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A REINVESTIGATION OF PHENYLENE- AND POLYPHENYLENE-MERCURIALS

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SUMMARY

Evidence is presented to show that ortho-phenylenemercury is a trimer; no evidence was obtained for the previously reported hexameric form. Similarly, ortho-biphenylenemercury and its perfluoro-analogue exist as trimers and not tetramers, while ortho-terphenylenemercury is a dimer.

INTRODUCTION

Wittig and his co-workers have described[1] the preparation of ortho-phenylenemercury, typically from the reaction between sodium amalgam and 1,2-dibromobenzene in an ether solvent. On the basis of molecular weight determinations in solution[1] and a partial X-ray structure[2] the compound was assigned a hexameric formula, $(C_6H_4Hg)_6$ see (II). We repeated this reaction and presented[3] mass spectral evidence to show that ortho-phenylenemercury could also exist as a trimer, $(C_6H_4Hg)_3$. To our knowledge there is no published infrared spectrum of hexameric ortho-phenylenemercury, the only data available for comparison of our trimer to Wittig's hexamer being Wittig's melting-decomposition point[4] of 325-326° and Grdenic's X-ray crystal measurements.

RESULTS AND DISCUSSION

On the hot-stage microscope ortho-phenylenemercury trimer begins to sublime slowly at about 260° but does not melt below 350°. We originally took this to mean that our trimer was a different compound from Wittig's ortho-phenylenemercury; to our surprise, however, we found that the trimer melts with decomposition at 325-326° when heated in a capillary tube. A possible explanation of this is that slight decomposition in one part of a crystal at 325-326° triggers off decomposition in the remaining material packed in the capillary tube; sometimes, one or two tiny crystals of the few hundred in the field of view on the hot-stage microscope were noted to spin round rapidly or move about on the surface of the slide at 325-327°. Thus the melting point data suggest that Wittig's ortho-phenylenemercury is identical to ours. Two crystalline forms of ortho-phenylenemercury trimer exist, neither of which is the same as that described by Gdrenic for the hexamer; possibly the crystal used in the X-ray studies was atypical of the ortho-phenylenemercury sample.

In an effort to obtain a sample of ortho-phenylenemercury hexamer we have tried all of the following reactions, but in each case the only ortho-phenylenemercury derivative to be isolated was the trimer (sometimes ortho-terphenylenemercury dimer, $(C_6H_4C_6H_4C_6H_4Hg)_2$, was also obtained) :

(a) 1,2-Diiodobenzene shaken with sodium amalgam in THF at room temperature;

(b) 1,2-Diiodobenzene shaken with potassium amalgam in THF at room temperature;

(c) 1,2-Dibromobenzene shaken or stirred with sodium amalgam in THF at room temperature;

(d) 1,2-Dibromobenzene shaken with potassium amalgam in THF at room temperature;

(e) 1,2-Dibromobenzene shaken with sodium amalgam in THF at 0°C;

(f) 1,2-Dibromobenzene refluxed with sodium amalgam in THF;

(g) 1,2-Dibromobenzene shaken with sodium amalgam in diethyl ether at room temperature;

(h) 1,2-Dibromobenzene shaken with sodium amalgam in a 50:50 mixture of diethyl ether and ethyl acetate;

(i) 1,2-Dibromobenzene shaken with sodium amalgam in a 50:50 mixture of petrol ether and ethyl acetate;

(j) 1,2-Dichlorobenzene shaken with either sodium or potassium amalgam in THF at room temperature;

(k) 1,2-Dichlorobenzene shaken with either sodium or potassium amalgam in diethyl ether at room temperature;

(l) 1-Bromo-2-fluorobenzene shaken with sodium amalgam in THF at room temperature.

The normal reaction times for these experiments was between 12 and 15 h, but essentially the same yields were obtained with reaction times varying from 30 m to 48 h. When 1,2-dibromobenzene was treated with sodium amalgam in monoglyme at room temperature, only ortho-terphenylenemercury dimer[1b] was isolated; mercuric iodide was the only tractable product when 1,2-diiodobenzene and mercury were heated together in sealed, evacuated tubes at temperatures up to 290°.

