Some studies in perhaloaromatic chemistry

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SOME STUDIES IN PERNHALOAROMATIC CHEMISTRY

by


A Doctoral Thesis submitted in partial
fulfilment of the requirements for the
award of Doctor of Philosophy of the
Loughborough University of Technology
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Above all, the author is deeply indebted to his family and friends, whose unfailing moral support and continued encouragement have made it all worthwhile.
To my parents and my Fiancée

with

much love and affection
Virtue is a ray
of heavenly beauty
prize of the soul, through which alone it is cherished.
The devastation of time
it does not fear; in man
the years make its splendour brighter,
Orpheus overcame Hell and was overcome
by his passions.
Eternal fame is deserved only by him
who overcomes himself.

A. Striggio.
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SUMMARY

A review of recent advances of the chemistry of polyhalogenaromatic compounds, with an emphasis placed on the uses of the corresponding lithium and Grignard derivatives in the formation of polyhalogenaromatic complexes of metals and metalloids is presented.

1,2,3-Tribromotrifluorobenzene was prepared by the decomposition of 1-lithio-2-bromotetrafluorobenzene in the presence of dry lithium bromide, and its structure elucidated from $^{19}$F and $^{13}$C nuclear magnetic resonance studies. Mass spectral analysis of the reaction products showed the presence of 1,2,3,4-tetrabromodifluorobenzene, formed by further attack of n-butyllithium on the tri-bromo-derivative with subsequent decomposition in the presence of lithium bromide. Polybromobiphenyls, having molecular formulae $C_{12}F_7Br_3$ and $C_{12}F_6Br_4$, were detected in the reaction products by mass spectrometry and mechanisms are given to account for their formation.

The isomeric 1-bromo-2,3-bis(pentafluorophenyl)- and 2-bromo-1,3-bis(pentafluorophenyl)-trifluorobenzenes, $C_{18}F_3Br$, were prepared via the intramolecular elimination of lithium fluoride from 2-lithio-nona-fluorobiphenyl, and their structures deduced from $^{19}$F and $^{13}$C nuclear magnetic resonance spectra. The unsymmetrical 1,2-bis(pentafluorophenyl)-3-hydrotrifluorobenzene is formulated by mass spectrometry and by interpretation of its $^{19}$F nuclear magnetic resonance spectrum.

Direct methods of synthesis of polyhalogenorganometallic complexes are discussed and these methods applied to the preparation of polychloroaromatic derivatives of main-group metals and metalloids.

Wittig has proposed a hexameric structure, $(C_{6}H_{4}Hg)_{6}$, for ortho-phenylenemercury prepared by the reaction between 1,2-dibromobenzene and sodium amalgam, whereas the fluoro-analogue is known to be trimeric, $(C_{6}F_{4}Hg)_{3}$. An extensive series of reactions was undertaken to check this apparent anomaly. X-ray and mass spectral analysis of ortho-phenylenemercury prepared in this work showed it to be trimeric. Wittig also claims a tetrameric structure for ortho-biphenylenemercury $(C_{12}H_{8}Hg)_{4}$, but mass spectral analysis of our samples gave a mass cut-off at the ion $(C_{12}H_{8}Hg)_{3}^+$ suggesting a trimeric structure. This is similar to the situation with the perfluoro-analogue which gave osmometric data suggesting $(C_{12}F_{8}Hg)_{4}$ as the formula, whereas mass spectra of three samples prepared in
different ways gave \((\text{C}_{12}\text{F}_6\text{Hg})_3^+\) as ion of highest mass. The formation of a by-product, 2,2'-bis(iodomercury)biphenyl, involves a chlorine-iodine exchange between Hg-Cl bonds and lithium iodide; mass spectral analysis of this latter mercurial under high-gain indicates the presence of several novel Hg
\text{I}_y^+ \) species.
INTRODUCTION TO POLYHALOAROMATIC CHEMISTRY
I.

NOMENCLATURE

In order to facilitate both the naming of fluoroaromatic and the diagrammatic representation of their formulae, a simple notation has been devised, which is now accepted in this field of Chemistry.

The basic units are taken from 1,2,3,4,5,6-hexafluorobenzene and 2,2',3,3',4,4',5,5',6,6'-decafluorobiphenyl, but the numerical prefixes are dropped to give hexafluorobenzene and decafluorobiphenyl respectively. The substitution of any atom or group for fluorine is then indicated in an analogous fashion to the substitution of hydrogen in organic aromatics; hence:

\[ \begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{I} & \quad \text{I} \\
\text{F} & \quad \text{F}
\end{align*} \]

1,2-Diiodotetrafluorobenzene

\[ \begin{align*}
\text{F} & \quad \text{Br} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*} \]

2-Bromonafluorophenyl

The system might lead to slight ambiguity only when hydrogen substituents are present, as in

\[ \begin{align*}
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H}
\end{align*} \]

2,2'-Dihydrooctafluorobiphenyl
In a few cases where the meaning is clear, the prefix perfluoro- may be used to signify that fluorine atoms fill all the available substitution positions in the aromatic system.

Decafluorobiphenyl or Perfluorobiphenyl

Bis(pentafluorophenyl)acetylene or Perfluorotolan

With regard to the nomenclature of the organometallic compounds, these will be considered mainly as derivatives of the elements e.g. bis(pentafluorophenyl)mercury, \( (C_6F_5)_2Hg \), and tetrakis(pentafluorophenyl)diphosphine, \( (C_6F_5)_2PP(C_6F_5)_2 \).

In the structural formulae the necessity of indicating every fluorine atom by "F" is alleviated by placing "F" within the ring and labelling only atoms or groups other than fluorine.
SYNTHESES OF POLYFLUOROAROMATIC COMPOUNDS

Rapid advances have been made in the chemistry of polyfluoroaromatic compounds in the last twenty years, facilitated by the commercial availability of hexafluorobenzene and many of its derivatives.

The classical method of introducing a fluorine atom into the aromatic nucleus had been the Balz-Schiemann reaction,

\[ \text{ArH} \rightarrow \text{ArNO}_2 \rightarrow \text{ArNH}_2 \rightarrow \text{ArH}^+\text{BF}_4^- \rightarrow \text{ArF} + \text{N}_2 + \text{BF}_3 \]

but extension of this method beyond the stepwise replacement of four hydrogen atoms in the benzene ring to produce 1,3- and 1,4- dihydrotetrafluorobenzene proved impossible. In the attempted conversion of 1,4-dihydrotetrafluorobenzene into pentafluorobenzene, the reaction failed at the nitration stage with the expulsion of two para-fluorine atoms yielding 2,5-difluoro-1,4-benzoquinone.
In the late 1940s McBee and his co-workers first reported the synthesis of hexafluorobenzene⁴ and then decafluorobiphenyl⁵ by the stepwise fluorination of hexachlorobenzene and decachlorobiphenyl, respectively, by bromine trifluoride and antimony pentafluoride followed by dechlorination using zinc dust. The high thermal stability of fluoroorganic compounds has made it possible to use high temperature processes for the synthesis of a wide range of fluorine containing products. Thermolytic reactions often prove to be the simplest and most convenient method for synthesising such compounds which can only be obtained with great difficulty using classical organic chemistry methods. The pyrolyses of tribromofluoromethane⁶, dibromofluoromethane⁷, dichlorofluoromethane⁷,⁸ and 1,2-dichloro-1,2-difluoroethane⁹ leading to the formation of hexafluorobenzene have been published⁶.

\[
\begin{align*}
6 & \quad \frac{\Delta}{\text{Pt tube}} \quad \frac{630^\circ}{\text{Pt tube}} \quad \frac{710^\circ}{\text{Pt tube}} \\
\begin{array}{c}
\text{C} \\
\text{Br}
\end{array}
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{C} \\
\text{H}
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{C} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
\begin{array}{c}
\text{F} \\
\text{F}
\end{array} \\
\quad + 3\text{X}_2 + 6\text{HX}
\end{align*}
\]

\( X = \text{Cl,Br} \)
Perfluoro-2-butyn on heating to $375^\circ$, trimerizes with the formation of hexaaxis(perfluoromethyl)benzene. By the addition of iodine or methyl iodide the reaction temperature can be lowered to $260^\circ$.

$$3 \text{F}_3\text{C} - \text{C} = \text{C} - \text{CF}_3 \xrightarrow{375^\circ} \begin{array}{c}
\text{CF}_3 \\
\text{F}_3\text{C} \\
\text{CF}_3 \\
\text{F}_3\text{C} \\
\text{CF}_3
\end{array}$$

Perfluorocyclohexene and the isomers of perfluorocyclohexadiene can be aromatized when their vapours are passed over a nickel or iron gauze at $450-500^\circ$, giving perfluorobenzene in good yield. Pyrolysis of perfluorocyclopentene and perfluorocyclohexene in an autoclave over nickel chips at $550^\circ$ proceeds differently to the vapour phase pyrolyses and gives for the both cycloalkenes practically the same products; namely

Perfluorocycloalkadienes readily form the corresponding Diels-Alder adducts; pyrolysis of the latter yields aromatic and heterocyclic compounds. Thus, thermal decomposition of perfluorocyclopentadiene dimer results in a triene formation, from which it is possible to obtain perfluoroindane.
b.

Pyrolysis of perfluorobenzene in a platinum tube at 900°-1000° gives perfluorotoluene in 63% yield per 2 mol of perfluorobenzene. On heating in an autoclave at 550°, perfluorotoluene undergoes disproportionation into perfluorobenzene and perfluoroxylenes.

\[
\begin{array}{c}
\text{F} & \text{CF}_3 \\
\text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F}
\end{array}
\stackrel{550°}{\text{autoclave}}
\rightarrow
\begin{array}{c}
\text{F} \\
\text{F}
\end{array}
36%
\]

\[
\begin{array}{c}
\text{F} & \text{CF}_3 \\
\text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F} & \text{F}
\end{array}
\]
30%

The results of thermolysis of hexakis(perfluoroethyl)benzene proved to be the quantitative transformation into the corresponding derivative of Dewar benzene.

\[
\begin{array}{c}
\text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 \\
\text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5
\end{array}
\stackrel{400°}{\text{Pt tube}}
\rightarrow
\begin{array}{c}
\text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5 & \text{C}_2\text{F}_5
\end{array}
\]

The application of thermolytic reactions for the syntheses of fluoroorganic compounds has recently been reviewed by Yakobson and Platonov.

The fluorination of benzene in mild conditions led to the formation of polyfluorocyclohexanes which were consecutively dehydrofluorinated and then defluorinated to afford hexafluorobenzene.
In a similar manner, defluorination of perfluorobicyclohexyl afforded decafluorobiphenyl.\textsuperscript{12,13}

This fluorination/defluorination procedure involves the destruction of an aromatic system in the initial fluorination stage followed by a re-creation of aromaticity in the defluorination stages, and led to investigations of a direct exchange of halogen/fluorine without the need for loss of aromaticity by Vorozhtsov\textsuperscript{14}, in which the reaction of hexachlorobenzene with anhydrous potassium fluoride at $450^\circ$-$500^\circ$ provides a direct route to hexafluorobenzene and perchlorofluorobenzenes.
Musgrave and his co-workers\textsuperscript{15} undertook the direct fluorination of hexachlorobenzene with fluorine. This yielded a mixture of perhalocyclohexanes, which were then dehalogenated to give hexafluorobenzene and perchlorofluorobenzenes.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\quad \xrightarrow{\text{KF} \ 300-350^\circ} \\
\begin{align*}
\text{Cl} & \quad \text{F} \\
\text{Cl} & \quad \text{F} \\
\end{align*}
\]

The above processes for the preparation of polyfluoroaromatic derivatives enabled the Imperial Smelting Corporation\textsuperscript{1} to synthesize large quantities of these compounds for commercial use.

The vapour phase photoisomerization of hexafluorobenzene\textsuperscript{16,17} and octafluorotoluene\textsuperscript{16} yields perfluoro-derivatives of bicyclo(2,2,0)hexa-2,5-diene, ("Dewar"benzene). Irradiation with ultraviolet light in cyclohexane or cyclooctane solution, however, leads to the formation of cyclohexyl-, or cyclooctylpentafluorobenzene, decafluorobiphenyl and many side products.\textsuperscript{18}
Hexafluorobenzene readily undergoes nucleophilic displacement of fluorine to form a variety of pentafluorophenyl derivatives.\textsuperscript{19,20,21}

\[
\begin{array}{c}
\text{F} \\
\rightarrow \text{F} \\
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
+ \text{nucleophile (X)} \\
\rightarrow \text{F} \\
\end{array}
\]

(X = OH, SH, OCH\textsubscript{3}, CH\textsubscript{3}, NH\textsubscript{2}, etc)

The conversion of pentafluorophenyl derivatives into a disubstituted tetrafluorobenzene may be accomplished by further treatment of nucleophilic reagents. For example, nucleophilic attack on decafluorobiphenyl leads to the formation of 4,4\textsuperscript{-}disubstituted octafluorobiphenyls.\textsuperscript{22,23,24,25}

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\rightarrow \text{X} \\
\end{array}
\]

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\rightarrow \text{X} \\
\end{array}
\]

X = OH, CH\textsubscript{3}, N(CH\textsubscript{3})\textsubscript{2}, NH\textsubscript{2} ref. 23, X = OC\textsubscript{6}H\textsubscript{5} ref. 25

X = NH.NH\textsubscript{2} refs. 22,23,25
A useful probe used in establishing the orientation of the isomers formed in the reactions such as these, is the highly developed interpretation of their $^1$H and $^{19}$F n.m.r. spectra. Generally the fluorine atom para to the first substituent (e.g. $X=H, \text{CH}_3, \text{CF}_3, N(\text{CH}_3)_2$) is replaced, but in a few cases replacement of the meta fluorine atom predominates ($X=\text{NH}_2$). A mechanistic interpretation rests on the fact that the five fluorine atoms direct replacement para to the substituent $X$ by virtue of combined mesomeric and inductive affects. Therefore, a group capable of deactivating ortho and para positions by a mesomeric effect would direct meta:

\[
\begin{align*}
\text{F} & \quad \text{NH}_2 \\
\text{F} & \quad +\text{NH}_2 \\
\text{F} & \quad +\text{NH}_2 \\
\text{F} & \quad +\text{NH}_2 \\
\text{F} & \quad +\text{NH}_2 \\
\end{align*}
\]

A group such as the nitro-group, capable of attracting electrons, will facilitate para substitution, and some ortho substitution as well. Burdon has proposed a further rationalization, where it is argued that the isomer distribution depends on the stability of the Wheland type transition leading to the various isomers:

\[
\begin{align*}
\text{F} & \quad \text{I} \\
\text{F} & \quad \text{II} \\
\end{align*}
\]

The resonance hybrid (I) is assumed to be the main contributor to the intermediate stage and the influence of the substituent attached to the carbon bearing negative charge, on that charge, is discussed. If a substituent $X (=\text{NO}_2, \text{CF}_3)$ stabilizes the charge, then nucleophilic attack occurs at the carbon para to it, and to a lesser extent, ortho. If $X(=\text{NH}_2)$ destabilizes the charge more than fluorine, then meta attack occurs.
Pentafluorophenyl free radicals have been proposed as intermediates in the oxidation of pentafluorophenylhydrazine in non-aqueous media, and in the pyrolysis of pentafluorophenylsulphonyl chloride. Some typical reactions can be summarized thus:

Valuable synthetic intermediates may be formed by the electrophilic replacement of hydrogen in pentafluorobenzene; e.g. the reaction of the appropriate halogen in oleum gives bromo- or iodopentafluorobenzene.

Also, similar reactions with tetrafluorobenzenes afford dihaloperfluoro-derivatives.

The halopentafluorobenzenes readily undergo an Ullmann reaction with copperbronze to give yields of decafluorobiphenyl:
Under the same conditions, 1,4-dibromo- and 1,4-diiodotetrafluorobenzenes formed low molecular weight para linked polymers containing halogen,

\[
\begin{align*}
\text{Br} & \quad \text{Cu} \quad \text{200 - 250°C} \\
\text{F} & \quad \text{X} \\
\text{Br} & \quad \text{Cu} \quad \text{DMF}
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{Br, } n = 4, 5, 8 \\
\text{X} & = \text{I, } n = 10
\end{align*}
\]

Several 2,2'-disubstituted octafluorobiphenyls have been prepared by heating 1-bromo-2-substituted tetrafluorobenzenes with copper in dimethylformamide:

\[
\begin{align*}
\text{Br} & \quad \text{Cu} \quad \text{DMF} \\
\text{F} & \quad \text{X} \\
\text{Br} & \quad \text{Cu} \quad \text{210°C/16 hrs.}
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{H, CH}_3, \text{CN, NO}_2
\end{align*}
\]

Crossed Ullmann reactions involving bromopentafluorobenzene and 1,2-dibromo- or 1-hydro-2-bromotetrafluorobenzene gave mixtures of the three predicted products;

\[
\begin{align*}
\text{Br} & \quad \text{Cu} \quad \text{Br}
\end{align*}
\]

whereas Falk has synthesized perfluoro-α- and -p-terphenyls in a similar reaction.

\[
\begin{align*}
\text{Br}_2 & \quad \text{Cl} \\
\text{Br} & \quad \text{Cu}
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{Cu} \quad \text{C}_6\text{F}_5 \\
\text{I} & \quad \text{Cu} \quad \text{C}_6\text{F}_5
\end{align*}
\]
POLYFLUOROAROMATIC LITHIUM DERIVATIVES

The relative ease (compared to fluorine) with which hydrogen or another halogen bonded to a fluoroaromatic nucleus will undergo lithium/X exchange with n-butyllithium\textsuperscript{36} has enabled a large number of lithium derivatives of polyfluoroaromatic systems to be synthesized and subsequently studied.

Pentafluorophenyllithium has received by far the most attention, and results from the action of lithium amalgam on bromopentafluorobenzene in ether or furan at \(0^\circ\text{C}\); by lithium/hydrogen exchange with halopentafluorobenzenes\textsuperscript{34,37-40} using n-butyllithium at \(-78^\circ\text{C}\):

\[
\begin{array}{c}
\text{Br} \\
F
\end{array}
\xrightarrow{n-C_4H_9Li} \text{ether/hexane} \xrightarrow{-78^\circ} \begin{array}{c}
\text{H} \\
F
\end{array} + \text{C}_4\text{H}_9\text{X} \\
X = H, Cl, Br
\]

The exchange reactions all take place with considerable ease. Within the range of solvents used (varying from ether\textsuperscript{37,41} or ether/hydrocarbon\textsuperscript{34,39,41} to a mixture of pure hydrocarbons\textsuperscript{40}), the lithium/X exchange proceeds quantitatively. Apparently lithium/bromine exchange occurs in preference to lithium/hydrogen exchange in ether/hexane\textsuperscript{42} as demonstrated by the reaction sequence:

\[
\begin{array}{c}
\text{Br} \\
F
\end{array} + \begin{array}{c}
\text{H} \\
F
\end{array} \xrightarrow{1) n-C_4H_9Li \text{ (one equiv.)}} \begin{array}{c}
\text{CO}_2\text{H} \\
F
\end{array} \xrightarrow{2) \text{CO}_2} \begin{array}{c}
\text{H} \\
F
\end{array} \xrightarrow{3) \text{H}^+} \begin{array}{c}
\text{H} \\
F
\end{array}
\]

Pentafluorophenyllithium reacts readily with water\textsuperscript{37}, halogens\textsuperscript{37}, sulphur\textsuperscript{43,44}, selenium\textsuperscript{45}, trimethylborate/hydrogen peroxide\textsuperscript{46}, and carbonyl compounds\textsuperscript{37,47,48}, as summarized below: (fig1)

Tatlow and co-workers have shown that pentafluorophenyllithium decomposes readily at \(0^\circ\text{C}\), via the intramolecular loss of lithium fluoride, forming transient
Figure No. 1
tetrafluorobenzyne in solution. This intermediate may be trapped by allowing pentafluorophenyllithium to decompose in the presence of furan or thiophen when 3,4- addition of tetrafluorobenzyne to the trapping agent occurs to afford derivatives of 1,2,3,4-tetrafluoro-5,8,-dihydronaphthalene.

![Diagram](image)

Similar derivatives are obtained via 1,4-addition with benzene and other substituted aromatic compounds:

![Diagram](image)

However, tetrafluorophenantherene is the major product of the reaction between styrene and tetrafluorobenzyne:

![Diagram](image)

If pentafluorophenyllithium is allowed to partially decompose at about 0°C in the presence of pentafluorobenzene, bromo- or iodopentafluorobenzene, a molecule of undecomposed pentafluorophenyllithium adds across the tetrafluorobenzyne.
to form 2-lithiononafluorobiphenyl, which then undergoes lithium/hydrogen or lithium/halogen exchange with the $C_6F_5X$ ($X = H, Br, I$) to give 2-hydro- or 2-halononafluorobiphenyl in high yield.

In these reactions, lithium is preferentially attached to the more electronegative organic radical, or the radical which would form the more stable carbanion.

Tatlow and his co-workers have shown\(^3\) that lithium halides add across tetrafluorobenzyne, thus the decomposition of pentafluorophenyllithium in the presence of both bromopentafluorobenzene and added lithium halides gives mainly 1,2-dihalotetrafluorobenzenes:

The formation of lithium derivatives becomes more complex when tetrafluorobenzene derivatives are used and often solvent effects become more important than in the formation of pentafluorophenyllithium. For example, 1,2-dibromotetrafluoro-
benzene gives a monolithio derivative in ether/hexane\(^{39,49,50,51}\), furan\(^{34}\) and benzene\(^{52}\), but apparently does not form a dilithio derivative\(^{53}\). However, 1,4-dibromo- and 1,4-dihydrotetrafluorobenzene react with n-butyllithium in ether/hexane or tetrahydrofuran/hexane to give a mixture of mono- and dilithio species\(^{41,50}\). Generally monolithiation occurs in ether/hexane, whereas dilithiation occurs to a greater extent in tetrahydrofuran/hexane. 1,2-dihydrotetrafluorobenzene readily forms a monolithio derivative in THF/hexane \(^{41,43,44,46}\), but little or no lithium/hydrogen exchange is detected in ether/hexane\(^{41}\). 1-Hydro-2-bromotetrafluorobenzene undergoes lithium/bromine exchange in ether/furan and benzene/petroleum ether, providing evidence of the relative ease with which lithium/bromine exchange occurs compared with lithium/hydrogen exchange.

Both 1-lithio-2-bromo- and 1-lithio-2-hydrotetrafluorobenzene lose lithium fluoride intramolecularly to form 1-bromo-\(^{54,44,55,51}\) and 1-hydro-2,3,4-trifluorobenzylene\(^{56}\) respectively, which form Diels-Alder addition products in the presence of either furan\(^{44,56}\) or benzene\(^{55,56,51}\):

![Diels-Alder reactions](attachment:image)

The decomposition\(^{54}\) of 1-lithio-2-bromotetrafluorobenzene in the presence of unreacted 1,2-dibromotetrafluorobenzene gives as the two main products the isomeric 2,6,2'- and 2,3,2'-tribromotetrafluorobiphenyls, formed by addition of a molecule of 1-lithio-2-bromotetrafluorobenzene to 1-bromo-2,3,4-trifluorobenzylene followed by lithium/bromine exchange between the intermediate lithium derivatives and 1,2-di-bromotetrafluorobenzene:
The presence of \(2,2'\)-dibromo-octafluorobiphenyl among the many reaction products suggests\(^5\) that some tetrafluorobenzylene is formed, by intramolecular loss of lithium bromide instead of lithium fluoride, but in low yield:
The elimination of lithium fluoride in preference to that of lithium bromide is explained on the basis that the lattice energy of lithium fluoride is much higher than that of lithium bromide, but the position is more complicated because lithium bromide has been shown to add across tetrafluorobenzene so that the elimination of lithium bromide might be reversible.

Both the mono- and dilithio- species undergo the conventional reactions of aryllithium reagents with bromine, carbon dioxide, sulphur, trimethylborate/hydrogen peroxide and on hydrolysis.

Both 1-lithio-4-bromo- and 1-lithio-4-hydro-tetrafluorobenzene undergo intramolecular loss of lithium fluoride to form the corresponding 2-substituted-1,3,4-trifluorobenzene which forms addition products analogous to those described above:

Tamborski has investigated the lithiation of 1-substituted-4-hydro-tetrafluorobenzenes, where the substituent para to the hydrogen is OH, NH₂, SH, CF₃ and CH₃; and other workers have separated similar lithium derivatives where the substituent para to the lithium is n-butyl and phenylethynyl.
1-Lithio-3-hydrotetrafluorobenzene has been obtained by reacting n-butyllithium with either 1,3-dihydro- or 1-bromo-3-hydrotetrafluorobenzene; it reacts with bromine in the normal manner and eliminates lithium fluoride to give the isomeric 1-hydro-2,3,4-trifluoro- and 2-hydro-1,3,4-trifluoro-benzynes which form addition products with furan.

\[
\begin{align*}
X = H, Br & \quad n-C_4H_9Li \\
\text{ether} & \quad \text{ether} \\
\end{align*}
\]

\[
\begin{align*}
\text{ether} & \quad \text{ether} \\
\text{ether} & \quad \text{ether} \\
\text{ether} & \quad \text{ether} \\
\end{align*}
\]

2-lithiononafluorobiphenyl is obtained by the action of n-butyllithium on the 2-halononafluorobiphenyls in ether/hexane, ether/heptane, ether/furan and benzene/hexane.

\[
\begin{align*}
X = Cl & \quad \text{ref. 38} \\
X = Br & \quad \text{ref. 34, 39} \\
X = I & \quad \text{ref. 60} \\
\end{align*}
\]

and reacts with water, chlorine, mercuric chloride and dimethyltin.
dichloride\textsuperscript{60} in an analogous manner to pentafluorophenyllithium. With bromo- and iodo-pentafluorobenzene, lithium/halogen exchange takes place at \(-78^\circ\) to give the corresponding 2-halononafluorobyphenyl:

\[
\begin{align*}
\text{Li} & \quad \text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} & \quad \text{F}
\end{align*}
\]

In benzene\textsuperscript{61} and furan\textsuperscript{55}, 2-lithiononafluorobiphenyl undergoes intramolecular loss of lithium fluoride to give 1-pentafluorophenyl-2,3,4-trifluorobenzyn which forms addition adducts with benzene or furan in a similar manner to tetrafluorobenzyn.

\(4,4'\)-Dihydrooctafluorobiphenyl reacts with n-BuLi in THF to give \(4,4'\)-dilithiooctafluorobiphenyl which reacts with carbon dioxide\textsuperscript{57} and other reagents in an analogous manner to \(1,4\)-dilithiotetrafluorobenzyn.

\(4,4'\)-Dilithio-3,3'-dihydro- and \(4,4'\)-dilithio-3,3'-dibromohexafluorobiphenyls have been prepared by the action of n-BuLi on the corresponding tetrahydro- and tetrabromohexafluorobiphenyls\textsuperscript{23}.
The reaction between the dihydrodicarboxylic acid and four equivalents of n-BuLi results in only a limited exchange between BuLi and the two aromatic protons of the intermediate dilithium salt of the acid

\[
\text{HO}_2\text{C} \quad \text{F} \quad \text{F} \quad \text{CO}_2\text{H} \quad \text{H} \quad \text{H} \quad 2\text{n-BuLi} \quad \rightarrow \\
\text{Li}_2\text{C} \quad \text{F} \quad \text{F} \quad \text{CO}_2\text{Li} \quad \text{H} \quad \text{H}
\]

but lithiation of the dibromodicarboxylic acid proceeds normally to give, after carbonation, hexafluorobiphenyl-3,3′,4,4′-tetracarboxylic acid in high yield.

Extensive studies have been carried out on 2,2′-dilithiooctafluorobiphenyl which is readily obtained by the reaction of n-BuLi with 2,2′-dibromo-octafluorobiphenyl in ether/hexane or tetrahydrofuran/hexane at low temperatures. It reacts with halogens in the normal way to give the corresponding 2,2′-di-halo-octafluorobiphenyl; carbonation yields octafluorodiphenic acid.

\[
\text{HO}_2\text{C} \quad \text{F} \quad \text{F} \quad \text{CO}_2\text{H} \quad \text{H} \quad \text{H} \quad \rightarrow \\
\text{L}_{i2}\text{C} \quad \text{F} \quad \text{F} \quad \text{CO}_2\text{Li} \quad \text{H} \quad \text{H} \\
1) \text{CO}_2 \\
2) \text{H}^+
\]

In the presence of furan, elimination of lithium fluoride from each 2-lithiotetrafluorophenyl ring affords two isomeric furan adducts. If the decomposition occurs between -78° and 0° in the absence of a benzyne trapping agent, one molecule of lithium fluoride is eliminated and this is apparently followed by an intramolecular addition of the intact half of the molecule to the benzyne forming 1-lithioheptafluorobiphenylene; this reacts with water, bromine and mercuric chloride in the conventional manner (fig.2).

Fluoroaromatic acetylenes may be prepared by the reaction of lithium derivative of an alkyl or aryl acetylene with a mono-substituted pentafluorobenzene in tetrahydrofuran:

\[
RC \equiv CLi + \begin{array}{c}
\text{THF} \\
\text{RC} \equiv C - F
\end{array} \rightarrow RC \equiv C - F + LiF
\]

\[
R = C_6H_5, C_3H_7, C_4H_9 \\
X = F, Cl, C_6F_5, C=CR
\]

When either pentafluorobenzene or iodopentafluorobenzene is used in the above preparation no isolable products are formed, probably because Li/H and Li/I exchange processes greatly complicate the reaction. Some reactions of 1-(phenylethynyl)-4-chlorotetrafluorobenzene are shown in fig.3. Lithium derivatives of polyfluoropyridines have been reported and can be synthesised by lithium/hydrogen or lithium/halogen exchange:

Although normal reactions are observed with carbon dioxide, no intramolecular elimination of lithium fluoride is observed in furan, suggesting
Figure No. 2
Figure No. 3
that the increased susceptibility of the pyridine system to nucleophilic attack favours intermolecular lithium fluoride elimination and the subsequent formation of polymers.\(^\text{68}\)

An unstable titanium species has been used to prepare substituted polyfluorobiphenyls\(^\text{49}\) by the reaction:

\[
\begin{align*}
\text{Br} \quad \text{F} \quad \text{Br} & \quad \overset{\text{LiBu, } -78^\circ}{\text{ether/hexane}} \quad \underset{\text{excess TiCl}_4, \text{warm slowly to room temperature}}{	ext{F}} \quad \text{Br} \\
\text{Br} \quad \text{Li} \quad \text{excess TiCl}_4, \text{warm slowly to room temperature} \quad \text{Br}
\end{align*}
\]

This product is thought to arise by thermal decomposition at, or below, room temperature, of the titanium species shown in the scheme below:

\[
\text{Ti(}C\text{F}_{6}^5\text{)}_2\text{Cl}_2 \quad \rightarrow \quad C\text{F}_{6}^5 - C\text{F}_{6}^5 \quad + \quad (\text{TiCl}_2) \quad \downarrow \quad \text{TiCl}_4 \quad 2\text{TiCl}_3
\]

In tetrahydrofuran the complex TiCl\(_3\).3THF can be isolated in good yields from these reactions.\(^\text{69}\)

1,3-Dibromotetrafluorobenzene reacts with n-butyllithium in ether to give 1-lithio-3-bromotetrafluorobenzene, as shown by the addition of titanium
tetrachloride to the monolithio-derivative, when a high yield of the coupled product, 3,3'-dibromo-octafluorobiphenyl is obtained, and hydrolysis gives 1-hydro-3-bromotetrafluorobenzene.

**POLYFLUOROAROMATIC GRIGNARD DERIVATIVES**

The greater stability of a polyfluoroaromatic Grignard reagent, compared with the corresponding lithium derivative, might suggest the former to be more suited for the preparation of polyfluoroaromatics as there would be no need for a strict temperature control during the reaction. The formation of the Grignard reagent from magnesium metal is, however, considerably more solvent dependent (as are many of its reactions) and it is generally more difficult to prepare than the lithium reagent. This has resulted in the preparation of relatively fewer Grignard reagents.

