

SUBSTITUTED PHENYLENE- AND BIPHENYLENE-MERCURIALS

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Summary

A variety of substituted phenylene- and biphenylene-mercurials has been prepared and each compound shown to be trimeric. However, there is mass spectral evidence that trace quantities of perfluorobiphenylenemercury tetramer exist in the bulk samples of trimer.

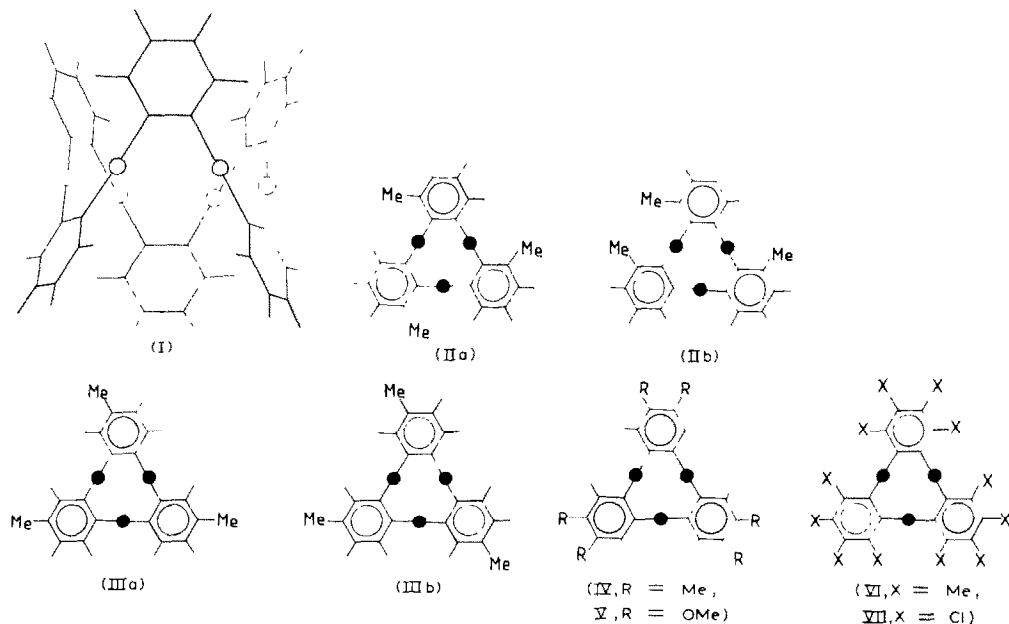
Introduction

ortho-Phenylenemercury was first described in 1930 by Vecchiotti [1] who prepared it by treating 1,2-dibromobenzene with sodium amalgam in a petroleum ether/ethyl acetate mixed solvent. Some years later Wittig and Bickelhaupt [2] determined the molecular weight in solution which suggested that the molecule was hexameric. The compound adopts two crystal forms, one orthorhombic the other monoclinic. Grdenic [3] studied the latter using X-ray crystallographic techniques and, via a Patterson projection, obtained the positions of the mercury atoms and hence deduced the hexameric structure shown in I. Although the hexamer is theoretically possible, when both crystal forms were subjected to a full, three-dimensional X-ray structure determination they were found to contain only trimeric molecules of *ortho*-phenylenemercury [4,5]; the fluoro analogue, tetrafluorophenylenemercury, is also trimeric [6,7]. By changing the electronic and/or steric properties of the phenylene groups we hoped to obtain evidence that some phenylenemercurials, at least, could exist in the hexameric form (or even as the tetramer which appears just as feasible structurally). To this end we have prepared a variety of substituted phenylenemercurials and checked their degree of polymerization using mass spectrometry. In all cases only the trimers were obtained.

Results and discussion

The methyl- and methoxy-phenylenemercurials (II-V) were prepared by vigorously stirring sodium amalgam with the corresponding 1,2-dibromobenzene deriva-

tive in a suitable solvent, usually tetrahydrofuran. Yields of mercurial were very low,



typically being about 1% based on the dibromobenzene used. Substituted 1-bromo-2-chlorobenzenes invariably failed to give any mercury-containing products and even 1-bromo-2-chlorobenzene itself gave only trace quantities of *ortho*-phenylenemercury trimer. Repeated failures attended our efforts to make "naphthalenemercury" using 2,3-dibromonaphthalene and either sodium or potassium amalgam. When 1,2-dibromobenzene reacts with sodium amalgam in 1,2-dimethoxyethane solvent fair yields of terphenylenemercury dimer, $(C_{18}H_{12}Hg)_2$, are produced [8,9]; no methyl-substituted terphenylenemercurials could be detected when 2,3-dibromotoluene or 3,4-dibromotoluene were treated with sodium amalgam in 1,2-dimethoxyethane. To our surprise we were unable to synthesise ethylphenylenemercury by treating 1-ethyl-2,3-dibromobenzene with alkali metal amalgams.

