Some Observations on the Minor Products of the Reaction of 2,2′-Dilithiobiphenyl with Mercuric Chloride

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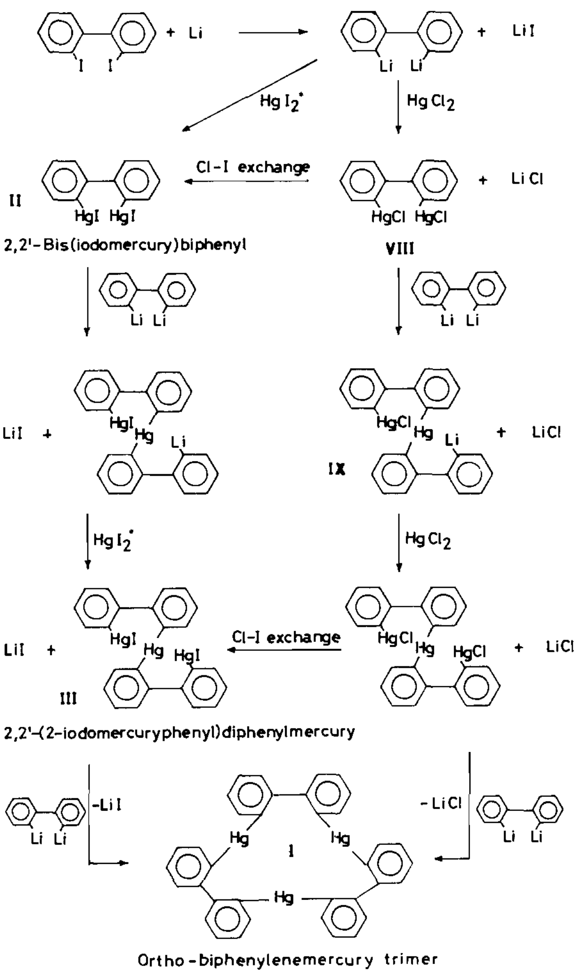
Abstract

Reaction of 2,2′-dilithiobiphenyl (formed from 2,2′-diiodobiphenyl and lithium in diethyl ether) with mercuric chloride gives the *ortho*-biphenylenemercury trimer (I) with 2,2′-bis(iodomercury)biphenyl (II) as an isolatable intermediate. The mass spectrum of impure 2,2′-bis(iodomercury)biphenyl at high sensitivity shows ion clusters which are interpreted as the ions of a polyphenyl iodomercury complex $[Hg_3(C_6H_4)_4I_2]$ (III) which is identified as a further intermediate in the production of *ortho*-biphenylenemercury trimer and several iodomercury cations of general formula $[Hg_xI_y]^+$, where $x,y = 1,2,3$. A fragmentation scheme is presented to account for these unusual iodomercury cations. Reaction mechanisms are presented to account for the production of II and III.

Introduction

In their studies on phenylene– and polyphenylene–mercury trimers, Massey *et al.* [1–3] have shown that the reaction of 2,2′-dilithiobiphenyl with mercuric chloride in diethyl ether gives trimeric *ortho*-biphenylenemercury (I) (see Scheme 1).



* Formed by exchange between $HgCl_2$ and LiI

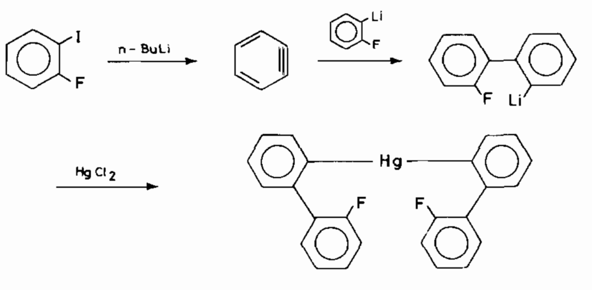
Scheme 1. Reaction pathway for formation of *ortho*-biphenylenemercury trimer.

In this work, evidence is presented for the occurrence in this reaction of two intermediate complexes: 2,2′-bis(iodomercury)biphenyl (II) and 2,2′-(2-iodomercuriphenyl)biphenylmercury (III).

2,2′-Bis(iodomercury)biphenyl (II) was an isolatable, colourless, slightly light-sensitive solid, identified by elemental analysis and mass spectrometry. 2,2′-(2-iodomercuriphenyl)biphenyl mercury (III) was not isolated and its presence in the reaction was inferred from careful analysis of the mass spectrum of impure samples of II.