Mixtures of ortho-phenylenemercury and ortho-terphenylenemercury dimer may be separated by heating them under vacuum (ca. 10^{-4} mm Hg) in a tube fitted with a cold finger. Ortho-phenylenemercury sublimes first at 160-200°, the pure ortho-terphenylenemercury dimer remaining may then be collected on the finger at 260°. For compounds having a similar structure (as probably do ortho-phenylenemercury hexamer and ortho-terphenylenemercury dimer, see II and III), volatility is proportional to molecular weight. Thus it is highly unlikely that the ortho-phenylenemercury used in these sublimation experiments is the hexamer (MW = 1656) when it sublimes at a lower temperature than ortho-terphenylenemercury dimer (MW = 858). The high thermal stability and volatility of ortho-phenylenemercury combine to make mass spectrometry an ideal method of establishing the molecular weight, as described in reference 3; the ion of highest mass, $(C_6H_4Hg)_3^+$, obtained by introducing the sample into the spectrometer at 140°, must surely represent the parent ion of ortho-phenylenemercury trimer and not the highest observable fragment ion of a hexamer. Three groups of workers[3,5] have described ortho-tetrafluorophenylenemercury as a trimer $(C_6F_4Hg)_3$; apparently without exception, perfluoro-derivatives of the elements have

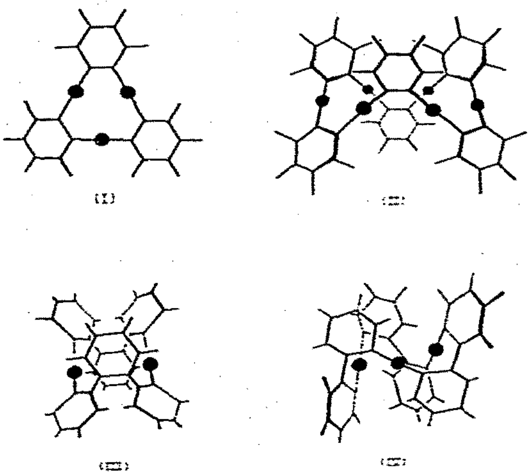


Figure 1. Probable molecular structures of the phenylenemercurials.

identical structures to their hydrogen analogues[6]. Thus there seems little doubt that our sample of ortho-phenylenemercury (and probably Wittig's) is the trimer (I). Preliminary X-ray studies on the contents of the unit cell of single crystals lead to the same conclusion.

An interesting feature in the mass spectrum of ortho-phenylenemercury trimer is the ion $(C_6H_4)_3Hg_2^{++}$, identified by the characteristic isotopic pattern, which has an intensity 15 times higher than the corresponding singly-charged ion. Unlike ortho-tetrafluorophenylenemercury trimer, which has a doubly-charged parent ion of intensity 9.4% relative to $(C_6F_4Hg)_3^+$, the ion $(C_6H_4Hg)_3^{++}$ in the mass spectrum of ortho-phenylenemercury trimer is barely visible even at very high gain. A broad meta-stable peak was observed at $^m/e = 62.8$ which corresponds to the transition :

$$(C_6H_4Hg)_3^+ \longrightarrow \text{"}Hg_3\text{"} + (C_6H_4)_3^+ ; \quad ^m/e \text{ calcd.} = 62.6$$

Whether these three mercurys are released as a trimeric cluster or as three separate atoms is not clear (the thermal decomposition of the trimer in a sealed, evacuated tube at 320° does not give simply triphenylene, although globules of mercury are formed : the crystalline material left behind melts over a wide range below 100° and clearly consists of a complex mixture of compounds; mass spectral analysis showed that three of the components were triphenylene, diphenylmercury and phenylbiphenylmercury). The base peak of the spectrum is due to the ion $C_{12}H_8^+$, the only other species of reasonable intensities being $C_6H_4^+$, 70%; $C_{18}H_n^+$, 68% and $(C_6H_4Hg)_3^+$, 53%; other mercury-containing ions, all of which were less than 0.5% relative abundance, included Hg_3^+, $Hg_2(C_6H_4)_2^+$, Hg_2^+, $Hg(C_6H_4)_2^+$, $Hg_2(C_6H_4)_3^{++}$, $HgC_6H_4^+$, Hg^+, $HgC_6H_4^{++}$ and Hg^{++}.