Monomethylphenylenemercury trimers can exist in two isomeric forms, IIa, IIb and IIIa, IIIb, depending on the relative positions of the three methyl groups. Presumably mixtures of the isomers were formed during the preparation of II and III but the very low solubility of the mercurials in all solvents hampered the isolation of the individual isomers when chromatography was attempted. Notwithstanding the isomeric mixtures present, samples of II and III melted sharply.

Tetramethylphenylenemercury was insoluble in all the solvents tried and the only way found to purify it was to remove any impurities by extracting them with boiling nitrobenzene. It could be made to sublime in vacuum (ca. 10^{-4} mmHg) on careful heating with a free flame, the volatility being similar to that of tetrachlorophenylenemercury.

The mass spectra of II-V show a mass cut-off at peaks representing the parent ion clusters, even at high gain there was no evidence of the corresponding tetrameric or hexameric mercurials. Apart from Hg^+ , in each case the molecular ion was the only other intense mercury-containing species and the base peak was due to the

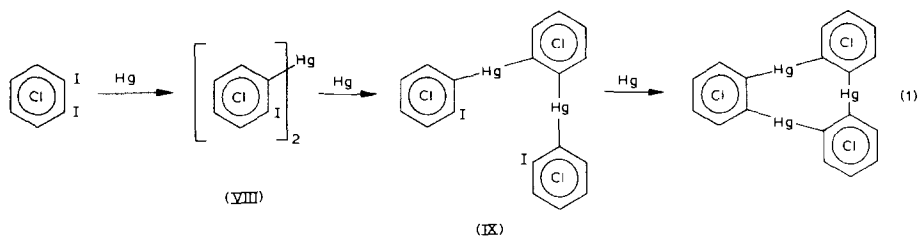
methyl- or methoxy-substituted phenylene ion. Typically, II showed a parent ion cluster of which the peak at 872 mass units had an intensity 26% relative to the base peak corresponding to $(C_6MeH_3)^+$; other ions of reasonable intensities were $(C_6MeH_3)_3^+$, $(C_6MeH_3)_2(C_6H_3)^+$, $(C_6MeH_3)(C_6H_3)_2^+$, Hg^+ , $(C_6MeH_3)(C_6H_3)^+$ and $C_6MeH_3^+$. Since all the mass spectra closely resemble that of *ortho*-phenylenemercury, now known from crystallographic studies to be trimeric, we are led to the conclusion that these methyl- and methoxy-substituted phenylenemercurials also exist only in the trimeric forms shown in II-V.

Typically, thermal decomposition of II at 320°C in a sealed, evacuated tube yielded metallic mercury together with a mixture of a liquid and some colourless crystals. Mass spectral analysis of the ether-soluble material showed that the main component of the liquid was dimethyldiphenyl and that the relatively involatile crystals were bis(methylphenyl)mercury.

Perfluorophenylenemercury trimer is best made by decarboxylating mercuric tetrafluorophthalate [6]. However, when decarboxylation of mercuric tetrachlorophthalate is attempted by heating it under vacuum chlorine-migration reactions occur to give mainly bis(pentachlorophenyl)mercury and some hexachlorobenzene; only tiny amounts of tetrachlorophenylenemercury can be sublimed from the involatile debris on strong heating with a free flame. A much more convenient synthesis of tetrachlorophenylenemercury is to heat together mercury and 1,2-diiodotetrachlorobenzene in a sealed, evacuated tube at 260–300°C for about four days. The yield is virtually quantitative; an off-white, analytical sample could be obtained simply by carefully subliming away the HgI_2 by-product and excess mercury. Tetrachlorophenylenemercury is highly insoluble in the common organic solvents and is only slightly soluble in boiling nitrobenzene or dimethylformamide; it separates from the latter, on cooling, in such a finely-divided state that the suspension has to be centrifuged at 3000 rpm to force the solid to settle. Unlike $(C_6F_4Hg)_3$ which exhibits solvates containing one, two and three molecules of solvent [7], tetrachlorophenylenemercury forms a solvate containing only half a mole of dimethylformamide (DMF). The broad carbonyl band of DMF (maximum intensity at 1690 cm^{-1}) shifts by 31 wavenumbers to 1659 cm^{-1} in the solvate; the band centred at 1080 cm^{-1} and the sharp peak at 457 cm^{-1} which occur in the spectrum of free DMF are essentially unchanged in the solvate. A similar "direct synthesis" in which a mixture of 1,2- $I_2C_6F_4$ and 1,2- $I_2C_6Cl_4$ was heated with mercury gave two expected products $(C_6F_4Hg)_3$ and $(C_6Cl_4Hg)_3$ as well as the "mixed" species $(C_6Cl_4)(C_6F_4)_2Hg_3$ and $(C_6Cl_4)_2(C_6F_4)Hg_3$. All four components gave molecular ion clusters in the mass spectrum, those of the latter two mixed species occurring at around 1112 and 1178 mass units, respectively.

