at 80°C giving a brown solid; this was triturated with cold chloroform to remove the brown impurity leaving white 2,2′-$C_{12}H_8(HgO_2CCH_3)_2$ (identified by its infrared spectrum).

(viii) Reaction of 2,2′-$C_{12}H_8(HgBr)_2$ with glacial acetic acid

The dibromide was refluxed for 2 h in glacial acetic acid and recovered unchanged on evaporation to small volume; m.p. 197°C, mixed m.p. 197°C and infrared identification.

(ix) Reaction of 2,2′-$C_{12}H_8(HgBr)_2$ with silver acetate

To a hot solution of 2,2′-$C_{12}H_8(HgBr)_2$ (557.0 mg, 0.781 mmol) in 20 ml of dimethylformamide was added a solution of silver acetate (261.3 mg, 1.565 mmol) in 50 ml of 5% aqueous acetic acid. Precipitated silver bromide was filtered off and the product deposited by addition of water (200 ml) to the filtrate and cooling. The grey solid was dried at 80°C before being recrystallized from methanol, m.p. 220–222°C (infrared identification).

(x) Reaction of 2,2′-$C_{12}H_8(HgO_2CCH_3)_2$ with hydrochloric acid

To the di-acetate in boiling methanol (5 ml) was added an excess of concentrated hydrochloric acid dropwise, giving a white precipitate; water was then added to complete the precipitation. The white solid product was washed copiously with distilled water, dried at 80°C and recrystallized from chloroform to give 2,2′-$C_{12}H_8(HgCl)_2$ m.p. 238°C; mixed m.p. 238°C (infrared identification).

(xi) Symmetrization of 2,2′-$C_{12}H_8(HgX)_2$ (X = Cl, Br, I) with sodium iodide

To a solution of 2,2′-$C_{12}H_8(HgX)_2$ in acetone was added an excess of sodium iodide and the mixture refluxed for 30 min giving a white precipitate which was collected and dried at 80°C. It had an infrared spectrum identical with that of biphenylenemercury trimer except that the medium-intensity peak at ca. 770 cm^{-1} showed no splitting. When the solid was recrystallized from toluene the usual doublet (774 and 769 cm^{-1}) was observed. The mass spectrum showed a mass cut-off at the parent ion cluster representing the trimer species.

The symmetrizations of 2,2′-$C_{12}H_8(HgBr)_2$ and 2,2′-$C_{12}H_8(HgI)_2$ with sodium iodide in refluxing aqueous ethanol were similarly achieved the infrared spectra of the crude and recrystallized products showed the same effects at ca. 770 cm^{-1} as described above.

(xii) Thermal symmetrization of 2,2′-$C_{12}H_8(HgX)_2$ (X = Br, I)

2,2′-$C_{12}H_8(HgI)_2$ was heated slowly in a sublimer under vacuum (ca. 10^{-4} mmHg). At about 150°C, a red sublimate of mercuric iodide was observed and the quantity increased as the temperature was raised to 200°C and held there for 1 h. An essentially quantitative residue of biphenylenemercury was obtained (infrared identification; no splitting of the band near 770 cm^{-1} until after recrystallization from toluene).

Similar treatment of the bromide (m.p. 198°C) gave partial melting of the solid, sublimation of $HgBr_2$ and then resolidification as the trimer formed (infrared identification). Only impure 2,2′-$C_{12}H_8(HgBr)_2$ was recovered on pyrolysis at 200°C for 4 h in the open air.

(xiv) Mixed reaction of 2,2′-$C_{12}H_8(HgCl)_2$ and 1,2-$C_6H_4(HgCl)_2$ with sodium iodide

Equimolar amounts of the two chlorides were refluxed with an excess of sodium iodide in aqueous ethanol when a white precipitate formed. The infrared spectra of various recrystallized fractions showed the presence of the expected products $(C_{12}H_8Hg)_3$ and $(C_6H_4Hg)_3$; a mass spectrum of the mixture also showed the two trimers to be present together with a substance which showed an Hg_3-cluster of peaks corresponding to a species $\overline{-C_6H_4HgC_6H_4HgC_{12}H_8Hg-}$. (Although an ion

$Hg_3(C_6H_4)_4^+$ could conceivably arise from biphenylenemercury trimer it is of such a low intensity as not to be observed from this source under the resolution of our instrument). However, we were unable to isolate this 'mixed' mercurial in the pure state.

(xv) Thermal decomposition of biphenylene trimer

The trimer was sealed under vacuum in a pyrex tube which had previously been throughly baked dry under high vacuum. After 2 h at 320°C, globules of metallic mercury were visible. After cooling and extraction of the products with a variety of solvents, only biphenyl (infrared identification) and a little unchanged trimer could be isolated.