Nevertheless, pentafluorophenylmagnesium halides were simultaneously reported by Tatlow and Wall in 1959, three years prior to that of pentafluorophenyllithium. They have since been prepared by the action of magnesium on chloro-, bromo-, and iodopentafluorobenzenes:

\[
\text{MgX} \quad \text{Et}_2\text{O or THF} \rightarrow \quad \text{MgX} \\
F \quad X = \text{Cl, Br, I.}
\]

and by the action of alkylmagnesium halides on both pentafluorobenzene and bromopentafluorobenzene. With chloropentafluorobenzene, the magnesium required activation by ethylene dibromide before the Grignard reagent would form.

The use of tetrahydrofuran does, however, have one drawback in that it favors nucleophilic reactions and the formation of polymeric by-products. Thus, although pentafluorophenylmagnesium bromide is stable in refluxing ether,
decomposition occurs in refluxing tetrahydrofuran to give bromopolyfluoropolyphenylenes\textsuperscript{74,75}. The decomposition is obviously temperature dependent since Tamborski\textsuperscript{73} reports no decomposition of pentafluorophenylmagnesium bromide in tetrahydrofuran after 5 days at room temperature; whereas carbonation at \(30-35^\circ\text{C}\)\textsuperscript{74} gave only half the yield of pentafluorobenzoic acid relative to that at \(20^\circ\text{C}\). By maintaining the temperature of pentafluorophenylmagnesium bromide in tetrahydrofuran at about \(-10^\circ\text{C}\) in the presence of pentafluoronitrobenzene\textsuperscript{76}, pentafluoropyridine\textsuperscript{77} or decafluorobiphenyl\textsuperscript{75}, controlled nucleophilic replacement of fluorine by the \(\text{C}_6\text{F}_5^-\) "anion" takes place:

\[
\text{C}_6\text{F}_5^- + \text{C}_6\text{F}_5\text{C}_6\text{F}_5 \rightarrow \text{C}_6\text{F}_5\left[\begin{array}{c}
\text{F} \\
\text{C}_6\text{F}_5 \\
n = 1, 2, 3
\end{array}\right]
\]

Similarly, during the reaction of pentafluorophenylmagnesium bromide with silicon tetrachloride, side reactions occurred\textsuperscript{78} to give, after hydrolysis, a mixture of \textit{para}-linked hydropolyfluoropolyphenyls: \(4-\text{HC}_6\text{F}_4(\text{C}_6\text{F}_4)_n\text{C}_6\text{F}_5\), \(n = 0, 1, 2\). These were thought to arise from attack of \(\text{C}_6\text{F}_5^-\) on the fluorine atom \textit{para} to the Grignard group:

\[
\text{MgBr} \rightarrow \text{C}_6\text{F}_5^- \rightarrow \text{F} - \text{F} \text{MgBr} \rightarrow \text{H} \text{H}
\]
followed by attack of the $\text{C}_6\text{F}_5\text{C}_6\text{F}_4^-$ anion on another $\text{C}_6\text{F}_5\text{MgBr}$ molecule or on the biphenyl Grignard:

\[
\begin{align*}
&\text{MgBr} \\
\text{F} &\xrightarrow{\text{C}_6\text{F}_5\text{C}_6\text{F}_4^-} \text{C}_6\text{F}_5 \\
&\text{MgBr}^+ \xrightarrow{\text{C}_6\text{F}_5\text{C}_6\text{F}_4^-} \text{C}_6\text{F}_5 \\
&\text{F} \\
\end{align*}
\]

The decomposition of pentafluorophenylmagnesium chloride and bromide in benzene\textsuperscript{79} gave the expected 1,4-Diels–Alder adduct, tetrafluorobenzobicyclo-\([2,2,2]\)octatriene,

\[
\text{F} \quad \text{H}
\]

together with 2-hydrononafluorobiphenyl, which presumably arose from addition of pentafluorophenylmagnesium halide across tetrafluorobenzyne:

\[
\begin{align*}
&\text{C}_6\text{F}_5\text{Mg} + \text{F} \\
\end{align*}
\]

\[
\begin{align*}
&\xrightarrow{\text{MgBr}} \text{F} \quad \text{F} \\
&\xrightarrow{\text{H}^+} \text{F} \quad \text{F}
\end{align*}
\]
A further by-product, 1-bromotrifluorobenzobicyclo[2,2,2]octatriene was formed by addition of magnesium bromide (formed during the activation of the magnesium by ethylene dibromide) across tetrafluorobenzyne, followed by elimination of magnesium bromofluoride:

\[
\begin{align*}
  &\text{F} + \text{MgBr} \rightarrow \text{F} \rightarrow \text{F} \rightarrow \text{Br} \rightarrow \text{Br} \\
\end{align*}
\]

Pentafluorophenylmagnesium halides undergo the typical reactions of Grignard reagents, see figure 4. Although 1,4-dihydrotetrafluorobenzene formed both the mono- and di- Grignard reagents when treated with ethylmagnesium bromide, 1,2-dihydrotetrafluorobenzene does not form even the mono-Grignard, under the same conditions.
$X = Br, R = CH_3, CF_3, CH_2Br,$ Ref: 80, 81
$X = I, R = CH_3,$ Ref: 80, 81
$R = C_6H_5, C_6F_5,$ Ref: 81
$R = CF_3, Ref: 82, 83$
$R = CCl_3, CHCl_2, CH_2Br,$ Ref: 83
$R = CClF_2,$ Ref: 82, 83

Figure No. 4
1,2-Dibromotetrafluorobenzene reacted with magnesium in ether\textsuperscript{51}, ether/THF\textsuperscript{39} or THF\textsuperscript{35} at 0°, the mono-Grignard reagent being formed:

\[ \text{F} \quad \text{Br} \quad \text{Mg} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{MgBr} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{H} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{30\%} \]

\[ \text{F} \quad \text{Br} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{COOH} \quad \text{81\%} \]

In benzene, benzyne formation occurred with magnesium bromofluoride and magnesium dibromide being eliminated intramolecularly in a 99:1 ratio\textsuperscript{51}:

\[ \text{F} \quad \text{Br} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{100\%} \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{100\%} \]

2-Bromononafluorobiphenyl reacted with magnesium in tetrahydrofuran over 5 hours to give 2-nafluorobiphenylmagnesium bromide\textsuperscript{39}, although the corresponding reaction in ether did not proceed even after 12 hours under reflux: hydrolysis gave 2-hydrononafluorobiphenyl;\textsuperscript{39}

\[ \text{F} \quad \text{Br} \quad \text{Mg} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{MgBr} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{H} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{39\%} \]

\[ \text{F} \quad \text{Br} \quad \text{F} \quad \text{Mg} \quad \text{THF} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{MgBr} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{H} \quad \rightarrow \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{F} \quad \text{Br} \quad \text{39\%} \]
4-Tetrafluoropyridylmagnesium bromide$^{77}$ and iodide$^{67}$ have been prepared by the action of magnesium in THF on 4-bromo- and 4-iodotetrafluoropyridine respectively:

$$\begin{align*}
\text{Br} & \quad \text{C}_2\text{H}_5 & \quad \text{CH}_3 \\
\text{I} & \quad \text{C}_6\text{H}_5 & \quad \text{H}
\end{align*}$$

POLYFLUORAROMATIC DERIVATIVES OF METALS AND METALLOIDS

The majority of polyfluoraromatic derivatives of metals and metalloids are prepared using lithium and Grignard reagents and metal and metalloid halides (Table No.1). Numerous pentafluorophenyl derivatives have been obtained by reacting the appropriate metal or metalloid halide (usually the chloride) with pentafluorophenylmagnesium halide in diethylether or tetrahydrofuran, the mixture being refluxed when necessary, (Table No.2). The above methods have also been used in the synthesis of polyfluorobiphenyl derivatives of metals and metalloids$^{60,61,114,126,127}$.

Several other distinct methods of preparation have been evolved. Pentafluorophenyl derivatives of boron$^{105,121,128,130}$, aluminium$^{130,131}$, phosphorus$^{131}$, arsenic$^{131}$ and germanium$^{131}$ have been obtained by the cleavage of pentafluorophenyl derivatives of titanium$^{105}$, tin$^{121,128,129}$ and mercury$^{128,131}$ by the corresponding halide:

$$\begin{align*}
\text{Sn(CH}_3)_3 & \quad \text{BX}_3 \quad \rightarrow \quad \text{Sn(BX}_2) \\
\text{HgCH}_3 & \quad \text{MX}_3 \quad \rightarrow \quad \text{Hg(MX}_2)
\end{align*}$$

ref. 121, 128

ref. 128

ref. 130, 131

ref. 131
Pentafluorophenyl derivatives of zinc\(^{94}\), cadmium\(^{95}\), and mercury\(^{132}\) result from decarboxylation of the corresponding pentafluorobenzoates:

\[
\text{(C}_6\text{F}_5\text{COO})_2\text{M} \xrightarrow{\Delta} \text{(C}_6\text{F}_5)_2\text{M} \\
\text{M = Zn, Cd, Hg}
\]

In sharp contrast decarboxylations\(^{94}\) of the pentafluorobenzoates of most other metals give only organic products:

\[
\text{(C}_6\text{F}_5\text{COO})_n\text{M} \xrightarrow{\Delta} \text{MF}_n + \text{CO}_2 + \text{(C}_6\text{F}_5)_n \\
n = 1, \text{M = Li, K, Cs} \\
n = 2, \text{M = Mg, Ca}
\]

\[
\text{(C}_6\text{F}_5\text{COO})_2\text{Si} \xrightarrow{\Delta} \text{SiO}_2 + \text{CO}_2 + \text{(C}_6\text{F}_5)_2\text{CO} \\
\text{(C}_6\text{F}_5\text{COO})_2\text{Cu} \xrightarrow{\Delta} 2\text{CO}_2 + \text{Cu} + \text{C}_6\text{F}_5 - \text{C}_6\text{F}_5
\]

Several pentafluorophenylmercurials have been obtained by the mercuration of pentafluorobenzene with mercuric carboxylates of the type \((\text{CH}_n\text{F}_{3-n}\text{CO}_2)_2\text{Hg}\)\(^{133,134}\),

\[
\text{C}_6\text{F}_5\text{H} + \text{(CH}_n\text{F}_{3-n}\text{COO})_2\text{Hg} \rightarrow \text{C}_6\text{F}_5\text{HgCOOCH}_n\text{F}_{3-n} \\
n = 0-3
\]

the order of reactivity of the carboxylates being:

\[
\text{CF}_3 > \text{CF}_2\text{H} > \text{CFH}_2 > \text{CH}_3
\]

Sulphur dioxide elimination (desulphination) reactions have been used extensively for the synthesis of monoaryl\(^{135-137}\) and diaryl mercurials\(^{138,139}\), but applications of this method to the derivatives of other main group elements is restricted to the preparation of a single organoarsenic compound\(^{140}\) and three organobismuth derivatives \(^{141}\). Only two syntheses of polyfluoroarylorgano-metallics by desulphination have been reported\(^{142-144}\):

\[
\text{(C}_6\text{F}_5\text{SO}_2)\text{Fe(\pi-C}_5\text{H}_5)(\text{CO}_2) \xrightarrow{\Delta} \text{C}_6\text{F}_5\text{Fe(\pi-C}_5\text{H}_5)(\text{CO})_2 \\
\text{(C}_6\text{F}_5\text{SO}_2)\text{IrCl}_2(\text{Ph}_3\text{P})_2 \xrightarrow{\Delta} \text{C}_6\text{F}_5\text{IrCl}_2(\text{Ph}_3\text{P})_2\text{SO}_2
\]

However, the recent preparation of lithium pentafluorobenzene sulphinate\(^{145}\) has made possible the extension of desulphination to the syntheses of polyfluoroarylmercurials\(^{146}\) and polyfluorophenylthallium compounds\(^{147}\) (Table No. 3).
<table>
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<th>Reactant</th>
<th>Product</th>
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<tr>
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<td>((C_6F_5)_2)Cd</td>
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<td>(C₆F₅)₃B</td>
<td>115,116</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>(C₆F₅)₃Al₂Et₂O</td>
<td>116</td>
</tr>
<tr>
<td>TlCl₃</td>
<td>(C₆F₅)₃Tl</td>
<td>124,125</td>
</tr>
<tr>
<td></td>
<td>(C₆F₅)₂TlBr</td>
<td>124,125</td>
</tr>
<tr>
<td>SiCl₄</td>
<td>(C₆F₅)₄Si</td>
<td>101,117</td>
</tr>
<tr>
<td>PCl₃</td>
<td>(C₆F₅)₃P</td>
<td>101,117</td>
</tr>
<tr>
<td>(π.C₅H₅)₂TiCl₂</td>
<td>(π.C₅H₅)₂Ti(C₆F₅)₂</td>
<td>118</td>
</tr>
<tr>
<td>Mn(CO)₅Br</td>
<td>C₆F₅Mn(CO)₅</td>
<td>118</td>
</tr>
<tr>
<td>π.C₅H₅Fe(CO)₂I</td>
<td>π.C₅H₅Fe(CO)₂(C₆F₅)</td>
<td>118</td>
</tr>
<tr>
<td>(R₃P)₂NiBr₂</td>
<td>(R₃P)₂Ni(C₆F₅)Br</td>
<td>110</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>(C₆F₅)₂Zn</td>
<td>119</td>
</tr>
<tr>
<td>GaCl₃</td>
<td>(C₆F₅)₃Ga₂Et₂O</td>
<td>116</td>
</tr>
<tr>
<td>InCl₃</td>
<td>(C₆F₅)₂InBr</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>(C₆F₅)₃In₂Et₂O</td>
<td>116</td>
</tr>
<tr>
<td>GeCl₄</td>
<td>(C₆F₅)₄Ge</td>
<td>96,97</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>(C₆F₅)₃As</td>
<td>101</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>(C₆F₅)₃Sb</td>
<td>101</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>(C₆F₅)₄Sn</td>
<td>120-122</td>
</tr>
<tr>
<td>PbCl₂+Br₂</td>
<td>(C₆F₅)₄Pb</td>
<td>100</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>(C₆F₅)₂Hg</td>
<td>123</td>
</tr>
</tbody>
</table>
### Table No. 3

**Preparations of Mono-organomercurials, RHgX, in Water**

<table>
<thead>
<tr>
<th>LiO₂SR</th>
<th>HgX₂</th>
<th>Product RHgX</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>C₆F₅</td>
<td>Cl</td>
<td>C₆F₅HgCl</td>
</tr>
<tr>
<td>C₆F₅</td>
<td>Br</td>
<td>C₆F₅HgBr</td>
</tr>
<tr>
<td>C₆F₅</td>
<td>CH₃COO</td>
<td>C₆F₅Hg(CH₃COO)</td>
</tr>
<tr>
<td>C₆F₅</td>
<td>PhSO₂</td>
<td>C₆F₅Hg(PhSO₂)</td>
</tr>
<tr>
<td>p-HC₆F₄</td>
<td>Cl</td>
<td>p-HC₆F₄HgCl</td>
</tr>
<tr>
<td>p-HC₆F₄</td>
<td>Br</td>
<td>p-HC₆F₄HgBr</td>
</tr>
<tr>
<td>p-HC₆F₄</td>
<td>CH₃COO</td>
<td>p-HC₆F₄Hg(CH₃COO)</td>
</tr>
<tr>
<td>m-HC₆F₄</td>
<td>Cl</td>
<td>m-HC₆F₄HgCl</td>
</tr>
<tr>
<td>m-HC₆F₄</td>
<td>Br</td>
<td>m-HC₆F₄HgBr</td>
</tr>
<tr>
<td>o-HC₆F₄</td>
<td>Cl</td>
<td>o-HC₆F₄HgCl</td>
</tr>
</tbody>
</table>

**Preparations of Di-mercurated Tetrafluorobenzenes in Water**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>HgX₂</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-(LiO₂S)₂C₆F₄</td>
<td>Cl</td>
<td>p-(ClHg)₂C₆F₄</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>p-(BrHg)₂C₆F₄</td>
</tr>
<tr>
<td></td>
<td>CH₃COO</td>
<td>p-(CH₃COOHg)₂C₆F₄</td>
</tr>
<tr>
<td>o-(LiO₂S)₂C₆F₄</td>
<td>Cl</td>
<td>o-(ClHg)₂C₆F₄</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>o-(BrHg)₂C₆F₄</td>
</tr>
</tbody>
</table>

**Preparations of Bispolyfluorophenylmercurials in aq. t-Butanol at Room Temp.**

<table>
<thead>
<tr>
<th>LiO₂SR</th>
<th>Hg compound</th>
<th>Product R₂Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆F₅</td>
<td>Hg(CH₃COO)₂</td>
<td>(C₆F₅)₂Hg</td>
</tr>
<tr>
<td>C₆F₅</td>
<td>HgCl₂</td>
<td>(C₆F₅)₂Hg</td>
</tr>
<tr>
<td>C₆F₅</td>
<td>C₆F₅HgCl</td>
<td>(C₆F₅)₂Hg</td>
</tr>
<tr>
<td>p-HC₆F₄</td>
<td>HgCl₂</td>
<td>(p-HC₆F₄)₂Hg</td>
</tr>
<tr>
<td>p-HC₆F₄</td>
<td>p-HC₆F₄HgBr</td>
<td>(p-HC₆F₄)₂Hg</td>
</tr>
<tr>
<td>m-HC₆F₄</td>
<td>Hg(CH₃COO)₂</td>
<td>(m-HC₆F₄)₂Hg</td>
</tr>
</tbody>
</table>

\[
\text{LiO}_2\text{SR} + \text{Tl}(\text{OCCF}_3)_3 \xrightarrow{\text{CH}_3\text{COOH}} R_2\text{TlO}_2\text{CCH}_3 \quad R = \text{C}_6\text{F}_5, \text{p}-, \text{o-}\text{HC}_6\text{F}_4
\]
Heptafluoro-n-propyl and -isopropyllithium\textsuperscript{148} have been synthesized by metal-halogen exchange reactions between \( \text{C}_3\text{F}_7\text{I} \) and lithium alkyls in ether at \(-78^\circ\). However, attempts to prepare trifluoromethyllithium by similar reactions have proved unsuccessful, due to the ease with which lithium fluoride is eliminated:

\[
\text{C}_3\text{F}_7\text{Li} \rightarrow :\text{CF}_2 + \text{LiF}
\]
\[
2:\text{CF}_2 \rightarrow \text{C}_2\text{F}_4
\]

In view of this difficulty to prepare perfluoroalkyl metal derivatives by the reaction of perfluoroalkyllithium and metal halides, the direct synthesis is found to be the more suitable route to obtain perfluoroalkyl metal and metalloid derivatives. The perfluoroalkyl iodides used for their remarkable thermal stability, have provided a starting point for the synthesis of many perfluoroorganometallic compounds, notably of sulphur\textsuperscript{149}, selenium\textsuperscript{150}, mercury\textsuperscript{150} and phosphorus\textsuperscript{151}

\[
\text{CF}_3\text{I} \rightarrow \text{CF}_2\text{I} + \text{LiF}
\]

The first success of the application of direct synthesis to prepare perfluoroaryl metal derivatives was met by Hazeldine\textsuperscript{152}, who obtained bis(pentafluorophenyl)mercury by heating iodopentafluorobenzene and mercury together in an evacuated sealed tube at \(300^\circ\) for 30 hours:

\[
2\text{C}_6\text{F}_5\text{I} + 2\text{Hg} \rightarrow (\text{C}_6\text{F}_5)_2\text{Hg} + \text{HgI}_2
\]

Subsequently, pentafluorophenyl derivatives of sulphur\textsuperscript{153}, selenium\textsuperscript{153}, tellurium\textsuperscript{153}, germanium\textsuperscript{153}, tin\textsuperscript{153}, phosphorus\textsuperscript{153}, arsenic\textsuperscript{153}, zinc\textsuperscript{153}, cadmium\textsuperscript{153} and indium\textsuperscript{154} have been synthesized by direct methods.

Several octafluorobiphenylene heterocyclic derivatives have been prepared by direct methods, involving the heating of 1,2-diiodotetrafluorobenzene or 2,2'-diiodoctafluorobiphenyl with a metal or metalloid\textsuperscript{153}(Fig.5).

When 1,2-diiodotetrafluorobenzene is heated with mercury to \(200^\circ\) tetrafluoro-ortho-phenylenemercuTrymer(III) is formed\textsuperscript{114}:
This mercurial has been made previously by both the decarboxylation\textsuperscript{155} and sulphur trioxide-elimination\textsuperscript{156} routes. Its mass spectrum verifies the trimer formulation. Normally, perfluoroaromatic organometallic compounds have similar structures to their hydrogen analogues, but ortho-phenylenemercury unlike tetrafluoro-ortho-phenylenemercury is known to be a hexamer\textsuperscript{157}. Wittig\textsuperscript{158,159} prepared the hydrogen analogue by reacting 1,2-dibromobenzene with sodium amalgam and molecular weight determination showed it to be a hexamer.

Attempts\textsuperscript{114} to verify Wittig's results have yielded only a trimeric structure for ortho-phenylenemercury. One might have expected the perfluoromercuronin to be hexameric, by direct analogy with o-phenylenemercury and it is unusual to experience an anomaly of this kind. Normally crystal structures of fluorine and hydrogen analogues are so alike that very similar melting points (± 15-20°) are observed for the two types of derivatives. Further studies on Wittig's compound are to be found in this work.
Figure No. 5
When 1,2-diiodotetrafluorobenzene and either arsenic or antimony are heated together, dodecafluoro-13,14-diarsatriptycene and dodecafluoro-13,14-distibatriptycene are formed:

\[
\begin{align*}
\text{I} & \quad \text{I} \\
\text{F} & \quad \text{M} \\
& \xrightarrow{300^\circ} \text{3 days} \\
\end{align*}
\]

\[\text{F} \quad \text{F} \quad \text{F} \quad \text{M} \quad \text{M} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \]

\[M = \text{As, Sb}\]

The reaction of 1,2-diiodotetrafluorobenzene with copper under vacuum at 230° gives a mixture of polyphenylenes \(\text{C}_6\text{F}_4\text{H}_x\) \((x = 2, 3, 4, \ldots)\), from which the interesting compound, perfluorotriphenylene, can be isolated. An X-ray structure determination shows distortion from planarity different from that expected, and unlike that of triphenylene itself.

Bis(pentafluorophenyl)mercury undergoes transmetallation reactions with germanium, tin, sulphur, selenium, tellurium.
Transmetallation has been used to prepare the first lanthanide fluoro-
carbon organometallic.\textsuperscript{163} The method differed from the above, in that
the reaction was carried out in dry THF at room temperature and not in a
sealed tube under vacuum.

\[
\begin{align*}
(C_{6}F_{5})_{2}Hg + Yb & \xrightarrow{\Delta \text{ in vacuo}} (C_{6}F_{5})_{n}M \quad \text{n=2, M=S, Se, Te} \\
& \quad \text{n=4, M=Ge, Sn}
\end{align*}
\]

Polyfluoroaromatic derivatives of transition metals have been obtained
by the nucleophilic replacement of fluorine by carboxylmetal anions, and
this replacement procedure has been applied to the synthesis of sulphur
derivatives.\textsuperscript{163-169}

\[
C_{6}F_{6} + [SH]^{-} \rightarrow C_{6}F_{5}SH
\]

\[
C_{6}F_{5}CF_{3} + [SR]^{-} \rightarrow F_{3}C-\begin{array}{c}
\text{F} \\
\text{SR}
\end{array}
\]

\[R = H, C_{6}H_{5}\]

Several polyfluoroaromatic silicon derivatives have been obtained by
reacting hexafluorobenzene with silanes under the influence of ultra-
violet radiation,\textsuperscript{170} and with silicon difluoride:\textsuperscript{171}

\[
C_{6}F_{6} + (CH_{3})_{3}SiH + C_{6}F_{5}Si(CH_{3})_{3}
\]

\[
C_{6}F_{6} + SiCl_{3}H + C_{6}F_{5}SiCl_{2}F + C_{6}F_{4}(SiCl_{2}F)_{2}
\]

\[
C_{6}F_{6} + SiF_{2} + C_{6}F_{5}SiF_{3} + C_{6}F_{4}(SiF_{3})_{2}
\]

The reactions proceed\textsuperscript{170} via attack of a free radical on hexafluorobenzene:

\[
(\text{CH}_{3})_{3}SiH \xrightarrow{\text{hv}} (\text{CH}_{3})_{3}Si^{\cdot} \xrightarrow{C_{6}F_{6}} \begin{array}{c}
\text{Si(CH}_{3}\text{)}_{3} \\
\text{F}
\end{array}
\]

\[
(\text{CH}_{3})_{3}SiF + \begin{array}{c}
\text{F}
\end{array} \xrightarrow{(\text{CH}_{3})_{3}Si} \begin{array}{c}
\text{Si(CH}_{3}\text{)}_{3}
\end{array}
\]
The formation of trimethylpentfluorophenylsilane from the action of bis(trimethylsilyl) mercury on bromopentafluorobenzene is thought to proceed by an electron-transfer mechanism:\textsuperscript{172}

\[
[(\text{CH}_3)_3\text{Si}]_2\text{Hg} + \text{C}_6\text{F}_5\text{Br} \rightarrow (\text{CH}_3)_3\text{Si}^+ + \text{C}_6\text{F}_5^- + (\text{CH}_3)_3\text{SiHgBr} \\
(\text{CH}_3)_3\text{Si}^+ + \text{C}_6\text{F}_5^- \rightarrow (\text{CH}_3)_3\text{Si}^+ + \text{C}_6\text{F}_5^- \rightarrow \text{C}_6\text{F}_5\cdot \text{Si(CH}_3)_3
\]

In addition to its preparation by the methods above, bis(pentafluorophenyl)mercury has been obtained by oxidizing pentafluorophenylhydrazine with mercuric oxide\textsuperscript{27} and by an exchange reaction between bis(pentafluorophenyl)thallic bromide and diphenylmercury:\textsuperscript{124}

\[
\text{C}_6\text{F}_5\text{NH.NH}_2 + \text{Hg/HgO} \xrightarrow{\text{C}_6\text{F}_5\text{Br}} (\text{C}_6\text{F}_5)_2\text{Hg} \quad \text{64}\%
\]

\[
(\text{C}_6\text{F}_5)_2\text{TIBr} + \text{Hg.(C}_6\text{H}_5)_2 \xrightarrow{\text{C}_6\text{F}_5\text{Br}} (\text{C}_6\text{F}_5)_2\text{Hg} + \text{C}_6\text{F}_5\text{HgC}_6\text{H}_5
\]

When pentafluorophenylhydrazine is used, the reaction proceeds\textsuperscript{27} via the pentafluorophenyl radical as evidenced by the formation of pentafluorobenzene and decafluorobiphenyl on replacing Hg/HgO by silver oxide in hexafluorobenzene:

\[
\text{C}_6\text{F}_5\text{NH.NH}_2 + \text{Ag}_2\text{O} \rightarrow \text{C}_6\text{F}_5^- \xrightarrow{\text{C}_6\text{F}_6} \text{C}_6\text{F}_5\text{H} \quad \text{64}\% \quad \text{C}_6\text{F}_5\cdot \text{C}_6\text{F}_5 \quad \text{2}\%
\]

The low yield of decafluorobiphenyl indicated the comparative inertness of hexafluorobenzene to attack by the pentafluorophenyl radical and it has been suggested\textsuperscript{27} that the decafluorobiphenyl is formed by the dimerization of C\textsubscript{6}F\textsubscript{5} radicals; pentafluorobenzene is formed by hydrogen abstraction from unreacted pentafluorohydrazine:

\[
\text{C}_6\text{F}_5^- + \text{C}_6\text{F}_5\text{NH.NH}_2 \rightarrow \text{C}_6\text{F}_5\text{H} \quad \text{C}_6\text{F}_5\cdot \text{C}_6\text{F}_5
\]

In recent years some novel direct synthetic methods have been utilized in the isolation of transition metal organoderivatives, notably by Timms\textsuperscript{173,174}, using low temperature co-condensation of metal atoms with organic ligand substrates. Evaporation of the metal can be accomplished by electrical heating of a crucible containing the metal, by electron bombardment
of a metal target or by laser evaporation\textsuperscript{175}. The co-condensation method has been utilized by Klabunde\textsuperscript{176} in the syntheses of perfluoroalkyl and perfluoroaryl derivatives of main group and transition metals e.g. CF\textsubscript{3}ZnI, C\textsubscript{6}F\textsubscript{5}CaF, C\textsubscript{6}F\textsubscript{5}PdBr and C\textsubscript{6}F\textsubscript{5}NiCl.

Fluoroaromatic organometallics have been reviewed\textsuperscript{52,177,178} several times over the years, the last review\textsuperscript{178} covering the period 1969-1972.

**POLYCHLOROAROMATIC DERIVATIVES OF METALS AND METALLOIDS**

Until a decade ago, only a small number of pentachlorophenyl-substituted derivatives had been reported. Chatt\textsuperscript{179-182} prepared the first transition metal derivatives using pentachlorophenylmagnesium chloride:

\[
\begin{align*}
\text{[Et}_2\text{Ph}P\text{Ni(C}_6\text{Cl}_5\text{)Cl}} & \\
\text{[Et}_3\text{P}2\text{Ni(C}_6\text{Cl}_5\text{)Cl}_2 & \\
\text{[Et}_2\text{PhP}2\text{M(C}_6\text{Cl}_5\text{)_2}} & \text{M = Co, Fe}
\end{align*}
\]

Five years later these compounds were again reported, together with the corresponding bis(pentachlorophenyl) cobalt complex, by Rau\textsuperscript{183}, Tibbetts and Gorden\textsuperscript{183}. These workers were the first to report\textsuperscript{183} the synthesis of pentachlorophenyllithium, C\textsubscript{6}Cl\textsubscript{5}Li, which was readily prepared by the addition of n-butyllithium in hexane to hexachlorobenzene in an ethereal solvent. When reactions were conducted in THF, it was found necessary to maintain the reaction temperature at about \(-78^\circ\) in order to obtain satisfactory yield\textsuperscript{183}, in diethylether, temperatures as high as \(-10^\circ\) could be employed (Fig. 6). Using this reagent they succeeded\textsuperscript{184,185}, in forming the first example of an organotransition metal compound in which two different highly electronegative aryl ligands are \(\sigma\)-bonded to the same transition metal:

\[
\begin{align*}
(C\text{H}_3)_2\text{P} & \\
C\text{Cl}\text{Ni} & \\
C\text{F}_5 & \\
P(C\text{H}_3)_2\text{CH}_3
\end{align*}
\]
Figure No. 6
and a series of perchloroaryl palladium compounds:

Using the Grignard reagent McKinnon and West\textsuperscript{186} prepared a series of derivatives of general formula:

\[(\text{Ph}_3\text{P})_2\text{M} (\text{C}_6\text{Cl}_5)X\]  

where \(X = \text{Cl}, \text{Br}, \text{I}\), which on heating above 160\(^\circ\)C, lose triphenylphosphine yielding dimeric products:

Recently\textsuperscript{187} much attention has been focused on the above compounds and there is now a large selection of new compounds of the type:

\[M \text{X(C}_6\text{Cl}_5)(\text{PPh}_3)_2\]  

where \(M = \text{Pd}\) or \(\text{Ni}\), and \(X = \text{Cl,Br,I,NCS,NCO,N}_3\)
Using allyl-Grignards, Wada\textsuperscript{190} has prepared a series of \( \pi \)-allylnickel compounds:

\[
(n^{-}\text{CHRCR'}\text{CH}_2)\text{Ni}(\text{PFMe}_2)\text{C}_6\text{Cl}_5
\]

\[
R = R' = \text{H}
\]

\[
R = \text{H}, R' = \text{CH}_3
\]

\[
R = \text{CH}_3, R' = \text{H}
\]

Uson and his co-workers\textsuperscript{191} have extended their researches in perhaloaryl complexes of gold(I) and (III) to prepare a number of pentachlorophenyl derivatives:

\[
\text{C}_6\text{Cl}_5\text{Au(AsPh}_3\text{)}
\]

\[
\text{C}_6\text{Cl}_5\text{Au(AsPh}_3\text{)}\text{X}_2
\]

\[
X = \text{Cl, Br, I}
\]

The pentachlorophenylgold(I) complex is prepared via the Grignard reagent and is oxidized to the gold(III) complex by halogens or with thallium(III) chloride. Also reaction of \( \text{C}_6\text{Cl}_5\text{Au(AsPh}_3\text{)} \) with methyl iodide results in the formation of:

\[
\text{IAu(}\text{C}_6\text{Cl}_5\text{)(CH}_3\text{)AsPh}_3
\]

All the above derivatives have involved the use of pentachlorophenyllithium or pentachlorophenylmagnesium chloride. A different synthetic approach has been used by Deacon\textsuperscript{192} for the preparation of bis(pentachlorophenyl)mercury compounds. Only three of the diarylmercurials had been prepared previously, viz. bis(pentachlorophenyl)mercury\textsuperscript{183,193-195}; bis(2,3,4-trichlorophenyl)mercury prepared by the pyrolysis of mercuric 2,3,4-trichlorobenzenesulphinate\textsuperscript{139}; and bis(2,5-dichlorophenyl)mercury by the symmetrization of 2,5-dichlorophenyldimercaptan acetate\textsuperscript{196}. From direct mercuration of polychlorobenzenes with mercuric trifluoroacetate, polychlorphenylmercuric trifluoroacetates were obtained. These undergo thermal...
decomposition into bis(polychlorophenyl)mercurials.

\[
2 \text{C}_6\text{H}_{6-n}\text{Cl}_n + \text{Hg(CF}_3\text{COO)}_2 \xrightarrow{\text{heat}} (\text{C}_6\text{H}_{5-n}\text{Cl}_n)_2\text{Hg} + 2\text{CF}_3\text{COOH}
\]

The mercurials \(R_2\text{Hg (R = o,m,p-C}_6\text{Cl}_4\text{NO}_2)\) were prepared\(^{197}\) in similar manner at \(220^\circ\) using the corresponding tetrachloronitrobenzenes.