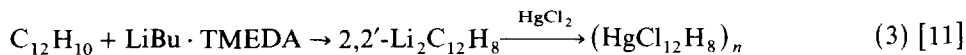
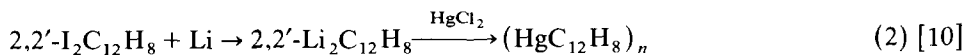
If the reaction between 1,2-diiodotetrachlorobenzene and mercury was stopped after only one day then bis(2-iodotetrachlorophenyl)mercury (VIII), occurred in large amounts among the products, and it could be obtained free of tetrachlorophenylenemercury by fractional vacuum sublimation. Presumably this compound is an intermediate in the formation of tetrachlorophenylenemercury (eq. 1). We have not, as yet, been able to obtain evidence for the occurrence of intermediate IX which, once formed, may well react rapidly with more mercury to give tetrachlorophenylenemercury. Attempts to chlorinate *ortho*-phenylenemercury directly with free chlorine gave only mercury(II) chloride.

In order to investigate if these phenylenemercurials would be useful in the



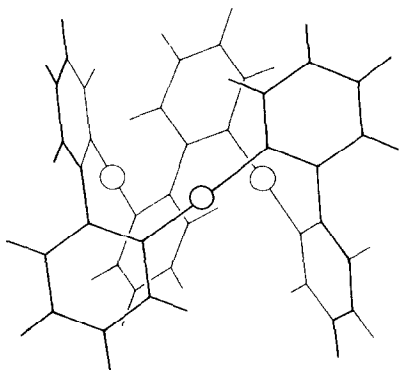
small-scale synthesis of other heterocyclic systems, *ortho*-phenylenemercury was heated with selenium to 250°C in a sealed tube. The product, extracted with 40–60°C petroleum ether, was essentially pure selenanthren, $\text{Se}_2(\text{C}_6\text{H}_4)_2$, as determined mass spectroscopically. In a similar manner sulphur gave $\text{S}_2(\text{C}_6\text{H}_4)_2$. A “mixed” reaction in which selenium was heated with $(\text{C}_6\text{F}_4\text{Hg})_3$ and $(\text{C}_6\text{H}_4\text{Hg})_3$, gave a product showing $\text{Se}_2(\text{C}_6\text{F}_4)_2^+$, $\text{Se}_2(\text{C}_6\text{H}_4)_2^+$ and $\text{Se}_2(\text{C}_6\text{H}_4)(\text{C}_6\text{F}_4)^+$ ions in its mass spectrum; no attempt was made to separate the components of the mixture.

Biphenylenemercury, $(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_n$, has been synthesised by both of the

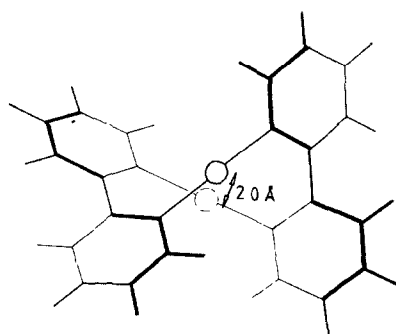


(TMEDA = tetramethylethylene diamine)

reaction sequences 2 and 3 and stated to be tetrameric. We have made biphenylenemercury by both routes and shown that the same compound is produced in each case and has a (sharp) melting point identical to that quoted by Witting for his tetramer. The mass spectrum of biphenylenemercury (repeated many times on different samples) has an ion cut-off at a cluster of isotopomeric ions centred at 1056 mass units, which represents the parent ion of the trimer; no peak corresponding to the ion $(\text{C}_6\text{H}_4)_8^+$ can be distinguished even at high gain. As all the phenylene- and polyphenylene-mercurials we have studied to date have shown easily identifiable parent ions in their mass spectra and furthermore, shown peaks of considerable



(X)

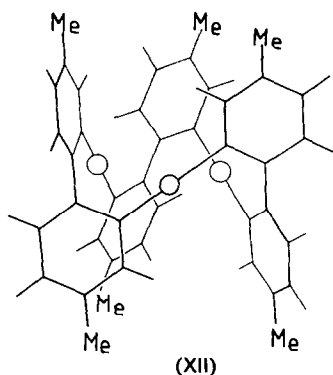


(XI)

intensity representing the parent ions stripped on all the mercury atoms it seems reasonable to assume that biphenylenemercury is trimeric (X), not tetrameric.

