Some bentafluorophenyl derivatives of tin and boron

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UNIVERSITY OF DURHAM

A THESIS

entitled

SOME BENTAFLUOROPHENYL DERIVATIVES OF TIN AND BORON.

submitted by

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SUMMARY

Pentafluorophenyl compounds of the series $Me_{4-x}Sn(C_6F_5)_x$, $Ph_{4-x}Sn(C_6F_5)_x$, where x = 1 → 4, and $(C_6F_5)_{4-x}Sn(p\text{-tolyl})_x$, where x = 1 and 2, have been prepared. These compounds undergo ready nucleophilic cleavage of pentafluorophenyl and an unusual halide- or cyanide-ion catalysed hydrolysis. Electrophilic cleavage by hydrogen chloride and boron halides has been studied as a route to some pentafluorophenyltin halides and pentafluorophenylboron halides respectively. Cleavage of methylpentafluorophenylmercury with stannic chloride provides an excellent route to pentafluorophenyltin trichloride.

Tris(pentafluorophenyl)tin chloride was obtained by the reaction of anhydrous hydrogen chloride with p-tolyltris(pentafluorophenyl)tin. It can be hydrolysed, without significant loss of pentafluorophenyl, using ammonium hydroxide.

Pentafluorophenylboron dihalides are air-sensitive liquids which tend to disproportionate on heating. However, they form 1:1 complexes with pyridine which are white air stable solids. Pentafluorophenylboronic acid was obtained by the low temperature hydrolysis of pentafluorophenylboron dichloride, and this is the first report of the isolation of a perfluorocarbon boronic acid.

Pentafluorophenylboronic acid exhibits several characteristic properties in which it differs from other arylboronic acids. Pentafluorophenol was obtained in good yield from pentafluorophenylboronic acid and 'high-test' hydrogen peroxide. Bis(pentafluorophenyl)borinic acid was obtained by the low temperature hydrolysis of bis(pentafluorophenyl)boron chloride.

Potassium pentafluorophenyltrifluoroborate, $K^+(C_6F_5BF_3)^-$, was obtained from pentafluorophenylboron difluoride and aqueous potassium fluoride. This salt is hydrolysed by boiling with water, and the thermal breakdown of the salt results in the formation of potassium fluoroborate and a perfluoropolyphenylene.

Dipole moments have been measured for some pentafluorophenyl derivatives of tin and mercury. Infra-red, ultraviolet and N.M.R. spectra of some pentafluorophenyl derivatives of mercury, tin and boron have been recorded.

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CHAPTER.1.

INTRODUCTION.

INTRODUCTION

The chemistry of fluorocarbon derivatives of both metallic and non-metallic elements has been the subject of several reviews.[1,2,3] These compounds often possess properties differing markedly from their hydrocarbon analogues. Pentafluorophenyl derivatives of metals and non-metals have only been reported during the last four years, and the work described in this thesis is mainly concerned with pentafluorophenyl derivatives of tin and boron. The introduction will deal with the general methods of preparation of fluorocarbon derivatives, followed by a detailed description of fluorocarbon derivatives of mercury, tin, and boron. A final section is devoted to pentafluorophenyl derivatives of other metals and non-metals.

General methods of preparation of fluorocarbon derivatives.

a) Perfluoroalkyl derivatives.

1) The reaction of perfluoroiodo-alkanes with metalloids, metals or their derivatives with heating or ultra-violet irradiation.

Although this method has now been successful in preparing perfluoroalkyl-metalloidal and -metallic compounds, it is restricted by the relatively small number of compounds which show reactivity towards perfluoroiodoalkanes. This method is particularly useful for the preparation of perfluoroalkyl derivatives of the group V elements phosphorus, arsenic, and antimony.

$$CF_3I + As \longrightarrow \begin{array}{ll} (CF_3)_3As & (78\%) \\ (CF_3)_2AsI & (13\%) \\ (CF_3)AsI_2 & (4\%) \end{array} \qquad (4)$$

A modification of this method involves the reaction of a perfluoroiodoalkane with an iodide in the presence of mercury; this gives only partially substituted compounds.

$$CH_3AsI_2 + 2Hg + 2CF_3I \longrightarrow (CF_3)_2AsCH_3 + 2HgI_2 \qquad (5)$$

2) <u>The reaction of unstable perfluoroalkyl intermediates with halogen compounds of metals and metalloids.</u>

This includes the use of perfluoroalkyl Grignard reagents and lithium perfluoroalkyls.

$$(CH_3)_2SiCl_2 + 2C_3F_7Li \longrightarrow (CH_3)_2Si(C_3F_7)_2 + 2LiCl \qquad (6)$$

$$(CH_3)_3SiCl + C_3F_7MgBr \longrightarrow (CH_3)_3SiC_3F_7 + MgBrCl \qquad (7)$$

The instability of such intermediates and the difficulties involved in their preparation have restricted their usefulness.

3) <u>Exchange reactions between perfluoroalkyl and alkyl compounds.</u>

This synthetic method is of very limited application, due to the lack of perfluoroalkyl compounds of a convenient degree of activity.

$$2(CH_3)_3M + CF_3I \longrightarrow CF_3M(CH_3)_2 + (CH_3)_4M^+I^- \qquad (8)$$

(M= P, As, or Sb)

4) Direct fluorination of alkyl compounds.

Owing to the ease of cleavage of most metal-carbon bonds on fluorination, this method is not suitable for the preparation of perfluoroalkyl-metallic derivatives, and it has only been used for the preparation of the nitrogen derivatives.

$$(C_2H_5)_3N \xrightarrow[N_2/270^\circ]{CoF_3} (C_2F_5)_3N \quad (0.8\%) \tag{9}$$

5) Electrochemical fluorination.[10,11,12]

This method utilises the fact that many organic compounds containing oxygen, nitrogen or sulphur are soluble in anhydrous hydrogen fluoride to give conducting solutions. Simons[13] has quoted a yield of 27% for the preparation of $(C_2F_5)_3N$ by this technique. The main advantage of the method is that fluorination occurs, if only in poor yield, without loss of functional groups.

6) The reaction of fluorides with fluoro-olefins.

This method is limited to the preparation of pentafluoroethyl and higher perfluoroalkyl derivatives.

$$HgF_2 + 2CF_2{=}CF_2 \xrightarrow[100^\circ/12\ \text{hours}]{AsF_3} Hg(C_2F_5)_2 \tag{14}$$

$$HgF_2 + 2CF_3CF{=}CF_2 \xrightarrow[100^\circ/12\ \text{hours}]{\text{liq: }HF} Hg\left[(CF_3)_2CF\right]_2 \tag{15}$$

Miller has suggested that this last reaction involves electrophilic attack by the metal cation on the olefin.[16]

7) The reaction of trifluoromethyl radicals with metals.

This procedure is derived from the classical one used by Paneth to prepare metal alkyls by the action of alkyl radicals on metal mirrors. Bis(trifluoromethyl)ditelluride has been prepared in this way,[17] using trifluoromethyl radicals generated by the pyrolysis of hexafluoroacetone.

b) Perfluorovinyl derivatives.

As in general organometallic chemistry, the first useful step was the preparation[18] of a Grignard reagent, in this case from trifluoroiodoethylene, $CF_2=CFI$. However, the inaccessibility of this iodoethylene limited application of the Grignard reagent. The use of commercially available bromotrifluoroethylene removed this restriction, since it forms a Grignard reagent in tetrahydrofuran solution.[19,20] The Grignard reagent has been successfully applied to the preparation of perfluorovinyl derivatives of silicon,[21] mercury,[22,25] phosphorus,[23] arsenic and antimony.[24] Some detailed work has been concerned with perfluorovinyltin compounds,[26] and this will be described later. Seyferth and coworkers[27] have prepared trifluorovinyllithium by the transmetallation reaction,

$$PhSn(CF=CF_2)_3 + 3PhLi \xrightarrow[-40^o]{ether} Ph_4Sn + 3CF_2=CFLi$$

but this is not a good preparative method. Trifluorovinyllithium has also been prepared by an ex-change reaction with bromotrifluoroethylene and an alkyllithium reagent.[28]

It was found to be stable at -78^{o}, and in reaction with mercuric chloride at 0^{o} gave better yields of bis(trifluorovinyl) mercury than were obtained with the corresponding Grignard reagent.

c) <u>Perfluoroaryl derivatives.</u>

As with perfluorovinyl derivatives the preparation of the Grignard reagent from magnesium and bromopentafluorobenzene or pentafluoroiodobenzene[29] provides a convenient route to the preparation of pentafluorophenyl derivatives of metals and metalloids by reaction with the appropriate metal or metalloid halide. In this manner, pentafluorophenyl derivatives of silicon and phosphorus,[30] mercury,[31] tin,[32] boron,[33] thallium,[34] lead,[35] and some transition metals[36] have been prepared. Other workers have reported the preparation of bis(pentafluorophenyl)mercury.[37,38] On carbonation in diethylether solution, pentafluorophenylmagnesium bromide gave a very low yield (3%) of pentafluorobenzoic acid.[29] However, when tetrahydrofuran is used as solvent the yield of acid is greatly increased (67%).[39] Chloropentafluorobenzene also forms a Grignard reagent,[40] though with more difficulty than the bromo-compound. It was found that formation of the Grignard reagent from chloropentafluorobenzene in tetrahydrofuran gave high molecular weight material (m.p$>360^{o}$). A similar observation was reported by Thrower,[41] who found that pentafluorophenylmagnesium bromide, although stable in refluxing ether, is decomposed in refluxing tetrahydrofuran to form perfluoropolyphenylenes, containing small amounts of bromine, together with minor products formed by attack on the solvent. Tetrahydrofuran is necessary for this decomposition, mixtures of tetrahydrofuran and ether being ineffective.

Tatlow and coworkers[37] have synthesised pentafluorophenyllithium by the exchange reaction between bromopentafluorobenzene and n-butyl lithium in diethyl ether at -78^{0}, and by direct metallation of bromopentafluorobenzene with lithium amalgam in ether at 0^{0}. The intermediate formation of tetrafluorobenzyne has been indicated in reactions with chlorine and bromine, and by the isolation of a Diels-Alder adduct with furan. However, these workers found that the Grignard reagent is easier to handle than the lithium compound, although the enhanced reactivity of the latter may be required for certain preparations.

In the preparation of tris(pentafluorophenyl)boron,[33] it was found advantageous to prepare pentafluorophenyllithium as a fine suspension in pentane, since difficulties were encountered in attempting to remove solvent when ether was used as the reaction medium. Indeed, it was found that formation of the lithium reagent in pentane rather than ether is advantageous in other syntheses.

Fluorocarbon derivatives of mercury.

a) Perfluoroalkyl derivatives.

Perfluoroalkylmercuric halides are readily obtained as white crystalline solids by the action of perfluoroiodoalkanes on mercury with heating or ultra-violet irradiation.[42] These like their alkyl analogues, can be converted to the bases, R_FHgOH, by treatment with an aqueous suspension of silver oxide. Bis(perfluoroalkyl)mercurials can be obtained by the reaction between anhydrous mercuric fluoride and fluoro-olefins, or by the reaction of the corresponding perfluoroalkylmercuric halide with cadmium amalgam.

$$CF_3HgI \xrightarrow{Cd/Hg,\ 120-130^{\circ}} (CF_3)_2Hg \quad (80-90\%) \qquad (43)$$

Bis(trifluoromethyl)mercury is also conveniently prepared by the reaction between tris(trifluoromethyl)phosphine and mercuric oxide.[44] Unlike dimethylmercury, which is a liquid boiling at 92°, it is a white crystalline solid with a cubic structure. Dialkylmercurials are practically insoluble in water, but both bis(trifluoromethyl)mercury and trifluoromethyl mercury halides are appreciably soluble and may be recovered unchanged from their aqueous solutions. Rather more unexpected is the appreciable conductivity of bis(trifluoromethyl)mercury solutions.[43] Conductometric titrations of aqueous solutions of $(CF_3)_2Hg$, CF_3HgI, and $n-C_3F_7HgI$ with potassium halides suggest the formation of the ionic species $Hg(R_F)_2X^-$, $Hg(R_F)_2X_2^{2-}$, HgR_FIX^-, and $HgR_FIX_2^{2-}$ where X = Cl, Br, or I.[45,46,47] Solid complexes believed to contain the anions $Hg(CF_3)I_3{}^{2-}$, $Hg(CF_3)_2I_2{}^{2-}$, and $Hg(C_3F_7)I_3{}^{2-}$, can be isolated by precipitation from aqueous solution as the salts of the ethylenediamine complex cations of zinc(II), copper(II), cadmium(II), or nickel(II).[45] However, recent work by Downs[49] on the spectroscopy of these solutions fails to support the postulated formation of complex anionic derivatives of bis(trifluoromethyl) mercury in solution. Although some form of weak association between the mercury compound and halide ions is indicated by slight modifications in the Raman and fluorine resonance spectra, and this is further supported by cryoscopic measurements.[50] Complexes of the type $Hg(R_F)_2L$ and $Hg(R_F)_2L_2$ (where R_F = fluoroalkyl or fluoroaryl; L = piperidine, pyridine, triphenylphosphine etc.,) have been shown to exist in benzene solution by oscillometric titrations.[48]

Bis(trifluoromethyl)mercury decomposes slowly above 160°,[43] and is thus less stable than dimethylmercury, which is only slightly decomposed at 300°. The photochemical and pyrolytic decomposition affords trifluoromethyl radicals which will initiate the polymerisation of olefins such as ethylene and terafluoroethylene.[47] The reaction of bis(perfluoroalkyl)-mercury derivatives with metal or metalloid halides does not yield the perfluoroalkyl derivatives expected by analogy with the corresponding alkyl compounds.[43,51,52]

Fluoroform is evolved after treatment of bis(trifluoromethyl)mercury with zinc or magnesium amalgam followed by addition of water, thus illustrating the pseudohalogen character of the perfluoroalkyl group.

$$Hg(CF_3)_2 + 2H_2O \xrightarrow{OH^-} 2CHF_3 + Hg(OH)_2$$

b) <u>Perfluorovinyl derivatives.</u>

Bis(trifluorovinyl)mercury can be prepared by the reaction of the Grignard reagent with mercuric chloride at -10° in ether solution, but, unlike bis(trifluoromethyl)mercury, it is a liquid (b.p. 65-6°/17mm.).[22] Seyferth and coworkers[25] have used the Grignard reagent to prepare trifluorovinylmercuric halides, and some unsymmetrical trifluorovinylmercurials have been prepared by the Grignard method in tetrahydrofuran.[53] The reactions of these unsymmetrical compounds with hydrogen chloride and arsenic trichloride were studied to determine the electronegativity of the perfluorovinyl radical.

$$(CF_2{=}CF)Hg(CH{=}CH_2) + HCl \longrightarrow CH_2{=}CHHgCl + CF_2{=}CFH \ (99\%)$$

$$(CF_2{=}CF)HgEt + HCl \longrightarrow EtHgCl + CF_2{=}CFH \ (98\%)$$

$$(CF_2{=}CF)HgPh + HCl \longrightarrow PhHgCl + CF_2{=}CFH \ (98\%)$$

Thus the position of the perfluorovinyl group in the cleavage series of organic groups from mercury by hydrogen chloride is:-

$$CF_2{=}CF- > Ph > CH_2{=}CH- > \text{Alkyl}$$

Some reactions of bis(trifluorovinyl)mercury have been described by Knunyants and his coworkers,[54] and these are summarised by equations.

$$(CF_2{=}CF)_2Hg + HgCl_2 \longrightarrow 2CF_2{=}CFHgCl \ (80\%)$$

$$(CF_2{=}CF)_2Hg + HgBr_2 \longrightarrow 2CF_2{=}CFHgBr \ (80\%)$$

$$(CF_2{=}CF)_2Hg + CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_2Hg \ (43\%)$$

$$(CF_2{=}CF)_2Hg + PhMgBr \longrightarrow Ph_2Hg \ (56\%)$$

$$(CF_2{=}CF)_2Hg + BCl_3 \longrightarrow CF_2{=}CFBCl_2 \ (45\%)$$

$$(CF_2{=}CF)_2Hg + AsCl_3 \longrightarrow CF_2{=}CFAsCl_2 \ (70\%)$$

The last two equations show that bis(trifluorovinyl)mercury differs from bis(trifluoromethyl)mercury in its reactions with inorganic halides, since bis(trifluoromethyl)mercury forms only decomposition products in its reactions with metal or metalloid halides.

Bis(trifluorovinyl)mercury has also been used for the synthesis of a perfluoroaluminium compound.[55]

$$3(CF_2{=}CF)_2Hg + 2AlH_3{:}NMe_3 \longrightarrow 2(CF_2{=}CF)_3Al{:}NMe_3 + 3H_2 + 3Hg$$

c) <u>Perfluoroaryl derivatives.</u>[31]

Bis(pentafluorophenyl)mercury was recovered unchanged after 5 hours at 250°, and can be recrystallised from concentrated sulphuric acid. It forms stable neutral coordination compounds with 2,2'-bipyridyl and 1,2-bis(diphenylphosphino)ethane. This is the first report that mercury involved in a linkage to carbon, other than in cyanide, has sufficient electron-accepting capacity to enable neutral coordination complexes to be isolated.

Bis(trifluoromethyl)mercury has a small but measureable conductivity in water, attributed to coordination of water to the mercury atom, followed by ionisation.[1]

$$(CF_3)_2Hg \longrightarrow (CF_3)_2Hg \leftarrow OH_2 \longrightarrow (CF_3)_2HgOH^- + H_3O^+$$

However, a solution of bis(pentafluorophenyl)mercury in 3:1 acetone-water has the same conductivity as pure solvent. This is surprising in view of the coordination complexes just mentioned.

With anhydrous hydrogen chloride, methylpentafluorophenylmercury undergoes preferential cleavage of a pentafluorophenyl group as pentafluorobenzene, but a phenyl group was cleaved from pentafluorophenylphenylmercury as benzene.

$$MeHgC_6F_5 + HCl \longrightarrow MeHgCl + C_6F_5H$$

$$C_6H_5HgC_6F_5 + HCl \longrightarrow C_6F_5HgCl + C_6H_6$$

Unexpectedly, cleavage with bromine removed a methyl group from methylpentafluorophenylmercury, but phenyl and pentafluorophenyl were cleaved from pentafluorophenylphenylmercury in equal amounts. It is apparent that different mechanisms must obtain for the reactions with bromine and hydrogen chloride.

Methylpentafluorophenylmercury was unchanged when heated at 100° in an evacuated tube, and, indeed, it can be prepared by the reaction between bis(pentafluorophenyl)mercury and dimethylmercury at 60°.

Fluorocarbon derivatives of tin.

a) Perfluoroalkyl derivatives.

Mixed alkyl-perfluoroalkyl and perfluoroalkyl halogen compounds have been described. The mixed alkyl-perfluoroalkyl compounds are of the types R_3SnR_F and $R_2Sn(R_F)_2$.

Compounds of the first type have been obtained by interaction of perfluoroiodoalkanes with hexaalkyl- or hexaaryl-ditin.[56,57] A more detailed study of the reaction,[58] for which the best yields are obtained by ultra-violet irradiation of the reactants, indicates that a radical-chain mechanism is operating, probably involving homolytic fission of the metal-metal bond as the first step.

$$\mathrm{Me_3Sn\text{-}SnMe_3} \xrightarrow{\mathrm{u\text{-}v}} \mathrm{2Me_3Sn^{\cdot}}$$

$$\mathrm{Me_3Sn^{\cdot} + CF_3I} \longrightarrow \mathrm{Me_3SnCF_3 + I^{\cdot}}$$

$$\mathrm{I^{\cdot} + Me_3Sn\text{-}SnMe_3} \longrightarrow \mathrm{Me_3SnI + Me_3Sn^{\cdot}}, \quad \text{etc.,}$$

This appears to be one of the instances where homolytic cleavage of a tin-tin bond seems likely.

Compounds of the type $R_2Sn(R_F)_2$ are prepared by treating dialkyltin dihalides with magnesium turnings and a perfluoroiodoalkane in tetrahydrofuran.[59] This reaction presumably involves the formation of a perfluoroalkyl Grignard reagent. However, trifluoromethyl derivatives have not been prepared in this way and the method may be limited to the preparation of derivatives of the higher perfluoroalkyl groups.

The chemistry of trimethyltrifluoromethyltin is interesting since the large electronegativity difference between tin and trifluoromethyl would be expected to produce at least partial polarisation of the Sn-CF_3 bond. This is apparent in the formation of trimethyltin trifluoromethylfluoroborate by the reaction of trimethyltrifluoromethyltin with boron trifluoride in carbon tetrachloride.[60,61]

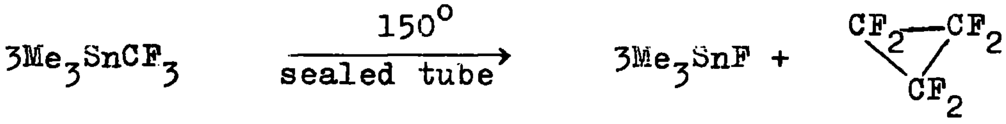
$$Me_3SnCF_3 + BF_3 \longrightarrow Me_3Sn^+[CF_3BF_3]^-$$

However, the strong Lewis acid boron trichloride reacted with trimethylpentafluoroethyltin to give a mixture of volatile products containing methyldichloroborane and unreacted boron trichloride.[62] Furthermore, in contrast to the reaction with boron trifluoride, the reaction of trimethyltrifluoromethyltin with the electrophilic reagents hydrogen chloride[62] and chlorine[57,63] leads to the cleavage of a methyl group as methane or chloromethane and the formation of dimethyltrifluoromethyltin chloride.