The chemistry of cyclopentadienylmetal compounds was aided by their convenient preparation using a variety of methods. However, the synthesis of penta-substituted-cyclopentadienyl complexes has presented problems. Some of which have been solved in the past few years.

The first such compounds, decachloroferrocene and decachlororuthenocene were obtained by repetitive metalation exchange-halogenation reactions\(^{198,199}\). Unsubstituted cyclopentadienyl complexes are conveniently prepared by the reactions of alkali metal, Grignard or thallium derivatives of \(C_5\text{H}_5^-\) with transition metal compounds\(^{200}\). Although \(\text{LiC}_5\text{Cl}_5\)\(^{201}\) and the corresponding Grignard reagent have been known for some time, attempts to use them as reagents for the preparation of transition metal - pentachlorocyclopentadienyl complexes have been unsuccessful\(^{199,202}\). More recently salts of the \(C_5\text{Cl}_5^-\) anion with large cations such as \(\text{Tl}^+, (\text{C}_4\text{H}_9)_4\text{P}^+\) and \((\text{C}_2\text{H}_5)_3\text{NH}^+\) were isolated\(^{203,204}\). These were found to be thermally unstable, decomposing in the solid above \(-15^\circ\) and in solution at \(-30^\circ\). All attempts to effect reaction of these compounds with transition metal halides failed. However, thallium pentachlorocyclopentadienide proved to be a useful reagent in the synthesis of a series of \(\sigma\)-bonded mercurial derivatives of the type:

\[
\text{Hg(C}_5\text{Cl}_5)_2
\]

\[
\text{Hg(C}_5\text{Cl}_5)\text{X X = Cl, Br, Ph}^{205,206}
\]

The reaction of diazocyclopentadiene \(C_5\text{H}_4\text{N}_2\) with dihalo-bridged rhodium dimers, such as \([\text{RhCl(1,5-C}_8\text{H}_{12})]_2\) and with manganese pentacarbonyl halides gives halo-substituted cyclopentadienyl complexes\(^{206}\). Following these observations, the chloro-substituted diazo-compound, 2,3,4,5-tetrachlorodiazocyclopentadiene has been used for the preparation of pentachlorocyclopentadienyl
Reaction of diazotetrachlorocyclopentadiene with di-μ-chlorobis(1,5-cyclooctadienierrhodium), [RhCl(1,5-C₈H₁₂)]₂ gives high yields of (π-pentachlorocyclopentadienyl)(1,5-cyclooctadiene)rhodium:

\[
C₅Cl₄N₂ + [RhCl(COD)]₂ \xrightarrow{10 \text{ hrs}} \xrightarrow{C₆H₆,RT} 2(COD)Rh
\]

A similar reaction with pentacarbonylchloromanganese, MnCl(CO)₅, gave two products: pentacarbonyl(σ-pentachlorocyclopentadienyl)manganese, Mn(σ-C₅Cl₅)(CO)₅ and tricarbonyl(π-pentachlorocyclopentadienyl)manganese, Mn(π-C₅Cl₅)(CO)₃. The σ-bonded complex is the first transition metal complex containing a σ-C₅Cl⁻ ring and for which there is no analogue in C₅H₅-Mn chemistry.

\[
\text{MnCl(CO)₅} + C₅Cl₄N₂ \xrightarrow{24 \text{ hrs}} \xrightarrow{\text{pentane,RT}} \text{pentane,RT}
\]

POLYBROMOAROMATIC DERIVATIVES OF METALS AND METALLOIDS

Although polyfluoro- and polychloroaromatic derivatives have been known for some years, very few polybromoaromatic derivatives are known. The lithium and Grignard reagents are prepared in the usual manner and have been used to synthesize C₆Br₅Si(CH₃)₃, C₆Br₅Si(CH₃)₅, C₆Br₅CuCan and C₆Br₅AuPPh₃.

This gold(I) complex is oxidized both by halogen and thallic chloride to the gold(III) complex:

\[
C₆Br₅AuPPh₃ + C₆Br₅MgBr \xrightarrow{\text{halogen, thallic chloride}} C₆Br₅AuPPh₃ + MgBrCl
\]

Deacon has extended his work on pentahalobenzoates of mercury to obtain a number of pentabromophenyl mercurials. Mercuric pentabromobenzoate and
phenylmercuric pentabromobenzoate undergo decarboxylation in boiling pyridine to give bis(pentabromophenyl)mercury and pentabromophenylphenylmercury, respectively, in good yield.

\[
\begin{align*}
(C_6\text{Br}_5\text{COO})_2\text{Hg} & \rightarrow (C_6\text{Br}_5)_2\text{Hg} + 2\text{CO}_2 \\
\text{PhHgCOOC}_6\text{Br}_5 & \rightarrow \text{PhHgC}_6\text{Br}_5 + \text{CO}_2
\end{align*}
\]

Bis(pentabromophenyl)mercury is readily cleaved by triiodide ions in N,N-dimethylformamide and by mercuric chloride and bromide in xylene/nitrobenzene giving iodopentabromobenzene and pentabromophenylmercuric chloride and bromide, respectively. On heating, solid pentabromophenylphenylmercury and pentabromophenylmercuric chloride and bromide, thermal symmetrization is observed prior to melting, in contrast with the behaviour of the corresponding pentachloromercurials\textsuperscript{193,214}

\[
\begin{align*}
2\text{PhHgC}_6\text{Br}_5 & \rightarrow 100^\circ \rightarrow \text{Ph}_2\text{Hg} + (C_6\text{Br}_5)_2\text{Hg} \\
2C_6\text{Br}_5\text{HgX} & \rightarrow 250^\circ \rightarrow (C_6\text{Br}_5)_2\text{Hg} + \text{HgX}_2 \\
X &= \text{Cl, Br}
\end{align*}
\]
EXPERIMENTAL
1. GENERAL TECHNIQUES

All operations that involved lithium reagents were carried out under an atmosphere of oxygen-free, dry nitrogen. "White Spot" nitrogen obtained from the British Oxygen Company was additionally purified by passing it through a column containing self-indicating silica-gel, the last traces of water were then removed using a double-surface liquid nitrogen trap of type shown in Figure No. 7.

A combined vacuum-nitrogen, double-manifold line was used for all air-sensitive manipulations, see Figure No. 8. Normally reactions were carried out in "Quickfit" round-bottomed flasks with high vacuum taps as side arms, isolated from the atmosphere but connected to the nitrogen-vacuum system by rubber tubing. Stirring was performed using a combined magnetic stirrer-hot plate and PTFE coated followers.

Before use, apparatus was cleaned in chromic acid, washed with distilled water and acetone and then dried at 110° in an oven.

2. PURIFICATION OF SOLVENTS AND REAGENTS

Solvents (e.g. ether, THF, pentane etc) for water-sensitive reactions were dried by first refluxing them over sodium wire and then distilling them under nitrogen, immediately prior to use. Liquid perfluoroaromatic compounds were dried by the addition of molecular sieves.

3. n-BUTYL LITHIUM

n-Butyllithium was either obtained commercially (Foote Mineral Company) in hexane, or prepared from n-butyl bromide and lithium wire in ether. In the case of the prepared reagent, the precipitated lithium salts were filtered off under dry nitrogen to yield a very pale yellow filtrate. In both cases, the n-butyllithium was standardized prior to use by the method of Gilman 249.

4. CHROMATOGRAPHY

Thin layer chromatography (TLC) was carried out on glass plates using...
Vapour phase chromatography (vpc) was performed on Pye-Unicam instruments (Model 104 for analysis and Model 105 for preparative work); in each case the column-packing material was Chromosorb P or G (60/80 mesh) with varying concentrations of SE30 as the stationary phase. Hydrogen was the most usual carrier gas.

5. SPECTRA

Infrared (ir) spectra were recorded on a Perkin Elmer 457 grating spectrophotometer (4000-250 cm⁻¹) using liquid paraffin (nujol) and hexachlorobutadiene (HCBD) mulls, and frequencies are considered to be accurate to ± 5 cm⁻¹.

Mass spectra were recorded on an A.E.I. MS12 spectrometer by Dr. L. Kumar of this department, the Physico-chemical Measurement Unit (Harwell), and Queen Mary College, London.

6. X-RAY DATA

X-ray powder diffraction analyses were performed using a Philips PW1010 generator and a PW1050/25 goniometer with a nickel filter and a copper target, running at 1000W. The detector unit was a Philips PW1051 X-ray diffractometer.
To Vac. Line

N₂ in

B55 joint

25 cm approx.

Double Surface Liquid Nitrogen Trap.

B24 joint

Inert Atmosphere Filtration Apparatus
B. Mercury diffusion pump.

C. Double Surface Liquid Nitrogen Trap.
Preparation of $\text{C}_6\text{F}_4\text{Br}_2$

(i) From 1,2-Dihydrotetrafluorobenzene.

The reaction was carried out in a three-necked round bottomed flask fitted with a nitrogen inlet, condenser and pressure equalizing dropping funnel. Under a nitrogen atmosphere, the vessel was charged with 70ml of oleum, 3g of aluminium bromide and 32g of elemental bromide; the contents stirred with a glass covered magnetic stirrer. CARE. The 1,2-dihydrotetrafluorobenzene (15g, 0.1mole) was placed in the dropping funnel and added dropwise to the rapidly stirring reaction mixture over a 45 minute period. When all the organic reagent has been added, the reaction mixture was very slowly brought to reflux temperature. The mixture was stirred at reflux for six hours.

The reaction mixture was cooled to room temperature and cautiously poured onto ice contained in a five-litre beaker. The resultant mixture was extracted with diethyl ether and washed with, consecutively, sodium metabisulphite, sodium carbonate and water. The ethereal layer was finally dried over magnesium sulphate.

The mixture was fractionally distilled, and the component distilling over at 198°C collected. This fraction was identified by I.R. Spectrum and GLC analysis to be 1,2-dibromotetrafluorobenzene (20.45g, 66.4% yield).

(ii) From Bromopentafluorobenzene.

$n$-Butyllithium (3.33ml, 0.01mole, 3M) was added to an ethereal solution (150ml) of bromopentafluorobenzene (2.5g, 0.01mole) at $-78^\circ$ and stirred for 30 minutes, the solution being pale yellow in colour. The reaction mixture was allowed to warm to $-35^\circ$ and 2ml of bromine added. The mixture was then stirred at room temperature overnight. The ethereal solution was washed with 10% aqueous sodium thiosulphate and then with water. The ether layer was separated and dried over magnesium sulphate.
The mixture was fractionally distilled and the component distilling over at 198°C collected. This fraction was identified by I.R. spectrum and GLC analysis to be 1,2-dibromotetrafluorobenzene (2.1g, 40.9% yield).

**Preparation of 1,2,3-Tribromotrifluorobenzene \( C_6F_3Br_3 \)**

1,2-Dibromotetrafluorobenzene (5g, 0.016 mole) dissolved in 50ml of dry ether in a pressure-equalizing dropping funnel, was run into an ethereal solution of n-butyllithium (5.7ml, 0.008 mole, 1.4M) held at -78°C, over a period of 45 minutes-1 hour. The mixture was stirred at -78°C for 30 minutes, after the addition of all the 1,2-dibromotetrafluorobenzene, when 5g dry lithium bromide (dried at 200°C for 2 days, and cooled in vacuo over silica gel) were added. The reaction mixture was allowed to slowly warm to room temperature with continual stirring. At approximately 5°C, the reaction mixture became pale purple in colour which gradually became greyish as the temperature reached ambient. The reaction was stirred at room temperature overnight, giving a yellow ethereal solution and a large amount of greyish solid. This solid was filtered off and the filtrate evaporated to low bulk; further lithium bromide precipitated by addition of more pentane was filtered off to leave a pale yellow pentane filtrate.

GLC/mass spectrographic analysis of this pentane solution showed the presence of 1,2,3-tribromotrifluorobenzene, a component whose retention time was identical to that of 2,2'-dibromo-octafluorobiphenyl and a complex mixture of brominated polyphenyls. The tribromotrifluorobenzene was extracted by either of two methods:

i) **Preparative gas-liquid chromatography**

The pentane solution was concentrated to low bulk and the 1,2,3-tribromotrifluorobenzene separated from the mixture of bromofluoroaromatics by use of a Pye-Unicam Series 105 chromatograph.

ii) **Steam distillation**

Steam distillation of the mixture of bromofluoroaromatics was found to be a quick and convenient method for the separation of the 1,2,3-tribromotrifluorobenzene.
The first components to distil over were unreacted starting material and 1,2-dihydrotetrafluorobenzene and as the temperature of the mixture rose, the 1,2,3-tribromotrifluorobenzene distilled over as a viscous oil which solidified to a white powder on standing. If the vessel containing the mixture was heated externally, the 2,2'-dibromo-octafluorobiphenyl distilled slowly over and solidified in the condenser. The solids remaining were found, by analytical GLC and mass spectrometry to be a mixture of brominated polyphenyls.

By both the extraction methods, approximately 3.5g, 58.5% yield, of 1,2,3-tribromotrifluorobenzene was obtained, identified by mass spectrometry, I.R. spectrum and m.pt.

Reaction of bromopentafluorobenzene with n-butyllithium in the presence of excess lithium bromide

Bromopentafluorobenzene (5g, 0.02 mole) was diluted with 50ml of dry ether in a pressure-equalizing dropping funnel. Over a period of 45 mins, this was run into an ethereal solution of n-butyllithium (10.75ml, 0.01 mole, 0.94M) held at -78° in an acetone-dry ice bath. After 30 mins at this temperature, excess dry lithium bromide (dried at 200° for 2 days, and cooled in vacuo over silica gel) was added and the reaction mixture allowed to reach room temperature with continual stirring. The mixture was stirred at room temperature overnight when it was worked as the previous reaction.

Analytical GLC of the concentrated pentane solution showed the presence of 1,2-dibromotetrafluorobenzene and also the presence of a substantial quantity of 1,2,3-tribromotrifluorobenzene.

Reaction of 1,2-dibromotetrafluorobenzene with n-butyllithium in the presence of bromine

1,2-Dibromotetrafluorobenzene (10g, 0.032 mole) was diluted with 50ml of dry ether. Over a 45 min period this was run into an ethereal solution of
n-butyllithium (34.41ml, 0.032 mole, 0.94M) held at -78° in an acetone-dry ice bath. After stirring for 1 hour at this temperature, the reaction mixture was warmed slowly to -35° when 2ml of elemental bromine were added. The mixture was stirred at room temperature overnight. The ethereal solution was washed with sodium thiosulphate to remove excess bromine, dried over magnesium sulphate and concentrated to low bulk. Analytical GLC of this solution showed the presence of 1,2,3-tribromotrifluorobenzene in the mixture.

Preparation of 2-Bromononafluorobiphenyl C_{12}F_{2}Br

n-Butyllithium (41ml, 1.2M, 0.005 mole) was added to a solution of bromopentafluorobenzene (24.7g, 0.1 mole) in dry ether (125ml) at -78° and stirred for 20 minutes, when the solution was pale yellow in colour. The mixture was allowed to slowly reach room temperature. (At approximately 18°C, a vigorous exothermic reaction is observed, and to avoid an explosion, the reaction must be cooled to moderate the evolution of ether or an effective condensing system be present), and stirred overnight during which time considerable clouding occurred. Removal of solvent gave a pale yellow-brown solid from which the 2-bromononafluorobiphenyl can be extracted in two ways:

a) Sublimation at 60° - 70° in vacuo (10^{-4} mm) gives 14.6g (75% yield) of white crystalline 2-bromononafluorobiphenyl, m.pt 66° (lit.216 69-71°).

b) Steam distillation of the crude solids gives approximately the same yield of the desired product. The 2-bromononafluorobiphenyl distils over as an oil which solidifies on standing or on scratching the sides of the receiving vessel.

Preparation of 2-Hydrononafluorobiphenyl C_{12}F_{2}H

This compound can be prepared in two ways:

i) From pentafluorobenzene C_{6}F_{5}H

n-Butyllithium (41ml, 1.2M, 0.005 mole) was added to a solution of pentafluorobenzene (16.8gm, 0.01 mole) in dry ether (125ml) at -78° and stirred
for 20 minutes, when the reaction mixture was pale yellow in colour. The mixture was allowed to slowly reach room temperature and stirred overnight. Considerable clouding occurred and removal of solvent gave a yellow-brown solid. Sublimation at approximately $50^\circ$, $10^{-4}$ mm pressure yielded 12.8g (81% yield) of white crystalline 2-hydrofluorobiphenyl, identified by its I.R. spectrum.

ii) From 2-bromononafluorobiphenyl

n-Butyllithium (8.2ml, 1.2M, 0.01 mole) was added to a solution of 2-bromonafluorobiphenyl (3.95g, 0.01 mole) in dry ether (100ml) at $-78^\circ$ and stirred for 20 minutes. The reaction mixture became deep bottle-green in colour. The reaction mixture was allowed to slowly rise to $-30^\circ$ and 50ml of distilled water added. On warming to room temperature, a pale yellow ethereal layer and a slightly coloured aqueous phase remained. The ethereal layer was dried over magnesium sulphate and evaporated under reduced pressure to yield a pale yellow-brown solid which on sublimation gave 13.4g (84.8% yield) of white crystalline 2-hydrononafluorobiphenyl, identified by its I.R. spectrum and melting point: $43^\circ$.

**Reaction of pentafluorophenyllithium with 2-bromonafluorobiphenyl**

n-Butyllithium (9.5ml, 2.7M, 0.026 mole) was added to a solution of bromopentafluorobenzene (6.2g, 0.026 mole) in ether (75ml) at $-78^\circ$ and stirred for 45 minutes. A solution of 2-bromonafluorobiphenyl (3.3g, 0.008 mole) in ether (50ml) was added and the mixture allowed to reach room temperature and stirred overnight. Evaporation of the solvent gave a yellow-brown solid; the lithium halides present were precipitated by the addition of pentane and removed by filtration. When the pentane was removed under vacuum, a yellow brown viscous liquid remained. Analytical GLC indicated the presence in this of bromopentafluorobenzene, 2-bromonafluorobiphenyl, 2-hydrononafluorobiphenyl, 1,2-bis(pentafluorophenyl) -3-hydrotrifluorobenzene and two compounds of longer retention time in the ratio 4:1. Preparative GLC enabled the isolation of the latter two compounds as white solids; the first to elute was 1,2-bis(pentaflu-
-orophenyl) -3-bromotrifluorobenzene, m.pt. 102-104°. The second component was 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene, m.pt. 99-101°.

The two triphenyls were also extracted from the mixture of products by steam distillation. It was found that this latter method of extraction was the more convenient and simple, even though steam at approx. 200° had to be used.

Reaction of pentafluorophenyllithium with 2-bromonafluorobiphenyl in the presence of liquid paraffin

i) Liquid paraffin before n-butyllithium addition

Liquid paraffin (10ml) was added to a stirred solution of bromopentafluorobenzene (6.2g, 0.025 mole) in ether (75ml) at -78° followed by n-butyllithium (20ml, 1.28M, 0.025 mole); the colour became bright green. After 45 mins. at -78°, 2-bromonafluorobiphenyl (3.3g, 0.008 mole) was added and the mixture allowed to reach room temperature and stirred overnight. (As the reaction warmed to ambient, the colour changed progressively from bright green, through blue-green to a final yellow-green). The solvent was removed under vacuum and pentane added; filtration followed by evaporation of the solvent gave a very viscous yellow oil. Analytical GLC indicated the presence of unreacted starting material, 2-hydrononafluorophenyl, a small amount of 1,2-bis(pentafluorophenyl)-3-hydrotrifluorobenzene and one component of longer retention time corresponding to that of 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene. The identity of this component was verified by its m.pt. (99°), infrared and mass spectra.

ii) Liquid paraffin after n-butyllithium addition

A similar procedure was followed to that above, except that the liquid paraffin (10ml) was added after the mixture of bromopentafluorobenzene and n-butyllithium had been stirred at -78° for 20 minutes. The colour of the reaction mixture did not alter on addition of the liquid paraffin and the final colour was canary-yellow. Analytical GLC of the viscous oil resulting from work up, showed the presence of only the symmetrical triphenyl isomer, 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene in approximately the same yield as previously. The isomer was extracted from the mixture by a combination of
preparative GLC and steam distillation.

iii) Liquid paraffin after n-butyllithium and 2-bromononafluorobiphenyl addition
In a similar experiment, liquid paraffin was added after both n-butyllithium and 2-bromonabiphenyl had been placed in the reaction mixture; analytical GLC showed both triphenyl-isomers present in similar ratio to that in reaction (i).

Reaction of pentafluorophenyllithium with 2-lithiononafluorobiphenyl
n-Butyllithium (21.93ml, 1.14M, 0.025 mole) was added to a stirred solution of 2-bromononafluorobiphenyl (10g, 0.025 mole) in ether (100ml) at -78°C and stirred for 45 minutes; (the colour rapidly becoming deep bottle green). In a separate flask, n-butyllithium (21.93ml, 1.14M, 0.025 mole) was added to a solution of bromopentafluorobenzene (6.25g, 0.025 mole) in ether (100ml) and stirred at -78°C for 45 minutes; (the colour becoming very pale yellow). The solution of 2-lithiononafluorobiphenyl was then poured rapidly into the solution of bromopentafluorophenyllithium, still held at -78°C. The mixture was allowed to slowly warm to room temperature (at -5°C, bromopentafluorobenzene (12.5g, 0.05 mole) was added) and stirred overnight. The mixture slowly became cloudy and orange-brown in colour. Normal work-up gave an orange-yellow viscous oil; analytical GLC of which indicated the presence of bromopentafluorobenzene, 2-bromononafluorobiphenyl, 2-hydrononafluorobiphenyl and a complex mixture of components of higher retention times, none of which could be safely assigned to the desired products: 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene and 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene.

Reaction of 2-lithiononafluorobiphenyl with pentafluorophenylmagnesium bromide
n-Butyllithium (17.5ml, 1.14M, 0.02 mole) was added to a solution of stirred 2-bromononafluorobiphenyl (8g, 0.02 mole) in ether (100ml) at -78°C and stirred for 45 minutes, (colour bottle green). After adding pentafluorophenylmagnesium bromide (0.02 mole), the reaction mixture was allowed to reach room temperature overnight. Analytical GLC of the products indicated the presence of pentafluorobenzene, 2-bromo- and 2-hydronafluorobiphenyls and a mixture of unassigned
components of higher retention time.

Reaction of 1,2-bis(pentafluorophenyl)-3-lithiotrifluorobenzene with pentafluorophenyllithium in the presence of bromine

n-Butyllithium (20.45 ml, 0.45M, 0.0092 mole) was added to a solution of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene (5g, 0.0092 mole) in ether at -78° and stirred for 45 minutes; the colour rapidly became deep bottle green. In a separate flask, n-butyllithium (20.45 ml, 0.45M, 0.0092 mole) was added to bromopentafluorobenzene (2.28g, 0.0092 mole) in ether at -78° and stirred for 45 minutes; on warming to -20° the two solids were mixed together and stirred for a further 30 minutes. The reaction mixture was warmed to -7° and bromine (0.75g, 0.25ml, 0.0092 mole) added before stirring was continued at room temperature overnight. Work-up and analytical GLC showed the presence in the products of bromopentafluorobenzene and a component of retention time corresponding to that of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene.

Preparation of Perchloryl Fluoride CLO₃F

The preparation was carried out in ordinary glass apparatus. Potassium perchlorate (10g, 0.08 mole) in a 250ml round-bottomed flask was treated with fluorosulphonic acid (100g, 1 mole) from a dropping funnel. Whilst slowly stirring the mixture, the temperature of the reaction vessel was raised cautiously; at about 50°C, perchloryl fluoride began to form and was passed, via PVC or Teflon tubing, over a solution of aqueous 10% sodium hydroxide containing 5% sodium thiosulphate and then bubbled through a similar solution. The scrubbed gases were passed over potassium hydroxide pellets and condensed in a trap cooled in acetone-dry ice. The reaction proceeded rapidly around 85°C and the product was finally swept out of the system with dry nitrogen. The reaction remained liquid at all times; the solution changing progressively from colourless through yellow, orange, dark brown, red and finally back to colourless; these changes are caused mainly by the decomposition of (ClO₂)₂S₃O₁₀. About 5g of pure perchloryl fluorine (67% based on potassium perchlorate) were produced in this way.
The product was further purified by fractional distillation in a glass vacuum system—the colourless, volatile liquid was stored at $-78^\circ$. It must be noted that on one occasion when air was let into the vacuum system, a violent explosion occurred due, possibly, to the presence of chlorine oxide by-products. The identity of the perchloryl fluoride was confirmed by gas-phase I.R. spectrum.

**Reaction of pentafluorophenyllithium with perchloryl fluoride**

n-Butyllithium (6.1ml, 0.012 mole, 2M) was added to a stirred solution of bromopentafluorobenzene (3g, 0.012 mole) in ether (100ml) held at $-78^\circ$. After stirring for 30 minutes, the reaction flask was frozen at $-196^\circ$ and approximately 2ml of perchloryl fluoride condensed in. The mixture was then stirred at $-78^\circ$ for 1 hour and slowly warmed to room temperature overnight. The resultant mixture was filtered and the filtrate concentrated; analytical GLC showed the presence of hexafluorobenzene, which was isolated by fractional distillation: 1.88g, (83%), boiling at 81$^\circ$C. The identity of the hexafluorobenzene was verified by its infrared and mass spectrometry.

**Reaction of 1-lithio-2-bromotetrafluorobenzene with perchloryl fluoride**

n-Butyllithium (4.9ml, 0.097 mole, 2M) was added to a stirred solution of 1,2-dibromotetrafluorobenzene (3g, 0.097 mole) in ether (100 ml), held at $-78^\circ$. After stirring for 30 minutes, the reaction flask was frozen at $-196^\circ$ and approximately 2ml of perchloryl fluoride condensed in. The reaction mixture was then stirred for 1 hour at $-78^\circ$ and slowly warmed to room temperature overnight. The resultant cloudy mixture was filtered and the filtrate concentrated. Analytical GLC showed the presence of bromopentafluorobenzene, which was fractionally distilled out as a liquid boiling at 137$^\circ$; 16g (68%) yield.

**Reaction of 2-lithiononafluorobiphenyl with perchloryl fluoride**

n-Butyllithium (3.8ml, 2M, 0.0076 mole) was added to a stirred solution of 2-bromononafluorobiphenyl (3g, 0.0076 mole) in ether (100 ml), held at $-78^\circ$. After stirring for 30 minutes, the reaction flask was frozen at $-196^\circ$ and approximately 2ml of perchloryl fluoride condensed in. The reaction mixture was then stirred for 1 hour at $-78^\circ$ and slowly warmed to room temperature overnight.
The resultant opaque pale yellow mixture was filtered and the filtrate concentrated. Analytical GLC showed the presence of decafluorobiphenyl. The mixture was sublimed at 100-120° at 10⁻⁴ mm to yield white crystals, 1.83g (73%) yield, identified by infrared and mass spectral analysis, m.pt. 67.5° (lit. 216 68-69°)

**Preparation of 1,2-diiodotetrachlorobenzene C₆Cl₄I₂**

To mercuric oxide (13g, 60m mole) in a 250ml flask were added 15ml trifluoroacetic acid and the mixture heated at reflux temperature until all the mercuric oxide had dissolved (a magnetic stirring bar-glass coated-greatly assisted the breaking up of the lumps of mercuric oxide). The temperature of the oil bath was raised to 230°C, to allow water and excess trifluoroacetic acid to distil out of the flask; a precipitate was sometimes observed at this point, but heating at 230 for about 30 minutes removed this, to give a clear melt of mercuric trifluoroacetate. 1,2-Dihydrotetrachlorobenzene (2.14g, 10m mole) was added in one portion A vigorous evolution of trifluoroacetic acid ensured and the reaction mixture solidified within 2 minutes. When no further reaction was evident (usually 10 minutes at 230° were sufficient), the flask was cooled to room temperature.

The mercurated residue was dissolved in approximately 50ml of dimethylformamide. This solution was added in one portion to a flask containing iodine (10.1g, 40m mole in 100ml of dimethylformamide. The mixture was stirred at 100°C for 30 minutes until the iodine colour had disappeared. 200ml of 10% aqueous potassium bromide was added to the cooled solution, which was shaken well and filtered. The product was dried over silica gel in vacuo and recrystallized from toluene/petrol (100-120°C). Yield 65%; M.pt. 230-234°C.

**Preparation of Iodopentachlorobenzene C₆Cl₅I**

A similar procedure, to that above, was followed except that pentachlorobenzene (20m mole) was used instead of 1,2-dihydrotetrachlorobenzene. In this instance, the reaction mixture of mercuric trifluoroacetate and pentachlorobenzene remained molten at 230°C.
Preparation of Bis(2,3,4,5-tetrachlorophenyl)mercury \((\text{C}_6\text{Cl}_6\text{H})_2\text{Hg}\)

1,2-Dihydrotetrachlorobenzene (10.5g, 48.5m mole) and mercuric trifluoroacetate (5.2g, 12.2m mole) were heated for 46 hours in a long open tube (approximately 1 foot in length) at 200°C. Evolution of trifluoroacetic acid was incomplete as evidenced by the presence of trifluoroacetate in the crude mercurial (4.2g, m.pt ca. 150°C). This crude material was washed with hexane to remove excess arene and then crystallized from xylene (100ml). A white flocculent material did not dissolve (0.4g, m.pt > 360°C) and this was filtered off. The filtrate was concentrated to 50ml when pure bis(2,3,4,5-tetrachlorophenyl)mercury crystallized out on cooling (1.1g, 12% yield). The filtrate was evaporated to 25ml and a further amount of product precipitated (1.6g, 18% yield). The I.R. spectrum was identical to that quoted by Deacon; m.pt 258°C; lit192 259-260°C.