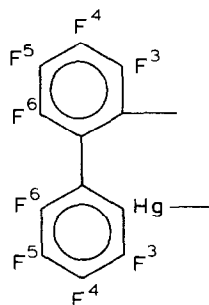
In the mass spectrum of biphenylenemercury there is a group of peaks, of almost equal intensity to the parent trimer ion, representing the isotopomeric species in the ion $(C_{12}H_8Hg)_2^+$. We have, therefore, to consider the possibility that biphenylenemercury can exist also as a dimer. Assuming that the C-Hg-C bond angle in a phenylenemercurial will be typically about 180° then it can be shown by consultation of scale Dreiding models that the two mercury atoms in a dimer would approach to within 2.0 Å of each other (XI). This is considerably less than twice the Van der Waals radius for mercury (ca. 3.1 Å) and suggests that the dimer molecule would be unstable sterically. Likewise there is a strong peak in the mass spectrum of perfluorobiphenylenemercury representing the ionized "dimer", $(C_{12}F_8Hg)_2^+$, as well as weak peaks due to $(C_{12}F_8Hg)_2^{2+}$. However, in this spectrum there is also a broad metastable peak at about 662 mass units corresponding to the transition $(C_{12}F_8Hg)_3^+ \rightarrow C_{12}F_8Hg + (C_{12}F_8Hg)_2^+$ (obs. 557-664, calcd. 662.3 m.u.) showing that most, if not all, of the "dimer" ions arise via fragmentation and not via molecular ionization.

More interestingly, some mass spectra of perfluorobiphenylenemercury show a group of peaks, visible only at high gain, corresponding to the tetramer (1992 m.u.). Thus trace amounts of tetramer must be present in some samples of perfluorobiphenylenemercury. Like the parent biphenylenemercury, 4,4'-dimethylbiphenylenemercury shows only a molecular ion representing the trimeric species XII in its mass spectrum.



Biphenylenemercury is too insoluble in all the solvents tried to carry out ^{13}C and 1H NMR searches for the presence of either tetramer or dimer within the trimer samples. However, octafluorobiphenylenemercury is much more soluble and shows four intense groups of peaks in its ^{19}F NMR spectrum at 120.6, 136.2, 154.2 and 154.9 ppm (relative to internal $CFCl_3$), corresponding to the F(3), F(6), F(5) and F(4) fluorine atoms of the trimer molecule. Tiny impurity peaks just observable above the background noise may be connected with the presence of the small amount of tetramer shown up by the mass spectrum.

Two peaks of almost equal intensities occur at 804 and 820 cm^{-1} in the infrared spectrum of perfluorobiphenylenemercury; this is the region where "Hg-C₆F₄" vibration peaks might be expected to occur. At face value this spectrum could be



taken as being indicative of about equal amounts of two perfluorobiphenylene-mercury species (trimer and tetramer) being present in the sample. The very weak peaks corresponding to the tetramer in the mass spectrum could then be attributed to the low relative volatility of the tetrameric species. However, the infrared spectrum of bis(perfluorobiphenylene)silane, $(C_{12}F_8)_2Si$, also shows two similar peaks of about equal intensity (at 884 and 864 cm^{-1}) attributable to “ $Si-C_6F_4$ ” vibrations. In view of this, and the lack of other evidence to suggest the presence of appreciable amounts of tetramer in perfluorobiphenylenemercury samples, we assume the two “ $Hg-C_6F_4$ ” peaks to be due to other effects within the crystals of trimer. In contrast, the “X-sensitive” peaks at 447 cm^{-1} in biphenylenemercury and at 405 cm^{-1} in dimethylbiphenylenemercury are very sharp and show no evidence of any splitting.

Experimental

The substituted dibromobenzenes and substituted 2,2'-diiodobiphenyls were prepared using standard procedures; 1,2-dimethoxy-4,5-dibromobenzene (4,5-dibromoveratrole) was purchased from Lancaster Synthesis and used without purification. All bench reactions were carried out in oven-dried glass-ware under an atmosphere of dry nitrogen; the sealed reaction tubes were made from pyrex glass and thoroughly baked out under vacuum with a free flame before use. Infrared spectra were recorded as Nujol or hexachlorobutadiene mulls.