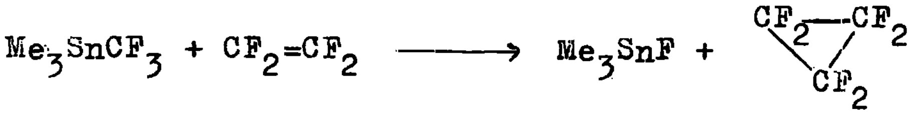
The high polarity of the Sn-R_F bond also explains the ready nucleophilic cleavage of perfluoroalkyl groups from perfluoroalkyltin compounds which these compounds have been shown to undergo. For example, dialkylbis(pentafluoroethyl)tin compounds release pentafluoroethane quantitatively on warming with aqueous base,[59] and trimethyltrifluoromethyltin evolves fluoroform under similar conditions.[62]

$$Me_3SnCF_3 + OH^- \longrightarrow Me_3SnOH + CF_3H$$

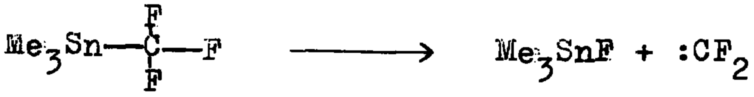
The thermal decomposition of trimethyltrifluoromethyltin[57] is also consistent with the polarisation of the Sn-CF_3 bond, since polarisation would encourage migration of fluoride ion to tin, and provides one of the first examples of the formation in good yield of difluorocarbene, which under the conditions of decomposition finally appears as perfluorocyclopropane.



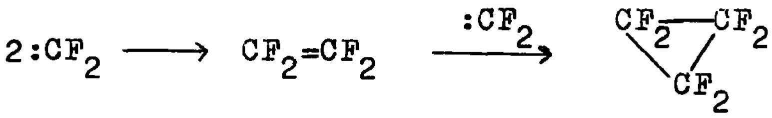
That difluorocarbene is produced in the decomposition is shown by the fact that when decomposition is carried out in the presence of tetrafluoroethylene there is a threefold increase in the yield of perfluorocyclopropane.



The decomposition of trimethyltrifluoromethyltin can therefore be expressed as,



$$Me_3Sn{-}CF_3 \longrightarrow Me_3SnF + :CF_2$$



The inductive effect of the trifluoromethyl group increases the acceptor properties of the tin atom in dimethyltrifluoromethyltin chloride, as is shown by the much higher conductivity of the chloride in nitrobenzene-pyridine solutions[63] as compared with trimethyltin chloride.

The ionisation process is probably,

$$Me_2SnCF_3Cl + Py \longrightarrow Me_2SnCF_3.Py^+ + Cl^-$$

Clark and Beg[64] have recently synthesised two interesting, new perfluoroalkyltin compounds by an extension of the reaction between trifluoroiodomethane and hexamethylditin. Addition of the white modification of diphenyltin to an equimolar amount of tetrafluoroethylene in carbon tetrachloride and exposure to ultra-violet irradiation for 72 hours gave diphenyltintetrafluoroethane as a white air-stable solid.

$$(C_6H_5)_2Sn + CF_2{=}CF_2 \longrightarrow (C_6H_5)_2SnC_2F_4$$

The reaction of hexamethylditin with tetrafluoroethylene was performed under similar conditions to give a hygroscopic oil as the mainproduct. This was characterised, by analysis, as 1,2-bis(trimethylstannyl)tetrafluoro-ethane, $Me_3SnC_2F_4SnMe_3$.

b) Perfluorovinyl derivatives.

Using trifluorovinyl Grignard reagents, compounds of the type $R_3SnCF{=}CF_2$, $R_2Sn(CF{=}CF_2)_2$, $RSn(CF{=}CF_2)_3$, and $Sn(CF{=}CF_2)_4$ have been prepared in good yield.[26,65] Their properties, particularly towards oxidation, differ markedly from those of vinyltin compounds. Thus, tetrakis(trifluorovinyl)tin apparently polymerises to a waxy white solid in the presence of dry oxygen, whereas tetravinyltin is not oxygen-sensitive. Also, trifluorovinyltin compounds are much more easily cleaved by base and by warm water than their vinyl analogues. For example, treatment of pure di-n-butylbis(trifluorovinyl)tin in ether solution with potassium fluoride solution caused partial cleavage, and ether-soluble di-n-butyltin oxide was formed. Ethanol alone, towards which vinyltin compounds are stable, caused cleavage of trifluorovinyl groups from tin in some cases. Thus, when an ethanolic solution of di-n-butylbis(trifluorovinyl)tin was heated at reflux for 20 hours, di-n-butyldiethoxytin was produced in almost quantitative yield. Triethyltrifluorovinyltin and triphenyltrifluorovinyltin were not attacked by ethanol under similar conditions.

The cleavage reactions of trifluorovinyltin compounds have been studied by two groups of workers.[26,65] Whereas in perfluoroalkyl compounds of the type, $R_3SnC_nF_{2n+1}$ (R = phenyl, alkyl), the alkyl or phenyl groups are released in preference to perfluoroalkyl groups on treatment with electrophilic reagents, in the case of trifluorovinyltin compounds the trifluorovinyl group is cleaved. In these compounds sp^2-hybridised carbon atoms are bonded simultaneously to fluorine and to the metal. In such compounds the presence of a filled p_π-orbital is apparently sufficient to attract the attacking electrophilic reagent. The position of the trifluorovinyl group in the cleavage series of organic groups from tin by protonic acids is,

$$CF_2{=}CF- > Ph > CH_2{=}CH- > \text{alkyl} > \text{perfluoroalkyl}$$

c) Perfluoroaryl derivatives.

A preliminary communication by Tatlow and coworkers[32] reports the preparation of five new pentafluorophenyltin compounds whose properties are listed in Table I.

TABLE I

Compound	M.p.	Method	Notes
$Sn(C_6F_5)_4$	221°	1	Stable to water
$SnMe_2(C_6F_5)_2$	liq:	2	Stable to water; b.p.94-6°/1·1 mm
$SnPh(C_6F_5)_3$	100-102°	3	Stable to water
$Sn(C_6F_5)_3Cl$	106°	1	Stable to water
$Sn(C_6F_5)_2Cl_2$	liq:	1,4	Reacts with water; b.p.130°/2 mm

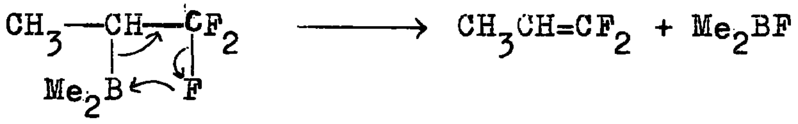
Methods: 1, Grignard + $SnCl_4$. 2, Grignard + Me_2SnCl_2.
3, Grignard + $PhSnCl_3$. 4, $SnMe_2(C_6F_5)_2$ + $SnCl_4$.

Tetrakis(pentafluorophenyl)tin was found to be unreactive, but the chloro-compounds were hydrolysed even by weak bases and were found to undergo a number of cleavages with loss of the pentafluorophenyl group. Preliminary measurements of the Mossbauer effect in tetrakis(pentafluorophenyl)tin suggest that the electronegativity of the pentafluorophenyl group is approximately the same as bromine.

Fluorocarbon derivatives of boron.

a) Perfluoroalkyl derivatives.

Many unsuccessful attempts to prepare perfluoroalkylboron compounds have been reported. For example, the reaction of boron halides or alkylboron halides with bis(perfluoroalkyl)-mercury compounds[62,66] leads only to the production of boron trifluoride. The low temperature reaction of heptafluoro-n-propyl lithium with boron trifluoride,[67] boron trichloride or boron tribromide[1] leads to extensive decomposition with formation of tetrafluoroborate ions. Stone and coworkers[68] found that the reaction between diborane and fluoroethylenes did not give fluoroalkylboron compounds, as expected by analogy with the reaction between diborane and ethylene, but instead mixtures of boron trifluoride and alkylboron fluorides were obtained. However, Haszeldine and others[69] found that 3,3,3,-trifluoropropene reacts readily with tetramethyldiborane to give dimethyltrifluoropropylboron (45%), together with methylbis(trifluoropropyl)boron (8%) and trimethylboron (30%). Dimethyltrifluoropropylboron decomposes very slowly at room temperature, and is stable for long periods at -78°. When it is heated at 100° for 27 hours, 75% decomposition takes place with the quantitative formation of 1,1,-difluoropropene and dimethylboron fluoride. These products probably result from internal nucleophilic attack by a β-fluorine atom on the boron atom, in a manner suggested for the decomposition of polyfluoroalkyl derivatives of silicon (see discussion).

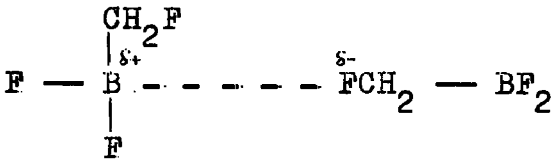


By contrast, compounds containing fluorine in the γ-position relative to boron are stable at 100°.[70] The gas-phase reaction between diborane and 3,3,3-trifluoropropene[71] gave a number of volatile products including 3,3,3,-trifluoropropylboron difluoride, which was only about 8% decomposed after 7 days at 160°, and 1,1-difluoropropene was not a decomposition product.

The lack of success in attempts to prepare perfluoroalkylboron compounds led to the suggestion that such compounds are inherently unstable, their instability resulting from the failure of perfluoroalkyl groups to satisfy the $2p_z$ orbital of the boron atom to the extent that fluorine or even a hydrocarbon group is able to do. Also, internal nucleophilic attack on boron by neighbouring fluorine atoms causes extensive decomposition.

The extreme case of tris(trifluoromethyl)boron has been discussed, with the conclusion that such a compound must easily lose CF_2 groups (as polymer) to form boron trifluoride.[66,72] However, the existence of compounds of the CF_3BX_2 type (where X is an atom or group contributing π-bonding electrons to boron) was not precluded, and, indeed, a recent communication[73] describes the preparation of trifluoromethylboron difluoride by two very different methods. Parsons and Baker reacted the product from the reaction between $KB(n\text{-}C_4H_9)_2$ and CF_3I with boron trifluoride and obtained butylboron difluoride and trifluoromethylboron difluoride, while Burg and Juvinall used the reaction between CF_3SCl with diborane at 60° in a sealed tube. The desired product was isolated as its etherate. Trifluoromethylboron difluoride was described as 'enduringly metastable' and is considered to be a stronger Lewis acid than boron trifluoride.

If the explanation given of the instability of boron perfluoroalkyls is correct, one might expect to obtain stable compounds in which the acceptor properties of the boron have been eliminated or substantially reduced e.g. by employing boron addition compounds or borazole derivatives.[66] This follows from observations on the physical and chemical properties of fluoromethylboron difluoride which is prepared in almost quantitative yield by the reaction of diazomethane with boron trifluoride in the gas phase at -40°.[74] This fluoroalkylboron compound has a value of 30.5 for Trouton's constant and an observed molecular weight 3.4% higher than that calculated for the monomer. It has been suggested that association occurs in both liquid and vapour phases, and that spectral data indicate association through the fluorine atom of the alkyl group.



$$\mathrm{F-\overset{\overset{\displaystyle CH_2F}{|}}{\underset{\underset{\displaystyle F}{|}}{B}}{}^{\delta+}\,-\,-\,-\,-\,-\,-\,\overset{\delta-}{F}CH_2-BF_2}$$

This suggestion is supported by the lack of association in methylboron difluoride and trimethylboron. Fluoromethylboron difluoride readily loses boron trifluoride.

A preliminary report has appeared of attempts to prepare a perfluoroalkyl borazole,[66] but the products were not identified. The most stable perfluoroalkylboron compounds known are the salts of trifluoromethylfluoroboric acid, HBF_3CF_3. Trimethyltin trifluoromethylfluoroborate[60] gives a stable aqueous solution from which potassium, barium and ammonium trifluoromethylfluoroborates are readily obtained.[61] The ion is destroyed by boiling with 50% sulphuric acid, the fluorine appearing entirely as fluoride ions rather than trifluoromethane. The high stability of the trifluoromethylfluoroborate ion can be attributed both to the complete filling of the second electronic shell of the boron atom and also to the shielding effect resulting from the distribution of the negative charge over all six fluorine atoms.

The thermal decomposition of trifluoromethylfluoroborates is similar to that of trimethyltrifluoromethyltin in that the elimination of difluorocarbene occurs, leaving fluoroborate ions and the difluorocarbene finally appears as tetrafluoroethylene, perfluorocyclopropane, or perfluorocyclobutane depending entirely on the temperature and pressure at which the decomposition is performed.

b) Perfluorovinyl derivatives.

Stafford and Stone[75] have reported the following perfluorovinylboron compounds:- trifluorovinylboron difluoride (b.p.-14°), trifluorovinylboron dichloride (b.p.48°), bis(trifluorovinyl)-boron chloride (b.p.100.5°), and tris(trifluorovinyl)boron (b.p.104.9o).

These compounds were the first reported examples of covalent boron compounds in which the organo-group is fully fluorinated. They are unstable over extended periods of time, even when kept at -78°. They are prepared by the reaction of boron trichloride with trifluorovinyltin compounds, as shown below.

$$Me_2Sn(CF{=}CF_2)_2 + 2BCl_3 \xrightarrow[70^\circ]{\text{1 hour}} Me_2SnCl_2 + 2CF_2{=}CFBCl_2 \text{ (93\%)}$$

$$Me_2Sn(CF{=}CF_2)_2 + BCl_3 \xrightarrow[70^\circ]{\text{1 hour}} Me_2SnCl_2 + (CF_2{=}CF)_2BCl \text{ (85\%)}$$

$$CF_2{=}CFBCl_2 \xrightarrow[-23^\circ;\text{ 12 hours}]{SbF_3} CF_2{=}CFBF_2 \text{ (59\%)}$$

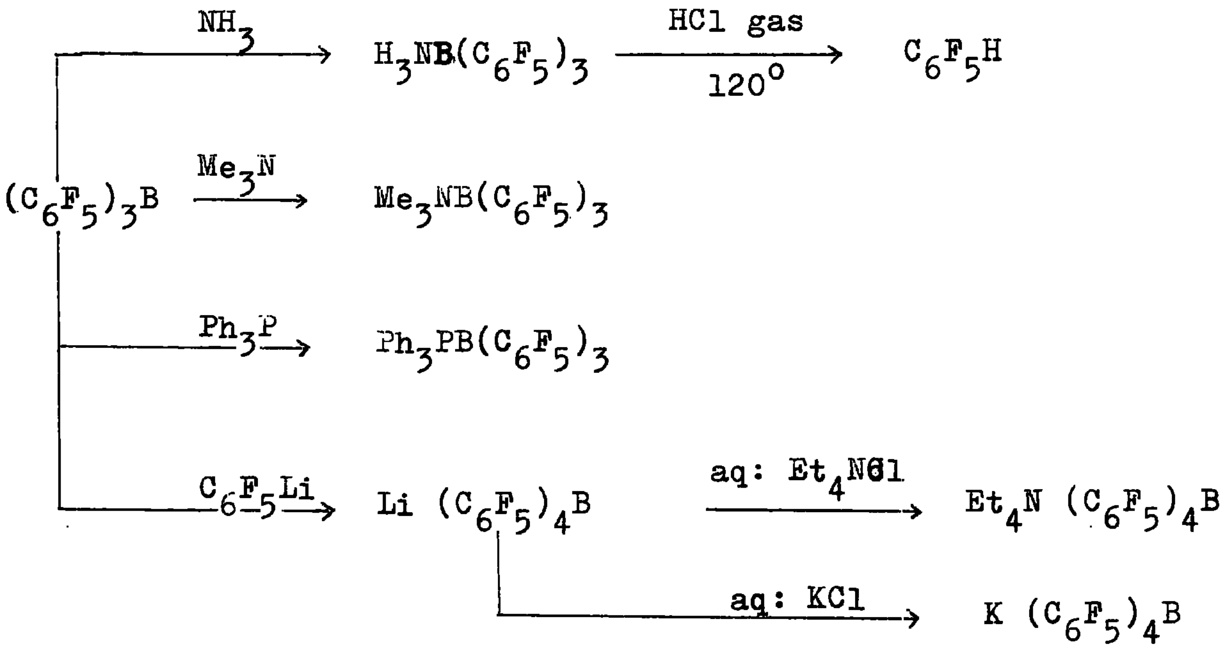
$$2(CF_2{=}CF)_2BCl + Me_2Sn(CF{=}CF_2)_2 \xrightarrow{50^\circ} Me_2SnCl_2 + 2(CF_2{=}CF)_3B$$

The trifluorovinylboron compounds are colourless, air-sensitive compounds, which, with water at elevated temperatures, release more than 90% of their trifluorovinyl groups as trifluoroethylene. In the gas phase at ambient temperatures trifluorovinylboron difluoride decomposes to form boron trifluoride at a rate of about 5% in a week. Trifluorovinylboron dichloride is able to withstand relatively short periods of heating (e.g. 5 hours at 100°) but on standing for a few days at room temperature partially decomposes giving boron trifluoride. Formation of the latter substance is of special interest since it shows that B-F bonds can be formed from these compounds by a route not involving simple disproportionation. This latter mode of disproportionation is, however, found with bis(trifluorovinyl)boron chloride, samples of which were observed to decompose completely into trifluorovinylboron dichloride and tris(trifluorovinyl)boron after one day at room temperature.

In view of the high stability of vinylboron difluoride[76] towards disproportionation it is likely that the tendency of trifluorovinylboron difluoride to give boron trifluoride does not involve disproportionation, but a fluorine-shift to the electronically unsaturated boron atom. Such a process is probably inhibited by a contribution of the π-electrons of the trifluorovinyl group to the p_{π}-orbital of the boron atom, with the result that trifluorovinylboron compounds might be thermally more stable than their perfluoroalkyl analogues, in which the p_{π}-orbital of the boron atom would be relatively less satisfied. That such an overlap does exist in the trifluorovinylboron compounds is supported by their infra-red spectra.[77]

c) Perfluoroaryl derivatives.

Stone and coworkers have reported the preparation of tris(pentafluorophenyl)boron from pentafluorophenyllithium and boron trichloride in pentane.[33] The product, although air-sensitive, is thermally stable at ambient temperatures, and shows marked acceptor properties as shown below.



Perfluoroaryl Derivatives of Other Metals and Metalloids.

a) Silicon and Phosphorus.[30]

The electron withdrawing character of the fluorine substituents in tris(pentafluorophenyl)phosphine appears to result in a stronger interaction between unshared electron pairs on the phosphorus atom with the π electrons of the aromatic nuclei than in triphenylphosphine. Thus, tris(pentafluorophenyl)phosphine is more acidic, and unlike triphenylphosphine does not form a phosphonium salt with methyl iodide, and is converted only through strong oxidation to the corresponding oxide.

Complete fluorination decreases the thermal stability of tetrakis(pentafluorophenyl)silane, but increases the thermal stability of tris(pentafluorophenyl)phosphine.

b) Thallium.

The recently reported compounds of the type $(C_6F_5)_2TlX$ (X = halogen, nitrate etc.,) are the first fluorocarbon derivatives of thallium to appear in the literature.[34] Bis(pentafluorophenyl)-thallium bromide was prepared from the Grignard reagent and thallium chloride in ether.

$$TlCl_3 + 2C_6F_5MgBr \longrightarrow (C_6F_5)_2TlBr + MgBr_2 + MgBrCl$$

Unlike most R_2TlX compounds, it is very soluble in organic solvents, and from the bromide, a chloride, nitrate, acetate- and a dipyridyl complex of the bromide - have been obtained. All the compounds except $(C_6F_5)_2$dipyTlBr are virtually non-electrolytes in acetone, the bromide, chloride, and nitrate being monomeric in this solvent. The molar conductance of $(C_6F_5)_2$TldipyBr is about ten times that of the bromide at comparable concentrations, hence some ionisation into $(C_6F_5)_2Tldipy^+$ and Br^- must occur, and this is confirmed by the low molecular weight in this solvent. The low conductance of $(C_6F_5)_2$TldipyBr could be explained by ion-pair formation, though the possibility that some of the compound is present as a five coordinate thallium derivative (like Sn in Me_3pySnCl)[78] cannot be ruled out. In benzene the molecular weight for the bromide suggests dimerisation. By contrast the dipyridyl complex is only slightly associated as expected for an ionic compound in benzene.

c) Transition Metals.