These complexes belong to the large family of halogenated polyphenyl mercurials and in order to place these compounds in some sort of context, two further reactions which give structurally related complexes are briefly described. Firstly, reaction [4] of the lithio derivative of 2-fluoroiodobenzene and $HgCl_2$ gave exclusively 2,2′-(2-fluorophenyl)biphenylmercury [IV].

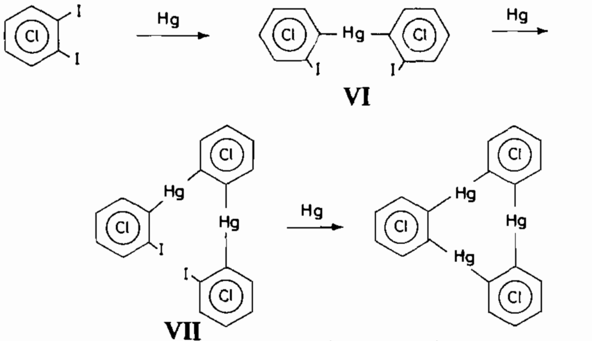
Secondly, tetrachlorophenylenemercury trimer (V) can be prepared [1] by heating together mercury and 1,2-diiodotetrachlorobenzene in a sealed



2,2'-(2-fluorophenyl)diphenylmercury

IV

evacuated tube for about 4 days. The reaction was postulated to proceed through two intermediate complexes and if the reaction is stopped after one day, the intermediate bis(2-iodotetrachlorophenyl)-mercury (VI) is obtained in large amounts among the products. However, no evidence for the occurrence in the reaction mixture of the second intermediate (VII) was obtained.



Tetrachlorophenylenemercury trimer

V

Experimental

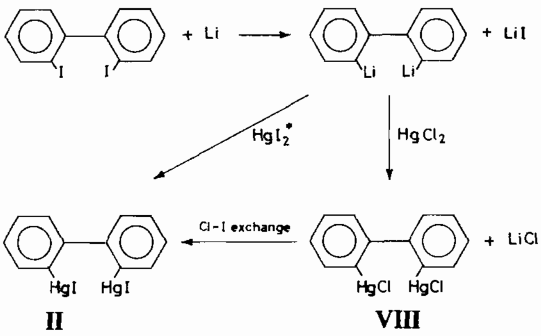
All operations that involved lithium reagents were carried out under an atmosphere of oxygen-free, dry nitrogen. Solvents were dried and distilled under dry nitrogen immediately before use. Mass spectra were recorded on an A.E.I. MS12 spectrometer, the samples being directly inserted into the mass spectrometer at 340 °C and 4×10^{-8} mm of Hg pressure; observed ion clusters were compared with computer calculated clusters [5] and were 'centered' using the isotopes of highest abundance, *i.e.* $_{80}Hg^{202}$, $_{53}I^{127}$, $_{6}C^{12}$, and $_{1}H^{1}$.

Preparation of the Major Project, ortho-Biphenylenemercury Trimer (I)

2,2'-Diiodobiphenyl was refluxed for 30 min with lithium chips in diethyl ether and stirred at room temperature overnight; mercuric chloride was then added and the mixture stirred for a further 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. *Anal.* Found: C, 40.6; H, 2.1. Calc. for $C_{36}H_{24}Hg_3$: C, 40.9; H, 2.3%.

Extraction of the Minor Product, 2,2'-Bis(iodomercury)biphenyl (II)

The above dichloromethane solution was evaporated and the residues extracted with ethanol to remove unused diiodobiphenyl. The remaining insoluble material was recrystallized from chloroform to give colourless crystals of 2,2'-bis(iodomercury)-biphenyl, melting point 198 °C. *Anal.* Found: C, 18.0; H, 1.0. Calc. for $C_{12}H_8Hg_2I_2$: C, 17.8; H, 1.0%. The 2,2'-bis(iodomercury)biphenyl presumably occurs via a chlorine–iodine exchange occurring between the Hg–Cl bonds in **VIII** and lithium iodide remaining from the preparation of the 2,2'-dilithiobiphenyl.



2,2'-Bis(iodomercury)biphenyl

*Formed by exchange between HgCl2 and LiI

Results and Discussion

2,2'-Bis(iodomercury)biphenyl was studied by mass spectral analysis, (see Table I). The parent ion cluster was centered at $m/z = 810$; the calculated and observed abundances for this molecular ion were in total agreement with the molecular formulation $[(C_6H_4)_2(HgI)_2]^+$. The base ion cluster at $m/z = 456$, which showed a simple 'Hg pattern' with no ^{13}C satellites, is due to $[HgI_2]^+$. It is noted that the doubly charged $[HgI_2]^{2+}$ cluster is almost 10 times as intense as the parent ion cluster at $m/z = 810$. Only two organic ion clusters are present: that of $[(C_6H_4)_2]^+$ at $m/z = 152$ and a small cluster at $m/z = 304$ corresponding to $[(C_6H_4)_4]^+$.