Preparation of ortho-phenylenemercury

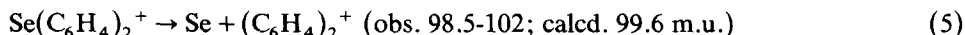
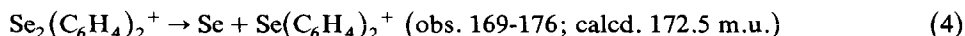
A solution of 20 mmol of 1,2-dibromobenzene (Aldrich) in 50 cm^3 of dry tetrahydrofuran was vigorously stirred with 50 mg atoms of 2% sodium amalgam. An exothermic reaction occurred which faded over about half an hour; stirring was continued for a further 2 h. Water was added until no more precipitate formed and the supernatant liquid separated from mercury and the precipitate, the latter being washed with water before removal of the mercury. A little hot toluene removed any organic material from the precipitate which was then extracted with hot dimethylformamide. The analytical samples were recrystallized from DMF and dried under vacuum or in an oven at 100°C (Found: C, 26.1; H, 1.5. $C_{18}H_{12}Hg_3$ calcd.: C, 26.0; H, 1.45%).

We have always found the yield from this reaction to be very low (usually 1–2%); even after 10 years experience in the field and having tried every conceivable change in reaction conditions we have been unable to obtain yields anywhere approaching those quoted by Wittig [2]. Infrared spectrum: 3090w; 3030m; 3005m; 2955w;

1425m; 1412m; 1259w; 1088m; 1021m; 866m; 745s; 679w; 479w; 422s; 325s; 289m cm^{-1} .

Reaction between $(\text{C}_6\text{H}_4\text{Hg})_3$ and Se

ortho-Phenylmercury (0.5 g) and selenium (0.5 g) were heated to 250 °C for 12 h in a sealed tube; metallic mercury could be seen in the tube after this time. After opening the tube, the contents were extracted with 40–60 °C petroleum ether to give 50 mg of a solid shown to be $\text{Se}_2(\text{C}_6\text{H}_4)_2$ by the ion cluster centred at 130 m.u. in the mass spectrum. Two large metastable peaks were observed for reactions 4 and 5.



A similar synthesis occurred when *ortho*-phenylmercury was heated with an excess of sulphur, the product $\text{S}_2(\text{C}_6\text{H}_4)_2$ again being identified mass spectrometrically.

Preparation of 4-methylphenylmercury (III)

Using similar conditions to those employed for *ortho*-phenylmercury, 3,4-dibromotoluene was treated with sodium amalgam in dry tetrahydrofuran. The analytical sample of 4-methylphenylmercury, m.p. 305–306 °C, was recrystallized from DMF and dried at 100 °C in an oven (Found: C, 29.4, 28.8; H, 2.0, 2.05. $\text{C}_{21}\text{H}_{18}\text{Hg}_3$ calcd.: C, 28.9; H, 2.1%). The same compound was obtained by stirring 3-bromo-4-fluorotoluene with sodium amalgam in 60–80 °C petroleum ether.

Infrared spectrum: 1568m; 1439m; 1365w; 1200m; 1085m; 872w; 797s; 716m; 570w; 510w; 492w; 414s; 387w; 293m; 275w cm^{-1} . The peak at 716 cm^{-1} is of variable intensity from sample to sample and may be due partially to the presence of impurity; the strong peak at 797 cm^{-1} is typical of a 1,2,4-substituted benzene. The aromatic C–H stretching frequency occurs at 3008 cm^{-1} with the asymmetric and symmetric C–H stretches of the methyl groups at 2908 and 2855 cm^{-1} , respectively.

Preparation of 3-methylphenylmercury (II)

Treatment of 2,3-dibromotoluene with sodium amalgam gave 3-methylphenylmercury, m.p. 323–325 °C (Found: C, 28.8; H, 2.0. $\text{C}_{21}\text{H}_{18}\text{Hg}_3$ calcd.: C, 28.9; H, 2.1%).

Infrared spectrum: 1130w, 1025w, 955w, 885w, 760s, 715m, 705w, 498w, 420w, 300w, 270s cm^{-1} .

The compound showed a parent ion cluster in its mass spectrum centred at 872 m.u., corresponding to the molecular weight of the trimer species. The main fragment ions were $(\text{C}_6\text{MeH}_3)_2\text{Hg}^+$, $\text{C}_6\text{MeH}_3\text{Hg}^+$, $(\text{C}_6\text{MeH}_3)_3^+$, $(\text{C}_6\text{MeH}_3)(\text{C}_6\text{H}_3)_2^+$, $(\text{C}_6\text{MeH}_3)_2^+$, $(\text{C}_6\text{MeH}_3)(\text{C}_6\text{H}_3)^+$, Hg^+ and C_6MeH_3^+ .