In a recent communication,[36] Stone and coworkers have reported the preparation and properties of some pentafluorophenyl derivatives of transition metals.

$$Mn(CO)_5Br + C_6F_5Li \longrightarrow C_6F_5Mn(CO)_5 \quad (29\%)$$

$$Fe(CO)_4I_2 + C_6F_5Li \longrightarrow C_6F_5Fe(CO)_4I \quad (2\%)$$

$$(\pi\text{-}C_5H_5)_2TiCl_2 + C_6F_5Li \longrightarrow (\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2 \quad (44\%)$$

$$+ (\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl \quad (29\%)$$

These compounds are chemically very robust for compounds containing organic groups bound to the metal by carbon-metal σ bonds. For example, pentafluorophenylmanganese pentacarbonyl was not decomposed after 72 hours at 138°, and after 72 hours at 162° it was recovered in 51% yield, and only 13% of the carbon monoxide expected for complete decomposition was obtained. Phenylmanganese pentacarbonyl decomposes at 100°.

Bis(cyclopentadienyl)bis(pentafluorophenyl)titanium was thermally stable at 110° in vacuo, but pyrolysis at 150° yielded small amounts of bis(cyclopentadienyl)pentaflurophenyltitanium fluoride, $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$.

Aqueous base had no apparent effect on these compounds, and bis(cyclopentadienyl)bis(pentafluorophenyl)titanium did not react with hydrogen chloride after 2 days at 110°. However, after 2 days at 150° the pentafluorophenyl groups were cleaved as pentafluorobenzene.

$$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2 + 2HCl \longrightarrow (\pi\text{-}C_5H_5)_2TiCl_2 + 2C_6F_5H \ (86\%)$$

Pentafluorophenylboron dichloride was obtained by the reaction between boron trichloride and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$.

Rausch has also reported the preparation of some pentafluorophenyl derivatives of some transition metals from the Grignard reagent[114].

$$Mn(CO)_5Br + C_6F_5MgBr \longrightarrow C_6F_5Mn(CO)_5 \qquad (47\%)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2I + C_6F_5MgBr \longrightarrow (\pi\text{-}C_5H_5)C_6F_5Fe(CO)_2 \qquad (7\%)$$

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2C_6F_5MgBr \longrightarrow (\pi\text{-}C_5H_5)_2(C_6F_5)TiCl$$

These new pentafluorophenyl derivatives of the transition metals exhibit remarkable thermal and oxidative stabilities compared to their hydrocarbon analogues.

d) Zinc.

Bis(pentafluorophenyl)zinc was obtained as a colourless, crystalline solid by the reaction shown below. [116]

$$ZnCl_2 + 2C_6F_5MgBr \longrightarrow (C_6F_5)_2Zn + MgCl_2 + MgBr_2$$

Bis(pentafluorophenyl)zinc was found to form coordination complexes readily with various oxygen-, nitrogen-, phosphorus- and arsenic-containing ligands. Bidentate ligands yield 1:1 complexes, but triphenylphosphine forms a 2:1 complex.

CHAPTER.2.

EXPERIMENTAL WORK.

EXPERIMENTAL.

Bromopentafluorobenzene was obtained from the Imperial Smelting Corporation, and by bromination of pentafluorobenzene.[29]

Preparation of Starting Materials.

Stannic Bromide.

Bromine (200g., 2.5 moles) was added dropwise to tin metal (60g., 0.5 moles), which had been cut into small pieces, in a 2Neck flask fitted with a dropping funnel and reflux condenser. The reaction was vigorous and sparks were observed. After 2 hours at reflux, excess of bromine was removed by distillation and the reaction mixture was distilled (b.p. 202°) to give stannic bromide (187.5g., 86%).

Tetramethyltin.

Methyl iodide (225g., 1.58 moles) in di-n-butyl ether (100ml) was added dropwise to magnesium (50g., 2.08 g-atoms) in di-n-butyl ether (600ml) in a 2 litre 3-neck flask fitted with a stirrer, dropping-funnel, and a reflux condenser. The reaction was initiated by the addition of a small crystal of iodine. The methyl iodide solution was added so as to maintain gentle reflux (3 hours). The reaction mixture was cooled to room temperature and stannic chloride (93.5g., 0.36 moles) was added dropwise. The reaction mixture was refluxed for 1½ hours, and then distilled, and the fraction boiling below 140° was collected. This fraction was fractionated using a glass helices column, and the fraction boiling at 76-78° was collected to give tetramethyltin (46.6g., 72.5%).

Tetraphenyltin.

Tetraphenyltin prepared by the standard procedure was available[79] in the department.

Tetra-p-tolyltin.

p-Bromotoluene (171g., 1 mole) in ether (100ml) was added to magnesium (24.3g., 1 g-atom) in ether (500ml) during 1½ hours. The reaction mixture was refluxed for ½ hour, and then allowed to cool to room temperature. Stannic bromide (76.5g., 0.175 moles) in benzene (100 ml) was added to the reaction mixture during 40 minutes, and then the reaction mixture was refluxed for 2¼ hours. The reaction mixture was cooled to room temperature and hydrolysed by the addition of ice-water (50 ml) and ice-cold 5% hydrochloric acid (200 ML). After filtration, the organic layer was separated, dried ($MgSO_4$), and solvent was removed under vacuum to give tetra-p-tolyltin (71g., 85%), which was recrystallised from benzene.

Alkyl- and Aryl-tin Halides.

With the exception of methyltintribromide, alkyl- and aryltin halides were obtained from the tetra-organotin compound by the redistribution reaction with stannic bromide or chloride.[80]

Methyltin Tribromide.

Bromine (25.1g., 0.31 moles) was added dropwise to dimethyltin dibromide (48.7g., 0.16 moles) in a 2-neck flask fitted with a dropping funnel and a reflux condenser, and the reaction mixture was heated until the colour due to bromine had disappeared. Distillation of the reaction mixture gave methyltin tribromide (b.p. 210°) (51g., 87%).

Methylmercury Iodide.

Mercury (53g.,) and methyl iodide (100g.,) were put into a Carius tube which was sealed off under vacuum and irradiated with ultra-violet light for 3 days with shaking. On opening the tube the solid product was recrystallised from benzene to give methylmercury iodide (55g., 61%) which had m.p.142-4°.

Preparation of Pentafluorophenyltin Compounds.

Trimethylpentafluorophenyltin.

Trimethyltin bromide (14g., 57.5 mmoles) in ether (25 ml) was added to a slight excess of pentafluorophenylmagnesium bromide prepared from magnesium (1.5g., 62.5 g-atoms) and bromopentafluorobenzene (15.5g., 62.5 mmoles) in ether (120 ml) and the mixture was heated under reflux for 48 hours. Hydrolysis was effected by 10% aqueous ammonium chloride (150 ml) to prevent the formation of an emulsion (halide-ion catalysed cleavage only occurs when alcohol is added as co-solvent). The ether layer was separated, dried ($MgSO_4$), and then the ether was removed under vacuum. Distillation

of the liquid residue ($34-6^{o}/10^{-2}$mm .) gave a colourless liquid, trimethylpentafluorophenyltin (11.5g., 60%).
(Found: F,28.2; Sn,35.6. $C_9H_9F_5Sn$ requires F,28.7; Sn,35.9%)
From trimethyltin iodide (50g), using a reflux time of 14 hours, trimethylpentafluorophenyltin was obtained in 70% yield, after distillation in vacuo.
The yields of trimethylpentafluorophenyltin from trimethyltin bromide are improved if a shorter reflux time (ca. 18 hours) than that described in the experiment above is used.

Dimethylbis(pentafluorophenyl)tin.

Dimethyltin dibromide (8.8g., 28.5 mmoles) in ether (25 ml) and pentafluorophenylmagnesium bromide (62.5 mmoles) in ether (120 ml) were heated at reflux for 48 hours, and then worked up in the manner described above to give dimethylbis(pentafluorophenyl)tin (8.0g., 58%) after distillation in vacuum ($74-6^{o}/10^{-2}$mm).
(Found: F,39.9; Sn,24.3. $C_{14}H_6F_{10}Sn$ requires F,39.3; Sn,24.6%)
In a later experiment using dimethyltin dibromide (17.6g) and a reflux time of 20 hours, dimethylbis(pentafluorophenyl)tin was obtained as a white solid (21.6g., 78%) which had m.p.35° after vacuum sublimation (60°/0.05mm).

Methyltris(pentafluorophenyl)tin.

Methyltin tribromide (7.2g., 19.2 mmoles) in ether (30 ml) and pentafluorophenylmagnesium bromide (62.5 mmoles) in ether (120 ml) after 3 days at reflux gave methyltris(pentafluorophenyl)tin (8.4g., 69%) which, after sublimation ($60-65^\circ/10^{-3}$mm) followed by recrystallisation from n-propanol had m.p.72-3°.

(Found: F,45.1; Sn,18.8. $C_{19}H_3F_{15}Sn$ requires F,44.9; Sn,18.7%)

Pentafluorophenyltriphenyltin.

Triphenyltin bromide (11.5g., 26.8 mmoles) in ether (30 ml) and pentafluorophenylmagnesium bromide (29.5 mmoles) in ether (100 ml), after 3 days at reflux, gave pentafluorophenyltriphenyltin (9.4g., 68%) which, after recrystallisation from ethanol and treatment with charcoal, had m.p.86°.

(Found: C,55.7; F,18.5. $C_{24}H_{15}F_5Sn$ requires C,55.7; F,18.4%)

Bis(pentafluorophenyl)diphenyltin.

Diphenyltin dibromide (12.4g., 28.7 mmoles) in ether (30 ml) and pentafluorophenylmagnesium bromide (62.5 mmoles) in ether (120 ml) after 48 hours at reflux gave bis(pentafluorophenyl)diphenyltin (9.5g., 54%) which, after recrystallisation from ethanol and treatment with charcoal, had m.p.85°.

(Found: C,47.8; F,30.6. $C_{24}H_{10}F_{10}Sn$ requires C,47.5; F,31.3%)

Tris(pentafluorophenyl)phenyltin.

Phenyltin tribromide (12.5g., 28.7 mmoles) in ether (30 ml) and pentafluorophenylmagnesium bromide (94 mmoles) in ether(180ml) after 3 days at reflux, gave tris(pentafluorophenyl)phenyltin (17.0g., 85%) which, after sublimation (80-90°/10^{-3}mm) and recrystallisation from ethanol, had m.p.95-6°. (Found: C,41.1; F,41.1. $C_{24}H_5F_{15}Sn$ requires C,41.3; F,40.9%)

Tetrakis(pentafluorophenyl)tin.

Stannic bromide (5g., 11.4 mmoles) in ether (25ml) and pentafluorophenylmagnesium bromide (48.8 mmoles) in ether (100 ml) after 3 days at reflux gave tetrakis(pentafluorophenyl)tin (4.6g., 51%) which, after sublimation (160°/10^{-3}mm) and recrystallisation from cyclohexane, had m.p.221°. (Found: F,47.9; Sn,14.9. $C_{24}F_{20}Sn$ requires F,48.3; Sn,15.1%)

p-Tolyltris(pentafluorophenyl)tin.

p-Tolyltin trichloride (10g., 31.6 mmoles) in ether (50 ml) and pentafluorophenylmagnesium bromide (122 mmoles) in ether (200 ml) after 19 hours at reflux gave a brown solid from which p-tolyltris(pentafluorophenyl)tin was obtained as white crystals by vacuum sublimation (140°/10^{-2}mm), and after recrystallisation from propanol the m.p. was 107°. (18g; 80% (Found: F,40.2; Sn,16.6. $C_{25}H_7F_{15}Sn$ requires F,40.1; Sn,16.7%)

Bis(p-tolyl)bis(pentafluorophenyl)tin.

Bis(p-tolyl)tin dichloride (7.4g., 20 mmoles) in ether (40 ml) and pentafluorophenylmagnesium bromide (50 mmoles) in ether (150 mmoles) after 11 hours at reflux gave a dark brown viscous liquid (8.1g). A portion of this liquid was distilled (160-164°/10^{-3}mm) to give a colourless liquid which deposited crystals, m.p.57-59°, on standing for several weeks. The rest of the product was eluted in petroleum (40-60°) over an alumina column. Removal of the solvent gave a light yellow liquid which, on standing, deposited crystals of bis(p-tolyl)bis(pentafluorophenyl)tin which had m.p. 73-5° after recrystallisation from isopropanol. (Found: C, 48.8; F, 30.3. $C_{26}H_{14}F_{10}Sn$ requires C, 49.2; F, 29.9%)

General Reaction Procedure.

The formation of pentafluorophenylmagnesium bromide took place readily without the addition of an initiator, and the reactions were performed in an atmosphere of nitrogen. In each case, the work-up procedure was that described for trimethylpentafluorophenyltin, and the reaction vessel was a 3-neck flask fitted with a stirrer, dropping funnel and reflux condenser.

Cleavage with Nucleophilic Reagents.

1) Alkali.

a) Trimethylpentafluorophenyltin (0.25g., 0.76 mmoles) was added to 50% aqueous-alcoholic potassium hydroxide (2ml., 4N). A white precipitate appeared on shaking, the mixture was acidified with hydrochloric acid, and then volatile product and solvent were removed by distillation, leaving a white solid from which was sublimed, trimethyltin hydroxide (0.12g., 0.66 mmoles), m.p.117°(subl.) (lit:118°d.)[81] The infra-red spectrum was identical with that of an authentic specimen. Pentafluorobenzene was shown to be present in the distillate by analytical-scale gas chromatography. When water alone is used as solvent (i.e. no alcohol present), the cleavage is very slow.

b) Triphenylpentafluorophenyltin (0.45g.,0.86 mmoles) was added to 10% aqueous-alcoholic potassium hydroxide (2ml, N/2) and the reaction mixture was refluxed for 20 minutes. Solvent was removed by distillation to give a white solid, triphenyltin hydroxide, which, after recrystallisation from ethanol-water had m.p. 117-8° (lit: 119-120°)[82]. The infra-red spectrum was identical with that of an authentic specimen.

2) <u>Potassium Fluoride in Anhydrous Ethanol.</u>

Trimethylpentafluorophenyltin (1.25g., 3.8 mmoles) and potassium fluoride (0.22g., 3.8 mmoles) in anhydrous ethanol (10 ml) were heated at reflux for 8 hours. Solid material was filtered off, washed with water and dried in an oven, and then identified as trimethyltin fluoride (0.22g., 1.2 mmoles) by comparison of its infra-red spectrum with that of an authentic specimen.

3) Aqueous-alcoholic Potassium Fluoride.

a) Trimethylpentafluorophenyltin (0.35g., 1.1 mmoles), which had been purified by preparative-scale gas chromatography, was shaken with 90% ethanol-water (2ml) and no reaction took place, (in a separate experiment the starting material was recovered unchanged). A small crystal of potassium fluoride was added to the mixture and a white precipitate appeared immediately. Solvent was removed by distillation and shown by gas chromatography to contain pentafluorobenzene. The residue was sublimed in vacuum to give trimethyltin hydroxide (0.19g., 1.1 mmoles) m.p.117°. Further experiments were carried out, similar to the one described above, except that potassium chloride or cyanide was used instead of potassium fluoride; trimethyltin hydroxide and pentafluorobenzene were obtained in each case, although the reactions were slower than in the case of potassium fluoride.

b) Dimethylbis(pentafluorophenyl)tin, when treated with aqueous-alcoholic potassium fluoride, as described above, gave dimethyltin oxide which gave an infra-red spectrum identical with that of an authentic specimen.

c) Pentafluorophenyltriphenyltin (0.25g) in 10% aqueous-ethanol solution was heated under reflux for 30 minutes. On cooling, a white solid appeared, which was filtered off. The infra-red spectrum of this solid was very similar to that of triphenyltin hydroxide, but it had a high m.p.(>300°) (c.f. Ph_3SnOH m.p.119-120°). However, the infra-red spectrum of this product was very similar to that of triphenyltin hydroxide except for a broad band at 3800 cm^{-1}, and from the spectrum there was no doubt that the pentafluorophenyl group had been cleaved.

d) Bis(pentafluorophenyl)diphenyltin was treated as described above, and diphenyltin oxide was obtained, which gave an infra-red spectrum identical with that of an authentic specimen.

e) Tetrakis(pentafluorophenyl)tin (0.62g) was treated as above, except that the reflux time was 5 minutes. Solvent was removed by vacuum transfer to give a white solid (m.p.>400°), which, from its infra-red spectrum, contained pentafluorophenyl and had a strong, broad band in the O-H stretch: region. (Found: Sn,31.8; C,27.0%). This corresponds to the stoicheiometric formula $(C_6F_5)_{1.4}SnO_{1.3}$.

f) When it was attempted to recrystallise methyltris(pentafluorophenyl)tin and tris(pentafluorophenyl)phenyltin from aqueous-ethanol, high-melting oxides were obtained. From the results of analyses, cleavage of two pentafluorophenyl groups from tin occurred in each case.

e.g. Product from $MeSn(C_6F_5)_3$ gave Sn = 38.2%

MeC_6F_5SnO requires Sn = 37.5%

Product from $PhSn(C_6F_5)_3$ gave Sn = 30.9%

PhC_6F_5SnO requires Sn = 31.3%.

Cleavage with Electrophilic Reagents.

1) Hydrogen Chloride gas.

The cleavage with hydrogen chloride was studied for both alkyl- and aryl-pentafluorophenyltin compounds. Since the experimental procedure was the same for each compound, the method is described for trimethylpentafluorophenyltin and the results of the other cleavages are summarised in Table II.

Hydrogen Chloride and Trimethylpentafluorophenyltin.

Hydrogen chloride was obtained from concentrated sulphuric acid and ammonium chloride. A known weight of gas was obtained by condensing the gas into a molecular weight bulb (which had been evacuated and weighed) on the vacuum line. Grease was removed from the bulb by means of tissue paper, and the bulb was reweighed, and thus the weight of hydrogen chloride in the bulb was obtained.

Hydrogen chloride gas (0.19g., 5.2 mmoles) was condensed into a Carius tube containing trimethylpentafluorophenyltin (1.72g., 5.2 mmoles). The tube was sealed off in vacuo, and allowed to stand at room temperature for 1 day. The tube was opened to the vacuum line and volatile material was collected, and shown by its infra-red spectrum and by analytical scale gas chromatography to be pentafluorobenzene (0.87g., 5.2 mmoles). The residue in the Carius tube was trimethyltin chloride (0.94g., 4.7 mmoles) which had m.p. 34.5-35.5° (lit: 37°),[83] and which was converted to a complex with ammonia, $Me_3SnCl.NH_3$, whose infra-red spectrum was identical with that of an authentic specimen.

Hydrogen Chloride and Pentafluorophenyltriphenyltin.

Hydrogen chloride gas (0.064g; 1.75 mmoles) was condensed into a Carius tube containing pentafluorophenyltriphenyltin (0.86g; 1.66 mmoles). The tube was sealed off, and a reaction occurred at 20°. After 3 days, volatile material was collected by vacuum transfer to give benzene (0.122g; 1.57 mmoles) identified by its infra-red spectrum and by gas chromatography. The residue in the tube was distilled (120-5°/0.005mm) to give a colourless liquid.

(Found: F,7.1; Cl,12.9. $C_{18}H_{10}ClF_5Sn$ requires F,20; Cl,7.5%) Disproportionation of the chloride may have occurred.

Hydrogen Chloride and Bis(pentafluorophenyl)diphenyltin.

Hydrogen chloride gas (0.045g; 1.23 mmoles) was condensed into a Carius tube containing bis(pentafluorophenyl)diphenyltin (0.67g; 1.10 mmoles). After 5 days at 20°, benzene (0.86g; 1.10 mmoles) was obtained by vacuum transfer. The residue in the tube was distilled (140-5°/0.005mm) to give a colourless liquid. (Found: F,32.4; Cl,8.2. $C_{18}H_5ClF_{10}Sn$ requires F,33.6; Cl,6.3%)

TABLE II

Reaction with HCl gas (1 mole)

Compound	Reaction Conditions	Composition of Volatiles	Yield of Volatiles
$Me_3SnC_6F_5$	20°; 24 hours	100% C_6F_5H	100%
* $Me_2Sn(C_6F_5)_2$	110°; 15 mins.	100% C_6F_5H	93%
$MeSn(C_6F_5)_3$	210°; 20 hours	100% C_6F_5H	30%
$(C_6H_5)_3SnC_6F_5$	20°; 15 mins.	100% C_6H_6	51%
"	20°; 3 days	100% C_6H_6	95%
† $(C_6H_5)_2Sn(C_6F_5)_2$	20°; 12 hours	100% C_6H_6	50%
"	20°; 5 days	100% C_6H_6	100%
$C_6H_5Sn(C_6F_5)_3$	170°; 12 hours	60% C_6H_6 40% C_6F_5H	80%
$(C_6F_5)_4Sn$	240°; 16 hours	100% C_6F_5H	10%
$(p\text{-}CH_3.C_6H_4)Sn(C_6F_5)_3$	100°; 17 hours	99% $C_6H_5.CH_3$ 1% C_6F_5H	87%
$(p\text{-}CH_3.C_6H_4)_2Sn(C_6F_5)_2$	95°; 7 hours	85% $C_6H_5.CH_3$ 15% C_6F_5H	80%

In each case volatile material was identified by its infra-red spectrum and by analytical scale gas chromatography.