Preparation of Bis(pentachlorophenyl)mercury \((\text{C}_6\text{Cl}_5\text{H})_2\text{Hg}\).

A similar procedure, to that above, using pentachlorobenzene gave bis(pentachlorophenyl)mercury in 32% yield; m.pt > 360°C (lit192 383°C).

Preparation of Pentachlorophenylmagnesium chloride \((\text{C}_6\text{Cl}_5\text{MgCl})\)

The preparation was carried out in a three-necked flask equipped with a nitrogen inlet, a condenser and a magnetic stirring bar. With dry nitrogen passing through the system, several ml of a solution of ethylmagnesium bromide, \(\text{C}_2\text{H}_5\text{MgBr}\) in THF (obtained previously from magnesium and ethyl bromide) were added to a warm suspension of magnesium (0.48gm, 0.02 mole) and hexachlorobenzene (5.69g, 0.02 mole) in 20ml of THF. The warming was effected by means of a magnetic stirrer-hotplate. The heating was discontinued when all the ethylmagnesium bromide solution has been added, but the stirring was maintained until the solution of pentachlorophenylmagnesium chloride reached room temperature. At the end of this period, no insoluble hexachlorobenzene was visible in the flask, and the solution was a clear deep magenta in colour.

Reaction of pentachlorophenylmagnesium chloride with sulphur dichloride

i) In situ method
A solution of hexachlorobenzene (5.69g, 0.02 mole), magnesium (0.48g, 0.02 mole), 0.6ml of benzyl chloride and sulphur dichloride (1.03gm, 0.01 mole) in 40ml THF/benzene was heated under nitrogen at reflux for several hours. This solution darkened and became orange-yellow in colour. On cooling the filtered solution was concentrated under reduced pressure, and the solid remaining washed with water to remove any magnesium chloride. The solid was dried over silica gel under vacuo and then placed in a sublimation apparatus. A white solid sublimed (at 120°C, 10⁻²mm) whose I.R. spectrum and GLC separation showed it to be unreacted hexachlorobenzene. No further sublimate was obtained between 120°C and 300°C.

ii) With the previous preparation of the Grignard reagent solution.

To a solution of pentachlorophenylmagnesium chloride (0.02 mole) in THF at room temperature, sulphur dichloride (1.03g, 0.01 mole) in 25ml dry THF was added dropwise, via a pressure equalizing funnel, over a period of 30 minutes. At the end of this period, the reaction mixture had darkened slightly and was slightly opaque. The mixture was stirred, at room temperature, for one hour when a white solid was precipitated. The THF was removed at reduced pressure and the solid washed with water and dried over silica gel to give a resultant grey-brown solid which gave a mixture of pentachlorobenzene and unreacted hexachlorobenzene on sublimation (identified by I.R. and GLC analyses).

iii) Heated at reflux.

An identical procedure was carried out to that in (ii) except that after the addition of all the sulphur dichloride solution, the reaction mixture was heated at reflux for four hours. The reaction mixture darkened and a white solid was precipitated. On working up, the reaction only yielded pentachlorobenzene and hexachlorobenzene as the major products.

Reaction of pentachlorophenylmagnesium chloride with disulphur dichloride

To a stirred solution of pentachlorophenylmagnesium chloride (0.02 mole) in THF, a solution of disulphur dichloride (1.35g, 0.01 mole) in THF was added dropwise over a period of 30 minutes. During the addition, a large amount of precipitation
was observed. The reaction mixture was stirred at room temperature for one hour after which time, the mixture was red-brown in colour. The THF was removed under reduced pressure and the solid washed with water, filtered and dried. Sublimation of the solid yielded only pentachlorobenzene and unreacted hexachlorobenzene.

The reaction was repeated in a similar manner, except that after the addition of the disulphur dichloride, the reaction mixture was refluxed for four hours. Pentachlorobenzene and unreacted hexachlorobenzene were the only identifiable products.

**Reaction of pentachlorophenylmagnesium chloride with selenium tetrachloride**

In a similar reaction to that described above, selenium tetrachloride (1.10g, 0.005 mole) was added to a stirred solution of pentachlorophenylmagnesium chloride in THF at room temperature. A reaction at reflux was also performed. In both cases pentachlorobenzene and hexachlorobenzene were the only identifiable products after working up of the reaction mixtures.

**Reaction of pentachlorophenylmagnesium chloride with silicon tetrachloride**

In a similar reaction to that described above, silicon tetrachloride (0.85g, 0.005 mole) was added to a stirred solution of pentachlorophenylmagnesium chloride in THF at room temperature. A reaction at reflux temperature was also carried out. Pentachlorobenzene and hexachlorobenzene were the only products after working up of the reaction mixtures.

**Reaction of pentachlorophenylmagnesium chloride with tellurium tetrachloride**

In a similar reaction to that described above, tellurium tetrachloride (1.35g, 0.005 mole) was added to a stirred solution of pentachlorophenylmagnesium chloride in THF at room temperature and at reflux. Hexachlorobenzene and pentachlorobenzene were the only products identified after work up.

**Reaction of pentachlorophenylmagnesium chloride with tetraphenylarsonium chloride**

To a stirred solution of pentachlorophenylmagnesium chloride (0.02 mole) in THF at room temperature, tetraphenylarsonium chloride, \( \text{Ph}_4\text{AsCl} \), (8.28g, 0.02 mole) was
added. The tetraphenylarsonium chloride dissolved and the clear magenta reaction mixture was refluxed for 18 hours. After which time the reaction mixture had darkened slightly and became opaque. The THF was removed under reduced pressure and water added to destroy any Grignard reagent present. The resultant solid was extracted with ether. The dark brown ethereal layer was dried over magnesium sulphate. Sublimation of the dark brown solid resulting from removal of ether yielded only unreacted tetraphenylarsonium chloride. Sublimation of the ether insoluble solid gave only pentachlorobenzene.

Reaction of pentachlorophenylmagnesium chloride with triphenylphosphine

In a similar reaction to that described above, triphenylphosphine (5.18g, 0.02 mole), was added to a stirred solution of Grignard reagent. After refluxing for 16 hours and working up only unreacted triphenylphosphine and pentachlorobenzene were the identifiable products.

Reaction of pentachlorophenylmagnesium chloride with triphenylarsine

In a similar reaction, triphenylarsine (6.06g, 0.02 mole) was added to a stirred solution of the Grignard reagent. After refluxing for 16 hours, and working up only unreacted triphenylarsine and pentachlorobenzene were the identifiable products.

Reaction of pentachlorophenylmagnesium chloride with diphenyldichlorosilane

Similarly, diphenyldichlorosilane (2.5g, 0.01 mole) was refluxed with a stirred solution of the Grignard reagent for 16 hours. Working up only yielded pentachlorobenzene.

Preparation of pentachlorophenyllithium \(C_6Cl_5\text{Li}\)

i) In diethyl ether

The reaction was carried out in a three-necked flask equipped with a nitrogen inlet, a condenser, a pressure-equalizing addition funnel and a magnetic stirring bar. With dry nitrogen passing through the system, hexachlorobenzene (5.69g, 0.02 mole) was added to the flask followed by 400ml of purified ethyl ether. An equimolar quantity of n-butyllithium in hexane was added to the addition funnel by means of a syringe. The contents of the flask were cooled to \(-10^\circ\text{C}\) by means
of an ice-salt bath. With rapid stirring, the n-butyllithium solution was added slowly over 30 to 45 minutes. At the end of this period, no insoluble hexachlorobenzene was visible in the flask and the solution of pentachlorophenyllithium was yellow-brown in colour.

ii) In tetrahydrofuran

A similar procedure was followed to that described in (i) except that a low temperature alcohol thermometer was inserted into the flask. The contents were cooled to approximately \(-78^\circ\) by means of an acetone-dry ice bath. The n-butyllithium solution was added dropwise, with stirring, so as to maintain the reaction at \(-78^\circ\). Following the addition the reaction mixture was stirred for an additional 20 minutes at \(-78^\circ\), after which time very little solid hexachlorobenzene was visible, and the reaction mixture had assumed a yellow-brown colour.

Reaction of pentachlorophenyllithium with sulphur dichloride

Sulphur dichloride (0.63ml, 1.03g, 0.01 mole) was diluted with approximately 50ml of dry ether and added via an addition funnel over a period of 30 minutes to pentachlorophenyllithium (0.02 mole) prepared in ethyl ether solution. The reaction mixture was maintained with stirring at \(-10^\circ\) during the addition and then allowed to warm to room temperature with stirring over a period of 24 hours. At the end of this period, the vessel contained an amount of yellow-orange solid and an orange ethereal solution. The solid was filtered off and washed with warm water to remove lithium salts, and then dried over silica gel in vacuo. This solid was extracted with chloroform to give a bright orange solution which yielded a quantity of orange-brown solid on removal of the solvent. Mass spectral analysis of this solid indicates a mixture of general formula \((C_6Cl_5)_2S_x, x = 1, 2, 3\).

Reaction of pentachlorophenyllithium with selenium tetrachloride

Selenium tetrachloride (1.1g, 0.005 mole) was added to pentachlorophenyllithium (0.02 mole) prepared in ethyl ether solution. The reaction mixture became immediately bottle green in colour, and was allowed to warm slowly from \(-10^\circ\) to room temperature with continual stirring over a period of 24 hours. The vessel, then contained some orangey solid and a yellow-orange ethereal solution. The
solid was filtered off, washed with warm water and dried over silica gel, under vacuo. This solid was then extracted with chloroform. On removal of the solvent from dark brown extract, a dark red-brown solid was obtained. This was sublimed to give a white product, identified as pentachlorobenzene by infrared and mass spectral analysis. The dark-brown solid was found to contain mostly pentachlorobenzene by mass spectral studies.

**Reaction of pentachlorophenyllithium with tellurium tetrachloride**

Tellurium tetrachloride (1.3g, 0.005 mole) was added to an ethereal solution of pentachlorophenyllithium (0.02 mole) held at -10° in an ice-salt mixture. The reaction mixture became pale yellow and a slight precipitate was observed. The mixture was allowed to reach room temperature and stirred for 24 hours. The bright orange-yellow precipitate was filtered off, washed with warm water, dried, and extracted with chloroform to yield an orange solid. This was sublimed at 70-80°C to give a white crystalline product which was identified as pentachlorobenzene by infrared and mass spectral analysis. Pentachlorobenzene was shown to be the main constituent of the orange solid by mass spectrometry.

**Reaction of pentachlorophenyllithium with silicon tetrachloride**

Silicon tetrachloride (0.6ml, 0.85gm, 0.005 mole) diluted in 50ml of dry ether, was added to an ethereal solution of pentachlorophenyllithium (0.02 mole) held at -10° over a period of 30 minutes. No colour change was observed, but on warming to room temperature, the mixture changed from a dark chocolate-brown to a dark yellow-brown. The reaction mixture was stirred for 24 hours at room temperature and filtered. The solid collected was washed with warm water, dried and extracted with chloroform to yield a honey-coloured product. This was sublimed at 70°-80°C to give a white crystalline product which was identified as pentachlorobenzene by infrared and mass spectral analysis. Pentachlorobenzene was shown to be the main constituent of the honey-coloured solid by mass spectrometry.
Reaction of bis(pentachlorophenyl)mercury with

i) Sulphur

Bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and sulphur (0.5g, 0.015 mole) were heated in an evacuated sealed tube at 250\(^\circ\) for 7 days; on cooling, the tube contained a quantity of charred material and some white crystals. When the tube was opened a distinct odour of sulphur dichloride was noticed. (The presence of sulphur dichloride as a product was verified in a separate experiment by its infrared spectrum). After extraction of the products with ether, removal of the solvent at 0\(^\circ\) yielded a pale yellow solid, which on vacuum sublimation at 50-60\(^\circ\) gave hexachlorobenzene (46%), m.pt 215\(^\circ\). Further sublimation at 100-120\(^\circ\) yielded a small quantity of reddish material, which was identified by X-ray powder diffraction as mercuric sulphide; further quantities of mercuric sulphide were identified in the involatile residues.

ii) Selenium

Bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and selenium (0.5g, 0.0063 mole) were heated in an evacuated sealed tube at 250\(^\circ\) for 7 days. On cooling, the tube was found to contain colourless crystals but the bulk solids were green flecked with red. The colourless crystals were identified as hexachlorobenzene (18%) by infrared spectroscopy; sublimation at 50-60\(^\circ\) yielded a further quantity of hexachlorobenzene (20%), but no further products were obtained on attempted sublimation between 60\(^\circ\) and 200\(^\circ\); X-ray powder diffraction analysis of the residual solid showed no identifiable products were present.

iii) Tellurium

Under the same conditions, bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and tellurium (0.5g, 0.004 mole) gave hexachlorobenzene as the only identifiable product; X-ray powder diffraction analysis of the bulk solids showed them to be mainly unreacted starting materials.

iv) Antimony

Bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and antimony (0.5g, 0.004 mole)
were heated in an evacuated sealed tube at 250° for 7 days. After this period, no reaction was observed. Analysis of the solids showed only unreacted starting materials.

v) Arsenic
Although, bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and arsenic (0.5g, 0.0067 mole) remained essentially unreacted after 7 days at 250°, a small amount of pentachlorobenzene was isolated.

vi) Germanium
Under the same conditions no reaction occurred between bis(pentachlorophenyl)mercury (1g, 0.0014 mole) and germanium (0.5g, 0.0069 mole).

The above transmetallations were attempted at temperatures ranging from 150° to 350° and with varying ratios of organomercurial to metal for varying lengths of time. In all cases, no reaction was observed at the low temperatures, whereas extensive charring occurred at high temperatures. In those cases where reactions did occur, hexachlorobenzene was the only identifiable organic product (except for the case of arsenic at 250°, mentioned above); X-ray powder diffraction analysis showed only inorganic mercury compounds in the residual solids. Attempts were made to extract the contents of each tube with ether, acetone, chloroform, hexane, benzene, toluene and xylene; the residues were subjected to sublimation at varying temperatures. The end result in all cases was confirmation of hexachlorobenzene, inorganic mercury compounds or unreacted starting materials.

Reaction of bis(2,3,4,5-tetrachlorophenyl)mercury with

i) Sulphur
Bis(2,3,4,5-tetrachlorophenyl)mercury (1g, 0.0016 mole) and sulphur (1g, 0.03 mole) were heated in an evacuated sealed tube at 250° for 7 days. After this time, the tube was found to contain a quantity of white crystals and black bulk solid.
On opening, pungent fumes were observed (these fumes were identified, later, as a mixture of hydrogen chloride and sulphur chlorides by vapour phase infrared analysis). The white crystals were removed and identified as 1,2-dihydrotetrachlorobenzene (38%) by infrared, mass spectral and X-ray diffraction studies, m.pt. 57°C. Sublimation at 120°C gave a reddish product whose infrared spectrum showed it to contain 1,2-dihydrotetrachlorobenzene; X-ray diffraction analysis identified the other component as mercuric sulphide. Mercuric sulphide was also the major constituent of the residues.

ii) Selenium
Similarly, bis(2,3,4,5-tetrachlorophenyl)mercury (1g, 0.0016 mole) and selenium (0.5g, 0.0063 mole) gave hydrogen selenide, 1,2-dihydrotetrachlorobenzene (23%) and mercury selenide as the identifiable products.

iii) Arsenic
Bis(2,3,4,5-tetrachlorophenyl)mercury (1g, 0.0016 mole) and arsenic (0.5g, 0.0067 mole) were heated in a sealed tube at 250°C for 7 days. On cooling, globules of mercury were observed, along with white crystals of 1,2-dihydrotetrachlorobenzene.

iv) Tellurium, Germanium, Antimony
Bis(2,3,4,5-tetrachlorophenyl)mercury did not react with tellurium, germanium or antimony on being heated to 250°C for 7 days.

In summary, it was found that at temperatures lower than 250°C, no reaction was observed, whereas, above 250°C extensive charring took place. At the intermediate temperature of 250°C, where reaction did occur, only 1,2-dihydrotetrachlorobenzene and inorganic mercury compounds could be identified.
Action of heat on bis(pentachlorophenyl)mercury

Bis(pentachlorophenyl)mercury (1g, 0.0014 mole) was heated in an evacuated sealed tube at 250° for 7 days. On cooling a quantity of white crystalline solid was observed in the cooler parts of the tube. (The tube was heated in a muffle furnace, there being a temperature gradient of a few °C from the front to the rear of the furnace). On opening, these crystals were proved to be sublimed starting material by I.R. spectroscopy. The bulk solid was also unreacted starting material.

When bis(pentachlorophenyl)mercury was heated in vacuo at 350° and the contents sublimed onto a -18° probe, a small quantity of white solid was collected. This was identified as hexachlorobenzene (12%) by I.R. and mass spectroscopy.

At higher temperatures, extensive charring occurs and no identifiable product was obtained.

Action of heat on bis(2,3,4,5-tetrachlorophenyl)mercury

Bis(2,3,4,5-tetrachlorophenyl)mercury was heated in vacuo at 275° for 7 days. Only starting material was found to be present. On heating at 375° for 7 days, some material sublimed to the cooler end of the tube; this was identified as 1,2-dihydrotetrachlorobenzene by I.R. and mass spectroscopy. A further quantity was isolated by sublimation at 75°. Total yield of 1,2-dihydrotetrachlorobenzene being 0.06g, 18%.

Reaction of iodopentachlorobenzene with

i) Sulphur

Iodopentachlorobenzene (0.5g, 0.0013 mole) and sulphur (0.15g, 0.0047 mole) were heated in a sealed evacuated tube at 210° for 3 days. (The tube became full of purple iodine fumes after approximately 1 hour at this temperature). After cooling the solids were extracted with ether to give a deep red-brown solution. This was washed first with aqueous thiosulphate (to remove dissolved iodine) then water, and then the ethereal layer dried over magnesium sulphate.
On removal of the solvent, a pale yellow solid was obtained, which on sublimation at $50^\circ$ gave a white crystalline product which was identified as iodopentachlorobenzene by I.R. spectroscopy. No further sublimate was obtained between $50^\circ$ and $200^\circ$; X-ray diffraction analysis of the residual solids indicated the presence of sulphur and iodopentachlorobenzene.

ii) Selenium

Iodopentachlorobenzene (0.5g, 0.0013 mole) and selenium (0.4g, 0.0052 mole) were heated in an evacuated sealed tube at $210^\circ$ for 3 days. (At the end of this time the tube was full of purple iodine fumes). On cooling, the content of the tube was extracted with ether. This was washed with aqueous sodium thiosulphate, to remove dissolved iodine, water and the pale yellow ethereal layer dried over magnesium sulphate. On the removal of the solvent, a pale yellow solid was obtained which on sublimation at $50^\circ$ gave a white solid product. This was identified as iodopentachlorobenzene by I.R. spectroscopy. No further sublimate was obtained between $50^\circ$ and $200^\circ$; X-ray diffraction analysis of the residual solids indicated the presence of selenium and iodopentachlorobenzene.

iii) Tellurium

Iodopentachlorobenzene (0.5g, 0.0013 mole) and tellurium (0.66g, 0.0052 mole) were heated in an evacuated sealed tube at $210^\circ$ for 3 days. (No iodine vapour was observed in the reaction tube). On extraction with ether, a pale yellow solid was obtained which was identified as unreacted iodopentachlorobenzene.

iv) Germanium

Iodopentachlorobenzene (0.5g, 0.0013 mole) and germanium (0.38g, 0.0052 mole) were heated in a sealed evacuated tube at $210^\circ$ for 3 days. (A very slight amount of iodine vapour was observed). On working up, only iodopentachlorobenzene was found.

v) Arsenic, Antimony

With these metals, reaction with iodopentachlorobenzene at $210^\circ$ for 3 days,
a small amount of reddish material was isolated. X-ray powder analysis showed this to be the corresponding inorganic iodides. The only other product to be found was unreacted iodopentachlorobenzene.

The above reactions were attempted at temperatures varying from $150^\circ$ to $350^\circ$ with varying ratio of iodopentachlorobenzene and metal, for varying lengths of time. It was found that at low temperatures, no reaction occurred; extensive charring occurring at high temperatures. At $275^\circ$, using an iodopentachlorobenzene: metal ratio of 1:4, however, reaction did occur. Although a large amount of charring occurred, it was possible to isolate a small quantity of white crystalline solid from all reactions; this was shown to be hexachlorobenzene by infrared and mass spectrometry. X-ray diffraction studies also proved the presence of the corresponding metal iodides.

Reaction of 1,2-diiodotetrachlorobenzene with

i) Sulphur

1,2-diiodotetrachlorobenzene (1g, 0.002 mole) and sulphur (0.5g, 0.016 mole) were heated in a sealed evacuated tube at $200^\circ$ overnight. The tube became full of purple iodine vapour over approximately 6 hours at this temperature. On cooling, the contents of the tube were extracted with ether, washed with aqueous sodium thiosulphate, water and the ether layer dried over magnesium sulphate. Removal of solvent yielded an off white solid. Sublimation at 50-60$^\circ$ gave a white solid (8%) identified as hexachlorobenzene by I.R. spectroscopy. No further sublimate was obtained between 50$^\circ$ and 200$^\circ$; X-ray diffraction analysis of the residual solids indicated the presence of sulphur, hexachlorobenzene and some 1,2-diiodotetrachlorobenzene.

ii) Selenium

1,2-Diiodotetrachlorobenzene (1g, 0.002 mole) and selenium (0.5g, 0.0064 mole) were heated in an evacuated sealed tube at $200^\circ$ for 3 days. (At the end of this time the tube was full of purple iodine vapour). On cooling, the contents of the tube were extracted with ether. This was washed with aqueous sodium thiosulphate, to remove dissolved iodine, water and the pale yellow ethereal
layer dried over magnesium sulphate. On removal of the solvent, a pale yellow solid was obtained which on sublimation at 50° gave a white solid product. This was identified as 1,2-diodotetrachlorobenzene by I.R. spectroscopy. No further sublimate was obtained between 50° and 200°; X-ray diffraction analysis of the residual solids indicated the presence of selenium and 1,2-diodotetrachlorobenzene.

iii) Tellurium

1,2-Diodotetrachlorobenzene (1g, 0.002 mole) and tellurium (0.5g, 0.0039 mole) were heated in an evacuated sealed tube at 200°C for 3 days (No iodine vapour was observed in the reaction tube). On extraction, with ether, a pale yellow solid was obtained which was identified as unreacted 1,2-diodotetrachlorobenzene.

iv) Germanium

1,2-Diodotetrachlorobenzene (1g, 0.002 mole) and germanium (0.5g, 0.0069 mole) were heated in a sealed evacuated tube at 200°C for 3 days. On working up, only diiodotetrachlorobenzene was found.

v) Arsenic, Antimony

With these metals, reaction with 1,2-diodotetrachlorobenzene at 200° for 3 days, a small amount of reddish material was isolated. X-ray analysis showed this to be the respective inorganic iodides. The only other product to be found was unreacted 1,2-diodotetrachlorobenzene.

vi) Mercury

1,2-Diodotetrachlorobenzene (1g, 0.002 mole) and mercury (1.5g, 0.0075 mole) were heated in an evacuated sealed tube at 200°C for 3 days. No reaction was observed and the temperature was increased to 300°C. Heating was continued for 7 days, after which time the tube contained a quantity of red crystals (identified as mercuric iodide by X-ray diffraction analysis) and white solid. This white solid proved insoluble in common organic solvents and sublimed in vacuo only at 300°. X-ray diffraction analysis showed the product not to be 1,2-diodotetrachlorobenzene. The compound was identified as bis(iodotetrachlorophenyl)mercury, Hg(C₆C₄I)₂, by mass spectrometry.
INFRARED SPECTRA
Infrared absorptions are quoted in cm$^{-1}$ for mulls in liquid paraffin, using CsI optics, except where otherwise stated.

(s-strong, m-medium, w-weak, sh-shoulder, d-doublet and br-broad).

$\text{C}_6\text{F}_5\text{Br}$ (neat liquid): 1599m, 1510sbr, 1433wbr, 1370m, 1339m, 1300wbr, 1200wbr, 1159m, 1125m, 1095s, 1085sh, 1071m, 1030sh, 1010s, 983s, 893s, 745w, 720m, 722m, 500m, 369m, 355m, 312m.

$\text{C}_6\text{F}_4\text{Br}_2$ (neat liquid): 1613m, 1572w, 1538m, 1510ssh, 1500s, 1465s, 1410w, 1355m, 1345w, 1315w, 1275m, 1121s, 1083w, 1039s, 1020w, 980wbr, 853s, 808s, 641w, 475w, 370w, 345w, 295w, 270w.

$\text{C}_6\text{F}_3\text{Br}_3$: 1593m, 1535w, 1508msh, 1415s, 1329w, 1319w, 1285w, 1238m, 1228m, 1090msh, 1075s, 960wbr, 946m, 935m, 920w, 858w, 843w, 803s, 795msh, 765w, 735s, 713m, 658s, 640w, 360m, 331w, 285w.

$\text{C}_{12}\text{F}_{19}$: 1629m, 1603wbr, 1404w, 1379sbr, 1309s, 1288w, 1275wsh, 1215sh, 1205m, 1170w, 1155w, 1140w, 1092s, 1071msh, 1040wsh, 1030s, 1008ssh, 992s, 940m, 865m, 795w, 745s, 725w, 700s, 690m, 651w, 582w, 562w, 470w, 335m.

$\text{C}_{12}\text{F}_{19}$: 1655m, 1630m, 1600w, 1528s, 1510ssh, 1502s, 1309m, 1280m, 1265w, 1150w, 1108s, 1052s, 1025m, 992s, 956s, 835s, 797w, 775w, 720s, 715ssh, 370wbr, 345m.

$\text{C}_{12}\text{F}_5\text{Br}_2$: 1620brd, 1510sh, 1502s, 1485s, 1421m, 1338w, 1330w, 1271m, 126m, 1139w, 1115s, 1090sh, 1075m, 1035s, 1028s, 948s, 835sh, 835s, 778w, 770w, 718s, 710sh, 640w, 465w, 415wbr, 370wbr, 350w.

$\text{C}_6\text{F}_3\text{Br}_2$ (sym): 1660mbr, 1615mbr, 1600w, 1540sh, 1530sbr, 1510sh, 1508s, 1415m, 1291w, 1267w, 1210wbr, 1150m, 1130-1105m, 1075s, 1060sh, 1020s, 995sbr, 945s, 855sh, 838s, 805wbr, 775s, 741sh, 731sh, 725m, 712m, 700w, 675w, 655s, 643m, 610w, 578w, 485w, 375w, 355w, 312w.

$\text{C}_6\text{F}_3\text{Br}_2$ (unsym): 1660mbr, 1622mbr, 1595m, 1545sh, 1530s, 1508s, 1490s, 1410m, 1360sh, 1335w, 1293m, 1265sh, 1255m, 1205wbr, 1155m, 1115s, 1110sh, 1080s, 1045w, 1020s, 1000s, 995sh, 947s, 852m, 805w, 770w, 743m, 721s, 711m, 675s, 661m, 640w, 632w, 609w, 580w, 495w, 480w, 455w, 385w, 352w, 339w, 313w.
$C_{6-3}F_{(C_{6-5})_{2}H_{(unsym)}}$: 1660m, 1611m, 1595m, 1528m, 1515s, 1475s, 1419m, 1380m, 1365m, 1300mbr, 1260mbr, 1200w, 1150mbr, 1115sh, 1100s, 1070s, 1010sh, 995s, 945m, 930m, 875m, 855w, 839m, 802m, 788sh, 775m, 759w, 745m, 725sh, 715s, 691w, 679wbr, 655m, 641w, 629m, 580w, 563w, 485wbr, 355w, 312w.

$C_{12-10}$: 1655mbr, 1595wbr, 1545sh, 1515s, 1495s, 1410w, 1395w, 1291m, 1275w, 1160w, 1150w, 1135w, 1110sh, 1080s, 1070sh, 1041m, 1012s, 1002s, 985s, 730s, 581w, 471w, 339m, 310w.

$C_{6Cl_{2}H}$: 1555w, 1525m, 1399s, 1335s, 1300m, 1229m, 1169s, 1089s, 867s, 825s, 704m, 685s, 564m, 558sh, 528m.

$C_{6Cl_{2}H_{2}}$: 1559m, 1550sh, 1262w, 1212w, 1179sbr, 1132m, 1078s, 1065sh, 1015w, 945w, 865w, 836s, 809s, 775s, 609s, 552s, 512s, 481s.

$C_{6Cl_{1}}$: 1329sbr, 1291m, 1275m, 845w, 685m, 632m.

$C_{6Cl_{2}}$: 1313sbr, 1280m, 1261m, 651m, 600m.

$C_{6Cl_{3}}$: 1345sbr, 1296m, 695sbr.

$C_{6-5}^{2}H_{2}$: 1331s, 1302s, 856m, 682s, 649w, 575w, 345w.

$C_{6-4}^{2}H_{2}$: 1331w, 1320w, 1301w, 1190m, 1170m, 1155m, 1070w, 890sh, 881m, 862m, 800m, 775wbr, 710w, 685wbr, 640m, 530w, 520w.
Figure No. 9  Bromopentafluorobenzene
Figure No. 10 1,2-Dibromotetrafluorobenzene
Figure No. 11 1,2,3-Tribromotrifluorobenzene
Figure No. 13 2-Bromononafluorobiphenyl
Figure No. 14 2,2'-Dibromo-octafluorobiphenyl
Figure No.15  1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene
Figure No.16 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene
Figure No. 17 1,3-bis(pentafluorophenyl)-2-hydrotrifluorobenzene
Figure No. 18  Decafluorobiphenyl
Figure No. 19 Pentachlorobenzene
Figure No. 20 1,2-Dihydrotetrachlorobenzene
Figure No. 21 Iodopentachlorobenzene
Figure No. 22 1,2-Diodotetrachlorobenzene
Figure No. 23 Hexachlorobenzene
Figure No. 24. Bis(pentachlorophenyl)mercury
Figure No. 25  Bis(2,3,4,5-tetrachlorophenyl)mercury
Preparation and Characterisation
of Tribromotrifluorobenzene
The organolithium compound, \(1\)-lithio-2-bromotetrafluorobenzene, is conveniently prepared by the following reaction:

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Li} & \quad \text{Li} \\
\text{F} & \quad \text{F}
\end{align*}
\]

\[\text{ether/hexane} \rightarrow \quad \text{Br} \quad \text{Br} \quad \text{Li} \quad \text{Br} \quad \text{F}\]

If the preparation is carried out using furan as the solvent, rather than the more normal diethyl ether, and the mixture allowed to warm to room temperature, the resultant product \(1,2,3\)-trifluoro-\(1\)-bromo-5,8-epoxy-5,8-dihydronaphthalene is in 91% yield.

In furan/ether mixture a significant quantity of the furan adduct is formed by lithium bromide loss:

From previous studies in benzyne chemistry one would expect that the \(1\)-lithio-2-bromotetrafluorobenzene would eliminate a bromide ion faster than fluoride.
to produce tetrafluorobenzyne instead of the observed bromotrifluorobenzyne. It has been suggested\textsuperscript{54,252} the preference for intramolecular elimination of lithium fluoride compared with lithium bromide is due to the higher lattice energy of lithium fluoride, but it is also possible for the greater solubility of lithium bromide to make its "elimination" reversible due to readdition to the benzyne intermediate.