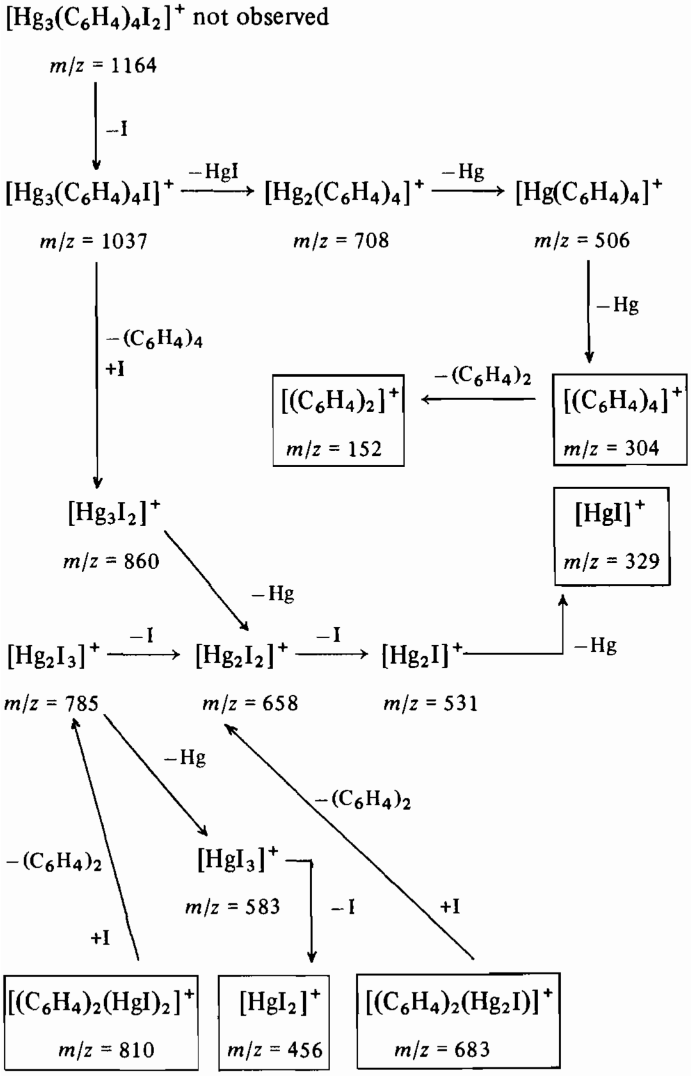
The mass spectra (see Scheme 2) of slightly impure samples of 2,2'-bis(iodomercury)biphenyl contained

TABLE I. Mass Spectrum of 2,2'-Bis(iodomercury)biphenyl

Mass number of cluster	Assignment	Relative abundance (%)
810	$[(C_6H_4)_2(HgI)_2]^+$	<0.5
683	$[(C_6H_4)_2(Hg_2I)]^+$	<0.5
456	$[HgI_2]^+$	100
329	$[HgI]^+$	19.4
304	$[(C_6H_4)_4]^+$	<0.5
254	$[I_2]^+$	3.9
228	$[HgI_2]^{2+}$	11.5
202	$[Hg]^+$	38.8
152	$[(C_6H_4)_2]^+$	3.9
128	$[HI]^+$	2.6
127	$[I]^+$	12.2
101	$[Hg]^{2+}$	4.6

unexpected ion clusters at $m/z = 1037$, 860, 785, 708, 658, 583, 531, and 506 when observed at high sensitivity and which were not present in the spectrum of the pure compound. Comparison with calculated [5] ion cluster patterns showed that the cluster centered at $m/z = 1037$ represents a species corresponding to $[Hg_3(C_6H_4)_4I]^+$ whilst the clusters at $m/z = 708$ and 506 have ion abundances showing they result from the loss of HgI and Hg_2I from the $[Hg_3(C_6H_4)_4I]^+$ forming $[Hg_2(C_6H_4)_4]^+$ and $[Hg(C_6H_4)_4]^+$; ions of 'unstable' mercurials predicted by Massey *et al.* [2].