When 1,2-dibromobenzene and sodium amalgam are allowed to react in dry monoglyme, ortho-terphenylenemercury dimer, (III), is formed as a very pale yellow, crystalline solid. In a capillary the powdered sample melted at 290-292° (lit.value[1b] 292-293°); a single, large crystal melted at 294°. On a larger scale, a sample of the dimer heated in an open tube using an oil bath melted at 290° and began to sublime at 320° forming large crystals on the sides of the tube; a brown, amorphous solid remained behind at the bottom of the tube. The sublimed crystals were of the pure dimer and melted at 290-292° in a capillary tube. The molecular weight was confirmed by the mass spectrum which showed a cluster of peaks around $^m/e = 858$ due to the parent ion $(C_{18}H_{12}Hg)_2^+$; the exceedingly intense base peak of the spectrum corresponded to $C_{18}H_{12}^{\ +}$. The ion $HgC_{36}H_{24}^+$ was of similar intensity in spectra of various samples of ortho-triphenylenemercury dimer and is thus a fragment ion and not due to hexaphenylenemercury present in the sample as an impurity; $Hg(C_6H_4)_6$ is considered[3] unlikely to be stable because of adverse steric interactions which would occur in the molecule. A meta-stable peak was observed at $^m/e = 60.7$ for the transition :

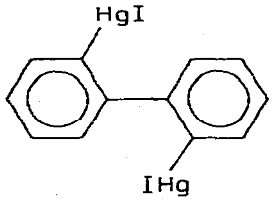
$$(C_6H_4)_6Hg_2^+ \longrightarrow (C_6H_4)_3^+ \quad + \quad (C_6H_4)_3Hg_2; \text{ calcd. } ^m/e = 60.6$$

The reaction of 2,2'-dilithiobiphenyl with mercuric chloride in diethyl ether gave an off-white solid which melted at 338° in a capillary and analysed as "$C_{12}H_8Hg$". Wittig[7] claims that a compound, having a melting point of 335-336° and prepared in the same manner, is the tetramer. The mass spectrum of our sample gave a mass cut-off at the ion $(C_{12}H_8Hg)_3^+$; the doubly-charged ion,

$(C_{12}H_8Hg)_3^{++}$, was also present at about 5% of the intensity of the parent ion. This is rather similar to the situation with the perfluoro-analogue which gave osmometric data[8] suggesting $(C_{12}F_8Hg)_4$ as the formula, whereas mass spectra of three samples prepared in different ways gave $(C_{12}F_8Hg)_3^+$ as the ion of highest mass with $(C_{12}F_8Hg)_3^{++}$ being present at about 6-7% of the parent ion's intensity. In view of the following facts : (a) the high thermal stability of ortho-biphenylenemercury in air (>340°); (b) the compound sublimes unchanged in both air or vacuum; (c) the mass spectra were recorded with the sample held at only 210-220°; and (d) the presence of the doubly-charged parent ion in the mass spectrum which demonstrates the stability of the compound to electron impact, we consider ortho-biphenylenemercury is the trimer (IV) and not the tetramer.

When 2,2'-diiodobiphenyl was treated with sodium amalgam in tetrahydrofuran no mercury-containing species could be isolated which implies that the intêrmediate sodio-biphenyl derivatives must rapidly polymerize, to give the observed brown gum, before sodium-mercury exchange can occur to give ortho-biphenylenemercury. This would explain the obvious absence of ortho-biphenylenemercury from the reaction between 1,2-dibromobenzene and sodium amalgam in monoglyme:polymerization passes rapidly through the biphenylene-stage to give the three ring system, the sodium intermediate then exists long enough to undergo sodium-mercury exchange and form ortho-terphenylenemercury. Although no mixed phenylene-biphenylene mercurials could be isolated from the reaction of 1,2-dibromobenzene and 2,2'-diiodobiphenyl with sodium amalgam in tetrahydrofuran (traces of such mixed derivatives apparently occur in some impure samples of ortho-phenylenemercury trimer[3]) the "coupled" organic product triphenylene was obtained in approximately 5% yield, lending some support for the above suggestion about the relative slowness of Na-Hg exchange reactions.