(xvi) Reaction of 2,2'-$Li_2C_{12}H_8$ · TMEDA with an excess mercuric chloride

Normally biphenylenemercury trimer is prepared from a 1/1 reaction mixture of 2,2'-$Li_2C_{12}H_8$, as its tetramethylethylenediamine (TMEDA) complex, and mercuric chloride [5,9]. After a similar reaction on a 1/2 mole ratio in 50/50 (v/v) ether/THF for 1 h, the mixture was filtered leaving a grey solid which was washed with hot chloroform. Evaporation of the combined washings and filtration under reduced pressure gave $HgCl_2$ · TMEDA, which was recrystallized from acetone, m.p. 162–164°C (Found: C, 18.8; H, 4.0; N, 6.9; $C_6H_{16}Cl_2N_2Hg$ calc: C, 18.6; H, 4.1; N, 7.2%). The acetone-insoluble residue (which sublimed above 240°C without melting) was identified as $C_{12}H_9HgCl$ from its mass spectrum. The chloroform-insoluble residue was extracted with boiling nitrobenzene to give biphenylenemercury trimer (m.p. and infrared identification). No 2,2'-$C_{12}H_8(HgCl)_2$) could be detected.

(b) Reaction of terphenylenemercury dimer with mercuric halides

(i) Mercuric chloride

Equimolar amounts of terphenylenemercury dimer and mercuric chloride in mesitylene were refluxed for 20 min. The white solid obtained on cooling was recrystallized from chloroform to give pure 1,2-bis(2'-chloromercuriophenyl)benzene, m.p. 250°C (Found: C, 29.8; H, 1.5; $C_{18}H_{12}Hg_2Cl_2$ calc: C, 30.9; H, 1.7%). Infrared spectrum; 1572w, 1417m, 1356w, 1022wb, 1001m, 997m, 949wsh, 941w, 874w, 779m, 776sh, 769m, 755vs, 748vs, 729vs, 648vw, 620w, 613w, 562m, 540wb, 445s, 437sh, 340w, 326mbr, 303w, 289vw.

(ii) Mercuric bromide

A similar preparation and purification gave 1,2-bis(2'-bromomercuriophenyl)benzene, m.p. 202–204°C (Found: C, 26.8; H, 1.4; Br, 21.4; $C_{18}H_{12}Hg_2Br_2$ calc: C, 27.4; H, 1.5; Br, 20.3%). Infrared spectrum: 1157w; 1022w; 1000m; 998m; 942w; 772s; 758wsh; 750vs; 744vs; 718wsh; 618w; 612w; 560w; 540w; 441s.

(iii) Mercuric iodide

A similar preparation gave 1,2-bis(2'-iodomercuriophenyl)benzene which was washed with boiling 40–60°C petroleum ether before recrystallization from chloroform, m.p. 230°C (Found: C, 23.9; H, 1.4; $C_{18}H_{12}Hg_2I_2$ calc: C, 24.5; H, 1.4%). Infrared spectrum: 1415m, 1208w, 1154vw, vbr, 1023wbr, 1001m, 997m, 941w, 870vw, 779m, 771s, 760sh, 751vs, 743vs, 727vs, 664vw, 620wsh, 614w, 560m, 539w, 443s, 436m.

(iv) Reaction of 1,2-bis(2′-chloromercuriophenyl)benzene with sodium iodide

1,2-Bis(2′-chloromercuriophenyl)benzene was refluxed with an excess of sodium iodide in 150 ml of ethanol giving a white precipitate of terphenylenemercury dimer on cooling the hot, cloudy solution. This was collected, washed well with distilled water and, after drying at 85 °C, was recrystallized from chloroform, m.p. 294–296 °C (Found: C, 50.45; H, 3.1; $C_{36}H_{24}Hg_2$ calc: C, 50.4; H, 2.8%).

(c) The ortho-phenylenemercury system

(i) Attempted synthesis of $(C_6H_4Hg)_3$ from $(2\text{-}ClC_6H_4)_2Hg$ and Na/Hg

No reaction could be detected when bis(2-chlorophenyl)mercury was vigorously stirred with sodium amalgam in dry THF under nitrogen.