[*] Me_2SnCl_2 was formed.

[†] Reaction with 2 moles of HCl gas:-

a) At room temperature; only 1 mole of HCl reacted.

b) 75°; 5 hours. 70% of HCl consumed. Volatiles contain 6% C_6F_5H.

2) Bromine in Ether.

As with hydrogen chloride, a typical experiment will be described, and the results of other experiments will be summarised in Table III. In this case, the progress of the reaction could be followed by observing the disappearance of the colour due to bromine.

Bromine and Triphenylpentafluorophenyltin in Ether.

Bromine (0.60g., 3.8 mmoles) was condensed into a Carius tube containing triphenylpentafluorophenyltin (1.95g., 3.8 mmoles) in diethyl ether (10 ml). The tube was allowed to reach room temperature, and after 1 day the colour due to bromine had disappeared. The tube was opened to the vacuum line and volatile material was collected, and shown by analytical scale gas chromatography to consist only of bromobenzene and ether. Bromobenzene was also identified by its infra-red spectrum after removal of ether by vacuum transfer. The residue in the Carius tube (1.87g.) was converted into a complex with ammonia by passage of dry ammonia gas into its ethereal solution. The ammonia complex was not characterised.

TABLE III. Reaction with Bromine in Ether (1 mole).

Compound	Reaction Conditions	Composition of Volatiles	Yield of Volatiles
$Me_3SnC_6F_5$			
$Me_2Sn(C_6F_5)_2$	20°; 3 days	100% C_6F_5Br	93%
$MeSn(C_6F_5)_3$	20°; 2½ hours	100% C_6F_5Br	85%
$(C_6H_5)_3SnC_6F_5$	20°; 24 hours	100% C_6H_5Br	
$(C_6H_5)_2Sn(C_6F_5)_2$	20°; 3 days	85% C_6H_5Br 15% C_6F_5Br	
$C_6H_5Sn(C_6F_5)_3$	20°; 10 days	2% C_6H_5Br 98% C_6F_5Br	96%
$(C_6F_5)_4Sn$	20°; 3 months	No Reaction	

Hydrogen Peroxide and Trimethylpentafluorophenyltin.

a) 'High test' (90%) hydrogen peroxide (1.9 ml) was added dropwise to trimethylpentafluorophenyltin (1.59g., 4.8 mmoles). There was no reaction at 20°, so the reaction mixture was heated on an oil bath. At 130° a violent reaction took place with ignition and extensive charring. The residue in the flask was extracted with methylene chloride, and solvent was removed by vacuum transfer to give crude pentafluorophenol (0.4g; 2.2mmoles) identified by its infra-red spectrum.

b) 'High test' hydrogen peroxide (1.2 ml) was added to trimethylpentafluorophenyltin (1.0g.) in carbon tetrachloride (3 ml). The reaction mixture was refluxed for several hours, but no pentafluorophenol was obtained, although a small amount of trimethyltin hydroxide sublimed onto the condenser.

Preparation of Tris(pentafluorophenyl)tin Chloride.

p-Tolyltris(pentafluorophenyl)tin (5.52g., 7.8 mmoles) and hydrogen chloride (0.26g., 7.3 mmoles) were heated in a sealed, evacuated, Carius tube at 100° for 17 hours. Volatile material, collected from the tube by vacuum transfer, was shown to be toluene (0.59 g., 6.5 mmoles) containing a trace of pentafluorobenzene by its infra-red spectrum and by analytical scale gas chromatography. The residue in the Carius tube (5.16g.) was recrystallised twice from petroleum (40-60°) to give white crystals of tris(pentafluorophenyl)tin chloride which had m.p. 108-9° (3.8g; 75%). (Found: C,33.0; Sn, 18.0. $C_{18}ClF_{15}Sn$ requires C,33.0; Sn,18.1%)

Reactions of Tris(pentafluorophenyl)tin Chloride.

With Alkali.

a) Tris(pentafluorophenyl)tin chloride (0.82g; 1.25 mmoles) in ether (10 ml) was added to 20% potassium hydroxide solution (2ml). A white precipitate appeared, which dissolved on shaking. The alkaline layer was separated, acidified, and the white precipitate was filtered off and dried in the oven (m.p. 300°). The infra-red spectrum of this material showed a broad band at 3400 cm^{-1}. (Found: C, 17.2%; Sn, 40.9%). This corresponds to the stoicheiometric formula $(C_6F_5)_{0.7}SnO_{1.65}$. On removal of the solvent from the organic layer, there was no residue.

b) Tris(pentafluorophenyl)tin chloride (0.46g; 0.71 mmoles) in ether (5 ml) was added to 2N ammonium hydroxide (2 ml). A white precipitate was formed, which dissolved on shaking. The ethereal layer was separated, dried ($MgSO_4$), and solvent was removed by vacuum transfer to give a white solid, tris(pentafluorophenyl)tin oxide (0.43g; 0.34 mmoles) (m.p.>300°). (Found: C,33.5; Sn,19.3. $C_{36}F_{30}OSn_2$ requires C,34.4; Sn,18.9%)

With Ammonia gas.

Dry ammonia gas was bubbled into a solution of tris(pentafluorophenyl)tin chloride (0.33g.) in petroleum (10 ml). A white precipitate of tris(pentafluorophenyl)tin chloride-2-ammonia was formed, which was filtered off (0.2g; m.p.155-170°). (Found: C, 31.4. $C_{18}H_6ClF_{15}N_2Sn$ requires C, 31.4%)

Thermal Stability of Pentafluorophenyltin Compounds.

Trimethylpentafluorophenyltin.

a) Trimethylpentafluorophenyltin (0.48g.) in a sealed, evacuated tube was heated at 250° for 20 hours. No discolouration of the liquid took place, and on opening the tube, trimethylpentafluorophenyltin (0.48g.) was recovered unchanged, as shown by its infra-red spectrum.

b) Trimethylpentafluorophenyltin (1.24g; 3.75 mmoles) in a sealed evacuated was heated at 400° for 2 hours. Considerable charring occurred, and, on opening the tube to the vacuum line, volatile material (0.26g.) was obtained. This had an infra-red similar to that of pentafluorobenzene, but, in addition, there were bands at 2980, 2916, 740, and 526 cms^{-1} which suggested the presence of a volatile methyltin compound. Analytical scale gas chromatography showed the volatile to consist of three components. The second and third components had retention times identical with those of tetramethyltin and pentafluorobenzene, respectively.

Methyltris(pentafluorophenyl)tin.

Methyltris(pentafluorophenyl)tin (0.39g.) was heated at 360° for 1 hour in a sealed, evacuated tube. Moderate charring occurred, and volatile material (0.0024g.) was obtained by vacuum transfer, and shown by its infra-red spectrum to be pentafluorobenzene.

Pentafluorophenyltriphenyltin.

Pentafluorophenyltriphenyltin (0.18g.) was heated for 2½ hours at 400° in a sealed, evacuated tube. Slight charring occurred, and volatile material (0.004g.) was collected by vacuum transfer and shown by analytical scale gas chromatography to contain only benzene.

Tetrakis(pentafluorophenyl)tin.

Tetrakis(pentafluorophenyl)tin was heated at 400° in a sealed, evacuated tube. Little change was observed after 2½ hours, but after 17 hours considerable charring had occurred. Volatile material (0.01g.) was collected by vacuum transfer, and shown by its infra-red spectrum to consist of a mixture of products with pentafluorobenzene as the major component.

Reaction of Pentafluorophenyltin Compounds with Donor Molecules.

2,2'-Bipyridyl.

2,2'-Bipyridyl (0.036g; 0.28 mmoles) in ether (10 ml) was added to methyltris(pentafluorophenyl)tin (0.147g; 0.23 mmoles) in ether (10 ml), and the mixture was allowed to stand at room temperature for 4 hours. No precipitate was obtained, and, after removal of solvent by vacuum transfer, sublimation (20°/0.005mm) gave a white solid, which was identified as unchanged 2,2'-bipyridyl by its infra-red spectrum.

Triethylamine.

Triethylamine in carbon tetrachloride solution was added in turn to separate solutions containing equimolar amounts of dimethylbis(pentafluorophenyl)tin, methyltris(pentafluorophenyl)tin, and pentafluorophenyltriphenyltin in carbon tetrachloride. In each case, white needles were slowly deposited. These crystals were filtered off and identified as triethylamine hydrofluoride by comparison of their infra-red spectra with that of an authentic specimen, which was prepared by passing anhydrous hydrogen fluoride into a solution of triethylamine in carbon tetrachloride.

Cleavage of Pentafluorophenyltin Compounds with Boron Halides.

A known weight of boron chloride or fluoride was obtained by filling a bulb of known volume, attached to the vacuum line, to a given pressure. The gas was then condensed into the reaction vessel.

Boron Trichloride and Trimethylpentafluorophenyltin.

Boron trichloride (10.04g; 86 mmoles) was condensed into a Carius tube containing trimethylpentafluorophenyltin (14.3g; 43 mmoles). The tube was sealed off under vacuum and allowed to stand at 20° overnight. White crystals appeared after 20 minutes at 20°. The tube was opened to the vacuum line and volatile material was fractionated through a trap at -78°. The volatile material in the -78° trap was pentafluorophenylboron dichloride (10.26g; 96%), which was hydrolysed to give pentafluorophenylboronic acid (see later).

The volatile material which passed through the -78° trap was condensed on to an equimolar of dry pyridine in pentane solution to give a white precipitate of methylboron dichloride -1-pyridine which, after recrystallisation from benzene-cyclohexane, had m.p. 107-9°
(Found: C,39.6; Cl,38.9. $C_6H_8BCl_2N$ requires C,41.0; Cl,40.3%)

The residue [illegible] in the Carius tube was shown to be dimethyltin dichloride (8.96g; 41 mmoles) by comparison of its infra-red spectrum with that of an authentic sample. After recrystallisation from cyclohexane it had m.p.106-7° (lit: 108°)[84].

Dimethyltin dichloride is also obtained if the molar ratio boron trichloride : trimethylpentafluorophenyltin is 1 : 1 instead of 2 : 1 as it was in this experiment. If the molar ratio is 1 : 1 , unreacted trimethylpentafluorophenyltin is also obtained.

Boron Trichloride (excess) and Dimethylbis(pentafluorophenyl)tin.

Boron trichloride (2.87g; 24.6 mmoles) was condensed into a Carius tube containing dimethylbis(pentafluorophenyl)tin (1.44g; 3.0 mmoles). The tube was sealed off under vacuum and allowed to stand at 20° for 34 hours. The tube was opened to the vacuum line, and volatile material was fractionated through a trap at -78° to give excess of boron trichloride (2.28g; 19.5 mmoles), identified by its infra-red spectrum. The residue in the Carius tube contained some unreacted dimethylbis(pentafluorophenyl)tin but was shown to be largely dimethyltin dichloride (0.75g;) from its infra-red spectrum and m.p.106° after recrystallisation from cyclohexane. The liquid in the -78° trap was shown to be pentafluorophenylboron dichloride (1.10g; 74%), which, on hydrolysis, gave pentafluorophenylboronic acid, identified by its infra-red spectrum.

Boron trichloride and dimethylbis(pentafluorophenyl)tin (1:1)

Preparation of bis(pentafluorophenyl)boron chloride.

Boron trichloride (3.11g., 26.5 mmoles) was condensed into a Carius tube containing dimethylbis(pentafluorophenyl)tin (12.8g., 26.5 mmoles). The tube was sealed off under vacuum and allowed to come to room temperature. White crystals appeared after 30 minutes at this temperature, and the tube was heated at 100° for 2 hours. On cooling, the contents of the tube were quickly transferred to a vacuum sublimation apparatus. Sublimation (20°/0.05mm) gave dimethyltin dichloride (4.0g., 18.3 mmoles) identified by its infra-red spectrum and m.p. after recrystallisation from cyclohexane. The residue was distilled (68-72°/0.02mm) to give bis(pentafluorophenyl)boron chloride (3.6g., 36%) which crystallised on cooling.

(Found: F,50.0; Cl,9.2. $C_{12}BClF_{10}$ requires F,49.5; Cl,9.2%)

Boron trifluoride and trimethylpentafluorophenyltin.

a) In carbon tetrachloride.

Boron trifluoride (1.68g., 24.8 mmoles) was condensed into a Carius tube containing trimethylpentafluorophenyltin (2.12g., 6.4 mmoles) in anhydrous (distilled from P_2O_5) carbon tetrachloride (10 ml). The tube was sealed off under vacuum and allowed to reach 20°. After 1 hour a large amount of white precipitate had appeared, and after

60 hours the tube was opened to the vacuum line and volatile material was fractionated through a trap at -78° to give excess of boron trifluoride (0.84g., 12.4 mmoles) identified by its infra-red spectrum. The liquid in the -78° trap, a mixture of carbon tetrachloride and pentafluorophenylboron difluoride, was hydrolysed by cautious addition of water, with cooling, to give pentafluorophenylboronic acid, identified by its infra-red spectrum and m.p.

The residue in the Carius tube was heated at 100° to give boron trifluoride (0.42g., 6.2 mmoles), identified by its infra-red spectrum. The residue in the tube, after washing with ether, was trimethyltin fluoride (1.11g., 6.4 mmoles) which had an infra-red spectrum identical with that of an authentic specimen. In a separate experiment, the residue in the Carius tube, which was extremely hygroscopic, was filtered off in a dry box and an infra-red spectrum was run as a KBr disc. This spectrum was identical with that expected for trimethyltin fluoroborate, and it had a strong, broad band centred at 1050 cm^{-1} which is characteristic of fluoroborates.

b) No solvent.

Boron trifluoride (1.08g., 16.0 mmoles) was condensed into a Carius tube containing trimethylpentafluorophenyltin (2.09g., 6.3 mmoles). The tube was sealed off under vacuum

and allowed to stand at 20° for 15 hours. A large amount of white solid was formed, and there was a dark liquid layer above the solid. The tube was opened to the vacuum line and volatile material was fractionated through a trap at -78° to give excess of boron trifluoride (0.69g., 10.2 mmoles) identified by its infra-red spectrum. The residue in the Carius tube was heated at 100° to give boron trifluoride (0.19g., 2.8 mmoles). The residue (2.15g.) was washed with ether to remove excess of trimethylpentafluorophenyltin. Insoluble material, a white solid, was dimethylpentafluorophenyltin fluoride (m.p.250°dec:), and an infra-red spectrum of this solid was recorded which showed bands characteristic of the pentafluorophenyl group.
(Found: C,28.6; F, . $C_8H_6F_6Sn$ requires C,28.7; F,36.7%)
However, methylboron difluoride was not detected spectroscopically in the volatile products.

Boron trifluoride and Dimethylbis(pentafluorophenyl)tin.

Boron trifluoride (0.38g., 5.6 mmoles) was condensed into a Carius tube containing dimethylbis(pentafluorophenyl)tin (0.78g., 1.6 mmoles). The tube was sealed off under vacuum. No reaction occurred at 20°, so the tube was heated at 70° for 2 days. On opening the tube to the vacuum line, excess of boron trifluoride (0.33g., 4.9 mmoles) was obtained by fractionation through a trap at -78°.

Pentafluorophenylboron Dichloride and Antimony Trifluoride.

Preparation of Pentafluorophenylboron Difluoride.

Anhydrous antimony trifluoride was obtained by continuous extraction with dry methanol, followed by removal of solvent by vacuum transfer. It was stored under vacuum.

a) Pentafluorophenylboron dichloride (10.7g., 43 mmoles) was condensed into a Carius tube containing antimony trifluoride (10.7g., 58 mmoles). The tube was sealed off under vacuum and allowed to stand at -15° for 4 hours. The tube was opened to the vacuum line, and volatile material was fractionated through a trap at -78° to give boron trifluoride (0.20g., 3.0 mmoles), identified by its infra-red spectrum. The volatile in the -78° trap was pentafluorophenylboron difluoride (6.8g., 73%), which was characterised by conversion to the 1:1 complex with pyridine (see later).

b) Pentafluorophenylboron dichloride (2.0g., 8.1 mmoles) was condensed into a Carius tube containing antimony trifluoride (4.5g., 25.0 mmoles). The tube was sealed off under vacuum, and heated at 45° for 1½ hours. The tube was opened to the vacuum line and volatile material was fractionated through a trap at -78° to give boron trifluoride (0.37g., 5.6 mmoles), identified by its infra-red spectrum. The -78° trap contained pentafluorophenylboron difluoride (0.33g., 18%), identified by its infra-red spectrum. The residue in the Carius tube

was extracted with ether (30 ml). The ethereal solution was dried ($MgSO_4$), and solvent was removed under vacuum to give a white solid, which, on sublimation in vacuo gave bis(pentafluorophenyl)antimony chloride (1.1g., 55%). The m.p was 68-71° after a second sublimation.
(Found: C,29.6; Cl,7.3; F,38.0. $C_{12}ClF_{10}Sb$ requires C,29.4; Cl,7.2; F,38.7%)

Preparation of Potassium Pentafluorophenylfluoroborate.

Pentafluorophenylboron Difluoride and Aqueous Potassium Fluoride.

Pentafluorophenylboron difluoride (5.19g., 24 mmoles) was condensed onto a solution of potassium fluoride (1.4g; 24mmoles) in water (20 ml). On warming to room temperature a white solid was rapidly formed. This solid was filtered off to give potassium pentafluorophenylfluoroborate (4.1g., 62%) which, after recrystallisation from water, had m.p.324°.
(Found: C,27·1; F,55·8. C_6BF_8K requires C,26.3; F,55.5%)

PENTAfluorophenylboron Difluoride and Aqueous Ammonium Fluoride.

Pentafluorophenylboron difluoride (0.99g., 4.6 mmoles) was condensed onto a solution of ammonium fluoride (0.34g; 9.2mmoles in water (5 ml). No white solid was formed on warming to room temperature, so the solution was evaporated to dryness to give a white solid, identified by its infra-red spectrum as ammonium fluoroborate (0.4g., 83%), which had m.p.306-312°.

Preparation of Pentafluorophenylboronic acid.

Pentafluorophenylboron dichloride (10.26g., 41.5 mmoles) was added dropwise to acetone (40 ml) at -78°, containing the calculated amount of water for hydrolysis. Solvent was removed by vacuum transfer to give pentafluorophenylboronic acid (7.85g., 89%) which, after sublimation in vacuo (140°/0.01mm), had m.p.290°. (Found:F,44.4. $C_6H_2BF_5O_2$ requires F,44.6%).

Determination of Neutralisation Equivalents.

Neutralisation equivalents were determined by titrating a weighed sample of the acid in 50% aqueous-ethanol solution, containing 20 times the solute weight of D-mannitol, against standard sodium hydroxide solution, using phenol phthalein as indicator. The values for the neutralisation equivalent were dependent on the method of purification of the acid. Samples purified by sublimation contained some anhydride, wheras samples purified by recrystallisation contained only acid.

Pentafluorophenylboronic acid requires Equivalent = 211.9

Pentafluorophenylboronic anhydride requires Equivalent = 193.9

Found:

a) Sample sublimed in vacuo (140°/0.01mm) Equivalent = 207.0

b) SAmple sublimed in vacuo and then recrystallised from toluene. Equivalent = 208.5

c) Sample recrystallised from toluene (not sublimed) Equiv; = 212.7

All three samples had a broad band centred at 3367 cm^{-1} in the infra-red spectrum. THis is characteristic of arylboronic acids, and is due to an intermolecular hydrogen bond.[85] However, the samples showed differences in the first order spectrum (see Chapter 4).

Preparation of Bis(pentafluorophenyl)borinic acid.

Bis(pentafluorophenyl)boron chloride (1.38g., 3.6 mmoles) in acetone (5 ml) was added to acetone (10 ml) at 20° containing the calculated amount of water for hydrolysis. Solvent was removed by vacuum transfer to give a colourless oil, which solidified after several hours pumping. This solid was twice sublimed in vacuo (90°/0.05mm) to give white crystals of bis(pentafluorophenyl)borinic acid (0.65g.,49%) which had m.p.102° (Found: F,52.5%; Neutralisation Equivalent, 356; 358. $C_{12}HBF_{10}O$ requires F,52.5%; Neutralisation Equivalent, 361.9)

Reactions of Pentafluorophenylboronic Acid.