The decomposition of 1-lithio-2-bromofluorobenzene in the presence of 1,2-dibromotetrafluorobenzene gave, in addition to the isomeric 2,2',3- and 2,2',6-tri-bromohexafluorobiphenyls, several by-products including small amounts of 2,2'-dibromoheptafluorobiphenyl. This biphenyl was thought\textsuperscript{54} to arise via the formation of tetrafluorobenzyne by intramolecular lithium bromide elimination from 1-lithio-2-bromotetrafluorobenzene:

\[
\begin{align*}
\text{Li} & \quad \text{Br} \\
\text{Br} & \quad \text{Li} \\
\text{Li} & \quad \text{Br} \\
\text{F} & \quad \text{Br} & \quad \text{Li} & \quad \text{Br}
\end{align*}
\]

The decomposition of pentafluorophenyllithium in the presence of 1,2-dibromotetrafluorobenzene\textsuperscript{54} gave 2,2'- and 2,6-dibromoheptafluorobiphenyls in addition to 2-bromononafluorobiphenyl. The formation of 2,6-dibromoheptafluorobiphenyl can be explained:

\[
\begin{align*}
\text{Br} & \quad \text{Li} \\
\text{F} & \quad \text{Br} \\
\text{Br} & \quad \text{Li} \\
\text{Br} & \quad \text{Li} & \quad \text{Br}
\end{align*}
\]
The reversibility of the elimination and addition of lithium halides to normal benzene has been studied by Wittig and Tatlow has shown the addition of lithium halides to tetrafluorobenzene to be a general reaction. In these latter experiments, pentafluorophenyllithium was formed in each case from bromopentafluorobenzene (2.5g). The results of Tatlow's experiments are shown below:

<table>
<thead>
<tr>
<th>Lithium Halide Added</th>
<th>Total Recovery (g)</th>
<th>C_{6}F_{4}BrH</th>
<th>C_{6}F_{5}I</th>
<th>C_{6}F_{4}Br_{2}</th>
<th>C_{6}F_{4}BrI</th>
<th>C_{6}F_{5}C_{6}F_{4}Br</th>
<th>C_{6}F_{5}C_{6}F_{4}Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>LiCl</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>LiCl, LiBr</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>LiI, LiBr</td>
<td>2.3</td>
<td>0.3</td>
<td>0.75</td>
<td>0.9</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LiI, LiCl</td>
<td>2.9</td>
<td>0.3</td>
<td>1.1</td>
<td>0.5</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
</tbody>
</table>

It can be seen that in those reactions where lithium halides have been added, the preparation of 1,2-dihalogeno-tetrafluorobenzenes in the product increases markedly. The formation of bromo-compounds when lithium iodide was added can be explained either by halogen-metal interchange starting from bromopentafluorobenzene or by the formation of lithium bromide in situ:

\[ n C_{4}H_{9}Br + I^- \rightarrow n C_{4}H_{9}I + Br^- \]

The formation of 1-bromo-2,3,4,5-tetrafluorobenzene is an indication that the reactions shown below are proceeding:

Cohen allowed 2-lithiononafluorobiphenyl to decompose in the presence of both lithium bromide and 2-bromononafluorobiphenyl. It was observed that lithium
bromide added across 1-pentafluorophenyl-2,3,4-trifluorobenzene, in an analogous fashion to the addition of lithium halides across tetrafluorobenzene\(^3\), the resultant isomeric 2-lithio-3-bromo- and 2-bromo-3-lithiooctafluorobiphenyls undergoing lithium/bromide exchange with added 2-bromononafluorobiphenyl to give 2,3-dibromooctafluorobiphenyl:

\[
\text{LiF} \quad \text{Li Br}
\]

Tatlow showed that 1,2-dibromotetrafluorobenzene was the major product when pentafluorophenyllithium was allowed to decompose in the presence of excess bromopentafluorobenzene and lithium bromide. This reaction was repeated, in this work, in an attempt to show the presence of 1,2,3-tribromotrifluorobenzene among the reaction products. Analytical GLC showed 1,2-dibromotetrafluorobenzene was indeed the major product but 1,2,3-tribromotrifluorobenzene was also shown to be present in the mixture of products.

In view of this, 1-lithio-2-bromotetrafluorobenzene was allowed to decompose in the presence of both lithium bromide and 1,2-dibromotetrafluorobenzene. It was hoped that the lithium bromide would add across 1-bromo-2,3,4-trifluorobenzene, and that the resultant isomeric 1-lithio-2,3-dibromo- and 1,3-dibromo-2-lithio-trifluorobenzenes would undergo lithium/bromide exchange with 1,2-dibromotetrafluorobenzene to yield 1,2,3-tribromotrifluorobenzene:
Previous work appears to indicate that lithium is attracted to the organo-system having the highest electronegativity. Hence, if fluorine is replaced by either a bromine or a pentafluorophenyl group, the electronegativity of the aromatic nucleus is reduced and the lithium moves to a more electronegative group.

In addition to 1,2-dihydrotetrafluorobenzene and 2,2'-dibromoocatfluorobipheny (presumably formed by the reaction scheme on page 100), a compound was indicated by analytical GLC which had an identical retention time to a pure sample of 1,2,3-tribromotrifluorobenzene. This was isolated using either preparative GLC or steam distillation and its identity confirmed by analysis and by n.m.r. and mass spectral measurements.

i) Elemental analysis
For C$_6$F$_3$Br$_3$ calcd.: C, 19.5; found: C, 19.8%.

ii) $^{19}$F n.m.r. spectrum
There are three possible isomeric structures for the molecular formula C$_6$F$_3$Br$_3$:

1,2,3-tribromotrifluorobenzene 1,3,5-tribromotrifluoro-1,2,5-tribromotrifluoro-
Figure No. 26 $^{19}$F n.m.r. spectrum of 1,2,3-Tribromotrifluorobenzene
Considering that the starting material contained two bromine atoms in positions ortho to each other, the symmetrical isomer 1,3,5-tribromotrifluorobenzene can be dismissed as being a highly unlikely product of this reaction. The $^{19}\text{F}$ n.m.r. spectrum of the product was very simple and consisted of only two sets of lines: a doublet centred at 116.7 p.p.m. and a triplet at 156.6 p.p.m. (relative to CFCl₃) showing that only two types of fluorine environment were present in the molecule. The relative intensities of the doublet and triplet were quite close to the 2:1 ratio expected for the 1,2,3-tribromotrifluorobenzene isomer.

![Diagram of 1,3,5-tribromotrifluorobenzene]

The signal for $F_2$ is split into a doublet by $F_1$, and the $F_1$ signal split into a symmetrical triplet by the two identical $F_2$ atoms. The coupling constants were $J_{F_2-F_1} 21.4$ Hz and $J_{F_1-F_2} 21.4$ Hz.

iii) $^{13}\text{C}$ n.m.r. spectrum

The spectrum consisted of four lines with approximate relative intensities 2,1,1,2 indicating that there were four different carbon environments present in the molecule. Relative to the internal TMS standard, their chemical shifts were: -109.9, -123.0, -146.2 and -148.5 p.p.m.

![Diagram of 1,2,3-tribromotrifluorobenzene]

It can be seen that a 2,1,1,2 pattern would arise from the symmetrical structure of 1,2,3-tribromotrifluorobenzene. By comparison with $^{13}\text{C}$ n.m.r. spectra of the three isomeric dibromotetrafluorobenzenes, it was possible to assign all the peaks in the spectrum of 1,2,3-tribromotrifluorobenzene:
Figure No. 27 $^{13}$C n.m.r. spectrum of 1,2,3-Tribromotrifluorobenzene.
Chemical shifts (-p.p.m.) relative to TMS

<table>
<thead>
<tr>
<th>C₆F₄Br₂</th>
<th>Chemical shift C-Br</th>
<th>Chemical shift C-F</th>
<th>Chemical shift C-F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm relative to TMS</td>
<td>ortho to C-Br</td>
<td>meta to C-Br</td>
</tr>
<tr>
<td>ortho</td>
<td>-109.06</td>
<td>-146.29</td>
<td>-140.71</td>
</tr>
<tr>
<td>meta</td>
<td>-95.13</td>
<td>-148.72</td>
<td>-138.14</td>
</tr>
<tr>
<td>para</td>
<td>-99.65</td>
<td>(-145.37)</td>
<td>(-145.37)</td>
</tr>
</tbody>
</table>

In 1,2,3-tribromotrifluorobenzene C₃ is ortho to two C₂-Br groups and can be assumed to give rise to the line at shift -148.5 p.p.m. (see data in col. 3 of table). Similarly, C₄ is meta to the two C₂-Br groups and consequently the line at shift -139.7 p.p.m. was assigned to this carbon atom. The atoms C₂-Br and C₁-Br are in the ratio 2:1 and the remaining lines in the spectrum at 123.0 and -109.9 p.p.m. were therefore considered to be due to these carbon atoms, respectively.

iv) Mass spectrum.

The parent ion, C₆F₃Br⁺, gives rise to the base peak in the mass spectrum of 1,2,3-tribromotrifluorobenzene. There is very little fragmentation of the compound, except for the successive loss of the three bromine atoms; a broad metastable peak
centred at m/e 226.1 corresponds to the loss of the first bromine atom:

\[
\text{C}_6\text{F}_3\text{Br}_3^+ - \text{Br} \rightarrow \text{C}_6\text{F}_3\text{Br}_2^+ \quad \text{Calcd.: m/e 226.3}
\]

The stability of 1,2,3-tribromotrifluorobenzene towards electron impact is demonstrated by the presence of a cluster of peaks centred at 184.5 due to the doubly-charged parent ion, \( \text{C}_6\text{F}_3\text{Br}_3^{2+} \). (Table 4)

Analytical GLC of the reaction mixture showed, besides 2,2'dibromo-octafluorobiphenyl and 1,2,3-tribromotrifluorobenzene, three further components of longer retention times. These were removed from the mixture by preparative GLC, and mass spectrometry showed that the principal component was of molecular weight 430, corresponding to a compound of molecular formula \( \text{C}_6\text{F}_2\text{Br}_4 \).

The other component had a molecular weight of 517, corresponding to \( \text{C}_{12}\text{F}_7\text{Br}_3 \); in some samples a trace amount of \( \text{C}_{12}\text{F}_6\text{Br}_4 \) was also detectable.

The mass spectrum of \( \text{C}_6\text{F}_2\text{Br}_4 \) showed that very little fragmentation occurred on electron bombardment until most of the bromine atoms had been lost: the
Table 4

Partial Mass Spectrum for 1,2,3-Tribromotrifluorobenzene

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>369</td>
<td>$C_6F_3Br_3^+$</td>
</tr>
<tr>
<td>350</td>
<td>$C_6F_2Br_3^+$</td>
</tr>
<tr>
<td>289</td>
<td>$C_6F_3Br_2^+$</td>
</tr>
<tr>
<td>270</td>
<td>$C_6F_2Br_2^+$</td>
</tr>
<tr>
<td>239</td>
<td>$C_5FBr_2^+$</td>
</tr>
<tr>
<td>207</td>
<td>$C_6F_3Br^+$</td>
</tr>
<tr>
<td>184.5</td>
<td>$C_6F_3Br_3^{2+}$</td>
</tr>
<tr>
<td>127</td>
<td>$C_6F^+$</td>
</tr>
<tr>
<td>109</td>
<td>$C_6F_2^+$</td>
</tr>
<tr>
<td>104</td>
<td>$C_5F^+$</td>
</tr>
<tr>
<td>98</td>
<td>$C_5^2F^+$</td>
</tr>
</tbody>
</table>

A metastable peak was observed for the loss:

<table>
<thead>
<tr>
<th></th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6F_3Br_3^+$</td>
<td>226.1</td>
<td>226.3</td>
</tr>
</tbody>
</table>
### Table 5

**Partial Mass Spectrum of 1,2,3,4-Tetrabromodifluorobenzene.**

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>$C_6F_2Br_4^+$</td>
</tr>
<tr>
<td>411</td>
<td>$C_6FBr_4^+$</td>
</tr>
<tr>
<td>350</td>
<td>$C_6F_2Br_3^+$</td>
</tr>
<tr>
<td>331</td>
<td>$C_6FBr_3^+$</td>
</tr>
<tr>
<td>270</td>
<td>$C_6F_2Br_2^+$</td>
</tr>
<tr>
<td>215</td>
<td>$C_6F_2Br_4^{2+}$</td>
</tr>
<tr>
<td>190</td>
<td>$C_6F_2^+$</td>
</tr>
<tr>
<td>171</td>
<td>$C_6FBr^+$</td>
</tr>
<tr>
<td>159</td>
<td>$C_5FBr^+$</td>
</tr>
<tr>
<td>135</td>
<td>$C_6F_2Br_2^{2+}$</td>
</tr>
<tr>
<td>110</td>
<td>$C_6F^+$</td>
</tr>
<tr>
<td>91</td>
<td>$C_5F^+$</td>
</tr>
<tr>
<td>79/81</td>
<td>Br$^+$</td>
</tr>
<tr>
<td>79</td>
<td>$C_5F^+$</td>
</tr>
</tbody>
</table>

A metastable peak was observed for the loss:

$$
C_6F_2Br_4^+ \quad \text{ Observed } \quad \text{ Calculated}
$$

\[ \text{C}_6F_2Br_4^+ \xrightarrow{-\text{Br}} C_6F_2Br_3^+ \]
Table 6

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>517</td>
<td>C_{12}F_{7}Br_{3}^{+}</td>
</tr>
<tr>
<td>437</td>
<td>C_{12}F_{7}Br_{2}^{+}</td>
</tr>
<tr>
<td>418</td>
<td>C_{12}F_{6}Br_{2}^{+}</td>
</tr>
<tr>
<td>382</td>
<td>C_{12}F_{4}Br_{2}^{+}</td>
</tr>
<tr>
<td>357</td>
<td>C_{12}F_{7}Br^{+}</td>
</tr>
<tr>
<td>338</td>
<td>C_{12}F_{6}Br^{+}</td>
</tr>
<tr>
<td>277</td>
<td>C_{12}F_{7}^{+}</td>
</tr>
<tr>
<td>258</td>
<td>C_{12}F_{6}^{+}</td>
</tr>
<tr>
<td>218.5</td>
<td>C_{12}F_{7}Br_{2}^{2+}</td>
</tr>
<tr>
<td>201</td>
<td>C_{12}F_{3}^{+}</td>
</tr>
<tr>
<td>178.5</td>
<td>C_{12}F_{7}Br_{2}^{2+}</td>
</tr>
<tr>
<td>182</td>
<td>C_{12}F_{2}^{+}</td>
</tr>
<tr>
<td>163</td>
<td>C_{12}F^{+}</td>
</tr>
<tr>
<td>144</td>
<td>C_{12}^{+}</td>
</tr>
</tbody>
</table>

Metastable peaks were observed for the transitions:

\[
\begin{align*}
C_{12}F_{7}Br_{3}^{+} & \rightarrow C_{12}F_{7}Br_{2}^{+} & \text{Observed} & 368.6 \\
C_{12}F_{7}Br_{2}^{+} & \rightarrow C_{12}F_{7}Br^{+} & \text{Observed} & 291.0 \\
C_{12}F_{7}Br^{+} & \rightarrow C_{12}F^{+} & \text{Observed} & 214.4
\end{align*}
\]
molecular ion $C_6F_2Br_4^+$ provides the base peak of the spectrum and a broad metastable peak centred at $m/e$ 284.8 corresponds to loss of the first bromine atom: (Table 5)

$$C_6F_2Br_4^+ \xrightarrow{-Br} C_6F_2Br_3^+ \text{ Calcd.: } 284.9$$

The compound, $C_6F_2Br_4$, is probably 1,2,3,4-tetrabromodifluorobenzene,

which can arise by further attack of n-butyllithium on 1,2,3-tribromotrifluorobenzene:

$$\text{Br}$$

which can arise by further attack of n-butyllithium on 1,2,3-tribromotrifluorobenzene:
The mass spectrum of $C_{12}F_7Br_3$ also showed that slight fragmentation occurred on electron bombardment, until two of the bromine atoms have been lost. The parent ion again provided the base peak of the spectrum; three metastable peaks were observed, corresponding to the progressive loss of bromine atoms from the compound:

\[
\begin{align*}
C_{12}F_7Br_3^+ & \xrightarrow{-\text{Br}} C_{12}F_7Br_2^+ & \text{Observed} & 368.6 & \text{Calculated} & m/e & 369.4 \\
C_{12}F_7Br_2^+ & \xrightarrow{-\text{Br}} C_{12}F_7Br^+ & 291.0 & 291.6 \\
C_{12}F_7Br^+ & \xrightarrow{-\text{Br}} C_{12}^F^+ & 214.35 & 214.9
\end{align*}
\]

The metastables were very broad due to the presence of bromine atoms (bromine has two isotopes $^{79}\text{Br}$ and $^{81}\text{Br}$) and this made accurate measurement of the midpoint difficult. (Table 6)

With the reaction conditions under consideration, two possible isomers of molecular formula $C_{12}F_7Br_3$ could be formed via a mechanism involving bromotri-fluorobenzene:

![Diagram](image-url)
The presence of three isomers in the product mixture was verified by checking their retention times with those of pure samples of the two compounds prepared previously by Dr. D.E. Fenton\textsuperscript{224}.

Four isomers of molecular formula \( \text{C}_{12}\text{F}_6\text{Br}_4 \) can be expected from a continuation of the reaction:

\[
\text{Br} \quad \text{Br} \quad \text{LiBu} \quad \rightarrow \quad \text{Li} \quad \text{Br} \quad \text{LiF} \quad \rightarrow \quad \text{Br} \quad \text{Br}
\]

\[
\text{Br} \quad \text{Li} \quad \text{Br} \quad \text{Li} \quad \text{Br} \quad \text{Br} \quad \text{Li} \quad \text{Br} \quad \text{Br} \quad \text{Li} \quad \text{Br}
\]

\[
\text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br}
\]

The two other isomers arise from \( 1,2,3 \)-tribromotrifluorobenzene:
The 2,2',3',6'-tribromohexafluorobiphenyl can also be formed from 2,2',6'-tribromoheptafluorobiphenyl by attack of n-butyl lithium to give 2,2'-dibromo-6'-lithioheptafluorobiphenyl. Lithium fluoride elimination gives the corresponding benzyne across which lithium bromide can add to form a new lithium derivative capable of undergoing lithium/bromine exchange to give 2,2',3',6'-tetrabromohexafluorobiphenyl.
A considerable amount of time was expended on unsuccessful attempts to isolate the tetrabromobiphenyls in a pure state. Preparative GLC proved ineffective, as the highest temperature, 300°C, the column support could withstand, was too low for movement of the compounds through the column. The success of steam distillation in isolating 2-bromonafluorobiphenyl and 1,2,3-tribromotrifluorobenzene prompted a series of experiments using steam superheated to 400°C to effect separation; however, although it was possible to steam distil the poly-bromobiphenyls only mixtures were obtained.
Preparation and Characterisation of Some Polyfluoroterphenyls
Several groups of workers have shown that pentafluorophenyllithium decomposes by intramolecular elimination of lithium fluoride. The formation of 2-halo- and 2-hydrononafluorobiphenyl has been explained by the addition of undecomposed pentafluorophenyllithium across tetrafluorobenzyne followed by Li/X exchange between the intermediate 2-lithiononafluorobiphenyl and unreacted \( C_{6}^{2}F_{5}X \).

There is no reason why 2-lithiononafluorobiphenyl should not itself eliminate lithium fluoride intramolecularly, and Tomlinson has decomposed 2-lithiononafluorobiphenyl in the presence of benzene or furan with the subsequent formation of Diels-Alder adducts derived from 1-pentafluorophenyl-2,3,4-trifluorobenzyne.

The formation of the 2-halo- and 2-hydrononafluorobiphenyls by lithium/X exchange between 2-lithiononafluorobiphenyl and \( C_{6}^{2}F_{5}X \) is an indication that the reactivity of the two lithium reagents towards this exchange is \( C_{6}^{2}F_{5}Li > 2-LiC_{12}^{2}F_{9} \) and that in the reaction:

\[
C_{6}^{2}F_{5}X + 2-LiC_{12}^{2}F_{9} \rightleftharpoons C_{6}^{2}F_{5}Li + 2X-C_{12}^{2}F_{9}
\]

the position of equilibrium lies well to the right. It has been demonstrated.
that this exchange does occur, by adding bromo- and iodopentafluorobenzene to 2-lithiononafluorobiphenyl at -78°C when the corresponding 2-halononafluorobiphenyl was obtained in high yield.

In the absence of pentafluorobenzene or halopentafluorobenzenes, the 2-lithiononafluorobiphenyl formed by decomposition of pentafluorophenyllithium would be expected to eliminate lithium fluoride intramolecularly and any undecomposed pentafluorophenyllithium remaining might add across the intermediate 1-pentafluorophenyl-2,3,4-trifluorobenzyne to give two isomeric polyfluoroterphenyllithium derivatives:

![Diagram of isomeric polyfluoroterphenyllithium derivatives]

Subsequently, pentafluorophenyllithium was allowed to decompose in the presence of 2-bromonafluorobiphenyl. Li/Br exchange occurred between the polyfluoroterphenyllithium derivatives, A and B, and 2-bromonafluorobiphenyl to give two isomeric bromopolyfluoroterphenyls in an analogous manner to Li/Br exchange between 2-lithiononafluorobiphenyl and bromopentafluorobenzene. These were separated by preparative scale GLC, the first to elute was shown by its $^{19}$F n.m.r. spectrum to be 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene, whereas the second was shown to be 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene. The bromoterphenyl-isomers were accompanied by 2-hydrononafluorobiphenyl and 1,2-bis(pentafluorophenyl)-3-hydrotrifluorobenzene formed by hydrolysis of the respective intermediate lithium reagents.
Both in this work and that of Cohen\textsuperscript{216}, the ratio of bromopolyfluoroterphenyls obtained was about 4:1 (a similar ratio was observed by Tomlinson\textsuperscript{55,61} in the preparation of the hydrofluoroterphenyls) in favour of the unsymmetrical isomer. The conversion of the benzene (shown in the reaction scheme on page 118) via A to the unsymmetrical isomer would therefore seem to be more favourable than the conversion of the benzene via B to the symmetrical isomer. Two possible explanations for these ratios have been put forward. Firstly, the benzene can be regarded as effectively ortho-substituted with an electron-donating C\textsubscript{6}F\textsubscript{5} group, since the electronegativity of this group has been shown\textsuperscript{218} to be about that of bromine and much less than fluorine. This would be expected to lead to preferential formation of the lithium reagent A. However, the decomposition of 1-lithio-2-bromotetrafluorobenzene in the presence of 1,2-dibromotetrafluorobenzene, in which the critical step is the addition of the lithium reagent to 3-bromotrifluorobenzene, led to the isolation of roughly equal amounts of the isomeric tribromoheptafluorobi-phenyls\textsuperscript{54}. In other words, the addition of a lithium reagent to this electronically similar benzene did not proceed preferentially in one direction to any marked extent, and there seems no reason why this should not also be the case in the present reaction.

Tomlinson\textsuperscript{55} and Cohen\textsuperscript{216} have suggested that on steric grounds, the addition of pentafluorophenyllithium across the benzene would be expected to be more favourable in the formation of the symmetrical isomer since the two pentafluorophenyl groups would be furthest apart in this case:

\[ \text{C}_{6}\text{F}_{5} \quad \text{Li} \quad \text{C}_{6}\text{F}_{5} \]

The Li/X exchange however, would be far less favourable in the case where the lithium atom is symmetrically placed between the two pentafluorophenyl groups, since the approach of X would almost certainly be hindered. Due to the smaller
size of hydrogen compared with bromine, the former would be expected to show
a larger proportion of the symmetrical isomer, as the formation of the lithium
derivatives must be the same in both cases, and this is found to be so. Li/X
exchange between the unsymmetrical terphenyllithium and either 2-bromo- or
2-hydronafluorobiphenyl would be expected to proceed without undue steric
hinderance to give high yields of the unsymmetrical isomers.

When pentafluorophenyllithium is decomposed in the presence of 2-bromonafluoro-
biphenyl and liquid paraffin, only one terphenyl is formed, namely the symmetrical
1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene. The large hydrocarbon
molecules in the liquid paraffin possibly prevent an "ortho" approach of the
pentafluorophenyl group of pentafluorophenyllithium to the pentafluorophenyl
group of 1-pentafluorophenyl-2,3,4-trifluorobenzene:

Because of the two large pentafluoro-phenyl groups and the intervening liquid
paraffin molecules, the lithium reagent cannot approach close enough to add
across the benzyne. However, a "meta" addition is still possible as the two
pentafluorophenyl rings are far enough apart to allow approach of the lithium
reagent, in spite of the hydrocarbon molecules. Addition across the benzyne
can take place, forming the symmetrical isomer after Li/X exchange has occurred.

Also, in the normal reaction, the lithium atom of pentafluorophenyllithium would
be expected to be solvated with ether molecules. The presence of liquid paraffin
may hinder this solvation and allow the "naked" lithium to readily approach the
benzyne in an "ortho" manner. When solvated the lithium atom is probably too
large to allow this ortho approach to the benzyne.
By a careful work-up of the products formed during the preparation of 2-bromo-
onafluorobiphenyl, from the decomposition of pentafluorophenyllithium in the
presence of bromopentafluorobenzene, two bromopolyfluoroterphenyls can be isolated
by preparative GLC. The first to elute was 1,2-bis(pentafluorophenyl)-3-bromo-
trifluorobenzene, whereas the second was not the 1,3-isomer but bromoperfluoro-p-
terphenyl. The apparent absence of 1,3-bis(pentafluorophenyl)-2-bromotrifluoro-
benzene might suggest that, in this reaction, the 1,2-isomer may be formed by
a mechanism other than that involving 1-pentafluorophenyl-2,3,4-trifluorobenzene.
The formation of bromoperfluoro-p-terphenyl can be explained in terms of a nucleo-
philic attack by the pentafluorophenyl "anion" $C_6F_5^-$ (derived from pentafluoro-
phenyllithium) on 2-bromonafluorobiphenyl. Tatlow \(^\text{34}\) has shown that the "anion"
$C_6F_5^-$ is capable of attacking pentafluorobenzene derivatives in a nucleophilic
manner; at $-40^\circ\text{C}$, the products due to nucleophilic attack greatly outweigh those
due to decomposition by intramolecular loss of lithium fluoride. In view of
the para directing effect of the pentafluorophenyl group, nucleophilic attack
on 2-bromonafluorobiphenyl would be expected to occur in the $4$ or $4'$ positions:

\[
\begin{array}{c}
\text{Br} \\
\text{F} \quad \text{F} \quad \text{F} \\
\text{} \quad \text{C}_6\text{F}_5^- \quad \text{+} \\
\text{Br} \\
\text{F} \quad \text{F} \quad \text{F}
\end{array}
\]

The formation of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene by a nucleo-
philic mechanism would require attack by $C_6F_5^-$ on the position ortho to the
pentafluorophenyl group i.e. at $F_6$:

\[
\begin{array}{c}
\text{Br} \\
\text{F} \quad \text{F} \\
\text{} \quad \text{C}_6\text{F}_5^- \quad \text{+} \\
\text{Br} \\
\text{F} \quad \text{F} \\
\end{array}
\]
Since nucleophilic attack on pentafluorophenyl derivatives generally gives rise to the para disubstituted tetrafluorobenzene\textsuperscript{19-21,217} it is most probable that 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene was, indeed, formed via the benzyne mechanism discussed above.

The reaction of pentafluorophenyllithium with titanium tetrachloride using a ratio of 4:1 or greater, gave several polyfluoropolyphenyl derivatives. As well as the terphenyl derivatives mentioned above, the formation of tris-, tetrakis- and pentakis-(pentafluorophenyl)benzene derivatives was detected by mass spectrometry. These compounds can be visualised to be formed via a series of intramolecular lithium fluoride eliminations followed by addition of pentafluorophenyllithium across a benzyne.
Li/Br exchange between the lithium reagents and unreacted pentafluorobromobenzene or hydrolysis, gives the corresponding bromo- or hydro- derivatives.

19F n.m.r. Spectra of Polyfluoropolyphenyls

The chemical shift, $\delta$, of a particular fluorine atom is measured in parts per million (p.p.m.) relative to an internal or external standard, usually trichlorofluoromethane ($\text{CFCl}_3$), hexafluorobenzene ($\text{C}_6\text{F}_6$) or trifluoroacetic acid ($\text{CF}_3\text{COOH}$).

The interconversion factors commonly used are:

$$\delta \text{CFCl}_3 = \delta \text{C}_6\text{F}_6 + 163.7 \quad \text{ref: 219}$$
$$\delta \text{CFCl}_3 = \delta \text{CF}_3\text{COOH} + 78.5 \quad \text{ref: 220}$$

Splitting of the resonance peak occurs due to the spin-spin coupling between the fluorine atom under observation and other atoms (normally fluorine or hydrogen) within the molecule. It has been observed$^{221}$ that fluorine-fluorine couplings are in the order:

$$J_{\text{ortho}} > J_{\text{para}} > J_{\text{meta}}$$

Whereas fluorine-hydrogen couplings are:

$$J_{\text{ortho}} > J_{\text{meta}} > J_{\text{para}}$$

The constants are quoted in hertz (Hz). The chemical shifts of fluorine atoms which are ortho to a substituent group $R$ are mainly influenced by inductive, resonance and steric effects and normally occur at lowest field; the meta fluorine shifts are more influenced by inductive effects whereas those of para fluorine atoms are often strongly influenced by $\pi$-bonding.$^{221}$ The pentafluorophenyl group shows three well-defined groups of peaks in the ratio 2:1:2 due to the ortho-, para- and meta- fluorines respectively, in order of increasing field. An effective analysis can be obtained by considering the five fluorine nuclei as an AA'XX' five-spin system$^{221}$:

![Five-spin system diagram](image-url)
In its simplest form, the P part of the spectrum consists of a triplet of triplets from which the coupling constants \( J_{P-X} (= J'_{P-X}) \) and \( J_{P-A} (= J'_{P-A}) \) can be obtained:

The basic ten-line spectrum of the AA'XX' system\(^{221}\) undergoes further splitting due to the coupling of \( F_A \) (or \( F_X \)) with \( F_P \). After removing these additional couplings (obtained from the spectrum of \( F_P \)) the AA'XX' system can itself be solved.\(^{221}\)

The effect of a group \( R \) on the chemical shifts of the ortho-, meta- and para-fluorines of pentafluorophenyl derivatives, compared with the single resonance of hexafluorobenzene has been shown\(^{34,76}\) to be approximately additive when applied to a polyfluoroaromatic system other than pentafluorophenyl. The differences between the chemical shifts of \( F_o' \), \( F_m' \), \( F_p' \) and that of hexafluorobenzene are known as substitution parameters and those for \( H \), \( Cl \), \( Br \), \( I \) and \( C_6F_5 \) are given in Table 7 below:

<table>
<thead>
<tr>
<th>Position relative to ( R )</th>
<th>( H )</th>
<th>( Cl )</th>
<th>( Br )</th>
<th>( I )</th>
<th>( C_6F_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ortho</td>
<td>23.4</td>
<td>21.7</td>
<td>29.7</td>
<td>43.1</td>
<td>24.0</td>
</tr>
<tr>
<td>meta</td>
<td>0.2</td>
<td>1.0</td>
<td>1.7</td>
<td>2.6</td>
<td>1.5</td>
</tr>
<tr>
<td>para</td>
<td>8.8</td>
<td>6.2</td>
<td>7.6</td>
<td>9.8</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Table 7
Substitution Parameters in Fluoroaromatic Systems derived from Pentafluorophenyl Derivatives, \( C_6F_5R^{222} \) (p.p.m. relative to \( C_6F_6 \))
Theoretical and Experimental $^{19}$F n.m.r. chemical shifts of the Trifluorobenzene Ring of the Terphenyls under discussion

<table>
<thead>
<tr>
<th></th>
<th>$F_4$</th>
<th>$F_5$</th>
<th>$F_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sym bromo-isomer</td>
<td>Calc: 124.6</td>
<td>151.7</td>
<td>124.7</td>
</tr>
<tr>
<td></td>
<td>Obs: 123.4</td>
<td>149.6</td>
<td>123.4</td>
</tr>
<tr>
<td>Unsym bromo-isomer</td>
<td>Calc: 119.1</td>
<td>147.1</td>
<td>129.2</td>
</tr>
<tr>
<td></td>
<td>Obs: 116.2</td>
<td>149.3</td>
<td>129.4</td>
</tr>
<tr>
<td>Unsym H-terphenyl</td>
<td>Calc: 123.7</td>
<td>148.2</td>
<td>127.3</td>
</tr>
<tr>
<td></td>
<td>Obs: (128.7)</td>
<td>154.6</td>
<td>(128.7)</td>
</tr>
</tbody>
</table>

The $^{19}$F n.m.r. Spectrum of 1,2-Bis(pentafluorophenyl)-3-bromofluorobenzene

The spectrum consists of eight groups of lines, although there appears to be only six due to partial overlap of peaks.