(ii) Reaction of phenylenemercury trimer with mercuric chloride

Equimolar amounts of the phenylenemercurial and mercuric chloride were heated in boiling dimethylformamide for 1 h on cooling, white 1,2-bis(chloromercurio)benzene was deposited, m.p. 322–324°C (lit. 2. 322–323°C). Infrared spectrum: 1268w, 1120w, 1032m, 970w, 775s, 739msh, 701w, 652w, 442s, 349s, 330s, 229msh, cm^{-1}. A similar preparation gave white 1,2-$C_6H_4(HgBr)_2$, which was recrystallized from DMF, m.p. 318–320°C (Found: C, 12.2; H, 0.6; Br, 24.7; $C_6H_4Hg_2Br_2$ calc: C, 11.3; H, 0.6; Br, 25.2%). Infrared spectrum: 1440s, 1400w, 1250s, 1025w, 1016s, 1006wsh, 950w, 874w, 764s, 755s, 720wsh, 635w, 422s, 316w, 298s cm^{-1}.

(iii) Reaction of 1,2-$C_6H_4(HgCl)_2$ with sodium iodide

A suspension of 1,2-$C_6H_4(HgCl)_2$ in a solution of sodium iodide in alcohol was heated under reflux for 2 h. After cooling, the supernatent liquor was decanted off, the residual white solid washed thoroughly with distilled water and dried at 85 °C, m.p. 327–329 °C. The *ortho*-phenylenemercury trimer was identified by its infrared spectrum.

(iv) Reaction of 1,2-$C_6H_4(HgBr)_2$ with sodium iodide

The mercurial and an excess of sodium iodide in dimethylformamide and ethanol (5/1, v/v) were refluxed for 0.5 h. The white precipitate of *ortho*-phenylenemercury trimer which formed was identified by infrared spectroscopy and shown to be the monoclinic form [3] by powder X-ray diffraction [15].

(v) Attempted thermal symmetrization of 1,2-$C_6H_4(HgBr)_2$

The mercurial was heated in a sublimer under vacuum (ca. 10^{-4} mmHg) to 220 °C for 1 h. No sublimate of $HgBr_2$ formed and the starting material was recovered (infrared identification).

(d) The tetrafluoro-ortho-phenylenemercury system

(i) Reaction of $(C_6F_4Hg)_3$ with mercuric chloride

The mercurial (0.515 mmol) and mercuric chloride (1.537 mmol) were refluxed for 45 min in methanol and 1,2-$(ClHg)_2C_6F_4$ crystallized on cooling, yield 87%, m.p. 316–318°C (lit. 1. ca. 300°C). The infrared spectrum was identical with that reported for the region 4000–400 cm^{-1} except that 868wbr [1] was not observed. Two strong ν(Hg–Cl) bands occurred at 331 and 313 cm^{-1}.

(ii) Reaction of $(C_6F_4Hg)_3$ with mercuric bromide

A similar synthesis gave fluffy, white crystals of 1,2-$(BrHg)_2C_6F_4$, which were separated by decantation, recrystallized from methanol and dried at 80°C; m.p. 312–314°C (lit. 1 > 300°C); infrared identification, see Ref. 1.

(iii) Reaction of 1,2-$(XHg)_2C_6F_4$ with sodium iodide (X = Cl, Br)

A solution of 1,2-$(XHg)_2C_6F_4$ in aqueous ethanol was refluxed with an excess of sodium iodide for 30 min. On cooling, a precipitate was formed which had an infrared spectrum identical with that of perfluorophenylenemercury trimer.

(iv) Preparation of mercuric 2,3,4,5-tetrafluorobenzoate

The benzoate was precipitated on addition of aqueous mercuric acetate to aqueous 2,3,4,5-tetrafluorobenzoic acid (mole ratio 1/2), 95% yield, m.p. (dec.) 284°C (Found: C, 28.4; H, 0.3; F, 25.6; $C_{14}H_2F_8O_2Hg$ calc: C, 28.7; H, 0.3; F, 25.9%). Infrared spectrum: 1592s, 1578s, 1531s, 1482s, 1462sh, 1374s, 1321m, 1308, 1299mbr, 1264s, 1199w, 1190w, 1108w, 1099w, 1046s, 915m, 903w, 895w, 885m, 791s, 783s, 730w, 718w, 665w, 518br cm^{-1}.

(v) Pyrolysis of mercuric 2,3,4,5-tetrafluorobenzoate

Mercuric 2,3,4,5-tetrafluorobenzoate was heated at 190°C under vacuum in a sublimer; the sublimate was recrystallized from petroleum ether (b.p. 60–80°C) giving 2,3,4,5-tetrafluorobenzoic acid (100% yield; infrared identification). An involatile residue of 2,3,4,5-tetrafluoro-6-mercuriobenzoate (88%) was recrystallized from acetone, m.p. (dec.) 291°C. The infrared spectrum was in agreement with that reported [7] except that additional medium bands were observed at 709, 690, 680 and 670 cm^{-1}.