Preparation of 4,5-dimethylphenylmercury (IV)

1,2-Dibromo-4,5-dimethylbenzene, on stirring with sodium amalgam in tetrahydrofuran, gave 4,5-dimethylphenylmercury, m.p. > 320 °C (Found: C, 32.2; H, 2.5. $\text{C}_{24}\text{H}_{24}\text{Hg}_3$ calcd.: C, 31.5; H, 2.6%). The parent ion cluster appeared at around 914 mass units in the mass spectrum; important fragmentation species were $(\text{C}_8\text{H}_8)_2\text{Hg}^+$, $\text{C}_8\text{H}_8\text{Hg}^+$, $(\text{C}_8\text{H}_8)_3^+$, $(\text{C}_8\text{H}_8)_2^+$, Hg^+ , C_8H_8^+ (base peak) and C_7H_5^+ .

Infrared spectrum: 1224w, 1150w, 1100w, 1015w, 868m, 720s, 640w, 430m cm^{-1} .

Preparation of 4,5-dimethoxyphenylenemercury (V)

1,2-Dibromo-4,5-dimethoxybenzene and sodium amalgam reacted in tetrahydrofuran to give 4,5-dimethoxyphenylenemercury, m.p. 300 °C (Found: C, 28.5; H, 2.5. $C_{24}H_{24}O_6Hg_3$ calcd.: C, 28.5; H, 2.4%). The parent ion cluster centred at 1010 mass units in the mass spectrum showed the trimeric nature of the compound.

Infrared spectrum: 1543m, 1330w, 1285s, 1260m, 1232s, 1195s, 1167s, 1106s, 858w, 838m, 764s, 718s, 400s br cm^{-1} .

Preparation of tetramethylphenylenemercury (VI)

Sodium amalgam and 1,2-dibromotetramethylbenzene were reacted together in refluxing decalin. The product proved highly insoluble even in such solvents as boiling DMF, dimethylsulphoxide or nitrobenzene. The analytical sample was refluxed with two portions of nitrobenzene, washed twice with boiling acetone and dried at room temperature in a vacuum, m.p. > 320 °C (Found: C, 36.0; H, 3.5. $C_{30}H_{36}Hg_3$ calcd.: C, 36.1; H, 3.6%). Although the compound did not melt below 320 °C, close observation showed that decomposition apparently occurred between 290 and 300 °C in the air; decomposition in a sealed, evacuated tube at 300 °C gave free mercury. Tetramethylphenylenemercury proved too involatile for a mass spectrum to be obtained but it would sublime on careful heating in a dynamic vacuum (ca. 10^{-4} mmHg). Virtually no infrared absorption occurred except in the 3000 and 1400 cm^{-1} regions: 2970m; 2955m; 2930m; 2870sh; 1445w,br, 1388m cm^{-1} .

Two very minor by-products, octamethylbiphenylene (Found: C, 90.0; H, 9.1. $C_{20}H_{24}$ calcd.: C, 90.8; H, 9.15%; mol.wt. 264 from mass spectrum) and bis(tetramethylphenyl)mercury, were found in the reaction. The latter is probably due to the presence of some 1-bromo-3,4,5,6-tetramethylbenzene in the starting material.

Decarboxylation of mercuric tetrachlorophthalate

Mercuric tetrachlorophthalate was cautiously heated in a continuously-evacuated tube using a free flame; considerable eruption of the solid occurred during the evolution of carbon dioxide. When no more gas was evolved the residue was fractionally sublimed to give mercury, C_6Cl_6 (containing a trace of decachlorobiphenyl), bis(pentachlorophenyl)mercury (major product; identified from its mass spectrum and by a comparison of its infrared spectrum with that of an authentic sample) and a solid of very low volatility which had properties similar to those of tetrachlorophenylenemercury described below.

Reaction of 1,2-diiodotetrachlorobenzene with mercury

Approximately 1.5 g of 1,2-diiodotetrachlorobenzene [12] was heated with an excess of mercury in a sealed, evacuated tube at 260 °C for 24 h; by arranging a slight thermal gradient in the furnace most of the HgI_2 by-product sublimed away from the off-white solid at the hotter, bottom of the tube. The remainder of the mercuric iodide was removed by opening the tube and subjecting the solid product to gentle warming under vacuum with a free flame; when all the yellow-to-red iodide had been removed further fractional sublimation produced a trace of white, volatile solid (shown to be bis(pentachlorophenyl)mercury using mass spectrometry) and a much less volatile, pale yellow component which proved to be bis(tetrachloroiodophenyl)mercury, m.p. > 330 °C (Found: C, 16.7; H, 0.0; Cl, 32.4; I, 28.9. $C_{12}Cl_8I_2Hg$ calcd.: C, 16.3; H, 0.0; Cl, 32.15; I, 28.8%). A mass spectrum verified

that the compound was $(C_6Cl_4I)_2Hg$ with a barely-detectable presence of $C_6Cl_4IHgC_6Cl_5$; a doubly-charged parent ion, $(C_6Cl_4I)_2Hg^{2+}$, was also present in the spectrum.