<table>
<thead>
<tr>
<th>Group</th>
<th>Centred position relative to $\text{CCl}_3F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>159.6 p.p.m.</td>
</tr>
<tr>
<td>B</td>
<td>150.8 p.p.m.</td>
</tr>
<tr>
<td>C</td>
<td>149.3 p.p.m.</td>
</tr>
<tr>
<td>D</td>
<td>137.9 p.p.m.</td>
</tr>
<tr>
<td>E</td>
<td>129.4 p.p.m.</td>
</tr>
<tr>
<td>F</td>
<td>116.2 p.p.m.</td>
</tr>
</tbody>
</table>

In order of decreasing field, they can be assigned as follows:

**Group A**

Two halves of two distinct AA'XX' (each split by an additional coupling) systems which partially overlap. The chemical shifts would indicate that these two
groups are due to the two sets of meta fluorine atoms of the pentafluorophenyl rings. Due to the overlap, a solution of the two line-groups cannot be readily obtained.

Group B

A triplet which arises from F₅; the latter presumably couples with F₄ and F₆ to an approximately equal extent since a difference in the values of \( J_{F_5-F_6} \) and \( J_{F_5-F_4} \) would have produced four lines.

Group C

Two partially overlapping triplets of triplets which arise from the para fluorines of the two pentafluorophenyl rings.

Group D

A complex pattern due to the overlap of the other halves of the two AA'XX' system. This arises from the two sets of ortho fluorines of the two pentafluorophenyl rings; in addition to coupling with the para fluorines of the pentafluorophenyl rings, further complication is caused by interannular coupling between F₆ and the ortho fluorines of the pentafluorophenyl ring ortho to F₆.

Group E

A quartet of triplets arising from F₆. The quartet is due to coupling of F₆ with F₅ and F₄, the ortho coupling \( J_{F_6-F_5} \) being considerably larger than the meta coupling \( J_{F_6-F_4} \). Each of these lines then becomes a triplet from inter-annular coupling between F₆ and the ortho fluorines of the pentafluorophenyl group ortho to F₆.

Group F

A four line pattern arising from F₄ which couples with F₅ and F₆ (in an analogous manner to F₆) but which does not take part in any inter-annular coupling.
Figure No. 28 $^{19}F$ n.m.r. Spectrum of 1,2-Bis(pentafluorophenyl)-3-bromotrifluorobenzene
Figure No. 29 $^{19}$F n.m.r. Spectrum of 1,3-Bis(pentafluorophenyl)-2-bromotrifluorobenzene
Figure No. 30 $^{19}$F n.m.r. Spectrum of 1,2-Bis(pentafluorophenyl)-3-hydrotrifluorobenzene
Figure No. 31  $^{13}$C n.m.r. Spectrum of 1,3-Bis(pentafluorophenyl)-2-bromotrifluorobenzene
Figure No. 32. $^{13}$C n.m.r. Spectrum of 1,2-Bis(pentafluorophenyl)-3-bromotrifluorobenzene

(not fully fluorine decoupled)
Unlike the unsymmetrical isomer discussed above, the symmetrical nature of 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene gives rise to fewer lines; F₄ and F₆ are now magnetically equivalent and the three sets of fluorines of the pentafluorophenyl rings will be identical.

<table>
<thead>
<tr>
<th>Group</th>
<th>Centred position relative to CCl₃F</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>159.9 p.p.m.</td>
</tr>
<tr>
<td>B</td>
<td>155.0 p.p.m.</td>
</tr>
<tr>
<td>C</td>
<td>149.6 p.p.m.</td>
</tr>
<tr>
<td>D</td>
<td>137.1 p.p.m.</td>
</tr>
<tr>
<td>E</td>
<td>123.4 p.p.m.</td>
</tr>
</tbody>
</table>

In order of decreasing field, they can be assigned as follows:

**Group A**

One half of an AA'DXX' system, arising from the four magnetically equivalent meta fluorines of the two pentafluorophenyl groups. The additional coupling between F₄ and F₆ is readily obtained from Group C and after removal from the total spectrum, the resultant ten lines treated as an AA'DXX' system.

**Group B**

A triplet arising from F₅. In this case J₅₋₄ and J₅₋₆ must be equal due to the magnetic equivalence of F₄ and F₆.

**Group C**

A triplet of triplets due to the equivalent para fluorines of the two pentafluorophenyl rings.
Group D

A complex multiplet from the other half of the $AA'XX'$ system, arising from the four magnetically equivalent ortho fluorines of the pentafluorophenyl rings. As in the unsymmetrical compound, this system is complicated by the coupling, $F_o-F_p$, and inter-annular coupling which now involves all four ortho fluorines.

Group E

A doublet of triplets arising from $F_4$ and $F_6$. The basic two lines are due to an ortho coupling with $F_5$ whereas the triplets arise from inter-annular coupling of $F_4$ (and $F_6$) with the ortho fluorines of the pentafluorophenyl rings.

The inter-annular coupling in the symmetrical isomer is less than half of that found for the unsymmetrical isomer. Whereas the quartet of triplets observed for $F_6$ in 1,2-isomer were fairly symmetrical, the triplets observed for $F_4$ and $F_6$ in the 1,3-isomer show considerable broadening and distortion. These observations can be interpreted as an indication of hindered rotation of the pentafluoro-groups in the symmetrical isomer due to steric factors caused by the presence of a bromine atom ortho to the pentafluorophenyl groups.

The $^{19}$F n.m.r. Spectrum of 1,2-Bis(pentafluorophenyl)-3-hydrotrifluorobenzene

The spectrum consists of nine groups of lines, although there appears to be only seven, due to overlapping of two groups of lines.
In order of decreasing field, they can be assigned as follows:

**Group A**

As in the case of the bromo-analogue, this group consists of two halves of two distinct AA'XX' systems which partially overlap. These two groups are due to the two sets of meta fluorine atoms of the pentafluorophenyl rings.

**Group B**

A triplet of doublets arising from F5. The expected eight-line multiplet was not observed, equal couplings $J_{F_5-F_4}$ and $J_{F_5-F_6}$ leading to a triplet which is further split by coupling with the meta hydrogen.

**Group C**

Two distinct sets of triplets which arise from the para fluorines of the two pentafluorophenyl rings. The parafluorine is split into a triplet by the meta fluorines and into further triplets by the ortho fluorines. Two sets are observed as the pentafluorophenyl rings are in slightly different environments to each other.

**Group D, Group E**

These groups are due to the other halves of the two AA'XX' systems. They arise from the two sets of ortho fluorines of the two pentafluorophenyl rings; in addition to coupling with the para fluorines of the pentafluorophenyl rings, further complication is caused by interannular coupling between F6 and the ortho fluorines of the pentafluorophenyl ring ortho to F6 and inter annular
coupling between the hydrogen atom and the corresponding ortho pentafluorophenyl ring.

**Group F**

Two groups of peaks which partially overlap, were assigned to F₆ and F₄ respectively, both are basically doublet of doublets, due to coupling with the fluorine atoms situated ortho and meta, but the F₄ multiplet has further doublet splitting caused by coupling with the ortho hydrogen atom. Likewise, the F₆ multiplet is further split by the hydrogen atom para to F₆. In addition, the F₆ multiplet is further complicated by a triplet splitting due to coupling with the ortho fluorine atoms of the adjacent pentafluorophenyl group.

**13C n.m.r. Spectra of isomeric bromoterphenyls**

The structures of the two isomeric bromopolyfluoroterphenyls under discussion was deduced from the pattern of their ¹⁹F n.m.r. spectral shifts, verified by consideration of their respective ¹³C n.m.r. patterns.

It has been shown that the electronegativity of the electron donating pentafluorophenyl group is similar to that of bromine. If the pentafluorophenyl groups are assumed to be bromines, then the spectra can be interpreted by comparison with ortho substituted di- and tri- bromofluorobenzenes and with 2-bromononafluorobiphenyl (this latter compound has an unsubstituted C₆F₅ group ortho to bromine).

The ¹³C n.m.r. spectrum of 1,2-dibromotetrafluorobenzene consists of three lines: in order of decreasing field relative to TMS; -109.1, -140.7 and -146.3 p.p.m. (Fig. No.33).
Figure No. 33 $^{13}$C n.m.r. Spectrum of 1,2-Dibromotetrafluorobenzene
Figure No. 34. $^{13}$C n.m.r. Spectrum of 2-Bromonafluorobiphenyl
In both bromobenzene and bromopentafluorobenzene, it is found that the order of chemical shifts of the unsubstituted carbons is:

\[
{\text{ortho}} > {\text{para}} > {\text{meta}}
\]

Hence, in \(1,2\)-dibromotetrafluorobenzene, the line at lowest field corresponds to \(C_2\) and the line at \(-140.7\) p.p.m. to \(C_3\). The line at \(-109.1\) p.p.m. is due to the two identical \(C_1\)-Br atoms (the corresponding shift in bromo-pentafluorobenzene is \(-94.7\) p.p.m., and the shift of the two ortho C-Br's in \(1,2,3\)-tribromotrifluorobenzene is \(-109.9\) p.p.m.)

![Diagram of chemical shifts](image)

The spectrum of \(2\)-bromonafluorobiphenyl (Fig. No. \(34\)) consists of two groups of lines.

![Diagram of 2-bromonafluorobiphenyl](image)

At highest field, there are three lines which are interpreted as being due to \(C_1\), \(C_6\) and \(C_7\). Assuming that the unsubstituted pentafluorophenyl ring is acting as another bromine atom, then the lines at \(107.2\) and \(-107.9\) p.p.m. compare favourably with the C-Br shifts in \(1,2\)-dibromotetrafluorobenzene, as the \(C_6\) group lies ortho to the Br in the molecule. It is difficult to distinguish between the shifts, but that at \(-107.9\) p.p.m. may be due to \(C_1\)-Br and that at \(-107.2\) p.p.m. to \(C_6\). \(C_7\) "sees" the substituted ring as a modified bromine of greater electronegativity than usual and the shift is
correspondingly greater than that of C_1 or C_6, lying as it does at -113.9 p.p.m.

The second group consists of five lines which can be assigned by considering 2-bromononafluorobiphenyl as two compounds:

We can look at A as a modified 1,2-dibromotetrafluorobenzene with the two C_1 atoms as being ortho to the "two" bromines and the two C_2 atoms, meta. By comparison with the shifts of the ortho and meta carbons in 1,2-dibromotetrafluorobenzene, the lines at -146.6 and -140.9 p.p.m. can be considered due, respectively, to C_1 and C_2 in the compound A.

Compound B can be looked on as a modified bromopentafluorobenzene. Since the order of chemical shifts is ortho > para > meta in "normal" bromopentafluorobenzene, the three remaining lines at -144.9, -142.6 and -138.5 p.p.m. can be assigned, respectively, to C_1, C_3 and C_2 in compound B.

The spectrum of 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene, likewise, consists of two sets of lines (Fig.No. 3).
The peak at highest field, -107.8 p.p.m. is undoubtedly that due to C₁, lying as it does in the region of C-Br chemical shifts:

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-Br shift relative to TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-C₆F₅</td>
<td>-94.7</td>
</tr>
<tr>
<td>1,2-Br₂-C₆F₄</td>
<td>-109.1</td>
</tr>
<tr>
<td>2-Br-C₁₂F₉</td>
<td>-107.8</td>
</tr>
<tr>
<td>1,2,3-Br₃-C₆F₃</td>
<td>-109.9, -123.0</td>
</tr>
</tbody>
</table>

The lines at -115.6 and -121.8 p.p.m. are thought to be due to the interannular carbons C₂, C₆, C₇ and C₁₃ but it is not possible to assign them to individual carbons.

The lines of the second groups can be assigned by assuming the compound to be modified tribromotrifluorobenzene:

By comparison with the known ¹³C shifts in 1,2,3-tribromotrifluorobenzene (Fig. No. 27) the line at lowest field, -150.7 p.p.m. is assumed to be due to the "identical" carbons C₃ and C₅; the C₄ resonance then lies at -139.9 p.p.m.

If we look on the unsubstituted pentafluorophenyl rings as being modified bromopentafluorobenzenes, then the three remaining lines can easily be assigned.
Assuming the order of chemical shifts to be the normal ortho > para > meta, the lines at -138.2, -142.8 and -144.6 can be assigned as below:

\[
\begin{array}{c}
\text{Br} \\
\begin{array}{c}
 F \\
145.2 \\
140.9 \\
\end{array} \\
\end{array} \quad \begin{array}{c}
\text{Br} \\
\begin{array}{c}
 F \\
144.6 \\
138.2 \\
\end{array}
\end{array}
\]

Hence the total assignment of lines in 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene is as follows, (excepting the interannular carbon atoms):

\[
\begin{array}{cccc}
138.2 & 144.6 & 150.7 & 139.9 \\
142.8 & 138.2 & 144.6 & 150.7 \\
\end{array}
\]

If we make the similar assumption that the \( \text{C}_6\text{F}_5^- \) groups act as bromines, in the interpretation of the spectrum of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene, a very similar result is obtained (Fig. No 30).

\[
\begin{array}{cccc}
137.9 & 144.5 & 149.1 & 141.5 \\
142.7 & 137.9 & 144.5 & 149.1 \\
\end{array}
\]

It can be seen that the line for the ortho carbons of the pentafluorophenyl rings is split (coupling constant 7.3Hz). The two pentafluorophenyl rings are in slightly differing environments, one being ortho to the bromine atom and the other meta, and this leads to the splitting of the line for the ortho carbons.

Infra-Red Spectra of Bromopolyfluorobiphenyl Isomers

Long and Steele have shown that the carbon- bromine stretching mode in
bromopentafluorobenzene (Fig. No. 9) occurs at 836 cm\(^{-1}\), whereas that of 2-bromononafluorobiphenyl (Fig. No. 13) is at 833 cm\(^{-1}\). From the infrared data of 2,2',6- and 2,2',3-tribromoheptafluorobiphenyl\(^{54}\), it has been shown that the carbon-bromine stretching frequency depends on the position of the bromine atom relative to a polyfluorobiphenyl system. In 2,2',6-tribromoheptafluorobiphenyl, any of the three bromine atoms can be viewed as ortho to the interannular carbon-carbon bond of the polyfluorobiphenyl system and only one carbon-bromine stretching absorption at 826 cm\(^{-1}\) is observed. In 2,2',3-tribromoheptafluorobiphenyl, however, two of the bromines, \(F_2\) and \(F_{2'}\), are ortho to the inter-annular carbon-carbon bond, whereas \(F_3\) is meta and three carbon bromine stretching absorptions are observed\(^{54}\), i.e. at 805, 827 and 869 cm\(^{-1}\).

1,3-Bis(pentafluorophenyl)-2-bromotrifluorobenzene (Fig. No 15) exhibits only one carbon-bromine stretching frequency at 833 cm\(^{-1}\) due to the bromine being ortho to the inter-annular carbon-carbon bond, but it is at 850 cm\(^{-1}\) in 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene (Fig. No 16) as the bromine atom can be regarded as either ortho or meta to the inter-annular carbon-carbon bonds.

**Mass spectrum of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene**

The parent ion, \(C_{18}F_{13}Br^+\), gives rise to the base peak in the spectrum of 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene. The only fragment ion of any size is that of \(C_{17}F_{11}^+\); the other fragments being of low relative intensities. The stability of the compound towards electron impact is demonstrated by the presence of a cluster of peaks centred at 272 due to the doubly-charged parent ion, \(C_{18}F_{13}Br_{2}^{2+}\). Metastables are observed for successive loss of \(Br\) and \(CF_2\) from the parent ion: loss of \(CF_3\) from \(C_{18}F_{12}^+\) is responsible for a metastable peak centred at \(m/e 315\). (Table 9).

**Mass spectrum of 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene**

As above, the parent ion, \(C_{18}F_{13}Br^+\), gives rise to the base peak in the spectrum of the symmetrical isomer. The compound shows more fragmentation than the
above; the ion $^{\text{C}18\text{F}_{13}}^+$ being some 3.4 times greater in relative intensity compared to the corresponding ion in the unsymmetrical isomer. This is probably due to the steric crowding of the bromine atom, making its loss easier and thereby relieving the strain on the molecule as a whole. However, the compound is relatively stable towards electron impact, as the doubly-charged parent ion, $^{\text{C}18\text{F}_{13}\text{Br}^{2+}}$, is present in a relatively large intensity. Metastables, corresponding to successive loss of Br and $\text{CF}_2$ from the parent ion are observed; loss of $\text{CF}_3$ from the ions $^{\text{C}18\text{F}_{13}}^+$ and $^{\text{C}18\text{F}_{12}}^+$ is also observed. (Table 10).

Mass spectrum of 1,2-bis(pentafluorophenyl)-3-hydrotrifluorobenzene

The compound proves to be relatively stable to electron impact. Very little fragmentation of the parent ion, $^{\text{C}18\text{F}_{13}}^+$ is observed. The $^{\text{C}18\text{F}_{13}}^+$ ion fragments by loss of F to give the $^{\text{C}18\text{F}_{12}}^+$ ion at $m/e$ 445, by loss of $\text{CF}_2$ to give $^{\text{C}17\text{F}_{11}}^+$ at $m/e$ 413 and by loss of $\text{CF}_3$, resulting in the formation of a peak at $m/e$ 395, corresponding to $^{\text{C}17\text{F}_{10}}^+$. These transitions are verified by the existence of the corresponding metastables. A metastable corresponding to loss of $\text{CF}_2$ by $^{\text{C}17\text{F}_{11}}^+$ is also observed. (Table 11).
Table 9

Partial Mass Spectrum of 1,2-Bis(pentafluorophenyl)-3-bromotrifluorobenzene

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>545/543</td>
<td>$^{13}C_{17}F_{13}Br^+$</td>
<td>29.75</td>
</tr>
<tr>
<td>544/542</td>
<td>$C_{18}F_{13}Br^+$</td>
<td>100</td>
</tr>
<tr>
<td>525</td>
<td>$C_{18}F_{12}Br^+$</td>
<td>2.47</td>
</tr>
<tr>
<td>474</td>
<td>$C_{17}F_{10}Br^+$</td>
<td>6.61</td>
</tr>
<tr>
<td>463</td>
<td>$C_{18}F_{13}$</td>
<td>7.85</td>
</tr>
<tr>
<td>444</td>
<td>$C_{18}F_{12}$</td>
<td>9.91</td>
</tr>
<tr>
<td>413</td>
<td>$C_{17}F_{11}$</td>
<td>25.61</td>
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<tr>
<td>406</td>
<td>$C_{18}F_{10}$</td>
<td>3.30</td>
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<tr>
<td>394</td>
<td>$C_{17}F_{10}$</td>
<td>3.71</td>
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<tr>
<td>382</td>
<td>$C_{16}F_{10}$</td>
<td>2.47</td>
</tr>
<tr>
<td>375</td>
<td>$C_{17}F_{9}$</td>
<td>8.67</td>
</tr>
<tr>
<td>344</td>
<td>$C_{16}F_{8}$</td>
<td>4.95</td>
</tr>
<tr>
<td>337</td>
<td>$C_{17}F_{7}$</td>
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<td>313</td>
<td>$C_{15}F_{7}$</td>
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<tr>
<td>296</td>
<td>$C_{12}F_{8}$</td>
<td>2.47</td>
</tr>
<tr>
<td>275</td>
<td>$C_{15}F_{5}$</td>
<td>1.65</td>
</tr>
<tr>
<td>272/271</td>
<td>$C_{18}F_{13}Br^{2+}$</td>
<td>7.02</td>
</tr>
<tr>
<td>227</td>
<td>$C_{11}F_{5}$</td>
<td>1.65</td>
</tr>
<tr>
<td>222</td>
<td>$C_{9}F_{6}^+/C_{16}F_{12}^{2+}$</td>
<td>5.37</td>
</tr>
<tr>
<td>203</td>
<td>$C_{9}F_{5}$</td>
<td>5.37</td>
</tr>
<tr>
<td>172</td>
<td>$C_{6}F_{4}$</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Metastable peaks were observed for the losses:

- $C_{18}F_{13}Br^+ - Br \rightarrow C_{18}F_{13}^+$ observed 394.0, calculated 394.7
- $C_{18}F_{13}^+ - CF_2 \rightarrow C_{17}F_{11}^+$ observed 369.0, calculated 368.9
- $C_{18}F_{12}^+ - CF_3 \rightarrow C_{17}F_{9}^+$ observed 315.0, calculated 316.7
Table 9 Cont'd.

A possible metastable corresponding to the loss:

\[
\text{Observed} \quad \text{Calculated}
\]

\[
\begin{align*}
\text{C}_{18}^{\text{F}}_{13} \text{Br}^+ & \rightarrow \text{C}_{17}^{\text{F}}_{10} \text{Br}^+ \\
413.0 & \quad 413.0
\end{align*}
\]

was obscured by the ion cluster \( m/e 413 \) of \( \text{C}_{17}^{\text{F}}_{11}^+ \).
Table 10

Partial Mass Spectrum of 1,3-Bis(pentafluorophenyl)-2-bromotrifluorobenzene

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>545/543</td>
<td>$^{13}$C$<em>{17}$F$</em>{13}$Br$^+$</td>
<td>26.66</td>
</tr>
<tr>
<td>544/542</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^+$</td>
<td>100</td>
</tr>
<tr>
<td>524</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^+$</td>
<td>3.92</td>
</tr>
<tr>
<td>474</td>
<td>$^{13}$C$<em>{17}$F$</em>{10}$Br$^+$</td>
<td>3.92</td>
</tr>
<tr>
<td>464</td>
<td>$^{13}$C$<em>{17}$F$</em>{13}$</td>
<td>5.49</td>
</tr>
<tr>
<td>463</td>
<td>$^{13}$C$<em>{17}$F$</em>{13}$</td>
<td>26.66</td>
</tr>
<tr>
<td>445</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>3.52</td>
</tr>
<tr>
<td>444</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
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<tr>
<td>414</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>4.70</td>
</tr>
<tr>
<td>413</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>23.13</td>
</tr>
<tr>
<td>406</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>4.70</td>
</tr>
<tr>
<td>394</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>17.25</td>
</tr>
<tr>
<td>382</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>2.74</td>
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<td>375</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>10.58</td>
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<td>344</td>
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</tr>
<tr>
<td>337</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>2.35</td>
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<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>5.09</td>
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<tr>
<td>296</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>4.31</td>
</tr>
<tr>
<td>275</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$</td>
<td>1.96</td>
</tr>
<tr>
<td>272/271</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>11.37</td>
</tr>
<tr>
<td>227</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>2.35</td>
</tr>
<tr>
<td>222</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>5.49</td>
</tr>
<tr>
<td>206.5</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>6.66</td>
</tr>
<tr>
<td>203</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>4.31</td>
</tr>
<tr>
<td>172</td>
<td>$^{13}$C$<em>{17}$F$</em>{12}$Br$^{2+}$</td>
<td>5.49</td>
</tr>
</tbody>
</table>
Metastable peaks were observed for the losses:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{+}\text{C}<em>{18}\text{F}</em>{13}\text{Br} \rightarrow \text{C}<em>{18}\text{F}</em>{13}$</td>
<td>-Br</td>
<td>394.0</td>
</tr>
<tr>
<td>$^{+}\text{C}<em>{18}\text{F}</em>{13} \rightarrow \text{C}<em>{17}\text{F}</em>{11}$</td>
<td>-CF$_2$</td>
<td>368.0</td>
</tr>
<tr>
<td>$^{+}\text{C}<em>{18}\text{F}</em>{13} \rightarrow \text{C}<em>{17}\text{F}</em>{10}$</td>
<td>-CF$_3$</td>
<td>336.0</td>
</tr>
<tr>
<td>$^{+}\text{C}<em>{18}\text{F}</em>{12} \rightarrow \text{C}<em>{17}\text{F}</em>{9}$</td>
<td>-CF$_3$</td>
<td>315.0</td>
</tr>
</tbody>
</table>

A possible metastable corresponding to the loss:

$^{+}\text{C}_{18}\text{F}_{13}\text{Br} \rightarrow \text{C}_{17}\text{F}_{10}\text{Br}^+$

was obscured by the ion cluster at m/e 413 of $^{+}\text{C}_{17}\text{F}_{11}$. 
Table 11

Partial Mass Spectrum of 1,2-Bis(pentafluorophenyl)-3-hydrotrifluorobenzene

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>465</td>
<td>$^{13}$CC$<em>{17}$F$</em>{13}$H$^+$</td>
<td>20.00</td>
</tr>
<tr>
<td>464</td>
<td>C$<em>{18}$F$</em>{13}$H$^+$</td>
<td>100.00</td>
</tr>
<tr>
<td>445</td>
<td>C$<em>{18}$F$</em>{12}$H$^+$</td>
<td>32.85</td>
</tr>
<tr>
<td>425</td>
<td>C$<em>{18}$F$</em>{11}$H$^+$</td>
<td>4.28</td>
</tr>
<tr>
<td>413</td>
<td>C$<em>{17}$F$</em>{11}$H$^+$</td>
<td>9.28</td>
</tr>
<tr>
<td>395</td>
<td>C$<em>{17}$F$</em>{10}$H$^+$</td>
<td>48.57</td>
</tr>
<tr>
<td>376</td>
<td>C$<em>{17}$F$</em>{9}$H$^+$</td>
<td>12.85</td>
</tr>
<tr>
<td>364</td>
<td>C$<em>{16}$F$</em>{9}$H$^+$</td>
<td>17.14</td>
</tr>
<tr>
<td>232</td>
<td>C$<em>{18}$F$</em>{13}$H$_{2}^+$</td>
<td>5.71</td>
</tr>
</tbody>
</table>

Metastable peaks were observed for the losses:

- $\text{C}_{18}F_{13}H^+ - F \rightarrow \text{C}_{18}F_{12}H^+$, Observed: 326.2, Calculated: 326.77
- $\text{C}_{18}F_{13}H^+ - \text{CF}_2 \rightarrow \text{C}_{17}F_{11}H^+$, Observed: 368.3, Calculated: 367.6
- $\text{C}_{18}F_{13}H^+ - \text{CF}_3 \rightarrow \text{C}_{17}F_{10}H^+$, Observed: 337.0, Calculated: 336.2
- $\text{C}_{17}F_{11}H^+ - \text{CF}_2 \rightarrow \text{C}_{16}F_9H^+$, Observed: 319.9, Calculated: 320.8

The metastable peaks were very broad and accurate judgement of position proved difficult.
Attempted Preparation of Polychloroaromatic Derivatives of Main-group Elements.
Direct synthesis may be defined as the preparation of an organometallic compound directly from the pertinent metallic element and a suitable alkyl or aryl halide, the reaction being carried out in vacuo at high temperature. The first direct synthesis of an organometallic compound was described by Frankland in 1849\textsuperscript{225}; he prepared ethylzinc iodide via the reaction of metallic zinc and ethyl iodide:

$$\text{Zn} + C_2H_5I \xrightarrow{72^\circ} C_2H_5ZnI$$

and also noted its thermal disproportionation at higher temperatures:

$$2 C_2H_5\text{ZnI} \xrightarrow{120^\circ} (C_2H_5)_2\text{Zn} + 2\text{ZnI}_2$$

Since that time, organometallic chemists have preferred to prepare compounds directly from the relevant metal, if at all possible. Twenty-four of the Main-Group elements are known now to participate in direct syntheses of organometallic derivatives. In those cases where the metal is insufficiently reactive, a catalyst, such as copper or silver is often used\textsuperscript{226}. Activation of the metal by free halogen is also a useful method and works particularly well with lithium, magnesium and aluminium.

Direct synthesis is often the only available synthetic route to perfluoroalkyl derivatives of metals and metalloids because of the instability of the corresponding Grignard and lithium reagents. For example, bis(trifluoromethyl)-disulphide and -diselenide may be prepared in high yield by the thermal reaction of sulphur (or selenium) with trifluoromethane\textsuperscript{227,228}.

Iodopentafluorobenzene has been found to be an extremely useful precursor in the direct synthesis of a range of pentafluorophenyl organometallic derivatives, since bis(pentafluorophenyl)mercury was first prepared by thermal reaction of iodine pentafluorobenzene with mercury at 300\textdegree\textsuperscript{152}. 
Low yields are obtained if the reactants are not free from moisture or air. When the reaction tubes are thoroughly evacuated and dried, almost theoretical yields are obtained in some cases.

When iodopentafluorobenzene is heated or irradiated with UV light, the C-I bond undergoes homolytic cleavage to yield a pentafluorophenyl radical and an iodine atom:

\[
C_6F_5I \rightleftharpoons C_6F_5^* + I
\]

The yield is low, since primary recombination occurs preferentially, but is increased considerably in the presence of a second component, e.g. a metal, that can react with either the organic radical or iodine atom or with both.

Direct methods are not amenable to the synthesis of perfluoroaromatic derivatives of transition metals. The reaction between iodopentafluorobenzene and copper powder at 130°, for example, affords decafluorobiphenyl in almost quantitative yield, while silver powder and iodopentafluorobenzene at 250° produces only trace amounts of decafluorobiphenyl. However, pentafluorophenyl-copper.
and pentafluorophenylsilver\(^{215,229}\) have been isolated by other methods and been found to be quite stable thermally. There is no reaction with gold powder after four weeks at 250\(^0\).

In similar fashion, 1,2-diodotetrafluorobenzene has been used in the direct synthesis of several novel compounds. Reaction with sulphur and selenium gives the respective octafluorothianthrene and -selanthrene\(^{114,153}\):

\[
\begin{array}{c}
\text{S} \\
\text{F} \\
\text{F} \\
\text{S} \\
\text{Se} \\
\text{F}
\end{array}
\quad \xrightarrow{\text{S, Se}}
\quad
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{S} \\
\text{Se} \\
\text{F}
\end{array}
\]

Direct reaction of germanium, tellurium and other main group metals with 1,2-diodotetrafluorobenzene has been shown to yield the corresponding derivatives\(^{114}\).

Direct synthetic methods have many inherent advantages, such as simplicity, ready availability of materials and potentially high yields. It was decided to attempt the extension of direct synthetic methods into the area of perchloroaromatic derivatives. A series of reactions was attempted of temperatures varying from 150-350\(^0\) with varying ratios of iodopentachlorobenzene (and 1,2-diodotetrachlorobenzene) and main-group metals. It was found that at low temperatures, no reaction occurred, whereas extensive charring occurred at high temperatures. At intermediate temperatures of 210\(^0\)-280\(^0\) some reaction did occur and identifiable products were obtained. However, these were not the expected polychloro-derivatives of Group V. In all cases, the respective metallic iodide and hexachlorobenzenes were the products, identifiable by a combination of infrared, mass spectral and X-ray diffraction techniques.

The synthesis of organometallic compounds which cannot be obtained by direct combination of metal and organic reagent, can sometimes be achieved using a transmetallation reaction. This involves the replacement of the metal in a given organometallic derivative by a different metal. Organomercury compounds are well known transmetallation reagents; the mercury being capable of replacement by many main-group elements\(^{52,114,161}\). Transmetallations
using bis(pentachlorophenyl)mercury were investigated as a means of preparing main-group polychloro-derivatives. The temperature range between "no reaction" and "extensive charring" was found to be lower than in the direct combination reactions. Hexachlorobenzene was the only tractable product found in those cases where the charring was not too extensive.