(e) Reactions of 2,3,4,5-tetrafluoro-6-mercuriobenzoate

(i) Iodomercuration

A solution of the benzoate and the stoichiometric amount of sodium triiodide in methanol was stirred until decolourised, when the methanol was evaporated and concentrated aqueous sodium iodide added. The solution was acidified with HCl, mercury was precipitated by H_2S, ether added and the mixture filtered. Ether extraction, evaporation, and recrystallization of the residue from petroleum ether (b.p. 60–80°C) gave 2,3,4,5-tetrafluoro-6-iodobenzoic acid (53%) which was sublimed (10^{-2} mmHg, 80°C) and recrystallized from ether/petroleum ether (1/9, v/v), m.p. 128–129°C [6] (Found: C, 26.7; H, 0.4; m/e, 320; $C_7HF_4IO_2$ calc: C, 26.3; H, 0.3%; mol. wt., 320). ^{19}F NMR spectrum ($((CD_3)_2CO)$): 114.7 (1F, F5), 139.2, (1F, F2), 152.3 (1F, F4), 154.3 (1F, F3). Infrared spectrum: 3200–2500mbr (ν(OH)), 1705vs, 1620s, 1504s, 1481vs, 1429s, 1355m, 1285s, 1249s, 1108m, 1044s, 913s, 816m, 783s, 707s, 483m cm^{-1}.

(ii) Protodemercuration

2,3,4,5-Tetrafluoro-6-mercuriobenzoate was boiled with acetone and concentrated HCl; extraction with diethyl ether, evaporation followed by recrystallization of the residue from petroleum ether (60–80°C) gave 2,3,4,5-tetrafluorobenzoic acid in 81% yield. M.p. 86–87°C (lit. 11 86–87°C), identified by infrared.

(iii) Thermal decomposition

The mercuriobenzoate, on pyrolysis at 300 °C under vacuum, gave a sublimate of tetrafluorophenylenemercury trimer which was purified by resublimation; 88% yield, m.p. > 300 °C (infrared identification). The non-availability of 3,4,5,6-tetrafluorophthalic acid at the present time makes this decomposition a useful source of $(C_6F_4Hg)_3$.

(f) The perfluorobiphenylenemercury system

(i) Preparation of perfluorobiphenylenemercury

Butyllithium (14 ml hexane solution; 10.9 mmol) and 2,2′-dibromooctafluorobiphenyl (4.95 g, 10.8 mmol) were stirred in 100 ml of ether for 30 min at −78 °C. After mercuric chloride (5.4 g, 10 mmol) was added, the stirred solution was allowed to warm to room temperature and stand for 15 h. The yellow solution was filtered to remove lithium chloride and the solvent evaporated giving a sticky, white solid. Addition of pentane gave a yellowish solid and an off-white solution which, on filtration and solvent removal yielded a little 2,2′-$H_2C_{12}F_8$ (infrared identification). The residue was crystallized from benzene to give $(C_{12}F_8Hg)_3$ (2.6 g, 48%), identified by its infrared spectrum [16]. The mercurial was also obtained by heating mercury with 2,2′-$I_2C_{12}F_8$ in a sealed tube to 310 °C.

(ii) Reaction of $(C_{12}F_8Hg)_3$ with bromine

The mercurial (260 mg) and bromine (0.2 ml) were heated in a sealed tube at 110 °C for 18 h. After cooling, the contents of the tube were extracted with ether and filtered; the clear ethereal solution was separated, dried over anhydrous $MgSO_4$ and evaporated under vacuum; sublimation (60–80 °C) of the residue gave 2,2′-dibromooctafluorobiphenyl (220 mg, 92%) identified by its infrared spectrum.

(iii) Reaction of $(C_{12}F_8Hg)_3$ with iodine

Iodine (320 mg) and $(C_{12}F_8Hg)_3$ (127 mg) were heated together at 230 °C in a sealed tube for 4 h. Work-up as for the bromine reaction yielded crystalline 2,2′-$I_2C_{12}F_8$ (125 mg, 89%) identified by its infrared spectrum.

(iv) Reaction of $(C_{12}F_8Hg)_3$ with sulphur

Mercurial (120 mg) and sulphur (140 mg) were heated in a sealed tube at 300 °C for 16 h. On extraction of the tube contents with ether and normal work-up only $(C_{12}F_8Hg)_3$, 80 mg, could be isolated (infrared identification).