With Hydrogen Peroxide.

a) 10% Hydrogen peroxide (7.7ml) was added dropwise to pentafluorophenylboronic acid (0.47g., 2.2 mmoles). The reaction mixture was heated at 100° for 15 minutes, and, on cooling, was extracted with methylene chloride (6 ml). The organic layer was separated, dried ($MgSO_4$), and solvent was removed by vacuum transfer to give pentafluorophenol (0.05g., 13%), identified by its infra-red spectrum. Solvent was shown to contain pentafluorobenzene by analytical-scale gas chromatography.

b) 'High test' (85%) hydrogen peroxide (10.1 ml) was added dropwise to pentafluorophenylboronic acid (5.4g., 25.4 mmoles) at -78° in a 2-neck flask fitted with a dropping funnel and reflux condenser. The reaction mixture was allowed to reach room temperature gradually, and, finally, heated to 50° to complete the reaction. The reaction mixture was extracted with methylene chloride (3 portions of 20 ml); the organic layer was separated, dried ($MgSO_4$), and solvent was removed under vacuum to give crude pentafluorophenol (4.25g., 91%). Distillation gave pentafluorophenol (b.p.143-147°., lit:143°)[36] (2.85g., 61%), identified by its infra-red spectrum.

With Diethanolamine.

Diethanolamine (o.42g., 4.0 mmoles) was added to pentafluorophenylboronic acid (0.85g., 4.0 mmoles) in dry benzene (40 ml). The reaction mixture was refluxed for 1 hour using a Dean-Stark head, and the solvent was distilled off to give a sticky white solid residue, which decomposed before an infra-red spectrum was recorded.

Hydrolytic Stability of PEntafluorophenylboronic Acid.

a) Pentafluorophenylboronic acid (0.132g., 0.62 mmoles) and water (0.76g.) in a sealed, evacuated tube were allowed to stand at 20° for 2 days. On opening the tube to the vacuum line, volatile material was obtained and shown by analytical scale gas chromatography to be pentafluorobenzene (0.02g., 20%).

b) Pentafluorophenylboronic acid (0.20g., 0.94 mmoles) was dissolved in 50% aqueous-ethanol (5 ml) and allowed to stand at 20° for 45 minutes. Solvent was removed by vacuum transfer to give boric acid (0.053g., 0.86 mmoles), identified by its infra-red spectrum. Pentafluorophenylboronic acid was stable in aqueous acetone under similar conditions, although hydrolysis also occurred in this solvent after several hours.

c) Pentafluorophenylboronic acid (0.087g.) was dissolved in aqueous-ethanol (4 ml) to which a few drops of 2N hydrochloric acid had been added. The solution was allowed to stand at 20° for 1 hour. Solvent was removed by vacuum transfer to give a white solid residue (0.074g.), which from its infra-red spectrum and m.p. 280-5° was mostly unchanged pentafluorophenylboronic acid. It appears that the addition of acid to the solution inhibits the hydrolysis of pentafluorophenylboronic acid.

Thermal Stability of Pentafluorophenylboron Compounds.

a) Pentafluorophenylboron Dichloride.

i) Pentafluorophenylboron dichloride (8g.) which had been standing in a sealed tube at room temperature for 6 weeks was fractionated through a trap at -20°. Volatile material which passed through this trap (0.2g.) was shown to be mainly boron trichloride, from its infra-red spectrum, but a weak band at 692 cm^{-1} indicated the presence of some boron trifluoride.

ii) Pentafluorophenylboron dichloride (0.82g., 3.3 mmoles) was heated in a sealed, evacuated tube at 130° for 19 hours. On cooling, the tube was opened to the vacuum line and volatile material was fractionated through a trap at -78°. Volatile material in the -78° trap was shown to be unchanged pentafluorophenylboron dichloride (0.60g., 2.4 mmoles) by its infra-red spectrum. The residue in the tube was bis(pentafluorophenyl)boron chloride (0.16g., 0.4 mmoles) which, on hydrolysis, gave bis(pentafluorophenyl)borinic acid, identified by its infra-red spectrum. Volatile material which passed through the -78° trap was shown to be boron trichloride (0.05g., 0.4 mmoles) by its infra-red spectrum.

iii) Pentafluorophenylboron dichloride (1.34g., 5.4 mmoles) was heated at 220° for 25 hours in a sealed, evacuated Carius tube. On cooling, volatile material was fractionated through a trap at -78° to give boron trichloride (0.21g., 67%), identified by its infra-red spectrum. The residue in the Carius tube was bis(pentafluorophenyl)boron chloride (0.6g; 59%), which, on hydrolysis, gave bis(pentafluorophenyl)borinic acid, identified by its infra-red spectrum. The volatile material in the -78° trap was shown to be unchanged pentafluorophenylboron dichloride (0.40g., 30%) from its infra-red spectrum.

b) Pentafluorophenylboron Difluoride.

i) Pentafluorophenylboron difluoride (0.90g., 4.2 mmoles) which had been standing in a sealed, evacuated tube at room temperature for 1 month was fractionated through a trap at -78° to give boron trifluoride (0.054g., 38%).

ii) Pentafluorophenylboron difluoride (0.90g., 4.2 mmoles) was heated at 95° for 16 hours in a sealed, evacuated tube. On cooling, volatile material was fractionated through a trap at -78° to give boron trifluoride (0.048g., 0.7 mmoles), identified by its infra-red spectrum. The material in the -78° trap was condensed into a tube, which was sealed off under vacuum, and heated at 194° for 18 hours. ON cooling, volatile material was fractionated through a trap at -78° to give boron trifluoride (0.062g., 0.9 mmoles). Thus, the total amount of boron trifluoride obtained from the decomposition is 0.11g., 77%. The white solid residue in the tube fumed in moist air, and, on hydrolysis, gave bis(pentafluorophenyl)-borinic acid (0.55g., 71%), identified by its infra-red spectrum. The volatile material in the -78° (0.19g.) trap was shown by its infra-red spectrum to be a mixture of pentafluorobenzene and unchanged pentafluorophenylboron difluoride.

c) Potassium Pentafluorophenyltrifluoroborate.

Potassium pentafluorophenyltrifluoroborate (0.56g., 2.0 mmoles) was heated for 4½ hours at 250° and very little decomposition occurred. The temperature was raised slowly to 295°, whereupon sudden decomposition, with charring, occurred. The contents of the tube were extracted with ether, and insoluble brown solid was filtered off (0.48g). This solid was boiled with water, and insoluble brown solid was filtered off. White crystals of potassium fluoroborate (0.14g., 54%), identified by its infra-red spectrum, were obtained from the filtrate on evaporation.

The brown solid (m.p.$>360^{\circ}$) was insoluble in acetone, benzene, methanol and THF. An infra-red spectrum was recorded, which was very similar to those of the perfluoropolyphenylenes obtained from the decomposition of pentafluorophenylmagnesium bromide in THF.[117] Major bands occurred at 1480, 995 and 980 (doublet), and 710 cms^{-1}.

Preparation of Pyridine Complexes of Pentafluorophenylboron Dihalides.

a) Pentafluorophenylboron Dichloride-1-Pyridine.

Pentafluorophenylboron dichloride (2.0g., 8.0 mmoles) was condensed onto an equimolar amount of anhydrous pyridine (distilled under N_2 from potassium hydroxide) in dry di-n-butyl ether (10 ml). On warming to room temperature a white solid was formed, which was filtered off to give pentafluorophenylboron dichloride-1-pyridine (0.15g., 57%), which, after recrystallisation from benzene/cyclohexane had m.p. 140-142°.

(Found: C,40·3 ; N,4·4. $C_{11}H_5Cl_2F_5NB$requires C,40.3; N,4.3%)

b) Pentafluorophenylboron Difluoride -1-Pyridine.

Pentafluorophenylboron difluoride (1.5g., 6.95 mmoles) was condensed onto an equimolar amount of anhydrous pyridine in dry petroleum (40-60°) (15ml). On warming to room temperature a white solid was formed, which was filtered off to give pentafluorophenylboron difluoride-1-pyridine (1.7g., 83%), which, after recrystallisation from chloroform/petroleum had m.p. 82-3°.

(Found: C, ; N, . $C_{11}H_5BF_7N$ requires C,44.8; N,4.9%)
F, 45·4 F, 45·1

Boron Trichloride and Pentafluorophenylboron Dichloride-1-Pyridine.

Boron trichloride (0.19g., 1.6 mmoles) was condensed into a Carius tube containing pentafluorophenylboron dichloride-1-pyridine (0.53g., 1.6 mmoles). The tube was sealed off under vacuum and heated at 110° for 6 hours. On cooling, volatile material was fractionated through a trap at -78° to give boron trichloride (0.10g., 53%), identified by its infra-red spectrum. The volatile material in the -78° trap was shown by its infra-red spectrum to be pentafluorophenylboron dichloride (0.14g., 35%). The residue in the Carius tube (0.47g.), after recrystallisation from benzene/cyclohexane, had m.p.83-5°, and from its infra-red spectrum was probably a mixture of the pyridine complexes of boron trichloride and pentafluorophenylboron dichloride.

Cleavage Reactions of Pentafluorophenylmercury Derivatives with Electrophilic Reagents.

Boron Trichloride and Methylpentafluorophenylmercury.

Boron trichloride (1.25g., 10.7 mmoles) was condensed into a Carius tube containing methylpentafluorophenylmercury[31] (1.98g., 5.3 mmoles). The tube was sealed off under vacuum and allowed to stand at 20° for 24 hours. The tube was then opened to the vacuum line and volatile material was fractionated through a trap at -78° to give excess of boron trichloride (0.70g., 6.0 mmoles), identified by its infra-red spectrum. The residue in the Carius tube, a white solid, was shown to be methylmercury (II) chloride (1.33g., 5.3 mmoles) by its infra-red spectrum and m.p.170 (lit: 167°)[162] after recrystallisation from ethanol-water. The volatile material in the -78° trap was pentafluorophenylboron dichloride (1.12g., 84%), identified by its infra-red spectrum.

Boron Trifluoride and Methylpentafluorophenylmercury.

Boron trifluoride (0.87g., 12.8 mmoles) was condensed into a Carius tube containing methylpentafluorophenylmercury (3.62g., 9.5 mmoles). The tube was sealed off under vacuum and allowed to stand at 20° for 2 days. The tube was opened to the vacuum line and volatile material was fractionated through atrap at -78° to give excess of boron trifluoride (0.37g., 5.5 mmoles), identified by its infra-red spectrum. The residue in the Carius tube was extracted with ether (25 ml), and the ethereal solution was decanted to give an insoluble liquid residue (1.14g.), which slowly deposited mercury on standing. The infra-red spectrum of this liquid showed a broad band between 1110 cm^{-1} and 835 cm^{-1}, which is characteristic of tetrafluoroborates.

Ether was removed from the organic layer by vacuum transfer to give a white solid residue (2.84g.), from which methylpentafluorophenylmercury (0.2g., 0.5 mmoles) was obtained by sublimation. The residue was recrystallised from benzene-cyclohexane to give bis(pentafluorophenyl)mercury (m.p.138-9°, lit:142°)[31], which was identified by its infra-red and N.M.R. spectra.

Stannic Chloride and Methylpentafluorophenylmercury (1:1).

Stannic chloride (0.64g., 2.5 mmoles) was condensed into a Carius tube containing methylpentafluorophenylmercury (0.94g., 2.5 mmoles). The tube was sealed off under vacuum and allowed to reach 20°. White solid appeared after 5 minutes at this temperature. After 20 hours, the contents of the tube were extracted with petroleum (40-60°; 4 ml), and insoluble white solid was filtered off and shown by its infra-red spectrum to be methylmercury (II) chloride (0.62g., 2.5 mmoles). Solvent was removed from the filtrate by vacuum transfer, and the liquid residue was distilled (54-6°/0.02mm) to give pentafluorophenyltin trichloride (0.9g., 90%).

(Found: F,23.9; Cl,27.3. $C_6Cl_3F_5Sn$ requires F,24.2; Cl,27.3%)

Stannic Chloride and Methylpentafluorophenylmercury (1:2).

Stannic chloride (1.80g., 6.9 mmoles) was condensed into a tube containing methylpentafluorophenylmercury (5.29g., 13.8 mmoles). The tube was sealed off under vacuum and heated at 100° for 1¼ hours. On cooling, the contents of the tube were extracted with petroleum (60-80°; 15 ml) and insoluble white solid was filtered off (4.0g., m.p.110-115°. Theoretical yield of methylmercury (II) chloride = 3.46g.). The infra-red spectrum of this solid showed strong bands characteristic of the pentafluorophenyl group, and the solid was probably a mixture of bis(pentafluorophenyl)-mercury and methylmercury (II) chloride.

Pentafluorophenyltin Trichloride and Methylpentafluorophenyl-Mercury.

Pentafluorophenyltin trichloride (1.3g., 3.4 mmoles) and methylpentafluorophenylmercury (1.3g., 3.4 mmoles) were allowed to react at 20° in a sealed, evacuated tube. Only a few white crystals had formed after 20 hours, but after standing for 14 days at 20° a large amount of white solid had formed. The contents of the tube were extracted with petroleum (40-60°; 10ml), and insoluble material was filtered off (0.5g.) and shown by its infra-red spectrum to be a mixture of methylmercury (II) chloride and bis(pentafluorophenyl)mercury.

Boron Trichloride and Bis(pentafluorophenyl)mercury.

Boron trichloride (1.34g., 11.5 mmoles) was condensed into a Carius tube containing bis(pentafluorophenyl)mercury (2.93g., 5.5 mmoles). The tube was sealed off under vacuum, and heated at 175° for 1 hour. On cooling, the tube was opened to the vacuum line and volatile material was fractionated through a trap at -78° to give excess of boron trichloride (0.43g., 3.7 mmoles), identified by its infra-red spectrum. However, it was very difficult to remove pentafluorophenylboron dichloride from the solid residue (3.57g.) in the tube by vacuum transfer, and only 0.25g; 9% of pentafluorophenylboron dichloride was obtained in the -78° trap.

Stannous Chloride and Bis(pentafluorophenyl)mercury.

Bis(pentafluorophenyl)mercury (1.96g., 3.7 mmoles) and anhydrous stannous chloride (0.92g., 4.9 mmoles) in dry acetone (20 ml) were heated at reflux for 22 hours . The reaction mixture gradually changed colour from yellow → orange → red → dark red. The solution was filtered, and solvent was removed by vacuum transfer to give a red-brown solid residue (2.15g.) which was sublimed ($80-100^\circ$/0.1mm) to give a viscous red liquid (0.65g.) and bis(pentafluorophenyl)mercury (1.1g., 56%), identified by its m.p. and infra-red spectrum. The infra-red spectrum of the red liquid suggested that it was polymeric, fluoroaromatic material.

When ethanol was used as solvent, a small amount of mercury was deposited, but bis(pentafluorophenyl)mercury was recovered in 56% yield after 40 hours at reflux.

Analyses.

Tin.

The gravimetric method used by Gilman and Rosenburg[87] for the determination of tin in organotin compounds was modified slightly.

A 150ml silica flask was heated strongly in a bunsen flame, allowed to cool in a dessicator (P_2O_5), and weighed. A piece of platinum wire was attached to the neck of the flask for suspension. Approximately 0.2g of the organotin compound was weighed into the flask. 1 ml of analar concentrated sulphuric acid was added by pipette and the flask was heated gently, at first, and then strongly in a bunsen flame. Finally, when all the fumes of sulphur trioxide had been driven from the flask, it was ignited for 1 hour to remove all carbonaceous material. This left a residue of tin (IV) oxide, which was allowed to cool in a dessicator and weighed.

Carbon and Fluorine.

Carbon and fluorine analyses were performed by Mr T. Holmes and Mr T. Caygill of this department.

CHAPTER 3.

DISCUSSION OF THE EXPERIMENTAL WORK.

DISCUSSION OF EXPERIMENTAL WORK

Preparation of Pentafluorophenyl Derivatives of Tin.

The following series of pentafluorophenyltin compounds have been prepared :- $Me_xSn(C_6F_5)_{4-x}$, $Ph_xSn(C_6F_5)_{4-x}$, where $x = 0 \rightarrow 4$, and $(p\text{-tolyl})_ySn(C_6F_5)_{4-y}$, where y = 1 or 2. These compounds have been prepared in good yield (>60%) by reaction of alkyl- or aryl-tin halides with pentafluorophenylmagnesium bromide in ether. The yield of tetrakis(pentafluorophenyl)tin is 50%. The m.p.'s of these compounds are listed in Table IV.

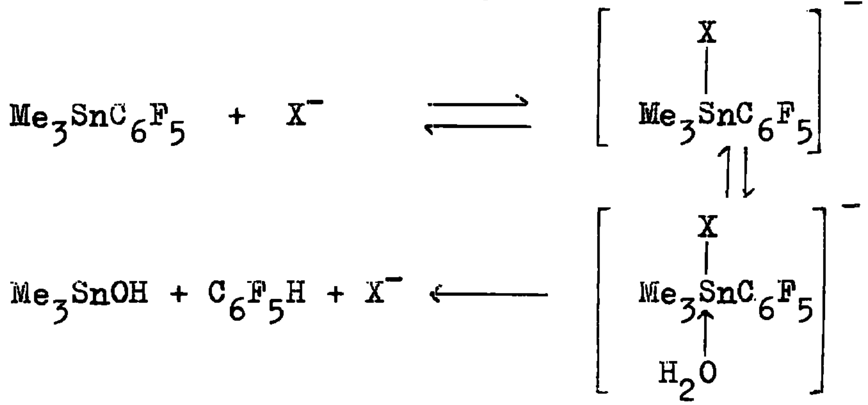
TABLE IV

Compound	M.p.	Compound	M.p.
$Me_3SnC_6F_5$	34-36°/0.01mm	$Ph_3SnC_6F_5$	86°
	186-187°/730mm	$Ph_2Sn(C_6F_5)_2$	85°
$Me_2Sn(C_6F_5)_2$	35°	$PhSn(C_6F_5)_3$	95-6°
	74-76°/0.01mm	p-tolyl$Sn(C_6F_5)_3$	107°
$MeSn(C_6F_5)_3$	72-3°	(p-tolyl)$_2Sn(C_6F_5)_2$	73-5°
$(C_6F_5)_4Sn$	221°		

Cleavage of Pentafluorophenyltin Compounds with Nucleophilic Reagents.

These compounds are white crystalline solids with the exception of the first member of the alkyl series, which is a colourless liquid at room temperature. In the absence of halide ions, they are stable to air and water. However, in the presence of halide ions these compounds were found to undergo an unusual halide-ion catalysed hydrolysis. This was observed because in the classical preparation of tetraorganotin compounds, excess of organotin halides is removed as the insoluble fluoride by shaking the reaction mixture with aqueous alcoholic potassium fluoride.[88] When this technique was employed in the preparation of pentafluorophenyltin compounds, rapid hydrolysis occurred with loss of pentafluorophenyl. For example, in the preparation of trimethylpentafluorophenyltin a large yield of trimethyltin hydroxide was obtained. Test tube experiments showed that the three entities water, alcohol, and fluoride ion were essential to this hydrolysis. Chloride ion and cyanide ion also caused hydrolysis of trimethylpentafluorophenyltin.

The most likely mechanism for this hydrolysis must involve initial coordination of halide ion to tin to give a five covalent species of tin. This would be followed by coordination of water, and elimination of pentafluorophenyl as pentafluorobenzene. Attempts to detect the intermediate species by spectroscopic studies were unsuccessful.



$$Me_3SnC_6F_5 + X^- \rightleftharpoons \left[\overset{X}{\underset{}{Me_3SnC_6F_5}}\right]^- \rightleftharpoons \left[\overset{X}{\underset{H_2O}{Me_3SnC_6F_5}}\right]^- \longrightarrow Me_3SnOH + C_6F_5H + X^-$$

Direct replacement of pentafluorophenyl by fluoride ion, followed by hydrolysis, is ruled out by the fact that trimethyltin fluoride is not readily hydrolysed in aqueous solution.

In the alkyl series hydrolysis occurred readily at room temperature, whereas in the aryl series short reflux periods were necessary. On hydrolysis, dimethylbis(pentafluorophenyl)tin gave dimethyltin oxide, and bis(pentafluorophenyl) diphenyltin gave diphenyltin oxide. Methyltris(pentafluorophenyl)tin and phenyltris(pentafluorophenyl)tin gave oxides which appear to have lost two pentafluorophenyl groups. Tetrakis(pentafluorophenyl)tin gave an oxide of ill-defined composition. In the absence of ethanol, however, pentafluorophenyltin compounds are distinctly water repellent.

This halide-ion catalysed hydrolysis may be a more general property of fluorocarbon tin compounds. Seyferth[65] has reported that hydrolysis takes place in the purification of perfluorovinyltin compounds containing two or more perfluorovinyl groups using aqueous alcoholic potassium fluoride solution.

$$(n\text{-}Bu)_2Sn(CF{=}CF_2)_2 \xrightarrow{F^-/H_2O} (n\text{-}Bu)_2SnO + 2CFH{=}CF_2$$

However, ethanol alone caused cleavage of perfluorovinyl from tin in some cases, whereas pentafluorophenyltin compounds were unaffected by refluxing in dry ethanol.

$$(n\text{-}Bu)_2Sn(CF{=}CF_2)_2 + 2EtOH \xrightarrow[\text{20 hours}]{\text{reflux}} (n\text{-}Bu)_2Sn(OEt)_2 + 2CFH{=}CF_2$$

It has also been observed[89] that trimethyltrifluoromethyltin containing halide impurities deposits a white solid on standing, whereas a sample purified by chromatography is quite stable.