When heated alone in vacuo, iodopentachlorobenzene, 1,2-diiodotetrachlorobenzene and bis(pentachlorophenyl)mercury all remain unaltered up to 350° when decomposition occurs and small quantities of hexachlorobenzene are isolated. It seems that the presence of the main-group element must in some way lower the thermal stability of the polychloro-derivative, facilitating the decomposition of a portion of the derivative to release chlorine atoms which attack the still-unde decomposed reagent; forming the hexachlorobenzene which is found in each case, e.g.

\[
\text{Cl}^- + C_6\text{Cl}_5^+ \rightarrow C_6\text{Cl}_5^- + \text{I}^- + \text{M} + \text{M-I}
\]

\[
C_6\text{Cl}_5^- + \text{Cl}^- \rightarrow C_6\text{Cl}_6
\]

When a series of trans metallation reactions were attempted with bis(2,3,4,5-tetrachlorophenyl)mercury, \((C_6\text{Cl}_4\text{H})_2\text{Hg}\), and several main-group elements, the only identifiable product was 1,2-dihydrotetrachlorobenzene. This is surprising, in the light of the above; pentachlorobenzene might have been expected as the product. In addition to the cleavage of the C-Hg-C bonds, a C-H linkage has to break in order to form the isolated product. However, comparison of the relative bond energies of the C-H bond (80.9 kcal mol\(^{-1}\)) and the C-Cl bond (93 kcal mol\(^{-1}\)) shows that the breaking of the carbon-hydrogen bond should be favoured in this case, with the corresponding formation of 1,2-dihydrotetrachlorobenzene.

Attempts were made to prepare main-group polychloroorganometallics by using the known Grignard and lithium reagents. In every reaction using pentachlorophenylmagnesium chloride, pentachlorobenzene was isolated. When pentachlorophenyllithium was used, the final product was invariably identified as pentachlorobenzene, except in one case. When sulphur dichloride was treated
with pentachlorophenyllithium, the product was a golden-brown solid, whose mass spectrum showed it to be a mixture of bis(pentachlorophenyl) polysulphides i.e. \((C_6Cl_5)_2S_x; x = 1, 2, 3\). Reaction of disulphur dichloride with pentachlorophenyllithium also gave a golden-brown product. Mass spectral analysis showed the solid to be a mixture of bis(pentachlorophenyl) polysulphides i.e. \((C_6Cl_5)_2S_x; x = 1, 2, 3, 4\). This series of bis(pentachlorophenyl) poly-sulphides does indicate that in the case of sulphur (as well as lithium and mercury), the formation of polychloroaromatic derivatives of the Main-Group elements is feasible.
A Reinvestigation of Phenylene- and Polyphenylene-Mercurials
Crystal structures of organomercury compounds indicate that the carbon-mercury-carbon bond angle is, with only a few exceptions, close to 180°. Mercury (II) cyanide exhibits an appreciable degree of coordination between the nitrogen and mercury atoms, which causes partial distortion of the metal's environment and consequently the C-Hg-C angle is only 171°232.

It has been shown by X-ray structure analysis that whereas diphenylmercury is linear and centrosymmetric in the solid state, crystal forces distort the bis(pentafluorophenyl)mercury molecule slightly, giving rise to a C-Hg-C angle of 176° and twisting the fluoroaromatic rings 60° apart234.

This tendency towards collinearity was not appreciated by earlier workers in the field and consequently they gave incorrect structures to a number of cyclic mercury compounds. In some instances, later investigations have shown that particular compounds are polymeric to an extent which allows collinear C-Hg-C bonds. For example, the compound originally described as (A) has in fact the structure (B), in which the shorter Hg-O distances (2.2A) are those expected for a chemical bond. Even so, the C-Hg-C angle is quoted as 176°235.

The compound 2,2'-biphenylenemercury, formed by the reaction of 2,2'-dilithiobiphenyl and mercuric chloride236 was originally assigned the structure (C). However, molecular weight determinations by Wittig158 indicated that the compound was tetrameric, presumably with the structure shown in (D), in which the phenyl groups are twisted relative to each other.
Similarly, the substance "o-phenylenemercury" resulting from the treatment of o-dibromobenzene with sodium amalgam in the presence of ethyl acetate\(^{237}\) was thought to have the structure:

![Chemical structure of o-phenylenemercury](image)

but was shown by a partial X-ray structure determination\(^{157}\) to be hexameric (see figure 33).

The perfluoroaromatic analogue of o-phenylenemercury, perfluorotribenzo(b,e,h)-(1,4,7)trimercuronin has been reported three times in the literature and may be synthesized by either thermal decarboxylation of mercuric tetrafluorophthalate, \([C_6F_5(CO_2)_2]Hg\)^\(^{155}\) which occurs in two stages, or by sulphur trioxide elimination by thermal decomposition of mercuritetrafluorobenzene-sulphonate, \((-HgC_6F_4SO_3^-)_n\)^\(^{156}\)

\[
\begin{align*}
\text{F} & \quad \text{CO}_2 \\
\text{Hg} & \quad 220^\circ \\
\text{F} & \quad \text{CO}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{Hg} \\
\text{CO}_2 & \quad 300^\circ \\
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{Hg} \\
\text{SO}_3 & \quad 300-400^\circ \\
\end{align*}
\]
For a small scale preparation, heating 1,2-diiodotetrafluorobenzene and mercury in an evacuated sealed tube at 300°, is by far the most practical. The reaction temperature is, however, fairly critical, for at 350° extensive charring occurs and yields of the product are very low, while at 250° only mercuric iodide is isolated. The remarkable thermal and oxidative stability of this compound can be judged by the fact that it can be purified by sublimation in an open tube at 320°.

It is insoluble in all common organic solvents except acetone, in which it is partially soluble. It may be cleaved by iodine and by silver powder, yielding 1,2-diiodotetrafluorobenzene and octafluorobiphenylene respectively. Reaction with sulphur and selenium at 300° in sealed tubes affords octafluorothianthrene and octafluoroselanthrene.

The infrared spectrum of \((C_6F_4Hg)_3\), figure 34, does not show the two bands at 940 cm\(^{-1}\) and 1210 cm\(^{-1}\) reported by Sartori\(^{155}\) and this anomaly has also been noted by Deacon\(^{156}\). Professor Sartori in a private communication has verified that these peaks should be absent and suggests that they were due to traces of \((C_6F_4)_2C_6F_3ClHg_3\) (arising from incomplete Cl-F exchange in his starting material preparation). The band at 940 cm\(^{-1}\) is likely to be due to a \(C_6F_4\)-to-\(C_6F_4\) vibration, considering the band at 939 cm\(^{-1}\) in \((C_{12}F_8Hg)_3\) and a large number of similar compounds (Table 11). The two bands at 1100 and 1015 cm\(^{-1}\)
Hexameric Structure of Ortho-phenylenemercury

Structure of Ortho-terphenylenemercury dimer

Trimeric Structure of Ortho-phenylenemercury
Infrared Spectrum of Perfluorotribenzo(b,e,h)(1,4,7)trimercuronin
**Table 11**

$C_6F_4$-to-$C_6F_4$ Stretching Vibrations of Substituted Octafluorobiphenyl Metal and Metalloidal Derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_6F_4$-to-$C_6F_4$ Stretching vibrations (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{12}F_8S$</td>
<td>948</td>
</tr>
<tr>
<td>$C_{12}F_8Se$</td>
<td>944</td>
</tr>
<tr>
<td>$C_{24}F_{16}$</td>
<td>962,970</td>
</tr>
<tr>
<td>$(C_{12}F_8)_2Si$</td>
<td>927</td>
</tr>
<tr>
<td>$(C_{12}F_8)_2Ge$</td>
<td>915</td>
</tr>
<tr>
<td>$(C_{12}F_8)_2Sn$</td>
<td>914</td>
</tr>
<tr>
<td>$C_{12}F_8Si(C_6H_5)_2$</td>
<td>921,996</td>
</tr>
<tr>
<td>$C_{12}F_8Ge(C_6H_5)_2$</td>
<td>921,996</td>
</tr>
<tr>
<td>$C_{12}F_8Sn(C_6H_5)_2$</td>
<td>914,997</td>
</tr>
<tr>
<td>$C_{12}F_8Ti(C_5H_5)_2$</td>
<td>962,970</td>
</tr>
<tr>
<td>2,2'-$Cl_{2}C_{12}F_8$</td>
<td>949</td>
</tr>
<tr>
<td>2,2'-$Br_{2}C_{12}F_8$</td>
<td>950</td>
</tr>
<tr>
<td>2,2'-$I_{2}C_{12}F_8$</td>
<td>947</td>
</tr>
<tr>
<td>2-$BrC_{12}F_9$</td>
<td>958</td>
</tr>
<tr>
<td>2,2'-$H_{2}C_{12}F_8$</td>
<td>929</td>
</tr>
<tr>
<td>2H,2'$Cl$-$C_{12}F_8$</td>
<td>941</td>
</tr>
<tr>
<td>2H,2'$Br$-$C_{12}F_8$</td>
<td>941</td>
</tr>
</tbody>
</table>
are due to the carbon-fluorine stretching frequencies, whilst the strong
band at 820 cm\(^{-1}\) may be assigned to the carbon-mercury stretching frequency,
since it lies in the expected range\(^{52}\) as seen below:

\[
\begin{array}{c|c}
\text{Compound} & \nu (\text{Hg-C}) \text{cm}^{-1} \\
(C_6F_5)_2\text{Hg} & 806 \\
(C_{12}F_8\text{Hg})_3 & 815 \\
(2-\text{BrC}_6F_4)_2\text{Hg} & 830 \\
(2-\text{HC}_6F_4)_2\text{Hg} & 813 \\
(C_{12}F_4)_2\text{Hg} & 819 \\
\end{array}
\]

Perfluorotribenzo(b,e,h)(1,4,7)mercuronin was proved to be trimeric by mass
spectral studies, the highest cluster of isotopomeric ions being centred at
\(m/e 1046,\) i.e. \((C_6F_4\text{Hg})_3^+\). Owing to the large number of naturally occurring
isotopes of mercury, ions containing one or more mercury atoms exhibit a
very complex pattern of peaks.

<table>
<thead>
<tr>
<th>Mass No.</th>
<th>% Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>0.14</td>
</tr>
<tr>
<td>198</td>
<td>10.02</td>
</tr>
<tr>
<td>199</td>
<td>16.84</td>
</tr>
<tr>
<td>200</td>
<td>23.13</td>
</tr>
<tr>
<td>201</td>
<td>13.22</td>
</tr>
<tr>
<td>202</td>
<td>29.80</td>
</tr>
<tr>
<td>204</td>
<td>6.85</td>
</tr>
</tbody>
</table>

As the pattern is unique to the number of Hg and C atoms, it enables rapid
and accurate identification of the various ion clusters.

One of the most interesting aspects of the mass spectrum of \((C_6F_4\text{Hg})_3\) is the
singly charged ion \(\text{Hg}_3^+\), unambiguously identified by comparison of observed
and calculated (using a published computer programme\(^{238}\)) intensities of peaks
in the ion cluster centred at \(m/e 602\) (fig.no.35 ). Absolute
Figure No. 5) Comparison of the observed (solid line) and theoretical (broken line) mass spectral intensities for important ions in \( (C_6F_4Hg)_3 \).
verification of the identity of $\text{Hg}_3^+$ was obtained by measuring the accurate mass of the peak at $m/e$ 593, $^{198}\text{Hg}$:

- Measured mass: 593.9000
- Calculated mass: 593.9001

The trimercuronin shows eleven mass spectral peaks containing mercury and $\text{C}_6\text{F}_4$ units, (Table 12), all of low relative abundance. The relative intensities within these peaks are in good agreement with the calculated patterns. The calculated and observed intensities for the molecular ion $(\text{C}_6\text{F}_4\text{Hg})_3$ is shown in Figure 35 as are those of the $\text{Hg}_3^+$ and $\text{Hg}_2^+$ ions. The two most intense peaks are due to the organic species $\text{C}_{12}\text{F}_{18}^+$ and $\text{C}_6\text{F}_4^+$ (base peak), and several peaks corresponding to the cracking patterns of these two ions are observed. By direct analogy with the o-phenylenemercury, one might have expected the perfluoromercuronin to be hexameric because normally structures of fluorine and hydrogen analogues are so alike that very similar melting points ($\pm$ 15-200) are observed for the two types of derivative. Indeed, in the cases of $(\text{C}_6\text{F}_5)_4\text{Sn}$, m.pt. 2210 and $(\text{C}_6\text{H}_5)_4\text{Sn}$, m.pt. 2270, the crystalline compounds appear to be physically so similar that the addition of one to the other causes little or no depression in the host's melting point. When the melting point does differ by more than 200, e.g. triphenylene and perfluorotriphenylene239, this is due to severe molecular twisting due to fluorine-fluorine steric interactions240.

Perfluorotriphenylene

Wittig and his co-workers described158 the preparation of ortho-phenylenemercury and on the basis of their molecular weight determinations in solution158 and Grädic's partial X-ray crystal measurements157, assigned the hexameric formula
### Table 12

**Partial Mass Spectrum of Perfluorotribenzo(b,e,h)(1,4,7)trimercuronin**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1046</td>
<td>(C₆F₅)₄Hg⁺</td>
<td>18.3</td>
</tr>
<tr>
<td>1027</td>
<td>(C₆F₄)₂C₆F₃Hg⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>844</td>
<td>(C₆F₅)₃Hg₂⁺</td>
<td>0.7</td>
</tr>
<tr>
<td>696</td>
<td>(C₆F₄)₂Hg⁺</td>
<td>7.2</td>
</tr>
<tr>
<td>677</td>
<td>(C₆F₃)C₆F₄Hg₂⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>644</td>
<td>(C₆F₄)₃Hg⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>632</td>
<td>Hg₃⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>548</td>
<td>C₆F₄Hg₂⁺</td>
<td>0.8</td>
</tr>
<tr>
<td>523</td>
<td>(C₆F₄Hg)₂⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>498</td>
<td>(C₆F₄)₂Hg⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>479</td>
<td>(C₆F₄)C₆F₃Hg⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>448</td>
<td>(C₆F₄)₂Hg⁺</td>
<td>0.1</td>
</tr>
<tr>
<td>444</td>
<td>C₁₈F₁₂⁺</td>
<td>4.4</td>
</tr>
<tr>
<td>402</td>
<td>Hg₂⁺</td>
<td>10.5</td>
</tr>
<tr>
<td>350</td>
<td>C₆F₄Hg⁺</td>
<td>1.0</td>
</tr>
<tr>
<td>348</td>
<td>(C₆F₄Hg)₂⁺</td>
<td>1.0</td>
</tr>
<tr>
<td>331</td>
<td>C₆F₃Hg⁺</td>
<td>0.7</td>
</tr>
<tr>
<td>296</td>
<td>C₁₂F⁺</td>
<td>89.2</td>
</tr>
<tr>
<td>277</td>
<td>C₁₂F⁺</td>
<td>3.3</td>
</tr>
<tr>
<td>246</td>
<td>C₁₁F⁺</td>
<td>4.4</td>
</tr>
<tr>
<td>m/e</td>
<td>Ion</td>
<td>Relative Abundance</td>
</tr>
<tr>
<td>-----</td>
<td>-------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>227</td>
<td>C_{11}F_{5}^+</td>
<td>6.7</td>
</tr>
<tr>
<td>202</td>
<td>Hg^+</td>
<td>7.2</td>
</tr>
<tr>
<td>148</td>
<td>C_{6}F_{4}^+</td>
<td>100.0</td>
</tr>
<tr>
<td>129</td>
<td>C_{6}F_{3}^+</td>
<td>34.5</td>
</tr>
<tr>
<td>117</td>
<td>C_{5}F_{3}^+</td>
<td>18.2</td>
</tr>
<tr>
<td>110</td>
<td>C_{6}F_{2}^+</td>
<td>7.3</td>
</tr>
<tr>
<td>98</td>
<td>C_{5}F_{2}^+</td>
<td>28.3</td>
</tr>
<tr>
<td>79</td>
<td>C_{2}F^+</td>
<td>21.4</td>
</tr>
</tbody>
</table>
(C₆H₄Hg)₆, see figure 33. Consultations of Dreiding models have shown that there are no steric reasons why a planar ortho-phenylenemercury trimer should not exist and recently¹¹4 mass spectral evidence has been advanced to show that the trimer (C₆H₄Hg)₃ can, indeed, exist. For this reason the following reactions were carried in order to repeat Wittig's preparation of the hexamer and so to clarify the "ortho-phenylenemercury" problem:

i) 1,2-Diodobenzene shaken with sodium amalgam in THF at room temperature;
ii) 1,2-Diodobenzene shaken with potassium amalgam in THF at room temperature;
iii) 1,2-Dibromobenzene shaken or stirred with sodium amalgam in THF at room temperature;
iv) 1,2-Dibromobenzene shaken with potassium amalgam in THF at room temperature;
v) 1,2-Dibromobenzene shaken with sodium amalgam in THF at 0°C;
vi) 1,2-Dibromobenzene refluxed with sodium amalgam in THF;
vii) 1,2-Dibromobenzene shaken with sodium amalgam in diethyl ether at room temperature;
viii) 1,2-Dibromobenzene shaken with sodium amalgam in a 50:50 mixture of diethyl ether and ethyl acetate;
ix) 1,2-Dichlorobenzene shaken with either sodium or potassium amalgam in THF at room temperature;
x) 1,2-Dichlorobenzene shaken with either sodium or potassium amalgam in diethyl ether at room temperature;
xi) 1-Bromo-2-fluorobenzene shaken with sodium amalgam in THF at room temperature.

In all cases, only ortho-phenylenemercury TRIMER was isolated.

The normal reaction time for these experiments was between 12 and 15 hours, but essentially the same yields of ortho-phenylenemercury were obtained with reaction times varying from 30 mins. to 48 hrs. (Sometimes, ortho-terphenylenemercury dimer, (C₆H₄C₆H₄C₆H₄Hg)₂ was also obtained). When 1,2-dibromobenzene was treated with sodium amalgam in monoglyme at room temperature, only
ortho-terphenylenemercury dimer 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 $290^\circ$. Analysis showed all the samples to be "ortho-phenylenemercury" but the mass spectrum of a typical analytical sample had a mass cut off at the ion $\left( C_6 H_4 Hg \right)_3^+$; the excellent fit between the observed and calculated values for the peaks in the parent ion cluster, figure no. 36, leave no doubt as to the identity of the ion and also show that very little fragmentation occurs by loss of $H$. It is apparent that this compound is the trimer of ortho-phenylenemercury and hence the hydrogen analogue of perfluorotribenzo(b,e,h)(1,4,7)trimercuronin.

There is, as yet, no published infrared spectrum of hexameric ortho-phenylenemercury, the only available data for comparison of the trimer to Wittig's hexamer being Wittig's melting-decomposition point $159$ of $325^\circ-326^\circ$ and Grdenic's X-ray crystal measurements. On the hot-stage microscope, ortho-phenylenemercury trimer begins to sublime slowly at about $260^\circ$ but does not melt below $350^\circ$. This was originally taken to mean that the trimer was a different compound to Wittig's ortho-phenylenemercury; however, it was found that the trimer melts with decomposition at $325-326^\circ$ when heated in a capillary tube. A possible explanation of this is that slight decomposition in one part of a crystal at $325-326^\circ$ triggers off decomposition in the remaining material packed in the capillary tube; sometimes, several crystals of the few hundred in the field of view on the hot-stage microscope were noted to spin rapidly or move about on the surface of the slide at $325-327^\circ$, a fact which lends some support for this idea. Thus the melting point data suggest Wittig's "hexamer" is identical to the ortho-phenylenemercury trimer.

Mixtures of ortho-phenylenemercury and ortho-terphenylenemercury dimer may be separated by sublimation at ca. $10^{-4}$ mmHg. Ortho-phenylenemercury sublimes first at $160-200^\circ$, the pure ortho-terphenylenemercury dimer remaining may then be collected at $260^\circ$. For compounds having a similar structure (as probably do ortho-phenylenemercury hexamer and ortho-terphenylenemercury dimer, see
Figure No. 36

Parent Ion Intensities for \( \text{HgC}_6\text{H}_4 \)
### Table 13
Partial Mass Spectrum of Ortho-phenylenemercury Trimer

<table>
<thead>
<tr>
<th>Mass No.</th>
<th>Assignment</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>828</td>
<td>$\text{(HgC}_6\text{H}_4)_3^+$</td>
<td>53.3</td>
</tr>
<tr>
<td>600</td>
<td>$\text{Hg}_3^+$</td>
<td>trace</td>
</tr>
<tr>
<td>550</td>
<td>$\text{Hg}_2\text{(C}_6\text{H}_4)_2^+$</td>
<td>trace</td>
</tr>
<tr>
<td>403</td>
<td>$\text{Hg}_2^+$</td>
<td>0.6</td>
</tr>
<tr>
<td>353</td>
<td>$\text{Hg(C}_6\text{H}_4)_2^+$</td>
<td>1.1</td>
</tr>
<tr>
<td>314</td>
<td>$[\text{Hg}_2\text{(C}_6\text{H}_4)_3]^2^+$</td>
<td>1.7</td>
</tr>
<tr>
<td>276</td>
<td>$\text{HgC}_6\text{H}_4^+$</td>
<td>7.8</td>
</tr>
<tr>
<td>228</td>
<td>$\text{(C}_6\text{H}_4)_3^+$</td>
<td>67.8</td>
</tr>
<tr>
<td>200</td>
<td>$\text{Hg}^+$</td>
<td>12.2</td>
</tr>
<tr>
<td>176</td>
<td>$\text{Hg(C}_6\text{H}_4)_2^{2+}$</td>
<td>2.8</td>
</tr>
<tr>
<td>152</td>
<td>$\text{(C}_6\text{H}_4)_2^+$</td>
<td>100</td>
</tr>
<tr>
<td>127</td>
<td>$\text{C}_{10}\text{H}_6^+$</td>
<td>8.9</td>
</tr>
<tr>
<td>113</td>
<td>$\text{(C}_6\text{H}_4)_3^{2+}$</td>
<td>5.6</td>
</tr>
<tr>
<td>100</td>
<td>$\text{Hg}^{2+}$</td>
<td>3.3</td>
</tr>
<tr>
<td>76</td>
<td>$\text{(C}_6\text{H}_4)_2^{2+}/\text{C}_6\text{H}_4^+$</td>
<td>71.1</td>
</tr>
</tbody>
</table>

Metastable peaks were observed for the losses:

<table>
<thead>
<tr>
<th>Equation</th>
<th>Observed</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Hg(C}_6\text{H}_4)_2^{2+} \rightarrow \text{Hg} \rightarrow (\text{C}_6\text{H}_4)_2^{2+}$</td>
<td>33.0</td>
<td>32.8</td>
</tr>
<tr>
<td>$\text{Hg}_3\text{(C}_6\text{H}_4)_3^+ \rightarrow \text{Hg}_3 \rightarrow (\text{C}_6\text{H}_4)_3^+$</td>
<td>63.0</td>
<td>62.8</td>
</tr>
<tr>
<td>$\text{Hg}_2\text{(C}_6\text{H}_4)_2^+ \rightarrow \text{Hg(C}_6\text{H}_4)_2^{2+}$</td>
<td>226.0</td>
<td>226.56</td>
</tr>
</tbody>
</table>
Predicted Stability of Ortho-Phenylenemercury Derivatives Using Dreiding Models

Criteria used were that the C-Hg-C angles had to be 180° and the Hg...Hg interactions ≥ 3.5 Å.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ((\text{C}_6\text{H}_4\text{Hg})_3)</td>
<td>detected 114 perfluoro analogue known155,156</td>
</tr>
<tr>
<td>2. ((\text{C}_6\text{H}_4\text{Hg})_4)</td>
<td>references157-159 non-rigid</td>
</tr>
<tr>
<td>3. ((\text{C}_6\text{H}_4\text{Hg})_6)</td>
<td>non-rigid</td>
</tr>
<tr>
<td>4. ((\text{C}_6\text{H}_4\text{Hg})_8)</td>
<td>this work; perfluoro analogue known reference158 two structural isomers possible, one being non-rigid formula &quot;isomer&quot; of 8 detected114</td>
</tr>
<tr>
<td>5. ((\text{C}_6\text{H}_4\text{Hg})_8)</td>
<td>detected114</td>
</tr>
<tr>
<td>6. ((\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_3)</td>
<td>detected114</td>
</tr>
<tr>
<td>7. ((\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_4)</td>
<td>two isomers possible depending on relative position of the single (\text{C}_6\text{H}_4) rings non-rigid</td>
</tr>
<tr>
<td>8. ((\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_2)</td>
<td>non-rigid</td>
</tr>
<tr>
<td>9. (\text{C}_6\text{H}_4\text{Hg}(\text{C}_6\text{H}<em>4)</em>{5}\text{Hg})</td>
<td>C-Hg-C bonds only slightly bent; possible borderline stability</td>
</tr>
<tr>
<td>10. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg}(\text{C}_6\text{H}_4\text{Hg})_4)</td>
<td></td>
</tr>
<tr>
<td>11. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg})</td>
<td></td>
</tr>
<tr>
<td>12. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg})</td>
<td></td>
</tr>
<tr>
<td>13. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg})</td>
<td></td>
</tr>
<tr>
<td>14. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg})</td>
<td></td>
</tr>
<tr>
<td>15. (\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg}))</td>
<td></td>
</tr>
<tr>
<td>16. ((\text{C}_6\text{H}<em>4)</em>{4}\text{Hg}(\text{C}_6\text{H}<em>4)</em>{4}\text{Hg})</td>
<td></td>
</tr>
<tr>
<td>17. ((\text{C}_6\text{H}_4\text{Hg})_5)</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Comments</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>18. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg}$</td>
<td>Hg...Hg separation too small</td>
</tr>
<tr>
<td>19. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg}$</td>
<td>C-Hg-C angle $&lt; 180^\circ$</td>
</tr>
<tr>
<td>20. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg}$</td>
<td>C-Hg-C angle $&lt; 180^\circ$</td>
</tr>
<tr>
<td>21. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg}$</td>
<td>ditto</td>
</tr>
<tr>
<td>22. $(\text{C}_6\text{H}_4)_4\text{Hg}$</td>
<td>ditto</td>
</tr>
<tr>
<td>23. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg}$</td>
<td>C-Hg-C angle $&lt; 180^\circ$; Hg...Hg distance only about 2.7 Å</td>
</tr>
<tr>
<td>24. $(\text{C}_6\text{H}_4)_5\text{Hg}$</td>
<td>C-Hg-C angle $&lt; 180^\circ$; two H atoms approach within 0.6 Å</td>
</tr>
<tr>
<td>25. $(\text{C}_6\text{H}_4)_6\text{Hg}$</td>
<td>two pairs of H atoms approach within 0.6 Å</td>
</tr>
</tbody>
</table>
figure 33), volatility is proportional to molecular weight. Thus it is highly unlikely that the ortho-phenylenemercury used in these sublimations is the hexamer (mol. wt. = 1656) when it sublimes at a lower temperature than ortho-terphenylenemercury dimer (mol. wt. = 858). The high thermal stability and volatility of ortho-phenylenemercury make mass spectrometry an ideal method of establishing the molecular weight; the ion of highest mass, \((C_6H_4Hg)_3^+\), obtained by introducing the sample into the spectrometer at 140°, must represent the parent ion of ortho-phenylenemercury trimer and not the highest observable fragment ion of a hexamer. The perfluoro-analogue of ortho-phenylenemercury has been described three times in the literature as a trimer and there can be little doubt that the samples of ortho-phenylenemercury prepared in this work (and probably Wittig's) are trimeric.

Dreiding models indicate that \((C_6H_4Hg)_n\) polymers should be stable for values of \(n = 3, 4, 6, 8\), see Table 14 and it is just possible that a range of such polymers is formed when ortho-dihalobenzenes react with sodium or potassium amalgams. The higher polymers with \(n = 4\) and 6 for example, are expected to have solubilities and volatilities which are considerably lower than those of the trimer and hence the least volatile and least soluble fractions in all the preparations listed above were closely examined. However, we have been unable to detect the presence of anything but the trimer, \(n = 3\).

Preliminary X-ray studies on the contents of the unit cell of single crystals lead to the same conclusion. 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, \(a = 5.59\); \(b = 23.06\); \(d_{001} = 12.23\) Å

Form 2: orthorhombic, \(a = 18.42\); \(b = 10.55\); \(c = 8.12\) Å; \(P2_12_12_1\); number of molecules, \(Z\), in unit cell = 4 for the trimer (for the hexamer \(Z = 2\), a result not possible on symmetry grounds).
The strong band at 745 cm\(^{-1}\) in the infrared spectrum of ortho-phenylene mercury, fig. no. 37, is due to the ring hydrogen out-of-plane, in-phase deformation vibration. (This is usually the strongest peak in an aromatic spectrum, as it is here in \((C_6H_6Hg)_3\).) Obviously from the planar, symmetrical structure of this molecule only a single peak would be expected in this region since there is only one type of \(C_6H_6\) group in the molecule; only a single band is observed in the structurally-related compound, triphenylene:

However, in several samples this band is found to be split even though the rest of the spectrum remains unchanged. This behaviour is probably associated with the different crystalline forms adopted by the trimer.

In mono-substituted benzenes, the 750 cm\(^{-1}\) band occasionally shows splitting due to steric affects or intermolecular forces in the solid state, e.g. in the infrared spectrum of triphenylbismuthine. In the solid state (nujol mull) A, the C-H out-of-plane deformation band is a doublet; whereas in carbon disulphide solution, B, a single band is observed:
Rao has also mentioned that the position of the 750 cm$^{-1}$ band is sensitive to mass effects.

**Triphenylene derivatives M(Ph)$_3$**

<table>
<thead>
<tr>
<th>M</th>
<th>C-H out of plane deformation cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>752</td>
</tr>
<tr>
<td>P</td>
<td>752</td>
</tr>
<tr>
<td>As</td>
<td>736</td>
</tr>
<tr>
<td>Sb</td>
<td>730</td>
</tr>
<tr>
<td>Bi</td>
<td>726</td>
</tr>
</tbody>
</table>

Two bands occur at 751 and 738 cm$^{-1}$ in the spectrum of ortho-biphenylenemercury trimer (fig.no.39) although the two C$_6$H$_4$ rings of the biphenylene groups are structurally identical in the free molecule.

In di-cyclopentadienylmercury (which is o-bonded) the Hg-C frequency is at 331 cm$^{-1}$ [242]. Possibly, the reasonably strong peak at 325 cm$^{-1}$ in ortho-phenylenemercury trimer is the Hg-C stretching frequency. In the other mercurials the relative strength of such a band would be expected to be lower: there are bands at 319 and 347 cm$^{-1}$ of weak intensity in ortho-biphenylenemercury trimer, and ortho-terphenylenemercury dimer respectively, and these are tentatively assigned to the Hg-C stretching frequencies.
An interesting feature in the mass spectrum of ortho-phenylenemercury trimer is the ion \((\text{C}_6\text{H}_4)_3\text{Hg}_2^{2+}\), 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 \((\text{C}_6\text{F}_4\text{Hg})_3^+\), the ion \((\text{C}_6\text{H}_4\text{Hg})_3^{2+}\) 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:

\[
(\text{C}_6\text{H}_4\text{Hg})_3^+ \xrightarrow{-\text{Hg}_3} (\text{C}_6\text{H}_4)_3^+ \quad \frac{m}{e \text{ calcld.}} = 62.6
\]

Whether these three mercury atoms 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, three of which mass spectral analysis showed were triphenylene, diphenylmercury and phenylbiphenylmercury). The basepeak of the spectrum is due to the ion \(\text{C}_{12}\text{H}_8^+\), the only other species of reasonable intensities being \(\text{C}_6\text{H}_4^+\), 70%; \(\text{C}_{18}\text{H}_n^+\), 68% and \((\text{C}_6\text{H}_4\text{Hg})_3^+\), 53%; nine other mercury-containing ions, all of which were less than 0.5% relative abundance were observed. (Table 13)

When 1,2-dibromobenzene and sodium amalgam are allowed to react in dry monoglym ortho-terphenylenemercury dimer, (fig.No. 33) is formed as a very pale yellow, crystalline solid. In a capillary tube the powdered sample melted at 290-292°
Figure No. 37  Ortho-phenylenemercuery trimer
Figure no. 38  Ortho-terphenylenemercuyry dimer.
Figure no. 39 Ortho-biphenylenemercu ry trimer
(lit. value158 292–293°); a single, large crystal melted at 294°. On the hot stage microscope the behaviour was completely different; the compound began to sublime at about 260° but did not melt until 340–342°. 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 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 \((\text{C}_{18}\text{H}_{12}\text{Hg})_2^+\);

the exceedingly intense base peak of the spectrum corresponded to \( \text{C}_{18}\text{H}_{12}^+ \).