An interesting by-product (intermediate?) in the formation of ortho-biphenylenemercury trimer from 2,2'-dilithiobiphenyl and mercuric chloride was a colourless, slightly light-sensitive solid, identified by analysis and mass spectrometry as 2,2'-bis(iodomercury)biphenyl (V). Obviously a chlorine-



(V)

iodine exchange has occurred between Hg-Cl bonds and lithium iodide, remaining from the <u>in situ</u> preparation of 2,2'-dilithiobiphenyl, at some stage of the reaction; a separate experiment demonstrated that mercuric iodide was formed almost instantaneously from a mixture of lithium iodide and mercuric chloride in diethyl ether. The base peak in the mass spectrum of (V) was due to the ion HgI_2^+ with the parent ion being only about 0.1% relative intensity; other mercury-containing ions included $C_{12}H_8Hg_2I^+$, $C_{12}H_8HgI^+$, HgI^+, HgI_2^{++}, Hg^+ and Hg^{++}.

The structures of (II), (III) and (IV) are all very closely related to that of ortho-hexaphenylene, spatial distortions occurring in the basic structure to allow for the long C-Hg-C bonds which replace some of the inter-ring C-C bonds. Although the ortho-phenylenemercury hexamer could not be isolated in this work, there are no steric reasons why it should not be isolated if the correct synthetic conditions are found. A compound containing six mercury atoms per molecule can be expected to be rather unsoluble in common organic solvents and, because of this, we carefully examined the least soluble products of all the reactions (a)-(l) (including the most unlikely of residues) using a combination of melting point, infrared and mass spectral techniques; only compounds (III) and/or (IV) could be isolated.

EXPERIMENTAL

All the reactions were carried out under nitrogen using solvents which had been refluxed with sodium wire and distilled from the sodium immediately before use.

Preparation of ortho-phenylenemercury trimer

Typical of the reactions (a)-(l), a solution of 20 m moles of 1,2-

diiodobenzene in 50 cm^3 of dry tetrahydrofuran was shaken under nitrogen with 50 mg. atoms of potassium amalgam (2 g of K in 102 g Hg). The exothermic reaction which occurred immediately began to fade after about 30 m; the shaking was continued for a further 48 h and then water added until no more precipitate formed. The supernatant liquid was separated from the mercury and the precipitate, the latter being washed with water before removal of the mercury. Any organic material was removed from the precipitate using a little hot toluene and then the undissolved ortho-phenylenemercury extracted with hot dimethylformamide. An analytical sample was recrystallized from DMF (Found : C, 26.1; H, 1.50%; $C_{18}H_{12}Hg_3$ calcd. : C, 26.0; H, 1.45%).

Identical mass spectra were obtained from this recrystallized sample and from one which had been sublimed under vacuum; these showed a mass cut-off at the ion $(C_6H_4Hg)_3^+$.

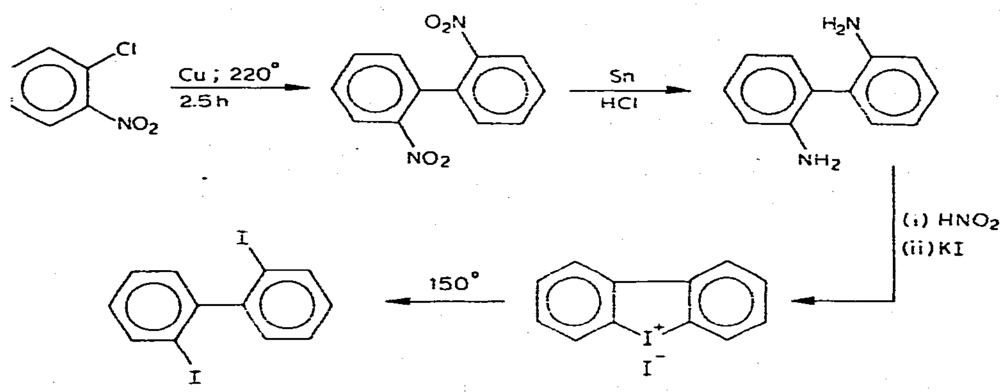
The sample giving the infrared spectrum shown in Figure 2 melted, with decomposition, in a capillary at 325-326° (Found : C, 26.3; H, 1.50%); most other samples possessed melting-decomposition points close to 325°. Sometimes, however, melting-decomposition points (measured in capillary tubes) as high as 332-334° were observed[4]; such samples still analysed as ortho-phenylenemercury trimer (Found : C, 25.8; H, 1.42%).