When the reaction was repeated but with a heating time of 4 d the product was tetrachlorophenylmercury (VII), purified by subliming away the excess mercury and the HgI_2 by-product, m.p. $> 330^\circ C$ (Found: C, 17.3; H, 0.0; Cl, 34.0. $C_{18}Cl_{12}Hg_3$ calcd.: C, 17.4; H, 0.0; Cl, 34.2%); the compound sublimes on strong heating in a vacuum.

The mercurial can be extracted from the reaction product by boiling with 5×50 cm^3 aliquots of DMF; on concentrating down the extracts, tetrachlorophenylmercury separated as an extremely finely-devided solid which had to be centrifuged from the mother liquor. The analytical sample was washed three times with acetone and dried for 20 m on a vacuum line (Found: C, 18.5; H, 0.35; N, 0.6; Cl, 34.6. $C_{18}Cl_{12}Hg_3 \cdot 0.5$ DMF calcd.: C, 18.3; H, 0.3; N, 0.55; Cl, 33.2%). A sample washed with acetone and air-dried at room temperature for 2 d gave similar analyses (Found: C, 18.1; H, 0.2; N, 0.5%).

When mercury was heated with a mixture of 1,2- $I_2C_6F_4$ and 1,2- $I_2C_6Cl_4$ a solid was formed which had a mass spectrum showing parent ion clusters of $(C_6F_4Hg)_3$, $(C_6F_4)_2(C_6Cl_4)Hg_3$, $(C_6F_4)(C_6Cl_4)_2Hg_3$ and $(C_6Cl_4Hg)_3$.

Infrared spectra: $Hg(C_6Cl_4I)_2$ 1322m sh; 1311s; 1283m; 1157w; 851w; 820w; 645m; 596w; 322vw cm^{-1} .

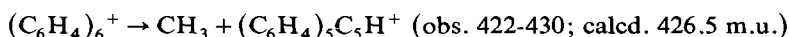
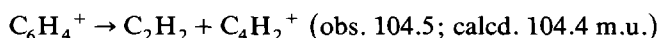
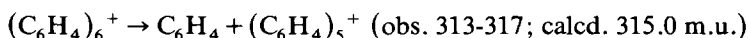
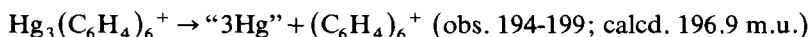
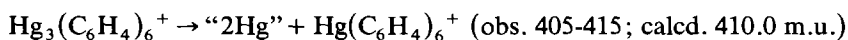
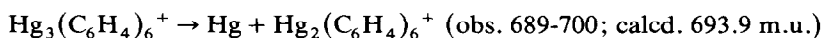
$(C_6Cl_4Hg)_3$: 1327m; 1310m; 1279m; 1160m; 1147m; 1066w; 844m; 825m; 640m; 350m cm^{-1} .

$(C_6Cl_4Hg)_3 \cdot 0.5$ DMF: 1659m; 1652sh; 1635sh br; 1326m; 1311m; 1287sh; 1282m; 1160m; 1151m; 844m; 831m br; 657w; 643m; 585w; 348m cm^{-1} .

Preparation of biphenylmercury (X)

This compound, m.p. $338^\circ C$, was formed by the reaction of 2,2'-dilithiobiphenyl with mercuric chloride in ether solution. The lithium reagent was made either by direct reaction of 2,2'-diiodobiphenyl with lithium [9,10] or by metallation of biphenyl with butyllithium in the presence of tetramethylethylene diamine [11] (Found: C, 40.6, 40.7; H, 2.1. 2.3. $C_{36}H_{24}Hg_3$ calcd.: C, 40.9; H, 2.3%).