(g) The perchlorophenylenemercury system

(i) Reaction of $(HgC_6Cl_4)_3$ with mercuric chloride

The mercurial (0.44 mmol) and $HgCl_2$ (1.32 mmol) were heated together in 70 ml of boiling dimethyl formamide, in which $(HgC_6Cl_4)_3$ is barely soluble. The suspension rapidly gave way to an almost clear solution which after 30 min, was filtered, evaporated to about 10 ml and left overnight. Large, transparent crystals formed which were washed quickly with two aliquots (ca. 50 ml) of cold acetone and dried at 70 °C when the crystals lost their brightness and collapsed to a white powder (Found: C, 10.5; H, 0.0; N, 0.0; Cl, 30.0; $C_6Cl_6Hg_2$ calc: C, 10.5; H, 0.0; N, 0.0; Cl, 31.0%). IR spectrum: 1491vw, 1413vw, 1325m, 1306s, 1281m, 1276m, 1269w, 1248vw, 1153wb, 1139vw, 1126vw, 1101s, 1061w, 861vw, 838w, 827w, 660vs, 643m, 582vw, 405vw, 370m, 338s, 328s, 322ssh cm^{-1}. The chloride was insoluble in acetone, methanol and toluene, but very soluble in DMF.

(ii) Reaction of $(HgCl_6Cl_4)_3$ *with mercurous chloride*

There was a virtually instantaneous blackening of the boiling suspension of $(HgC_6Cl_4)_3$ (0.383 mmol) in 70 ml of DMF when mercurous chloride (1.15 mmol) was added. The reaction mixture was boiled for 1 h, filtered and the volume reduced to 10 ml before the flask was left overnight. Large transparent crystals formed which were washed with acetone and dried at 70°C when they collapsed to a white powder. The infrared spectrum proved identical to that of a sample of $C_6Cl_4(HgCl)_2$ produced in the previous experiment (Found: C, 10.35; H, 0.0; N, 0.0; Cl, 31.0; $C_6Cl_6Hg_2$ calc: C, 10.5; H, 0.0; N, 0.0; Cl, 31.0%).

(iii) Reaction of $(HgC_6Cl_4)_3$ *with mercuric bromide and other mercuric compounds*

There appeared to be only an incomplete reaction when $HgBr_2$ (1.32 mmol) was refluxed with 0.44 mmol of $(HgC_6Cl_4)_3$ in 70 ml of DMF. On cooling, the unreacted mercurial separated out rapidly and was filtered off before the solution was evaporated down and allowed to crystallize. The colourless product had an infrared spectrum virtually the same as $C_6Cl_4(HgCl)_2$ (Found: C, 9.6; Cl, Br combined and quoted as 'chloride', 26.9; $C_6Cl_4Br_2Hg_2$ calc: C, 9.3; Cl + Br as 'Cl', 27.5%). Chloride and bromide co-precipitate during a silver potentiometric titration [12] and, therefore, in this analysis they were titrated as 'total chloride'.

There was no reaction in either boiling DMF or boiling nitrobenzene when $(HgC_6Cl_4)_3$ was treated with HgO, HgI_2, $HgSO_4$ and $Hg(SCN)_2$. There was no apparent reaction with mercuric acetate in boiling ethanol, ethyl acetate or DMF; although no reaction was evident in boiling nitrobenzene a small amount of crystalline material was isolated which had a different infrared spectrum to the starting materials and analysis showed to be the diacetate $C_6Cl_4(CH_3COOHg)_2$ (Found: C, 16.5; H, 0.6; N, 0.0; Cl, 19.0; $C_{10}H_6Cl_4O_4Hg_2$ calc: C, 16.5; H, 0.8; N, 0.0; Cl, 19.3%).

The product obtained by refluxing $(C_6Cl_4Hg)_3$ and damp mercuric nitrate in nitrobenzene was $Hg(C_6H_4NO_2)_2$ formed by mercuration of the solvent; it was presumably a mixture of several isomers and no attempt was made to separate them (Found: C, 32.4; H, 1.8; N, 6.35; Cl, 0.0; $C_{12}H_8N_2O_4Hg$ calc: C, 32.4; H, 1.8; N, 6.3; Cl, 0.0%).

(iv) Reaction of $(C_6Cl_4Hg)_3$ *with water*

Although the mercurial resisted attack by boiling acids such as hydrochloric, nitric, acetic and aqua regia, ready and quantitative cleavage of the tetrachlorophenyl groups (as 1,2-$H_2C_6Cl_4$) occurred when $(C_6Cl_4Hg)_3$ was heated with water vapour at 250°C in a sealed, evacuated tube.

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