Preparation of ortho-terphenylenemercury dimer

The above procedure was followed for the reaction of 1,2-dibromobenzene with sodium amalgam except that dry monoglyme was used as the solvent. The only mercury-containing product was ortho-terphenylenemercury dimer; the analytical sample was recrystallized from chloroform (Found : C, 50.6; H, 2.7%; $C_{36}H_{24}Hg_2$ calcd. : C, 50.4; H, 2.8%).

Preparation of 2,2'-diiodobiphenyl

2,2'-Diiodobiphenyl, m. pt. 108-109°; was prepared from 1-chloro-2-nitrobenzene using the following sequence of reactions :



Preparation of ortho-biphenylenemercury trimer

2,2'-Diodobiphenyl (2.5 g) was refluxed for 30 m with 0.5 g of lithium in 80 cm^3 of diethyl ether and then stirred at room temperature overnight. Mercuric chloride (1.8 g) was added and the mixture stirred for 48 h before the ether solvent was removed under vacuum. The solid remaining after the residues had been leached with boiling dichloromethane was recrystallized from nitrobenzene to give pure ortho-biphenylenemercury trimer (Found : C, 40.6; H, 2.1%; $C_{36}H_{24}Hg_3$ calcd. : C, 40.9; H, 2.3%).

The dichloromethane was evaporated and the residues extracted with ethanol, the ethanol-soluble part being unchanged 2,2'-diiodobiphenyl. The insoluble material was recrystallized from chloroform to give colourless crystals of 2,2'-bis(iodomercury)biphenyl, m. pt. 198° (Found : C, 18.0; H, 1.0%; $C_{12}H_8Hg_2I_2$ calcd. : C, 17.8; H, 1.0%).

X-ray crystal data on ortho-phenylenemercury

Although all the crystals examined were too small for a full structure determination to be carried out, two different modifications were recognised.

Form 1 : monoclinic, a = 5.59; b = 23.06; d_{001} = 12.23Å.

Form 2 : orthorhombic, a = 18.42; b = 10.55; c = 8.12Å; $P2_12_12_1$; number of molecules, z, in the unit cell = 4 for the trimer (for the hexamer z = 2, a result not possible on symmetry grounds).

Infrared spectra (nujol mulls, 1300-250 cm^{-1})

$C_{62}H_4Hg)_3$: 1259 w; 1088 m; 866 m; 745 s; 679 w; 479 w; 422 s; 325 s; 289 m.

$(C_6H_4C_6H_4Hg)_3$: 1255 w; 1157 w; 1109 w; 1005 w; 785, 780 md; 751 s; 734, 738 sd; 621 w; 556 w; 452 m sh; 446 s; 428 w; 361 w; 320 w.

$(C_6H_4C_6H_4C_6H_4Hg)_2$: 1162 w; 1107 w; 1076 w; 1033 w; 1009 m; 979 w; 944 w; 875 w; 786 w sh; 780, 775 md; 756 s; 749 s; 736, 730 sd; 692 m; 625 w; 570 m; 458 s; 737 m; 348 m (d = doublet).

The strong bond at 745 cm^{-1} in the spectrum of ortho-phenylenemercury trimer is due to the ring hydrogen out-of-plane, in-phase deformation vibration. Obviously from the planar, symmetrical structure of this molecule only a single peak would be expected at ca. 745 cm^{-1} as shown in Figure 2; however, in several samples this band is found to the split even though the rest of the spectrum remains unchanged. We assume this behaviour to be associated with the different crystalline forms adopted by ortho-phenylenemercury trimer.