The mass spectrum of biphenylmercury showed a mass cut-off at the cluster of peaks centred around 1058 mass units corresponding to the parent ion of the trimer, $(C_{12}H_8Hg)_3$; other mercury-containing ions present in the spectrum were $Hg_2(C_6H_4)_6^+$, $Hg(C_6H_4)_6^+$, $Hg_2(C_6H_4)_4^+$, $Hg(C_6H_4)_4^+$ and $Hg_3(C_6H_4)_6^{2+}$ (very weak). Several metastable peaks were also present which could be ascribed to the transitions:



Preparation of perfluorobiphenylenemercury

2,2'-Dibromooctafluorobiphenyl was lithiated at -78°C in ether/hexane solvent by butyllithium and mercuric chloride added. After removal of the solvent the mercurial, m.p. $> 330^{\circ}\text{C}$, was extracted with carbon tetrachloride (yield 64%). (Found: C, 28.6; 30.0; H, 0.0; F, 28.5, 31.4. $\text{C}_{36}\text{F}_{24}\text{Hg}_3$ calcd.: C, 29.0; H, 0.0; F, 30.6%). The osmometric molecular weight determined in benzene solution appeared to be 2038 (calcd. for tetramer 1988). However, the mass spectrum of several samples of perfluorobiphenylenemercury showed a mass cut-off at the parent ion of the trimer with only one sample having a very weak group of peaks around 1992 mass units corresponding to the ionized tetramer. The intensity ratio of trimer/tetramer parent ions was approximately 100/1.

Infrared spectrum (KBr disc): 1623m; 1605m; 1590m; 1493s; 1462s; 1445s; 1403m, sh; 1374w; 1364w; 1302s; 1282m; 1269m; 1127w; 1104s,sh; 1101s; 1063s; 1029m,sh; 1017s; 934m; 815m; 799m; 775w; 708m; 640w cm^{-1} .

Preparation of 4,4'-dimethylbiphenylenemercury (XI)

2,2'-Diiodo-4,4'-dimethylbiphenyl was stirred for 3 h in ether with butyllithium; mercuric chloride was then added and stirring continued for a further 2 h. The ether solvent was removed under vacuum and the mercurial extracted with hot DMF and recrystallized; the analytical sample was dried in an oven at 100°C . m.p. $316\text{--}318^{\circ}\text{C}$ with decomposition (Found: C, 43.8; H, 3.5. $\text{C}_{42}\text{H}_{36}\text{Hg}_3$ calcd.: C, 44.1; H, 3.2%). The parent ion cluster around 1140 m.u. in the mass spectrum demonstrates the trimeric nature of the mercurial; the more important ions present in the spectrum were $(\text{C}_{14}\text{H}_{12}\text{Hg})_3^+$, $(\text{C}_{14}\text{H}_{12}\text{Hg})_2^+$, $(\text{C}_{14}\text{H}_{12})_2\text{Hg}^+$, $(\text{C}_{14}\text{H}_{12})_2^+$, $\text{C}_{14}\text{H}_{12}^+$ (base ion), $\text{C}_{13}\text{H}_9^+$, Hg^+ and C_7H_6^+ .

Infrared spectrum: 1587w, 1258w, 1134m sh, 1035w, 1002m, 884m, 835m, 830m, 817s, 811s, 722m, 563m, 549w, 472m, 415s, 353w, 327w, 298w cm^{-1} .

References

- 1 L. Vecchiotti, *Chem. Ber.*, 63 (1930) 2275.
- 2 G. Wittig and F. Bickelhaupt, *Chem. Ber.*, 91 (1958) 883.
- 3 D. Grdenic, *Chem. Ber.*, 92 (1959) 231.
- 4 D.S. Brown, A.G. Massey and D.A. Wickens, *Acta Cryst. B* 34 (1978) 1695.
- 5 D.S. Brown, A.G. Massey and D.A. Wickens, *Inorg. Chim. Acta*, 44 (1980) L193.
- 6 P. Sartori and A. Golloch, *Chem. Ber.*, 101 (1968) 2004.
- 7 M.C. Ball, D.S. Brown, A.G. Massey and D.A. Wickens, *J. Organomet. Chem.*, 206 (1981) 265.
- 8 G. Wittig, E. Hahn and W. Tochtermann, *Chem. Ber.*, 95 (1962) 431.
- 9 S.B. Awad, D.S. Brown, S.C. Cohen, R.E. Humphries and A.G. Massey, *J. Organomet. Chem.*, 127 (1977) 127.
- 10 G. Wittig and W. Herwig, *Chem. Ber.*, 87 (1954) 1511; G. Wittig and G. Lehmann, *ibid.* 90 (1957) 875.
- 11 W. Neugebauer, A.J. Kos and P. von Ragué Schleyer, *J. Organomet. Chem.*, 228 (1982) 107.
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Note added in proof. Biphenylenemercury, when purified by several recrystallizations, has a melting point of $358\text{--}360^{\circ}\text{C}$. Two different crystal modifications have been identified and, by using density measurements combined with symmetry properties to define the number of molecules per unit cell, it has proved possible to calculate the molecular weight of biphenylenemercury in each form: monoclinic (from *p*-xylene), MW 1056.1; orthorhombic (from toluene), MW 1053.2. The calculated molecular weight for the trimer is 1058.2.