Pentafluorophenyltin compounds are very susceptible to nucleophilic attack (in the presence of ethanol as co-solvent) losing pentafluorophenyl as pentafluorobenzene.

$$Me_3SnC_6F_5 + OH^- \xrightarrow{EtOH} Me_3SnOH + C_6F_5H$$

$$Ph_3SnC_6F_5 + OH^- \xrightarrow{EtOH} Ph_3SnOH + C_6F_5H$$

In the absence of ethanol, cleavage by alkali is very slow. This ready cleavage by nucleophilic reagents is a general property of fluorocarbon tin compounds, and is probably due to the high polarity of the bond between the metal and the fluorocarbon group.

Trimethylpentafluorophenyltin is even cleaved by potassium fluoride, on refluxing in dry ethanol.

$$Me_3SnC_6F_5 + KF \xrightarrow[\text{reflux; 8 hours}]{\text{EtOH}} Me_3SnF\ (30\%) + C_6F_5H$$

Cleavage of Pentafluorophenyltin Compounds by Electrophilic Reagents.

There has been considerable interest in the electrophilic cleavage of organic groups from metals, and the idea which persisted for some time was that the ease of cleavage of a group depends on its electronegativity (more electronegative groups being most easily cleaved). Kharasch[90] determined for a large number of mixed mercury dialkyls and diaryls which of the two groups in the reaction,

$$RHgR' + HCl \xrightarrow[\text{solvent}]{\text{inert}} RHgCl + R'H$$

is removed from the mercury atom. He drew up a list of radicals classified according to electronegativity which is known as Kharasch's list.

tolyl > phenyl > benzyl > methyl > ethyl etc.,

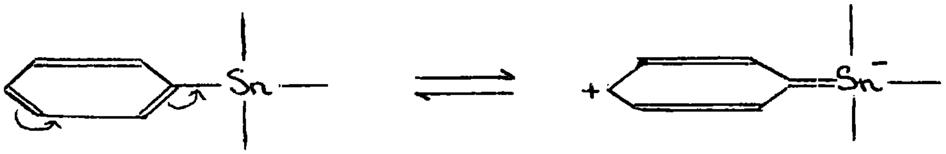
This list strictly holds only for mercury compounds reacting in an inert solvent with hydrogen chloride. Experiments carried out with compounds of other metals showed, however, that the sequence in which groups are removed by iodine, bromine, hydrogen chloride and some other polar reagents is always the same but for a few exceptions.

That the concept of group electronegativity is not very meaningful in these reactions has recently been discounted by several authors.[62,91,92] In a series of papers Eaborn and coworkers[91] have shown that substituent effects on the rates of cleavage of aryl-metal bonds (metal = Si, Ge, Sn, or Pb) by acids can be quantitatively explained in terms of ease of electrophilic attack at the metal-bonded carbon atom. Furthermore, after an intensive investigation of the reaction between hydrogen chloride and unsymmetrical mercury compounds, Dessy[92] concludes that the cleavage of these compounds is a good measure of the electron availability at the attacked carbon atom, and not of the electronegativity of the departing group, as indicated by Kharasch. Finally, the preferential cleavage of phenyl and alkyl groups by electrophilic reagents from perfluoroalkyltin compounds is surprising, 62,63 since perfluoroalkyl groups are obviously very electronegative. However, this is easily explained if one considers the electron density at the tin-bonded carbon atoms. In the perfluoroalkyltin compounds, because of the inductive factor, an unfluorinated carbon atom is more electron rich than a fluorinated carbon atom, and, therefore, the unfluorinated group is preferentially cleaved by acids. It would therefore appear that in the cleavage of organic groups from metals by electrophilic reagents, the important factor in deciding which organic group will be cleaved is the electron density at the metal-bonded carbon atom, and not the electronegativity of the organic group.

The order of cleavage of pentafluorophenyl could not be predicted with certainty since the balance between retarding inductive electron withdrawal and assisting mesomeric electron release by aromatic fluorine varies with the reaction system, (c.f. chlorination and nitration of fluorobenzene).[93] The electrophilic cleavage of pentafluorophenyltin derivatives has been studied with a view to the preparation of pentafluorophenyltin halides and pentafluorophenylboron dihalides. Particular regard has been paid to a comparison of the reactivity of the various derivatives and to decide whether cleavage of specific groups could be achieved. Cleavage reactions using anhydrous hydrogen chloride (see Table II) show that the overall ease of electrophilic cleavage of groups from tin is,

p-tolyl > phenyl > pentafluorophenyl > methyl

which is consistent with the results of cleavage from mercury.[31] This series is obviously determined by the ease of electrophilic substitution at the various groups, but overall reactivity is governed by the number of pentafluorophenyl groups in the molecule. An increase in the number of pentafluorophenyls leads to a decrease in reactivity in both the methyl and the phenyl series. Tetra-aryl derivatives are usually considerably less reactive to electrophilic cleavage than trialkyl-aryl derivatives, and this has been attributed to inductive electron withdrawal by phenyl.[94] It is therefore surprising to note the considerable reactivity of pentafluorophenyltriphenyltin, which is comparable to that of trimethylpentafluorophenyltin. This indicates that mesomeric electron release from phenyl(i.e.d_π-p_π interaction with tin) occurs in the cleavage of pentafluorophenyltriphenyltin.



The cleavage of pentafluorophenyltin derivatives in ether solution by bromine was also studied. In the phenyl series, the overall reactivity of pentafluorophenyl compounds was the same as with hydrogen chloride, but, unlike hydrogen chloride, bromine cleaved a pentafluorophenyl group exclusively from tris(pentafluorophenyl)phenyltin. In the reaction with hydrogen chloride both phenyl and pentafluorophenyl groups were cleaved. In the alkyl series, bromine cleaved pentafluorophenyl groups preferentially.

Preparation of Pentafluorophenyltin Halides.

It was possible to replace one phenyl exclusively by chlorine (see Table II) in pentafluorophenyltriphenyltin and in bis(pentafluorophenyl)diphenyltin using hydrogen chloride. In both cases benzene, but no pentafluorobenzene, was obtained. This is a convenient method for the preparation of the corresponding chlorides,

$$Ph_2Sn(C_6F_5)_2 + HCl \longrightarrow Ph(C_6F_5)_2SnCl + C_6H_6$$

but the chlorides so prepared could not be distilled without disproportionation, as shown by the fluorine and chlorine analyses of the distillate. Reaction with two molecular proportions of hydrogen chloride was more difficult, and cleavage of pentafluorophenyl as well as phenyl occurred from bis(pentafluorophenyl)diphenyltin. This difficulty also arose in the reaction of tris(pentafluorophenyl)phenyltin with one molecular proportion of hydrogen chloride. However, specific cleavage of p-tolyl from tris(pentafluorophenyl)-p-tolyltin occurred to give tris(pentafluorophenyl)tin chloride in excellent yield.

$$(C_6F_5)_3Snp\text{-}tolyl + HCl \longrightarrow (C_6F_5)_3SnCl + C_6H_5.CH_3$$

Pentafluorophenyltin trichloride and bis(pentafluorophenyl)tin dichloride could not be prepared by preferential cleavage of groups with hydrogen chloride, but the trichloride was prepared by the reaction of stannic chloride with methylpentafluorophenylmercury.

$$MeHgC_6F_5 + SnCl_4 \longrightarrow MeHgCl + C_6F_5SnCl_3$$

The dichloride could not be prepared by this route since reaction of pentafluorophenyltin trichloride with methylpentafluorophenylmercury was very slow, and the trichloride caused disproportionation of the mercurial into dimethyl- and bis(pentafluorophenyl)-mercury. However, the preparation of the dichloride from dimethylbis(pentafluorophenyl)tin and stannic chloride has been communicated recently.[32]

$$Me_2Sn(C_6F_5)_2 + SnCl_4 \longrightarrow Me_2SnCl_2 + (C_6F_5)_2SnCl_2$$

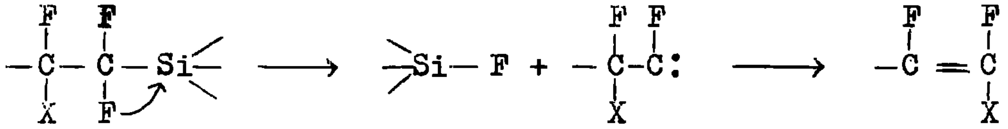
Hydrolysis of tris(pentafluorophenyl)tin chloride required very mild conditions since cleavage of pentafluorophenyl occurred with strong alkali, but this cleavage was avoided by using ammonium hydroxide and tris(pentafluorophenyl)tin oxide was isolated. Reaction of the chloride with ammonia gas in dry ether gave a complex containing two molecular proportions of ammonia.

$$(C_6F_5)_3SnCl \xrightarrow{NH_4OH} \left[(C_6F_5)_3Sn\right]_2O$$

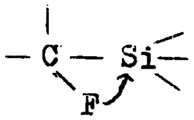
$$\xrightarrow{NH_3} (C_6F_5)_3SnCl.2NH_3$$

Thermal Stability of Pentafluorophenyltin Compounds.

Fluorocarbon derivatives of metals and metalloids have often been observed to be thermally unstable due to internal nucleophilic attack on the metal atom by fluoride ion. Haszeldine[95] has shown that for polyfluoroalkylpolysiloxanes, when fluorine is in the α-position, thermal breakdown appears to occur by α-elimination of fluorine initiated by an internal nucleophilic attack on silicon by the α-fluorine, and followed by rearrangement of the carbene thus formed.



Evidence for the carbene-type mechanism has been obtained in separate experiments using the compounds $CHFCl.CF_2.SiCl_3$ and $CFCl_2.CF_2.SiCl_3$.[96] The pyrolysis of the first of these compounds yields the olefin CHF:CFCl as the major organic product together with small amounts of CF_2:CHCl. The primary step in this pyrolysis is considered to be an internal nucleophilic attack on silicon by a fluorine in the α-position,



followed, or possibly accompanied, by migration of a chlorine atom from the β-carbon atom, thus giving rise to the olefin, CHF:CFCl. The other olefin, CF_2CHCl, results from βeliminationof fluorine following simple C-Si fission, or from internal nucleophilic attack on silicon by a fluorine in the β-position, or from a combination of both. Similarly the thermal decomposition of trimethyltrifluoromethyltin[57] at 150° gives rise to difluorocarbene in good yield.

Unlike trifluoromethyl, pentafluorophenyl attached to tin is not inherently thermally unstable e.g. trimethylpentafluorophenyltin was recovered unchanged after 20 hours at 250°, although rapid decomposition did occur at 350° to give pentafluorobenzene and tetramethyltin. The phenylpentafluorophenyltin compounds were more stable at this temperature but decomposed quickly at 400°, and tetrakis-(pentafluorophenyl)tin was unchanged after 2 hours at 400°, but charred after a prolonged time at this temperature.

The mechanism of thermal decomposition of pentafluorophenyltin compounds is interesting since if internal nucleophilic attack by o-fluorine on tin occurred this would result in the loss of pentafluorophenyl from tin as tetrafluorobenzyne. However, no evidence for this type of mechanism was obtained, although the report by Stone[36] of the isolation of bis(π-cyclopentadienyl)pentafluorophenyltitanium fluoride from the thermal decomposition of bis(π-cyclopentadienyl)bis(pentafluorophenyl)titanium strongly suggests that this mechanism does occur in the thermal breakdown of pentafluorophenyl derivatives of transition metals.

Reaction of Pentafluorophenyltin Compounds with Donor Molecules.

Pentafluorophenyl enhances the acceptor propertiesof mercury since bis(pentafluorophenyl)mercury forms some stable, neutral coordination complexes,[31] but attempts to isolate similar complexes with tetrakis(pentafluorophenyl)tin or other tetra-organo derivatives of tin have been unsuccessful. Addition of triethylamine to solutions of pentafluorophenyltin compounds in carbon tetrachloride resulted in the formation of triethylamine hydrofluoride. No explanation can be given for the formation of the latter.

Cleavage of Pentafluorophenyltin Compounds with Boron Halides.

Preparation of Pentafluorophenylboron Derivatives.

The reaction between boron trihalides and tetra-organotin compounds has been used in several instances for the preparation of organoboron compounds.[75,97,98,99] This reaction has now been shown to provide an excellent route to pentafluorophenylboron derivatives. For example, pentafluorophenylboron dichloride is obtained in about 90% yield from the reaction between boron trichloride and trimethylpentafluorophenyltin at room temperature in the absence of solvent.

$$Me_3SnC_6F_5 + 2BCl_3 \longrightarrow C_6F_5BCl_2 + Me_2SnCl_2 + MeBCl_2$$

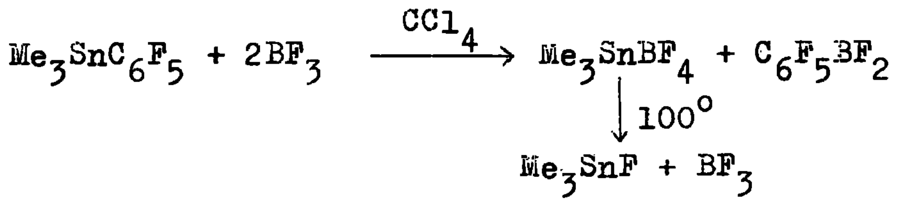
Pentafluorophenylboron dichloride can also be obtained from dimethylbis(pentafluorophenyl)tin and boron trichloride under similar conditions.

$$Me_2Sn(C_6F_5)_2 + 2BCl_3 \longrightarrow 2C_6F_5BCl_2 + Me_2SnCl_2$$

If the molar ratio of the reactants in the above reaction is 1:1, bis(pentafluorophenyl)boron chloride can be obtained after 2 hours at 100°.

$$Me_2Sn(C_6F_5)_2 + BCl_3 \longrightarrow (C_6F_5)_2BCl + Me_2SnCl_2$$

The reaction between boron trifluoride and trimethylpentafluorophenyltin in anhydrous carbon tetrachloride gave trimethyltin fluoroborate and pentafluorophenylboron difluoride.



$$\begin{tikzcd}[column sep=small] Me_3SnC_6F_5 + 2BF_3 \arrow[r, "CCl_4"] & Me_3SnBF_4 \arrow[d, "100^{o}"] + C_6F_5BF_2 \\ & Me_3SnF + BF_3 \end{tikzcd}$$

It is interesting to compare this reaction with the reaction between boron trifluoride and trimethyltrifluoromethyltin in which trimethyltin trifluoromethylfluoroborate is obtained.[60]

$$Me_3SnCF_3 + BF_3 \longrightarrow Me_3Sn^{+}(CF_3BF_3)^{-}$$

The formation of trimethyltin fluoroborate in the reaction between boron trifluoride and trimethylpentafluorophenyltin indicates that pentafluorophenylboron difluoride is a weaker Lewis acid than boron trifluoride.

In the absence of solvent, however, pentafluorophenylboron difluoride was not obtained from the reaction of boron trifluoride with trimethylpentafluorophenyltin. Instead, cleavage of a methyl group occurred to give dimethylpentafluorophenyltin fluoride.

$$Me_3SnC_6F_5 + BF_3 \xrightarrow{\text{No solvent}} Me_2(C_6F_5)SnF + MeBF_2$$

Inthe reaction between boron trifluoride (excess of) and dimethylbis(pentafluorophenyl)tin in the absence of solvent more than 85% of the boron trifluoride was recovered after

2 days at 70°. However, pentafluorophenylborom difluoride is obtained in good yield from the reaction between pentafluorophenylboron dichloride and antimony trifluoride at -15°

$$C_6F_5BCl_2 \xrightarrow[-15^{\circ}]{SbF_3} C_6F_5BF_2$$

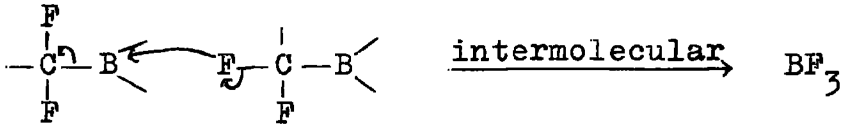
This is the most convenient route to pentafluorophenylboron difluoride, since in the reaction between boron trifluoride and trimethylpentafluorophenyltin it was found to be very difficult to separate pentafluorophenylboron difluoride from solvent. The low temperature is important in the reaction above, since at higher temperatures a transfer of pentafluorophenyl from boron to antimony occurs, and bis(pentafluorophenyl)antimony chloride is obtained.

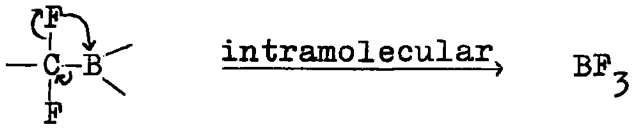
$$C_6F_5BCl_2 \xrightarrow[30^{\circ}]{SbF_3} (C_6F_5)_2SbCl + BF_3$$

Pentafluorophenylboron dihalides are colourless liquids, which fume strongly in moist air. They are conveniently characterised as their 1:1 complexes with pyridine, which are white air-stable solids, although the complex derived from the difluoride becomes sticky after about 2 months in a sample bottle.

Thermal Stability of Pentafluorophenylboron Dihalides.

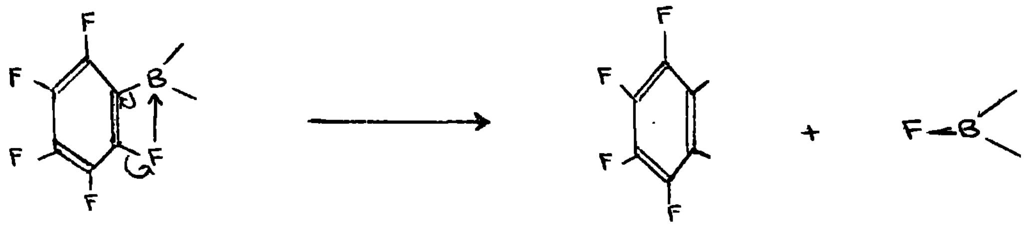
Fluorocarbon derivatives of boron have been shown to be unstable with respect to boron trifluoride. This appears to be due to a tendency for nucleophilic attack on boron by neighbouring fluorine atoms to occur. This can take place by an intermolecular or by an intramolecular process, and, in either case, boron trifluoride will be formed and the organic group will be eliminated as a carbene.





Thus perfluorovinylboron dichloride decomposes at 100° to boron trifluoride as well as boron trichloride.

It was therefore of interest to determine if the thermal breakdown of pentafluorophenylboron compounds occurs by a similar mechanism. If the decomposition involves internal nucleophilic attack on boron by an o-fluorine atom, one might expect the intermediate formation of tetrafluorobenzyne.



It was found, however, that both pentafluorophenylboron dichloride and pentafluorophenylboron difluoride decompose by simple disproportionation. Thus, after 25 hours at 220°, pentafluorophenylboron dichloride was shown to undergo 67% decomposition to give bis(pentafluorophenyl)boron chloride and boron trichloride.

$$2C_6F_5BCl_2 \longrightarrow (C_6F_5)_2BCl + BCl_3$$

Pentafluorophenylboron dichloride could be distilled, under nitrogen, at atmospheric pressure with only slight decomposition After 6 weeks at room temperature in a sealed tube, pentafluorophenylboron dichloride gave mainly boron trichloride in about 5% yield. However, the infra-red spectrum of the volatile decomposition product showed a weak band at 692 cm^{-1}, which is diagnostic of the presence of boron trifluoride.[100] This band was not present in the infra-red spectrum of the volatile product obtained from the thermal decomposition of pentafluorophenylboron dichloride. The difference in thermal behaviour between pentafluorophenylboron dichloride and perfluorovinylboron dichloride can be attributed to the stronger C-F bonds in the aromatic compound. Also, if the decomposition is intramolecular, the formation of boron trifluoride from pentafluorophenylboron dichloride is less likely than from perfluorovinylboron dichloride, since in pentafluorophenylboron dichloride there is no fluorine on the α-carbon atom.

Similarly, pentafluorophenylboron difluoride gave bis(pentafluorophenyl)boron fluoride and boron trifluoride in 77% yield after 18 hours at 194°.

$$2C_6F_5BF_2 \longrightarrow (C_6F_5)_2BF + BF_3$$

Pentafluorophenylboron difluoride was also observed to undergo decomposition at room temperature in a sealed tube to give boron trifluoride at the rate of about 40% in a month.

Preparation and Thermal Stability of Potassium Pentafluorophenyltrifluoroborate.

Only three mixed organohaloborate anions have been characterised previously. These are $(C_6H_5)_3BF^-$,[101] $[CF_3BF_3]^-$,[60.61] and $CH_2{=}CHBF_3^-$.[102] As would be expected, these anions show greater hydrolytic stability than do the organoboron compounds from which they are derived. Vinylboron difluoride was regenerated in a high state of purity when potassium vinyltrifluoroborate was heated at 250° on the vacuum line. Thus, salts of organohaloborates may be an excellent means of storing and handling organoboron halides, and of regenerating these compounds in a highly pure form. In view of the tendency of pentafluorophenylboron difluoride to decompose to boron trifluoride, potassium pentafluorophenyltrifluoroborate was prepared by condensing pentafluorophenylboron difluoride onto an aqueous solution containing an equimolar amount of potassium fluoride.

$$KF + C_6F_5BF_2 \longrightarrow K^+(C_6F_5BF_3)^-$$

An attempt to prepare the ammonium salt in a similar way resulted mainly in the formation of ammonium fluoroborate.