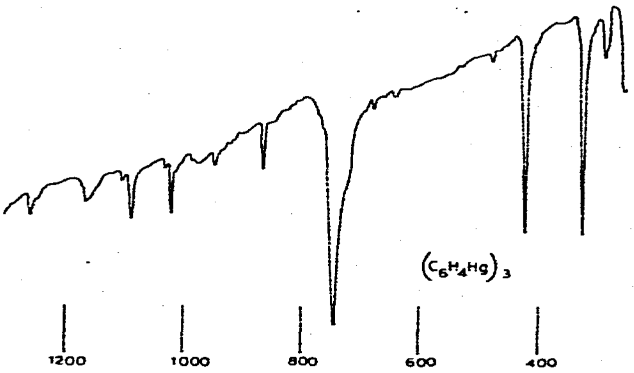


Figure 2. Partial infrared spectrum of ortho-phenylenemercury trimer.

Preparation and mass spectrum of perfluoro-biphenylenemercury trimer

This compound was prepared by the following methods :

(i) decarboxylation of 2,2'-$C_{12}F_8(COO)_2Hg$; (ii) reaction of 2,2'-dilithiooctafluorobiphenyl with mercuric chloride in ether, and (iii) direct reaction of 2,2'-diiodooctafluorobiphenyl with mercury in a sealed, evacuated tube. An analytical sample was obtained by sublimation in an open tube held at 300° in a furnace; m. pt. >370° (Found : C, 28.6; H, 0.0; F, 31.4% $C_{12}F_8Hg$ calcd. : C, 29.0; H, 0.0; F, 30.6%).

The volatility and thermal stability of perfluoro-biphenylenemercury are amply demonstrated by the method used in purification. Direct insertion into the mass spectrometer at 340° (4×10^{-8} mm) gave a parent ion cluster for the trimer at around 1490 m.u. with no peaks of higher mass visible even at high gain; a check on the molecular weight was provided by the doubly-charged parent ion centred at $^{m}/e = 745$. The identity of the parent was unambiguously confirmed by comparison of the calculated and observed peak intensities in both the parent and doubly-charged parent ion clusters, see Table. The only other mercury-carbon fragment ion of significant intensity was $(HgC_{12}F_8)_2^+$, the majority of the peaks in the spectrum being due to C_nF_m fragments of which $C_{12}F_8^+$ (presumably ionized octafluorobiphenylene) was the base peak.

Table

Calculated and Experimental intensities of the peaks in the ion clusters for $(C_{12}F_8Hg)_3^+$ and $(C_{12}F_8Hg)_3^{++}$

$^{m}/e$	calcd.	$(C_{12}F_8Hg)_3^+$	$(C_{12}F_8Hg)^{++}$
1483	0.4	-	0.3
1484	1.2	1.0	1.3
1485	2.6	3.0	2.8
1486	4.9	5.0	5.4
1487	7.6	7.8	7.6
1488	10.6	10.6	10.4
1489	12.4	12.4	12.5
1490	13.7	13.4	13.3
1491	12.8	12.7	12.5
1492	11.5	11.3	12.0
1493	8.3	8.2	7.8
1494	6.5	6.5	6.2
1495	3.3	3.5	3.3
1496	2.3	2.4	2.5
1497	0.8	0.9	1.1
1498	0.4	0.4	0.5

(The observed $^{m}/e$ values have been multiplied by two for the peaks in the doubly-charged ion).

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REFERENCES

1. (a) G. Wittig and F. Bickelhaupt, Chem.Ber. 91 (1958) 883;
   (b) G. Wittig, E. Hahn and W. Tochtermann, Chem.Ber. 95 (1962) 431
2. D. Grdenic, Chem.Ber. 92 (1959) 231
3. C.M. Woodard, G. Hughes and A.G. Massey, J.Organometal.Chem. 112 (1976) 9
4. Sometimes a melting-decomposition point as high as 332-334° is observed; see HJS Winkler and G. Wittig, J.Organic Chem. 28 (1963) 1735
5. P. Sartori and A. Golloch, Chem.Ber. 101 (1968) 2004; P.G. Cookson and G.B. Deacon, Aust.J.Chem. 26 (1973) 541
6. S.C. Cohen and A.G. Massey, Adv. in Fluoric Chem. 6 (1970) 83
7. G. Wittig and W. Herwig, Chem.Ber. 87 (1954) 1511; G. Wittig and G. Lehmann, Chem.Ber. 90 (1957) 875
8. S.C. Cohen and A.G. Massey, J.Organometal.Chem. 10 (1967) 471