The ion cluster at $m/z = 531$ has an 'Hg_2 pattern' which shows no ^{13}C satellite peaks indicating that the cluster is not due to an organomercury species; furthermore, no additional lines attributable to the isotopes of hydrogen and/or chlorine are present and



Scheme 2. Fragmentation pathways of impure 2,2'-bis(iodomercury)biphenyl. Ion clusters in square boxes appear in the spectrum of pure 2,2'-bis(iodomercury)biphenyl as well as the spectrum of the impure compound.

the cluster analysed as $[Hg_2I]^+$. Similarly, the ion clusters at $m/z = 583$, 658 and 785 have simple 'Hg patterns'; with no ^{13}C satellite peaks and are due to $[HgI_3]^+$, $[Hg_2I_2]^+$ and $[Hg_2I_3]^+$. Both the latter clusters are 25 mass units away from those species containing the $(C_6H_4)_2$ grouping and at least one iodine, namely $[(C_6H_4)_2Hg_2I]^+$, $m/z = 683$ and $[(C_6H_4)_2Hg_2I_2]^+$, $m/z = 810$. Assuming the difference of 25 mass units is due to the loss of a $(C_6H_4)_2$ grouping and the addition of one iodine atom (*i.e.*, $-152 + 127 = -25$), then the assignment of the formulae $[Hg_2I_2]^+$ and $[Hg_2I_3]^+$ to the clusters at $m/z = 658$ and 785 is reinforced. The cluster at $m/z = 860$ possesses ^{13}C satellites and could be due to $[(C_6H_4C_6H_4)_3Hg_2]^+$, $m/z = 860$, an ion which occurs in the mass spectrum of the *ortho*-biphenylenemercury trimer. The presence of the trimer (**I**) in the impure sample was demonstrated by a small cluster at $m/z = 1062$ which corresponds to $[(C_6H_4C_6H_4Hg)_3]^+$. However, the cluster shape at $m/z = 860$ is closer to that of an 'Hg_3 pattern' than an 'Hg_2 pattern'; if an Hg_3 species is present, then the most likely formulation is $[Hg_3I_2]^+$, $m/z = 860$. Overlap of the inorgano-Hg_3 and organo-Hg_2 species is possible, giving the observed shape of the ion cluster. Recently, confirmation of the existence of the $Hg_2I_3^+$ and HgI_3^+ has been reported by Massey [6] in a spectrum of 2,2′-bis(iodomercury)biphenyl. In this case the parent ion of the biphenyl–HgI species was absent with $Hg_2I_3^+$ as the highest mass cluster.

It is possible to draw a fragmentation scheme (Scheme 2) to account for the ion clusters under discussion. The clusters were in 'very low' abundance even at high sensitivity, sometimes masked by the extremely large clusters of 2,2′-bis(iodomercury)-biphenyl (**II**) and it proved impossible to calculate relative abundances for the ions or to measure accurate mass values.

Having invoked a mechanism involving the loss of $(C_6H_4)_2$ with gain of iodine to explain $[Hg_2I_3]^+$ and $[Hg_2I_2]^+$, an analogous loss of $(C_6H_4)_4$ (*i.e.* two $(C_6H_4)_2$) units) with gain of iodine from $[Hg_3(C_6H_4)_4I]^+$ would account for $[Hg_3I_2]^+$.

Conclusions

2,2′-Bis(iodomercury)biphenyl is an isolatable intermediate in the formation of *ortho*-biphenylenemercury trimer. It is probable that $[Hg_3(C_6H_4)_4I]^+$ is the daughter ion, through loss of iodine, of an unobserved $[Hg_3(C_6H_4)_4I_2]^+$, which would be the ion of the intermediate (**III**) in the formation of the major product, *o*-biphenylenemercury trimer (**I**). This intermediate (**III**) may have arisen via a similar mechanism to that proposed in a previous paper [3], where 2,2′-diiodobiphenyl was treated with sodium amalgam in THF. The non-isolation of mercury containing species implied that the sodium–biphenyl derivatives were polymerizing before mercury–sodium exchange could take place to give the desired *ortho*-biphenylenemercury. Here, coupling of 2,2′-dilithiobiphenyl with a partially lithiated mercury species gives the $(C_6H_4)_4$ grouping. The lithium intermediate (**IX**) exists long enough to undergo lithium–mercury exchange with subsequent chlorine–iodine interchange to form $Hg_3(C_6H_4)_4I_2$; 2,2′-(2-iodomercuriphenyl)biphenylmercury (**III**).

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