Potassium pentafluorophenyltrifluoroborate can be recrystallised from its aqueous solution, but prolonged boiling with water results in hydrolysis. Pentafluorophenylboron difluoride was not regenerated when the salt was heated. Instead, thermal decomposition took place quite suddenly at about 300° to give potassium fluoroborate and a perfluoropolyphenylene. Clearly, attack on the boron atom by fluorine from an organic group must occur, but, as pointed out previously, the mechanism of the decomposition can be unimolecular or bimolecular. A unimolecular mechanism would give rise to a polyphenylene with predominantly ortho linkages, whereas a bimolecular mechanism would yield a polyphenylene with mainly meta or para linkages. The perfluoropolyphenylene was not sufficiently soluble for an N.M.R. spectrum to be recorded, but the infrared spectrum was similar to those of the perfluoropolyphenylenes obtained from the decomposition of pentafluorophenylmagnesium bromide in THF.

Preparation and Properties of Pentafluorophenylboronic Acid.

Pentafluorophenylboronic acid was obtained by the low temperature (-78°) hydrolysis of pentafluorophenylboron dichloride, using the exact amount of water required for hydrolysis, in acetone solution. This is the first report of the isolation of a perfluorocarbon boronic acid.

$$C_6F_5BCl_2 + 2H_2O \xrightarrow{-78^{\circ}} C_6F_5B(OH)_2 + 2HCl$$

If the hydrolysis is done at higher temperatures there is a tendency for cleavage of the pentafluorophenyl group to occur, and, indeed, in aqueous-ethanolic solution pentafluorophenylboronic acid was hydrolysed to boric acid and pentafluorobenzene after 45 minutes at room temperature.

$$C_6F_5B(OH)_2 + H_2O \longrightarrow C_6F_5H + H_3BO_3$$

This hydrolysis was inhibited by the addition of dilute mineral acid to the ethanolic solution. These observations indicate that the anion derived from pentafluorophenylboronic acid is unstable, readily losing pentafluorophenyl as a carbanion. The ease of nucleophilic displacement of the pentafluorophenyl group from the boronic acid also accounts for the fact that it was not possible to isolate a diethanolamine ester of pentafluorophenylboronic acid. These esters are usually the most stable derivatives for the characterisation of arylboronic acids.[103]

The ready hydrolysis of pentafluorophenylboronic acid in ethanolic solution thwarted attempts to measure the ionisation of this acid. Certain arylboronic acids are known to hydrolyse and oxidise in the presence of dilute base e.g. o-chlorophenylboronic acid. However, Povlevy[104] has determined the ionisation constants of a number of substituted arylboronic acids by potentiometric titration, and he checked that hydrolysis did not occur during the titrations by comparing the ultra-violet spectra of solutions of arylboronic acids before and after titration.

Unlike phenylboronic acid, pentafluorophenylboronic acid is not readily dehydrated to a boroxine, even at 140°/0.01mm. A sample purified by vacuum sublimation under these conditions has a broad band centred at 3367 cm^{-1} in the infra-red spectrum, which has been observed by other workers for a number of arylboronic acids,[105] and which is considered to be due to an intermolecular hydrogen bond. Povlevy[104] found that this broad band was resolved into two bands for most o-substituted arylboronic acids, when the spectrum was recorded in diethyleneglycoldimethyl ether solution. However, when the spectrum of pentafluorophenylboronic acid was recorded in this solvent, resolution of this band did not occur. The neutralisation equivalent of a sample of pentafluorophenylboronic acid purified by vacuum sublimation is 207, which indicates the presence of some anhydride. However, a sample recrystallised from toluene (not sublimed) has a neutralisation equivalent corresponding to that expected for the acid i.e. 212.

Conversion of Pentafluorophenylboronic Acid to Pentafluorophenol by Reaction with 'High-test' Hydrogen Peroxide.

A relatively rapid and efficient route from aryl halides to the corresponding phenols involves the intermediate formation of arylboronic acids (which need not be isolated), followed by treatment with 10% hydrogen peroxide.[106]

$$\mathrm{ArX} \longrightarrow \mathrm{ArMgX} \xrightarrow[2.\mathrm{H_2O},\ \mathrm{H^+}]{1.\mathrm{B(OMe)_3}} \mathrm{ArB(OH)_2} \xrightarrow{10\%\ \mathrm{H_2O_2}} \mathrm{ArOH} + \mathrm{B(OH)_3}$$

When pentafluorophenylboronic acid was treated with 10% hydrogen peroxide, both pentafluorobenzene and pentafluorophenol were obtained. However, treatment of the acid with 'high-test' hydrogen peroxide at low temperature gave only pentafluorophenol in good yield. At room temperature the reaction is very vigorous. Thus, the following series of reactions provide a convenient route to pentafluorophenol from pentafluorobenzene. The overall yield of pentafluorophenol is about 45%.

$$\begin{tikzcd}
C_6F_5H \arrow[r, "Br_2/\text{oleum}"] & C_6F_5Br \arrow[r, "\text{i. } Mg/Et_2O", "2.\ Me_3SnBr"'] & Me_3SnC_6F_5 \arrow[d, "BCl_3"] \\
C_6F_5OH & C_6F_5B(OH)_2 \arrow[l, "\text{'high test'}"', "H_2O_2"] & C_6F_5BCl_2 \arrow[l, "H_2O"', "-78^\circ"]
\end{tikzcd}$$

This reaction may provide a convenient route to substituted perfluorophenols, which cannot be prepared from the parent aromatic fluorine compound by the standard reaction with potassium hydroxide,[107] because of secondary reactions between the substituent and alkali.

Preparation of Bis(pentafluorophenyl)borinic Acid.

Bis(pentafluorophenyl)borinic acid was obtained by the hydrolysis of bis(pentafluorophenyl)boron chloride in acetone solution at -78°.

$$(C_6F_5)_2BCl + H_2O \longrightarrow (C_6F_5)_2BOH + HCl$$

Bis(pentafluorophenyl)borinic acid was readily hydrolysed by the addition of water to give pentafluorobenzene and pentafluorophenylboronic acid.

$$(C_6F_5)_2BOH + H_2O \longrightarrow C_6F_5B(OH)_2 + C_6F_5H$$

An attempt to prepare the borinic acid by the method due to Coates and Livingstone[108] was unsuccessful, as also was the reaction between pentafluorophenylmagnesium bromide and trimethyl borate[109] for the preparation of pentafluorophenylboronic acid. This lack of success in the preparation of pentafluorophenylboron derivatives by the Grignard procedure, which is used for their hydrocarbon analogues, is probably due to the hydrolytic instability of the C-B bond in pentafluorophenylboron compounds. Since, in these reactions the work-up procedure involves destroying excess of the Grignard reagent by hydrolysis.

Reaction of Boron Trihalides with the Pyridine Complexes of Pentafluorophenylboron Dihalides.

The reaction between boron trihalides and the complexes formed between other boron halides and a reference base has been used to determine the relative Lewis acidities of boron trihalides.[110] The stronger Lewis acid displaces the weaker one from the reference base, and the results were in accord with those obtained by measurements of the physical properties of boron trihalide complexes. When boron trichloride and pentafluorophenylboron dichloride -1-pyridine were heated together in a sealed tube at 110° for 6 hours, pentafluorophenylboron dichloride was obtained in 35% yield.

$$C_6F_5BCl_2.Py + BCl_3 \longrightarrow C_6F_5BCl_2 + BCl_3.Py$$

This indicates that, as expected, pentafluorophenylboron dichloride is a weaker Lewis acid than boron trichloride. Boron trifluoride did not replace pentafluorophenylboron difluoride from its pyridine complex at room temperature, and, on heating, pentafluorophenylboron difluoride-1-pyridine decomposes to give boron trifluoride so that no information about the relative Lewis acidities of boron trifluoride and pentafluorophenylboron difluoride could be obtained by this method.

Cleavage Reactions of Pentafluorophenylmercury Compounds with Inorganic Halides.

Mercury diaryls were the first reagents to be used for the attachment of aryl to boron, giving directly the arylboron dihalide.[111, 112] The high temperature and pressure quoted by early workers are not necessary, and Gilman and Moore[113] have found that the reaction of boron trichloride with diphenylmercury occurs very readily at room temperature and atmospheric pressure. Groups attached to the aryl radical of the organomercury compound have a distinct effect on the reaction. The hydroxy and amino groups, which aid electrophilic substitution reactions, not only seem to aid the displacement of mercury by boron, but also the displacement of boron by a proton. The carboxyl group decreases the reactivity of the aryl radical, so that mercury is not displaced by boron even at elevated temperatures.

a) Bis(pentafluorophenyl)mercury.

It has previously been noted[31] that bis(pentafluorophenyl)-mercury is extremely resistant to protonic acids, and reacts only slowly with bromine in carbon tetrachloride. Further reactions have been carried out which confirm the lack of reactivity of bis(pentafluorophenyl)mercury towards electrophilic reagents.

Diphenylmercury is known to react readily with stannous chloride in ethanol to give diphenyltin dichloride and mercury metal.[118]

$$Ph_2Hg + SnCl_2 \longrightarrow Ph_2SnCl_2 + Hg$$

However, the reaction between bis(pentafluorophenyl)mercury and stannous chloride in ethanol solution did not give mercury metal, even when heated at reflux for 40 hours, and bis(pentafluorophenyl)mercury was recovered in 56% yield. When acetone was used as solvent, the solution was dark red after 22 hours at reflux, but bis(pentafluorophenyl)mercury was again recovered in 56% yield. The other product was a viscous red liquid, which, from its infra-red spectrum, was probably some polymeric fluoroaromatic material.

When boron trichloride and bis(pentafluorophenyl)mercury were heated together (molar ratio 2:1) at 175° for 1 hour in a sealed tube, 68% of the boron trichloride was consumed. However, it was very difficult to remove pentafluorophenylboron dichloride from the solid reaction product when the tube was opened to the vacuum line, and the method was, therefore, impractical as a route to pentafluorophenylboron dichloride. This reaction illustrates the considerable decrease in reactivity which accompanies the substitution of fluorine in the aryl radicals of diarylmercurials.

b) Methylpentafluorophenylmercury.

In contrast to the lack of reactivity of bis(pentafluorophenyl)mercury towards protonic acids, methylpentafluorophenylmercury undergoes ready cleavage of pentafluorophenyl when reacted with anhydrous hydrogen chloride. With this in mind, the reactions between methylpentafluorophenylmercury and some inorganic halides have been investigated with a view to the preparation of pentafluorophenyl derivatives of other metals or metalloids.

Cleavage of pentafluorophenyl by boron trichloride occurs readily at room temperature, in the absence of a solvent, to give pentafluorophenylboron dichloride in 84% yield.

$$MeHgC_6F_5 + BCl_3 \longrightarrow MeHgCl + C_6F_5BCl_2$$

However, the difficulty encountered in removing the desired product from methyl mercury (II) chloride makes this route inferior to the one involving the use of alkylpentafluorophenyltin compounds for the preparation of pentafluorophenylboron dichloride.

The reaction between boron trifluoride and methylpentafluorophenylmercury in the absence of solvent gave, rather unexpectedly, bis(pentafluorophenyl)mercury in almost quantitative yield. The other product was insoluble in ether, and from its infra-red spectrum it was probably a fluoroborate. Furthermore, it deposited mercury metal on standing and was therefore probably methylmercury (II) fluoroborate. Unsymmetrical organomercury compounds have been observed to disproportionate in the presence of RHgX impurities.[115] It seems likely that boron trifluoride catalyses this disproportionation in the case of methylpentafluorophenylmercury.

Stannic chloride and methylpentafluorophenylmercury, at room temperature and in the absence of a solvent, readily gave pentafluorophenyltin trichloride in excellent yield.

$$MeHgC_6F_5 + SnCl_4 \longrightarrow MeHgCl + C_6F_5SnCl_3$$

However, the reaction between pentafluorophenyltin trichloride and methylpentafluorophenylmercury was much slower, and bis(pentafluorophenyl)tin dichloride could not be prepared by this method. In addition to cleavage of pentafluorophenyl from mercury, disproportionation of the mercurial also occurred and both bis(pentafluorophenyl)mercury and methylmercury (II) chloride were identified in the solid reaction products.

This preliminary investigation indicates that cleavage reactions of methylpentafluorophenylmercury with inorganic halides of sufficient reactivity will provide a convenient route to pentafluorophenyl derivatives of other metals or metalloids. However, if the inorganic halide is not sufficiently reactive, the reactions may be complicated by disproportionation of the mercurial.

CHAPTER 4.

PHYSICAL MEASUREMENTS.

DIPOLE MOMENT MEASUREMENTS.

Theory of Dipole Moment Measurements.

It was pointed out by Faraday[119] that the molecules of a dielectric when placed in an electric field become 'polarised' i.e. a separation of charge takes place. One end of the molecule acquires a small positive charge, the other a negative charge of equal magnitude.

Mathematical treatment of this statement led to the derivation of the Clausius and Mosotti law[120,121]

$$\frac{\varepsilon - 1}{\varepsilon + 2} \, \frac{1}{d} = p \qquad \ldots\ldots\ldots\ldots (1)$$

where p is the specific polarisation, d is the density and ε the dielectric constant of the substance.

For a number of materials of low dielectric constant p remains constant despite changes in temperature and pressure, and is almost the same for the liquid or solid states.

It was shown by Maxwell[122] that for such materials the dielectric constant is related to the refractive index n for the same frequency of radiation by

$$n^2 = \varepsilon \emptyset \qquad \ldots\ldots\ldots\ldots (2)$$

where ϕ is the magnetic permeability of the material.

As ϕ is almost equal to unity for all except ferromagnetic substances, then if the values of the refractive index obtained in the visible region of the spectrum are extrapolated to the wavelength at which the dielectric constant is measured (virtually infinite wavelength)

$$\varepsilon = n^2 \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

For substances of high dielectric constant ε is almost invariably greater than n^2.

It was shown by Lorenz[123] and Lorentz[124] that $\frac{n^2 - 1}{n^2 + 2}\,\frac{1}{d} = r$ where r is a constant, independent of temperature, known as the specific refraction. The product of the molecular weight M and the specific refraction is known as the molecular refraction R.

$$R = \frac{n^2 - 1}{n^2 + 2}\,\frac{M}{d} \qquad \ldots\ldots\ldots\ldots\ldots (4)$$

Molecular refractions are additive, within certain limits, and by allocation of certain values to certain atoms and bonds, molecular refractions may be compiled. Molecular polarisation P obtained by multiplying the specific polarisation by the molecular weight would also be expected to be additive. It is found, however, that P is only additive for compounds of low dielectric constant where $\varepsilon = n^2$.

Debye[125,126] indicated that this behaviour could be explained by assuming that although a molecule as a whole is neutral, the centres of positive and negative charge do not usually coincide and the molecule has a permanent doublet or dipole which tends to orientate itself in an electric field of relatively low intensity, (i.e. radio frequency). Thus the molecule shows polarisation by orientation besides charge displacement.

Indeed it would be fortuitous if any molecule other than a symmetrical one did not have some net permanent dipole due to the variation in electronegativity of the atoms of the molecule.

The magnitude of the electronic charge is 4.8×10^{-10} e.s.u. and distances between small atoms are 1 to 2×10^{-8} cms. It is found that dipole moments of most molecules lie between 0 and 9×10^{-18} e.s.u. or 0 to 9 Debye. A further contribution to the total polarisation of a molecule is that due to the relative displacement of the atoms of the molecule in an electric field.

If a molecule contains polar bonds so that the atoms carry different effective charges, then the nuclei are displaced with respect to one another and this produces an induced dipole the effect of which is superimposed on the permanent dipole, if present, and the dipole due to the displacement of the electrons with respect to the nucleus.

This type of polarisation is known as atom polarisation and together with orientation polarisation (due to orienting of permanent dipoles) and electron polarisation (due to displacement of electrons) goes to make up the total polarisation.

Thus, $$TP = AP + OP + EP \quad \ldots\ldots\ldots\ldots \quad (5)$$

For molecules with no permanent dipole and no atom polarisation, the total polarisation is the same as the electron polarisation or TP = EP, and is identical with R if the value of n is obtained by extrapolation to infinite wavelength. As the values of R obtained for infinite wavelength usually only differ by 1 or 2 c.c. from those obtained at visible frequencies, often no correction for the difference is made in dipole moment calculations.

The Clausius and Mosotti theory considers each molecule as a sphere of dielectric and assumes that for small displacements of electrons with respect to the nucleus the induced moment m is proportional to the field F.

i.e. $$m = \gamma F \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

γ is called the polarisability of the molecule and is equal to the moment induced by a field of unit strength.

The treatment gives an equation for the molecular polarisation known as distortion polarisation, $P = \frac{4}{3}\pi N\gamma$ where N is Avogadro's number.

The Debye treatment, which is concerned with a molecule with a permanent dipole μ inclined at an angle to an electric field F, gives an expression for the molecular orientation polarisation,

$$OP = \frac{4}{3}\pi\frac{N\mu^2}{3kT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where k is Boltzmann's constant and T is the absolute temperature.

Thus the total polarisation is given by,

$$TP = \frac{4}{3}\pi N\left(\gamma + \frac{\mu^2}{3kT}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

$\frac{4}{3}\pi N\gamma$ represents the polarisation a molecule would have in the absence of a permanent dipole, and this may be divided up into atom polarisation and electron polarisation. From equation (7):

$$\mu = \sqrt{\frac{9kT}{4\pi N}OP} = 0.012812\sqrt{OP.T}$$

As all dipole moment measurements were carried out at 25°, this can further be reduced to,

$$\mu = 0.2212\sqrt{OP} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Evaluation of Results.

The expression for the polarisation of a solution, due to Debye[127,128] is:-

$$P = P_1f_1 + P_2f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \; \frac{M_1f_1 + M_2f_2}{d} \quad \ldots\ldots\ldots (1)$$

where P_1, P_2, f_1, f_2, are the total polarisations and mole fractions of solvent and solute respectively.

Halverstadt and Kumler,[129] used specific volumes instead of densities and weight fractions instead of mole fractions. By assuming that the specific volume and dielectric constant of the solution are linear functions of the weight fraction (i.e. $\varepsilon = a + \alpha w_2$ and $v = b + \beta w_2$ where a and b are the dielectric constant and specific volume of the solvent, w_2 is the weight fraction of the solute), they derived an expression for the total specific polarisation at infinite dilution of the solute, p_2.

$$p_2 = \frac{3\alpha v_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} (v_1 + \beta) \quad \ldots\ldots\ldots\ldots (2)$$

By plotting ε against w_2 and v against w_2, α and β may be evaluated.

In a similar manner the electron polarisation Ep_2 can be expressed as,

$$Ep_2 = \frac{6\gamma n_1 v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n^2 + 2}(v_1 + \beta) \quad \ldots\ldots\ (3)$$

where the assumption is made that $n = n_1 + \gamma w_2$ where n_1 is the refractive index of the solvent.

To obtain dipole moments by measurements on solutions the dielectric constant, refractive index and density of a number of solutions must be determined. By plotting ε, v, and n against w_2, obtaining α, β, and γ from the graphs, and fitting them in the equations, the total polarisation and electron polarisation of the compound being studied may be obtained.

At low concentrations ($w \ll 0.02$) the plots are usually close to linear[130] and linear plots of n against w_2 may be obtained at still higher concentrations.

Dielectric Constant Measurements.

Benzene was used as solvent in all cases and the dielectric constants of air (ε_1) and benzene (ε_2) were assumed to be 1.0006 and 2.2727 respectively.

The change in capacitance which occurred when the dielectric of a capacitor (the dielectric cell) was altered was measured. The cell of the Sayce-Briscoe type[131] with plates of platinum burnt on to the glass could be filled with benzene or the benzene solution of the compound, and solutions could be changed easily by blowing out with nitrogen, washing with pure benzene and refilling with the required solution. It was immersed in a thermostat, which was filled with transformer oil to reduce stray capacitances.