The ion \( \text{HgC}_{36}\text{H}_{24}^+ \) 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; \( \text{Hg(C}_6\text{H}_4)_6 \) is considered17 unlikely to be stable, as stated previously in Table 14, because of adverse steric interactions which occur in the molecule.

A meta-stable peak was observed at \( m/e = 60.7 \) for the transition:
Table 15

Partial Mass Spectrum of Ortho-Biphenylenemercury Trimer and Ortho-Terphenylene Dimer

<table>
<thead>
<tr>
<th>Ortho-Biphenylenemercury</th>
<th>Ortho-Terphenylene Dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Number</td>
<td>Assignment</td>
</tr>
<tr>
<td>1056</td>
<td>Hg$_3$(C$_6$H$_4$C$_6$H$_4$)$_3$</td>
</tr>
<tr>
<td>856</td>
<td>Hg$_2$(C$_6$H$_4$C$_6$H$_4$)$_3$</td>
</tr>
<tr>
<td>704</td>
<td>Hg$_2$(C$_6$H$_4$C$_6$H$_4$)$_2$</td>
</tr>
<tr>
<td>504</td>
<td>Hg(C$_6$H$_4$C$_6$H$_4$)$_2$</td>
</tr>
<tr>
<td>456</td>
<td>(C$_6$H$_4$)$_6$</td>
</tr>
<tr>
<td>380</td>
<td>(C$_6$H$_4$)$_5$</td>
</tr>
<tr>
<td>304</td>
<td>(C$_6$H$_4$)$_4$</td>
</tr>
<tr>
<td>290</td>
<td>C$<em>{23}$H$</em>{14}$</td>
</tr>
<tr>
<td>276</td>
<td>C$<em>{22}$H$</em>{12}$</td>
</tr>
<tr>
<td>228</td>
<td>(C$_6$H$_4$)$_3$</td>
</tr>
<tr>
<td>200</td>
<td>Hg$^+$</td>
</tr>
<tr>
<td>152</td>
<td>(C$_6$H$_4$)$_2$</td>
</tr>
<tr>
<td>100</td>
<td>Hg$^{2+}$</td>
</tr>
<tr>
<td>77</td>
<td>C$_6$H$_5$</td>
</tr>
<tr>
<td>76</td>
<td>C$_6$H$_4$</td>
</tr>
</tbody>
</table>

Metastable peak observed for loss:

Hg$_2$(C$_6$H$_4$)$_6$ $^+$ + (C$_6$H$_4$)$_3$ $^+$ 60.6 60.73

Obs.  Calcd.
The reaction of 2,2'-dilithiobiphenyl with mercuric chloride in diethyl ether gave an off-white solid, melted at 336° in a capillary and analysed as \( \text{C}_{12} \text{H}_8 \text{Hg} \). Wittig claims that a compound, having a melting point of 335-336° and prepared in the same manner, is a tetramer. The mass spectrum of the sample of ortho-biphenylmercury prepared here, showed a mass cut off at the ion \( (\text{C}_6 \text{H}_4 \text{C}_6 \text{H}_4 \text{Hg})^+ \). There is little doubt as to the identity of this ion since the mass (m/e = 1059) was established by extrapolation from a reference peak only seven mass units away at m/e 1066. A feature in the spectrum was a doubly-charged parent ion of about 5% relative intensity to the parent. In view of the following facts: a) the high thermal stability of the ortho-biphenylmercury 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, it can be considered that ortho-biphenylmercury is the trimer (fig.no. 33) and not the tetramer.

This is rather similar to the situation with the perfluoro analogue which gave osmometric data suggesting \( \text{C}_{12} \text{F}_8 \text{Hg} \) as the formula, whereas mass spectra showed \( (\text{C}_{12} \text{F}_8 \text{Hg})^+ \) as the ion of highest mass, with \( (\text{C}_{12} \text{F}_8 \text{Hg})^+ \) being present at about 6-7% of the parent ion's intensity. The perfluorobiphenylmercury trimer was prepared by three methods: (i) decarboxylation of \( 2,2'-\text{C}_{12} \text{F}_8(\text{COO})_2 \text{Hg} \); (ii) reaction of 2,2'-dilithiooctafluorobiphenyl with mercuric chloride in
Table 16
Partial Mass Spectrum of Ortho-octafluorobiphenylene-
mercury trimer.

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1488</td>
<td>$\text{C}<em>{36}\text{F}</em>{24}\text{Hg}_3^+$</td>
<td>56.8</td>
</tr>
<tr>
<td>1469</td>
<td>$\text{C}<em>{36}\text{F}</em>{23}\text{Hg}_3^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>992</td>
<td>$[\text{HgC}_{12}\text{F}_8]_2^+$</td>
<td>2.8</td>
</tr>
<tr>
<td>744</td>
<td>$(\text{HgC}_{12}\text{F}_8)_3^{2+}$</td>
<td>7.0</td>
</tr>
<tr>
<td>592</td>
<td>$\text{C}<em>{24}\text{F}</em>{16}^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>573</td>
<td>$\text{C}<em>{24}\text{F}</em>{15}^+$</td>
<td>1.4</td>
</tr>
<tr>
<td>554</td>
<td>$\text{C}<em>{24}\text{F}</em>{14}^+$</td>
<td>1.4</td>
</tr>
<tr>
<td>526</td>
<td>$\text{C}<em>{23}\text{F}</em>{13}^+$</td>
<td>3.2</td>
</tr>
<tr>
<td>496</td>
<td>$\text{Hg(C}_{12}\text{F}_8)_2^+$</td>
<td>2.6</td>
</tr>
<tr>
<td>495.5</td>
<td>$[\text{Hg(C}_{12}\text{F}_8)_2^+]_2^{2+}$</td>
<td></td>
</tr>
<tr>
<td>485</td>
<td>$\text{C}<em>{23}\text{F}</em>{11}^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>400</td>
<td>$\text{Hg}_2^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>327</td>
<td>$\text{C}_{13}\text{F}_9^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>315</td>
<td>$\text{C}_{12}\text{F}_9^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>296</td>
<td>$\text{C}_{12}\text{F}_8^+$</td>
<td>100</td>
</tr>
<tr>
<td>277</td>
<td>$\text{C}_{12}\text{F}_7^+$</td>
<td>10.7</td>
</tr>
<tr>
<td>265</td>
<td>$\text{C}_{11}\text{F}_7^+$</td>
<td>4.6</td>
</tr>
<tr>
<td>258</td>
<td>$\text{C}_{12}\text{F}_6^+$</td>
<td>3.7</td>
</tr>
<tr>
<td>246</td>
<td>$\text{C}_{11}\text{F}_6^+$</td>
<td>8.1</td>
</tr>
<tr>
<td>227</td>
<td>$\text{C}_{11}\text{F}_5^+$</td>
<td>9.1</td>
</tr>
<tr>
<td>208</td>
<td>$\text{C}_{11}\text{F}_4^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>200</td>
<td>$\text{Hg}_2^+$</td>
<td>2.9</td>
</tr>
<tr>
<td>196</td>
<td>$\text{C}_{10}\text{F}_4^+$</td>
<td>1.2</td>
</tr>
<tr>
<td>189</td>
<td>$\text{C}_{11}\text{F}_3^+$</td>
<td>0.5</td>
</tr>
<tr>
<td>177</td>
<td>$\text{C}_{10}\text{F}_3^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>165</td>
<td>$\text{C}_{9}\text{F}_3^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>158</td>
<td>$\text{C}_{10}\text{F}_2^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>Mass Number</td>
<td>Assignment</td>
<td>Relative Intensity</td>
</tr>
<tr>
<td>-------------</td>
<td>------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>100</td>
<td>Hg$^{2+}$</td>
<td>$&gt; 0.5$</td>
</tr>
<tr>
<td>93</td>
<td>$C_3F_3^+$</td>
<td>$&gt; 0.5$</td>
</tr>
</tbody>
</table>

Metastable peaks:

\[
\begin{align*}
C_{12}F_8^+ & \xrightarrow{-\text{CF}_2} C_{11}F_6^+ & \text{Observed: } 204.5 & \text{Calculated: } 204.44 \\
C_{12}F_8^+ & \xrightarrow{-\text{CF}} C_{11}F_7^+ & \text{Observed: } 237.2 & \text{Calculated: } 237.24 \\
C_{12}F_8^+ & \xrightarrow{-\text{F}} C_{12}F_7^+ & \text{Observed: } 259.2 & \text{Calculated: } 259.21
\end{align*}
\]
Table 17

Calculated and Experimental intensities of the peaks in the ion clusters for

\[(C_{12}F_8Hg)_3^+ \text{ and } (C_{12}F_8Hg)_3^{2+}\]

<table>
<thead>
<tr>
<th>m/e</th>
<th>Calcd.</th>
<th>((C_{12}F_8Hg)_3^+)</th>
<th>((C_{12}F_8Hg)_3^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1483</td>
<td>0.4</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>1484</td>
<td>1.2</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>1485</td>
<td>2.6</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>1486</td>
<td>4.9</td>
<td>5.0</td>
<td>5.4</td>
</tr>
<tr>
<td>1487</td>
<td>7.6</td>
<td>7.8</td>
<td>7.6</td>
</tr>
<tr>
<td>1488</td>
<td>10.6</td>
<td>10.6</td>
<td>10.4</td>
</tr>
<tr>
<td>1489</td>
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<td>12.4</td>
<td>12.5</td>
</tr>
<tr>
<td>1490</td>
<td>13.7</td>
<td>13.4</td>
<td>13.3</td>
</tr>
<tr>
<td>1491</td>
<td>12.8</td>
<td>12.7</td>
<td>12.5</td>
</tr>
<tr>
<td>1492</td>
<td>11.5</td>
<td>11.3</td>
<td>12.0</td>
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<td>1493</td>
<td>8.3</td>
<td>8.2</td>
<td>7.8</td>
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<tr>
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<td>6.5</td>
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<tr>
<td>1495</td>
<td>3.3</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>1496</td>
<td>2.3</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>1497</td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>1498</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The observed \(m/e\) values have been multiplied by two for the peaks in the doubly-charged ion.
Table 18

Partial Mass Spectrum of 2,2'-Bis(iodomercury)biphenyl

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>808</td>
<td>$C_{12}H_8(HgI)_2^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>680</td>
<td>$C_{12}H_8Hg_2I^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>455</td>
<td>$HgI_2^+$</td>
<td>100</td>
</tr>
<tr>
<td>342</td>
<td>$HgI^+$</td>
<td>19.4</td>
</tr>
<tr>
<td>304</td>
<td>$(C_{12}H_8)_2^+$</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>254</td>
<td>$I_2^+$</td>
<td>3.9</td>
</tr>
<tr>
<td>226</td>
<td>$HgI_2^{2+}$</td>
<td>11.5</td>
</tr>
<tr>
<td>200</td>
<td>$Hg^+$</td>
<td>38.8</td>
</tr>
<tr>
<td>152</td>
<td>$(C_6H_4)_2^+$</td>
<td>3.9</td>
</tr>
<tr>
<td>128</td>
<td>$HI$</td>
<td>2.6</td>
</tr>
<tr>
<td>127</td>
<td>$I$</td>
<td>12.2</td>
</tr>
<tr>
<td>100</td>
<td>$Hg^{2+}$</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure No. 40  2,2'-Bis(iodomercury)biphenyl
ether, and (iii) direct reaction of 2,2'-diiodooctafluorobiphenyl with mercury in a sealed, evacuated tube. Direct insertion into a mass spectrometer at 340° (4 x 10⁻⁸ mm) gave an 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 trimer ion centred at $\frac{M}{2} = 745$. The identity of the trimer was unambiguously confirmed by comparison of the calculated and observed peak intensities in both the singly- and doubly-charged ion clusters, see Table 17. The only other mercury-carbon fragment ion of significant intensity was $(C_{12}F_8Hg)_2^+$, 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.

The exceptionally high general stability of perfluorobiphenylenemercury is shown by the fact that it can be purified by sublimation at 300° in the open air. Due to this stability and the proven volatility, we are led to the conclusion that the ion $(C_{12}F_8Hg)_3^+$ in the mass spectrum represents the parent ion of the compound and hence that perfluorobiphenylenemercury, like its hydrogen analogue, is a trimer.

An interesting by-product 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(iodo-mercury)biphenyl:

```
\begin{center}
\includegraphics[width=0.2\textwidth]{structure.png}
\end{center}
```

The parent ion cluster was centred at $m/e = 808$, the calculated and observed intensities for this molecular ion being in good agreement with the formulation $C_{12}H_8Hg_2I_2^-$. 
The base peak, centred at \( m = 455 \), showed a simple "Hg pattern" with no \( ^{13}C \) satellites and is no doubt due to the ion \( \text{HgI}_2^+ \). The spectrum consists of 14 ion clusters, mostly low intensity 2,2'-bis(iodomercury)-biphenyl cracking patterns; the doubly charged \( \text{HgI}_2^{2+} \) cluster is about 10 times as intense as the parent ion at \( m = 808 \). The peaks between 808 and 455 were clusters at \( m = 680 \) and \( m = 480 \), corresponding to \( \text{C}_{12} \text{H}_8 \text{Hg}_2^+ \) and \( \text{C}_{12} \text{H}_8 \text{HgI}^+ \) respectively. There were only two organic ions present; \( \text{C}_{12} \text{H}_8 \text{Hg}^+ \), \( m = 152 \) and a small cluster at \( m = 304 \) which corresponds to \( (\text{C}_{12} \text{H}_8)^+ \). Obviously, a chlorine-iodine exchange has occurred between Hg-Cl bonds and lithium iodide, remaining in situ from the preparation of 2,2'-dilithiobiphenyl. A separate experiment demonstrated that mercuric iodide was formed almost instantaneously from a mixture of lithium iodide and mercuric chloride in diethyl ether.
The mass spectrum of a relatively impure sample of 2,2'-bis(iodomercury)-biphenyl showed some interesting and unexpected ions when observed at high gain. The ion cluster of highest mass number was centred at \( m/e = 1059 \) and several ion clusters not present in a spectrum of the pure compound were observed at \( m/e = 1023, 854, 781, 704, 654, 581, 527 \) and 504. Comparison with calculated data showed that the ion cluster centred at \( m/e = 1023 \) represents a \( \text{Hg}_3\text{C}_{24} \) species and is probably due to the ion \( \text{Hg}_3(\text{C}_6\text{H}_4)_4\text{I}^+ \). The ion clusters at \( m/e = 704 \) and 504 compare favourably with calculated intensities for \( \text{Hg}_2\text{C}_{24} \) and \( \text{HgC}_{24} \) ions respectively, caused by loss of \( \text{HgI} \) and \( \text{Hg}_2\text{I} \) from the \( \text{Hg}_3(\text{C}_6\text{H}_4)_4\text{I}^- \), forming \( \text{Hg}_2(\text{C}_6\text{H}_4)_4^+ \) and \( \text{Hg}(\text{C}_6\text{H}_4)_4^+ \). The cluster at \( m/e = 1059 \) is twenty five mass units away from the cluster of the ion \( \text{Hg}_3(\text{C}_6\text{H}_4)_4\text{I}^+ \). This is the mass difference between a \( (\text{C}_6\text{H}_4)_2 \) group and an iodine atom. \( \text{Hg}_3(\text{C}_6\text{H}_4)_6^+ \) is a possible candidate as its molecular weight is 1056 and the observed intensity of the lines in the ion cluster compare favourably with the calculated \( \text{Hg}_3\text{C}_{36} \) intensities. The ion cluster centred at \( m/e = 527 \) has an \( \text{Hg}_2 \) pattern but contains no \( ^{13}\text{C} \) peaks indicating that the cluster is not caused by an organomercury species. Combination of mercury with hydrogen, chlorine or iodine is possible, theoretically, in the system under discussion. The cluster is, however, an \( \text{Hg}_2 \) pattern with no additional lines attributable to the isotopes of hydrogen or chlorine and as iodine has only one naturally occurring isotope, the cluster must be due to the ion \( \text{Hg}_2\text{I}^+ \).
The cluster at \( m/e = 581 \) compares well with a simple Hg pattern; no \(^{13}\text{C}\) satellite peaks being observable; the most likely identity of this ion is \( \text{HgI}_3^+ \).

**Calculated:** \( \text{Hg} \)

**----------**

**----------**

**----------**

**----------**

**----------**

The ion clusters at \( m/e = 654 \) and 781 also analyse as inorganic mercury species; no \(^{13}\text{C}\) satellite peaks being present in either cluster. Both clusters have Hg\(_2\) patterns and are probably due to \( \text{Hg}_2\text{I}_2^+ \) and \( \text{Hg}_2\text{I}_3^+ \) ions respectively. Both clusters are twenty five mass units away from species containing the \((C_6H_4)_2\) group and at least one iodine, namely \((C_6H_4)_2\text{Hg}_2\text{I}^+\) and \((C_6H_4)_2\text{Hg}_2\text{I}_2^+\).

If we assume the difference of twenty five mass units is due to the loss of the \((C_6H_4)_2\) group and the addition of one iodine atom, then the assignment of the formulae \( \text{Hg}_2\text{I}_2^+ \) and \( \text{Hg}_2\text{I}_3^+ \) to the clusters at \( m/e = 654 \) and 781 is reinforced.

The cluster at \( m/e = 854 \) does contain some \(^{13}\text{C}\) lines and could be caused by the ion \( \text{Hg}_2(C_6H_4C_6H_4)_2^+; m/e = 856 \), which does occur in the spectrum of pure orthobiphenylenemercury trimer. (The presence of the trimer in the impure sample is shown by the cluster at \( m/e = 1059 \) which corresponds to \((C_6H_4C_6H_4\text{Hg})^+; m/e = 1059\)) However, the shape of the cluster is nearer to that of an Hg\(_3\) pattern than an Hg\(_2\) pattern.

If an Hg\(_3\) species is present, then the most likely compound is \( \text{Hg}_3\text{I}_2^+; m/e = 854 \). Overlap of the inorganic - Hg\(_3\) species and the organo-Hg\(_2\) species is possible, giving the observed shape for the ion cluster.
These unusual $\text{Hg}_x \text{I}_y^+$ ions are particularly interesting because they do not occur in the mass spectrum of $\text{HgI}_2$ itself. They obviously raise some fundamental bonding questions which cannot be fully answered at the present time. The presence of $\text{Hg}_x \text{I}_y^+$ and $\text{Hg}_3^+$ species in the mass spectra studied in this work suggests that organometallic compounds might be used generally to form a variety of other unusual ions.

When 2,2'-diiodobiphenyl was treated with sodium amalgam in THF no mercury-containing species could be isolated, which implies that the intermediate sodiobiphenyl 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 trimer from the reaction between 1,2-dibromobenzene and sodium amalgam in monoglyme: polymerization passes rapidly through the biphenylene-stage to give the threering system, the sodium intermediate then exists long enough to undergo sodium-mercury exchange and form ortho-terphenylenemercury dimer. Although no mixed phenylene-biphenylene mercurials could be isolated from the reaction of 1,2-dibromobenzene and 2,2'-diiodobiphenyl with sodium amalgam in THF, 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 on biphenyl systems. (Traces of mixed derivatives apparently occur in some impure samples of ortho-phenylenemercury trimer; a group of peaks around $m/e = 906$ representing the ion $\text{C}_{24}\text{H}_{16}\text{Hg}_3^+$ have been observed in mass spectra of such samples. This may be the parent ion cluster of compound 11 in Table 14;
In some spectra very weak peaks also appear at around e = 985 and could be due to compound 12 in Table 14:

\[
\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{HgC}_6\text{H}_4\text{HgC}_6\text{H}_4\text{Hg}
\]

Schorigin\(^2\) allowed lithium to react with a benzene solution of diethylmercury and obtained ethyllithium as evidenced by the formation of propionic acid on carbonation. Schlenck and Holtz\(^2\) prepared methyl-, ethyl-, propyl- and benzyl lithium by the action of lithium on the corresponding \(R_2\text{Hg}\).

\[
2\text{Li} + R_2\text{Hg} \quad \leftrightarrow \quad 2\text{RLi} + \text{Hg}
\]

The reversibility of this reaction was demonstrated by shaking a cyclohexane solution of butyllithium with metallic mercury: di-\(n\)-butylmercury and lithium amalgam were formed\(^2\)\(^4\)\(^6\). Likewise dibenzyllmercury was formed by shaking an ether solution of benzyllithium with mercury\(^2\)\(^4\)\(^7\). Thus a possible mechanism for the formation of the phenylenemercurials is as follows:

\[
\begin{align*}
2 \text{BrB}r & \quad + \quad 2\text{Na} \quad \rightarrow \quad 2 \text{BrNa} + \text{NaBr} \\
\text{Hg} & \quad \rightarrow \quad \text{HgB}r \quad \text{B}r \quad \text{B}r \\
\text{Na} & \quad \rightarrow \quad \text{Na} \quad \text{Hg} \quad \text{Na}
\end{align*}
\]

Formation of benzyne to build up biphenyl and terphenyl systems.

Build up polymeric mercurials

Wittig\(^2\)\(^8\) has demonstrated this reaction to be reversible by forming 1,2-di-lithiobenzene from \((\text{C}_6\text{H}_4\text{Hg})\)_\(_n\) polymer and lithium metal in ether.
In an attempt to prepare the perchloro-analogue of ortho-phenylenemercury trimer, 1,2-diodotetrachlorobenzene was heated in a sealed evacuated tube with elemental mercury. The resultant white solid proved to be insoluble in common organic solvents, but did sublime at 300° at 10⁻³ mm pressure. Mass spectral analysis showed that this solid was not ortho-perchlorophenylene-mercury trimer, but bis(iodotetrachlorobenzene)mercury, Hg(C₆Cl₄I)₂.

\[
\begin{align*}
\text{Cl} & \quad \text{I} \\
\phantom{+} & + \text{Hg} \\
\rightarrow & \\
\text{Cl} & \quad \text{Hg} \quad \text{Cl}
\end{align*}
\]

The parent ion, Hg(C₆Cl₄I)₂⁺, occurs centred at \( m/e = 881 \). The base peak is centred at \( m/e = 342 \) and corresponds to C₆Cl₄I⁺. Other major ion clusters in the spectrum are Hg(C₆Cl₄)₂I, C₆Cl₄HgI₂⁺, C₆Cl₄HgI, C₆Cl₄⁺, and fragment ions of the latter ion, (Table no.19).

---

197.
Table 19

Partial Mass Spectrum of Bis(iodotetrachlorophenyl)mercury Hg(C₆Cl₄I)₂

<table>
<thead>
<tr>
<th>Mass Number</th>
<th>Assignment</th>
<th>Relative Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>881</td>
<td>Hg(C₆Cl₄I)₂⁺</td>
<td>94.23</td>
</tr>
<tr>
<td>754</td>
<td>Hg(C₆Cl₄)₂⁺I⁺</td>
<td>21.15</td>
</tr>
<tr>
<td>664</td>
<td>Hg(C₆Cl₄)₂⁺I₂⁺</td>
<td>42.30</td>
</tr>
<tr>
<td>537</td>
<td>Hg(C₆Cl₄)⁺I⁺</td>
<td>42.94</td>
</tr>
<tr>
<td>464</td>
<td>C₆Cl₄I⁺₂</td>
<td>33.33</td>
</tr>
<tr>
<td>455</td>
<td>HgI₂⁺</td>
<td>28.84</td>
</tr>
<tr>
<td>440.5</td>
<td>Hg(C₆Cl₄I)₂⁺²⁺</td>
<td>8.97</td>
</tr>
<tr>
<td>415</td>
<td>Hg(C₆Cl₄)⁺</td>
<td>6.41</td>
</tr>
<tr>
<td>342</td>
<td>C₆Cl₄I⁺,C₆Cl₄HI</td>
<td>100</td>
</tr>
<tr>
<td>327</td>
<td>HgI⁺</td>
<td>7.05</td>
</tr>
<tr>
<td>254</td>
<td>I₂⁺</td>
<td>3.84</td>
</tr>
<tr>
<td>212</td>
<td>C₆Cl₄⁺</td>
<td>92.30</td>
</tr>
<tr>
<td>200</td>
<td>Hg⁺</td>
<td>37.17</td>
</tr>
<tr>
<td>177</td>
<td>C₆Cl₃⁺</td>
<td>40.38</td>
</tr>
<tr>
<td>142</td>
<td>C₆Cl₂⁺</td>
<td>44.87</td>
</tr>
<tr>
<td>128</td>
<td>HI⁺</td>
<td>7.69</td>
</tr>
<tr>
<td>127</td>
<td>I⁺</td>
<td>11.54</td>
</tr>
<tr>
<td>107</td>
<td>C₆Cl⁺</td>
<td>23.07</td>
</tr>
</tbody>
</table>
Experimental for Phenylene- and Polyphenylene-Mercurials.
Reaction of Ortho-Dihalobenzenes with Alkali Metal Amalgams.

1) A solution of 1,2-diiodobenzene (20 mol) in dry tetrahydrofuran (50 cm³) was shaken under an atmosphere of nitrogen with potassium amalgam (50 mg atoms; 2 gm K in 102 gm Hg), whereupon an exothermic reaction began and appeared to be essentially complete after 30 minutes. Shaking was continued for a further 48 hours after which time water was added until no more precipitate formed. The supernatent liquid was separated from the precipitate and the mercury, the precipitate being first washed with water and then extracted with a little hot toluene to remove soluble organic material. The remaining ortho-phenylenemercury was extracted with hot dimethylformamide (DMF) and recrystallized as small needles from the same solvent. The yield was variable, usually being 10-20%. Found: C, 26.1; H, 1.5%; Calcd. for C₆H₄Hg: C, 26.0; H, 1.45%. The molecular weight was obtained mass spectrometrically, the parent ion cluster appearing at around m/e = 830 (see page for a discussion of the relative peak intensities in this parent ion). Thus the product from the reaction would appear to be ortho-phenylenemercury trimer, (C₆H₄Hg)₃; its infrared spectrum is shown in figure.

In capillary tubes, the products from this and similar reactions melted and decomposed at about 325-326°, the value quoted by Wittig for his ortho-phenylenemercury hexamer, (C₆H₄Hg)₆. Examination of the melting point tubes with a magnifying glass showed the presence of mercury globules among the decomposition products.

On the hot-stage microscope, the crystals partially sublimed from about 260° onwards, but did not melt or show any outward signs of decomposition up to 350°; large crystals sometimes lost their transparency at about 330°. A sample of ortho-phenylenemercury was sublimed at 10⁻⁴ mm and 260°; the mass spectrum of the sublimed material showed a mass cut-off at the ion (C₆H₄Hg)₃⁺. This experiment demonstrates the high thermal stability and volatility of ortho-phenylenemercury, very strongly suggesting that (C₆H₄Hg)₃⁺ is the parent ion of the compound and not the first fragment ion to be observed for ortho-phenylenemercury hexamer.
ii) A similar reaction, carried out using 1,2-dibromobenzene and potassium amalgam, also gave ortho-phenylenemercury trimer. A small amount of ortho-terphenylenemercury dimer, \( (C_6H_4)_2C_6H_4C_6H_4Hg \), was detected mass spectrometrically.

iii) 1,2-Dibromobenzene and potassium amalgam were shaken in dry tetrahydrofuran at \( 0^\circ \) for only 30 minutes. Even under these conditions of low temperature and short reaction time, the main product was ortho-phenylenemercury trimer, together with Wittig's ortho-terphenylenemercury dimer.

iv) A mixture of 1,2-dibromobenzene and sodium amalgam was shaken in dry tetrahydrofuran at room temperature for 30 minutes. The reaction was not very exothermic in comparison to the potassium reactions; water was added until no more precipitate formed and the filtered precipitate extracted with hot toluene. The remaining solid was extracted with hot DMF to give ortho-phenylenemercury trimer. Crystals from the toluene fraction had a melting point of about \( 190^\circ \) which is near that of triphenylene, \( 198^\circ \); a mass spectrum confirmed the presence of triphenylene.

v) No mercury-containing products could be isolated from a reaction between 1,2-dibromotetrafluorobenzene (6.2gm) and sodium amalgam (1.7gm Na in 100gm Hg) in dry tetrahydrofuran.

vi) 1,2-Dibromobenzene and sodium amalgam again gave ortho-phenylenemercury trimer, although in reduced yield, when reacted together in refluxing tetrahydrofuran. A few flat, plate-like crystals were isolated from a DMF extraction of the residues; these had a melting point on the hot stage microscope of 289-290\(^\circ\); melting point of ortho-terphenylenemercury dimer is 292-293\(^\circ\).

vii) Sodium-amalgam and 1-bromo-2-fluorobenzene shaken together in tetrahydrofuran at room temperature give ortho-phenylenemercury trimer.

**Preparation of ortho-terphenylenemercury dimer**

The above procedures were 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 via the following scheme:

\[
\text{Cl} \underset{Cu}{\xrightarrow{220°C, 24h}} \text{H-} \overset{O_2N}{\text{NO}_2} \overset{\text{Sn}}{\xrightarrow{\text{HCl}}} \text{H}_{2N} \overset{(i)}{\xrightarrow{\text{HNO}_2}} \text{H}_{2N} \overset{(ii)}{\xrightarrow{\text{KI}}} \text{I} \overset{150°}{\xrightarrow{\text{I}}} \text{I}.
\]

Preparation of ortho-biphenylenemercury trimer

$2,2'$-Diiodobiphenyl (2.5g) was refluxed for 30 minutes with lithium (0.5g) in 80cm$^3$ of diethyl ether and then stirred at room temperature overnight. Mercuric chloride (1.8g) was added and the mixture stirred for 48 hours 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 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%).
Infrared absorptions are quoted in cm$^{-1}$ for mulls in liquid paraffin, using CsI optics, except where otherwise stated.

(s-strong, m-medium, w-weak, sh-shoulder, d-doublet, br-broad).

$(\text{C}_6\text{H}_4\text{Hg})_3$: 1259w, 1088m, 1021m, 866m, 745s, 679w, 479w, 422s, 325s, 289m.

$(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_3$: 1255w, 1157w, 1109w, 1005w, 785, 780md, 751s, 734, 738sd, 621w, 536w, 452msh, 446s, 428w, 361w, 320v.

$(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Hg})_2$: 1162w, 1107w, 1076w, 1033w, 1009m, 979w, 944w, 875w, 786wsh, 780, 775md, 756s, 749s, 736, 730sd, 692m, 625w, 621m, 570m, 458s, 348m.

$\text{C}_{12}\text{H}_8(\text{HgI})_2$: 1575m, 1418m, 1289w, 1162w, 1120w, 1110w, 1075w, 1047w, 1026m, 1001s, 955, 950wd, 879w, 779s, 755ssh, 749s, 739, 731sd, 725sh, 659, 665wd, 645w, 620m, 555w, 535w, 451, 439md.
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