The cell used was not the one used by Dixon[132], and a calibration was there fore necessary. If ε_3 is the dielectric constant of the solution and C_1, C_2, and C_3 are the capacitances of the cell filled with air, benzene and solution respectively, then provided the lead capacitances remain constant,

$$\frac{C_3 - C_1}{C_2 - C_1} = \frac{\varepsilon_3 - \varepsilon_1}{\varepsilon_2 - \varepsilon_1}$$

$$\begin{aligned}\varepsilon_3 &= \frac{C_3 - C_1}{C_2 - C_1}(\varepsilon_2 - \varepsilon_1) + \varepsilon_1 \\ &= \left(\frac{C_3 - C_2}{C_2 - C_1} + 1\right)(\varepsilon_2 - \varepsilon_1) + \varepsilon_1 \quad \ldots\ldots\ldots (1)\end{aligned}$$

$C_2 - C_1 = 29.40$ pfs. was measured by connecting an N.P.L. calibrated condenser in parallel with the cell and finding the necessary change in capacitance to restore the balance when the dielectric was changed from air to benzene. $C_3 - C_2 = C$ was the change in capacitance measured on M, and since l is the reading on the condenser in cms, and the capacitance change per cm. was 3.38 pfs, then from equation (1),

$$\varepsilon_3 = \left[\frac{3.38\ l}{29.4} + 1 \right] 1.2721 + 1.0006$$

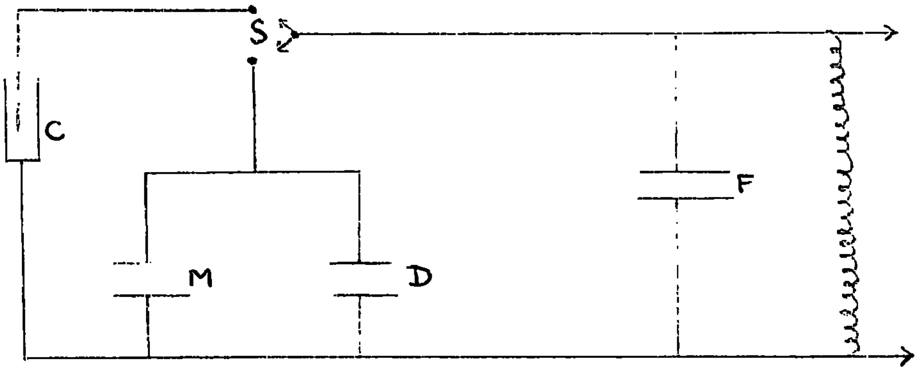
$$\frac{d\varepsilon}{dw} = \left[\frac{3.38\delta l}{29.4} \right] \times 1.2721$$

$$\alpha = \frac{d\varepsilon}{dw} = \frac{3.38 \times 1.2721}{29.4} \frac{dl}{dw} = 0.14625 \frac{dl}{dw}$$

$\frac{dl}{dw}$ is the slope of the graph obtained by plotting the reading on the calibrated condenser against weight fraction.

A heterodyne beat capacitance meter of the type described by Hill and Sutton[133] was used to measure the capacitance change in the cell. The X plates of the cathode ray tube carried the output from a beat frequency generator which consisted of two oscillators, one of fixed frequency, f_0 (ca. 10^5 c.p.s.), and the other of variable frequency, f_1, incorporating the measuring system. The circuits of the oscillators were as nearly identical as possible. The Y plates carried the output from an audiofrequency oscillator, f_2 (ca. 1000 c.p.s.). The measuring system, shown below, consisted of the cell C, two air-spaced uncalibrated variable capacitors D and F, and a calibrated concentric cylinder variable capacitor, M, with a micrometer screw having a capacitance change of 3.38 pfs. per cm. length. The cell and the calibrated capacitor could be interchanged by the switch, S.

Circuit Diagram of Measuring System.



C = the cell. S = switch for changing circuits.
D, F = uncalibrated variable condensers.
M = calibrated variable condenser with micrometer screw.

D was adjusted until the output of the beat frequency generator gave a figure of eight on the cathode ray tube corresponding to $f_1 - f_o = \frac{f_2}{2}$ which was used as a balance point througnout all the measurements. After filling the cell and allowing it to reach thermal equilibrium (about 10 minutes) D was adjusted. M was then switched in to replace the cell, and adjusted in order to reobtain the figure of eight. After adjusting each circuit several times, and when a steady figure of eight was obtained on both sides of the switch, the value of M was noted (arranging that for pure benzene the balance occurred with the calibrated capacitor reading about 2.4 cm, since its range was 0 to 2.5 cm.) After blowing out the benzene, the cell was washed out (twice with benzene) and then filled with a solution of the compound, and the balance point was again obtained. The difference in M, gave the difference in capacitance between the solution and pure benzene, $\Delta\epsilon$. Readings of M, with pure benzene in the cell, were taken after each solution, and an average value taken if a slight drift occurred. $\frac{dl}{dw}$ is the slope of the straight line obtained when $\Delta\epsilon$ is plotted against weight fraction, w.

Refractive Index Measurements.

A Pulfrich refractometer with a divided cell attached to the prism with silicone rubber was used. The refractometer was enclosed in a box fitted with a glove and a window which could be lifted on a hinge. When closed the window rested on polyurethane foam to avoid draughts. The temperature was kept at 25 ± 0.2° throughout the box by means of a fan and a heater in circuit with a thermostatted thermometer. A sodium lamp was used as a light source. Pure benzene was placed in one side of the cell and a solution in the other, a polythene cap being placed over the cell to prevent evaporation. The difference in extinction angles, Δn, between the solution and pure solvent was measured. A graph of extinction angle against refractive index is linear and shows that 1 minute of arc = 1087×10^{-7}. γ is the slope of the graph obtained when Δn is plotted against weight fraction, w.

Specific Volume Measurements.

A pyknometer with ground glass caps to prevent evaporation was used. It had been calibrated previously[132] (volume = 12.1208 cc.) using distilled water. The dry pyknometer was filled with a solution and placed in a 25° thermostat for 20 minutes. The meniscus of the liquid was adjusted to the graduation mark by applying a piece of filter paper to the tip of the opposite limb. The pyknometer was removed from the thermostat, dried with tissue paper, and the caps put in place. It was hung on the balance for 10 minutes, before weighing, to allow thermal equilibrium to be attained.

$$\text{Specific Volume, } \bar{V} = \frac{12.1208}{\text{weight of solution in the pyknometer}}$$

β is the slope of the graph of specific volume against w.

Example of Dipole Moment Calculation from Experimental Results.

$Me_3SnC_6F_5$

Wt. of flask	40.1520	41.9910	31.7974	37.1994
Wt. of flask + cpd.	40.2323	42.1852	32.1470	37.7306
Wt. of flask + cpd. + benzene	66.4975	67.2590	64.1583	66.4974
Wt. of cpd.	0.0803	0.1942	0.3496	0.5312
Wt. of cpd. + benzene	26.3455	25.2680	32.3609	29.2980
Wt. fraction, $w \times 10^6$	3048	7686	10803	18131

Dielectric Measurements.

Pure benzene reading	2.340	2.340	2.340	2.340
Solution reading	2.286	2.228	2.146	2.016
$\Delta\epsilon$ (cms.) $(= \nu)$	0.054	0.112	0.194	0.324

Refractivity Measurements.

Δn	1' 10"	3' 0"	3' 35"	5' 15"
$1087 \times 10^7 . \Delta n$	1268	3261	3985	5707

Density Measurements.

(Wt. of pyknometer = 20.6438g.)

Wt. of pyknometer + solution	31.2444	31.2693	31.2811	31.3172
Wt. of solution	10.6006	10.6255	10.6373	10.6734
Specific volume $\left(\frac{12.1208}{\text{wt. of solution}} \right)$	1.14341	1.14073	1.13946	1.13561

Graphs of $\Delta\epsilon$, $1087 \times 10^{7}\Delta n$, and V against weight fraction give:-

$$\alpha = 0.14625 \times \frac{d\Delta\epsilon}{dw} = 0.14625 \times 17.95 = 2.62519$$

$\beta = -0.5150$ $\gamma = 0.0353$ Mol; Wt. = 330.9

Substituting these values in the equations for total polarisation and electron polarisation, we have

$$Tp_2 = 330.9[0.1881 \times 2.62519 + 0.2979(1.1445 - 0.5150)]$$

$$= 225.5 \text{ c.c.}$$

$$Ep_2 = 330.9[0.5712 \times 0.0353 + 0.2931(1.1445 - 0.5150)]$$

$$= 68 \text{ c.c.}$$

Assuming atom polarisation $Ap_2 = 6.8$ c.c. (i.e. 10% of Ep_2)

Then, $Op_2 = Tp_2 - (Ep_2 + Ap_2)$

$$= 150.7 \text{ c.c.}$$

Hence, dipole moment, $\mu = 0.2212\sqrt{150.7}$

$$= \underline{2.7 \text{ D.}}$$

Experimental Results.

Dipole moments were measured in benzene solution at 25°. B.D.H. Analar benzene was purified by fractional crystallisation, followed by refluxing with potassium for 3 hours, and finally distillation under nitrogen.

$MeHgC_6F_5$

10^3w	$\frac{\Delta\varepsilon}{w}$	$\frac{10^2\Delta n}{w}$	$\frac{-\Delta v}{w}$
4.620	16.667	--	-
10.241	-	0.442	-
12.058	16.248	-	0.731
14.249	-	-	0.739
14.487	16.113	0.500	-
17.833	16.128	-	0.734

$PhHgC_6F_5$

10^3w	$\frac{\Delta\varepsilon}{w}$	$\frac{10^2\Delta n}{w}$	$\frac{-\Delta v}{w}$
3.682	11.678	1.475	0.682
7.126	-	1.525	0.699
9.061	11.919	-	0.691
13.371	12.191	-	-
16.360	-	2.104	-

$(C_6F_5)_2Hg$

3.473	-	-	0.749
7.133	2.102	1.524	0.782
10.995	2.002	1.318	0.753
14.521	1.860	1.497	0.751

C_6F_5HgBr

3.546	-	3.065	0.877
6.520	2.607	2.500	0.857
11.839	2.449	-	0.869
15.951	2.508	2.215	-

$Me_3SnC_6F_5$

3.048	1.739	4.160	0.489
7.686	-	4.243	-
10.803	1.833	3.689	0.512
18.131	1.793	-	0.518

$Me_2Sn(C_6F_5)_2$

3.180	1.478	-	0.566
8.304	1.517	2.618	0.561
12.925	1.524	2.733	-
17.192	1.524	2.634	0.571

$MeSn(C_6F_5)_3$

3.640	0.769	-	-
7.063	0.807	1.767	0.793
10.760	-	-	-
11.670	0.848	2.001	-
16.200	0.753	1.889	0.706

$Ph_3SnC_6F_5$

2.409	-	-	-
3.210	1.215	-	0.477
7.354	1.197	5.296	-
8.596	1.105	5.058	0.526
12.928	1.214	5.886	0.506

$Ph_2Sn(C_6F_5)_2$

3.794	1.133	1.908	0.674
7.816	-	-	0.729
10.469	1.127	1.903	-
14.244	1.151	2.226	0.689
17.467	-	2.385	-

$PhSn(C_6F_5)_3$

3.751	0.906	0	0.581
7.284	0.851	0	0.636
11.203	0.893	0	0.609
17.214	0.819	0	0.622

Compound	T_{p_2}	E_{p_2}	A_{p_2}	O_{p_2}	μ (D)
$MeHgC_6F_5$	211	45	12	154	2.8
$PhHgC_6F_5$	207	64	14	129	2.5
$(C_6F_5)_2Hg$	91	66	25	0	0
C_6F_5HgBr	69.5	44	12	13	(<1)
$Me_3SnC_6F_5$	225.5	68	7	150.5	2.7
$Me_2Sn(C_6F_5)_2$	284	93	9	182	3.0
$MeSn(C_6F_5)_3$	215	81	8	126	2.5
$Ph_3SnC_6F_5$	267	112	11	144	2.65
$Ph_2Sn(C_6F_5)_2$	276	90	9	177	2.95
$PhSn(C_6F_5)_3$	250	87	9	154	2.75

Discussion of Dipole Moment Results.

In the early days of dipole moment determinations, atom polarisation was regarded as a factor of minor importance in the evaluation of dipole moments from dielectric constant and refractivity measurements. In the absence of the necessary data, it is still inevitable that any allowance made for atom polarisation in evaluating dipole moments must generally be assessed arbitrarily, but it is now realised that the atom polarisation may assume a considerable magnitude. For the reasons discussed below, the latter may be the case for pentafluorophenylmercury compounds. However, for pentafluorophenyltin compounds atom polarisation is taken as 10% of the electron polarisation.

The symmetrical mercury diaryls belong to a group of compounds which display apparent permanent dipole moments in solution, though X-ray and other evidence indicates non-polarity. Compounds of this type which can be examined as gases have been shown to be non-polar, by the temperature-invariance of their total polarisation. The anomalous moments apparent from measurements of solutions have been ascribe to unusually large atom polarisations,[134] and this view has been strongly supported by recent calculations of atom polarisations from infra-red frequencies.[135] Since atom polarisations are the sum of terms of the type, constant $\times \nu^{-2}$, the bending modes of lowest frequency, least accessible to observation, make the biggest contributions. Very recently, the atom polarisation of p-benzoquinone was calculated from the infra-red frequencies and intensities;[136] most of the anomalously large atom polarisation was accounted for, and 85% of the calculated (65-70% of the observed) atom polarisation was due to the vibration at 108 cm^{-1}.

Diphenylmercury is centrosymmetric,[137] and the difference[138] between its total polarisation (Tp) and its electron polarisation (Ep) is 4c.c. Bis(pentafluorophenyl)mercury is probably also centrosymmetric, and thus its atom polarisation is approximately Tp - Ep = 25 c.c. In calculating orientation polarisation of pentafluorophenylmercury compounds an allowance of 2 c.c. for the atom polarisation of a PhHg group, and 12 c.c. for that of a C_6F_5Hg group has been made. The bending frequency of mercury (II) bromide vapour is only 41 cm^{-1},[162] which suggests that the HgBr group has an appreciable atom polarisation. This would in turn further reduce the apparent dipole moment of pentafluorophenylmercuric bromide. The moments of the analagous compounds $MeHgC_6F_5$ and $PhHgC_6F_5$ are a little less than those of alkyl- and phenyl-mercury (II) bromides (3.1-3.5D).[139]

That high atom polarisation is responsible for the apparent moments of mercury compounds, R_2Hg, has been denied by

Wright[140] who found low atom polarisation by dielectric constant measurements on the compressed solid compounds. The molecules would not, however, be expected to be quite as flexible when constrained in a crystal lattice as in the dissolved or gaseous states. It is fairly clear that at least a significant proportion of these molecules are bent in the dissolved state. If the bending is mainly due to the electric field applied in order to measure the dipole moment, then the apparent moment can be ascribed to atom polarisation. If it is due to thermal agitation, and the thermally bent molecules remain in that condition long enough to orientate in the applied field, then the moments can be reasonably ascribed to orientation polarisation and are thus 'real'.

For the pentafluorophenyltin compounds, assuming a tetrahedral structure, the moment of compounds of the type $R_2SnR'_2$, should be 15% larger than that of R_3SnR'.[141] Furthermore, in the absence of distortion and other complicating effects the moment of R_3SnR' should be the sum of the moments R-Sn and Sn-R', and should therefore be equal to the moment of $RSnR'_3$.

$Me_2Sn(C_6F_5)_2$ / $Me_3SnC_6F_5$ = 1.11

$Me_2Sn(C_6F_5)_2$ / $MeSn(C_6F_5)_3$ = 1.20

$Ph_2Sn(C_6F_5)_2$ / $Ph_3SnC_6F_5$ = 1.10

$Ph_2Sn(C_6F_5)_2$ / $PhSn(C_6F_5)_3$ = 1.07

The low value for the moment of $MeSn(C_6F_5)_3$ can be explained in terms of distortion of the pentafluorophenyl groups from the tetrahedral positions towards the methyl group, which would give the compound a lower moment than expected.

INFRA-RED SPECTRA.

Infra-red spectra were recorded by Mr. G. Collier and Miss D. A. Chapman of these laboratories using a Grubb-Parsons GS2A grating spectrometer.

Discussion of Infra-red Spectra.

For the pentafluorophenyl-tin and -boron compounds there are several well-defined regions which are common to all the compounds, and these must therefore be associated with pentafluorophenyl, at approximately 1640, 1510 and 1460 (doublet), 1370, 1270, 1080, 1070, 1020, 1010, 960, and 600 cms^{-1}. A doublet in the region 1500 and a band at 1640 cm^{-1} appear to be the most useful diagnostic features for pentafluorophenyl compounds since they are contained in the spectra of pentafluorophenyl derivatives of boron, tin, mercury,[31] and phosphorus.[30] Absorption in the region 1300-1000 cm^{-1} can be attributed to C-F stretch:. The spectra of a number of methyltin compounds have been analysed[142] and from this we can assign some bands in the methyl series of pentafluorophenyltin compounds, in the regions 780, 730 ($Sn-CH_3$ rock), 540 (assym: Sn-C stretch:), and 520 cm^{-1} (sym: Sn-C stretch:).

Snyder has reported[143] that the change of an arylboronic acid to its anhydride, which sometimes occurs when the acid is simply warmed in an anhydrous solvent, can be detected by examination of the infra-red absorption spectrum of the sample. As a result of the change, the hydroxyl absorption band of the acid disappears and a new absorption near 700 cm^{-1}, characteristic of the anhydride, appears. Santucci and Gilman[144] have reported that a band at 1030-1020 cm^{-1} present in all the acids invariably disappeared from the anhydrides. However, Povlevy found that neither criterion was applicable to o-hydroxyphenylboronic acid.[104] The broad band at 3340-3190 cm^{-1} present in arylboronic acids has been attributed to intermolecular hydrogen-bonding.[105] A band at 1028 cm^{-1}, present in the spectrum of a recrystallised sample of pentafluorophenylboronic acid, completely disappears in the spectrum of a sublimed sample. However, there was no band at 700 cm^{-1} in the spectrum of a sublimed sample, and both samples showed a strong, broad band centred at 3367 cm^{-1}. The latter absorption, in agreement with determinations of neutralisation equivalents (see experimental), points to the fact that a sample of pentafluorophenylboronic acid purified by sublimation contains mainly acid and not much anhydride.

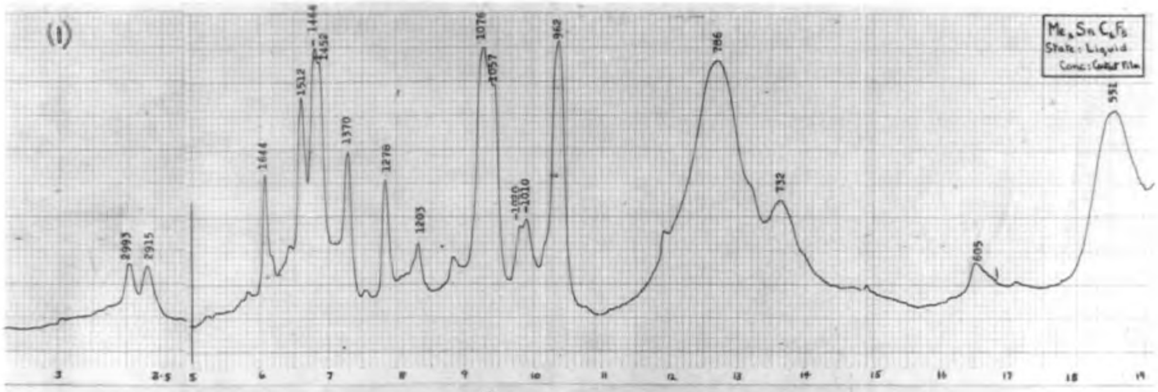
The spectrum of potassium fluoroborate has been closely studied by Cote and Thompson[145], who assign the strong absorptions in the region 1040-1090 cm^{-1} to asymmetric B-F stretching frequencies, and similar absorptions at

1041, 1063, 1090 cm^{-1} were present in the spectrum of potassium trifluoromethylfluoroborate.[61] However, in the spectrum of potassium pentafluorophenylfluoroborate there is no absorption in this region, and it is likely that the strong band at 950 cm^{-1} is attributable to asymmetric B-F stretching frequencies in this compound. It is noteworthy that this band is not nearly as broad as the corresponding band in other fluoroborates.

A strong band at 360-370 cm^{-1}, present in the spectra of all the pentafluorophenyltin compounds which were studied, was not present in the spectra of tetraphenyltin, triphenyltin bromide or pentafluorophenylboron derivatives.

The following infra-red spectra are included in this thesis:-

1) $Me_3SnC_6F_5$
2) $Me_2Sn(C_6F_5)_2$
3) $MeSn(C_6F_5)_3$
4) $Me_2Sn(C_6F_5)F$
5) $Ph_3SnC_6F_5$
6) $Ph_2Sn(C_6F_5)_2$
7) $PhSn(C_6F_5)_3$
8) $(C_6F_5)_4Sn$
9) (p-tolyl)$_2$Sn(C$_6$F$_5$)$_2$
10) p-tolylSn(C$_6$F$_5$)$_3$
11) $(C_6F_5)_3SnCl$
12) $C_6F_5SnCl_3$
13) $[(C_6F_5)_3Sn]_2O$
14) $(C_6F_5)_3SnCl.2NH_3$
15) $(C_6F_5)_2SbCl$
16) $K^+(C_6F_5BF_3)^-$
17) $C_6F_5BCl_2$
18) $C_6F_5BCl_2$.py
19) $C_6F_5BF_2$
20) $C_6F_5BF_2$.py
21) $C_6F_5B(OH)_2$ (sublimed)
22) $C_6F_5B(OH)_2$ (recrystallised)
23) $(C_6F_5)_2BOH$


(1)
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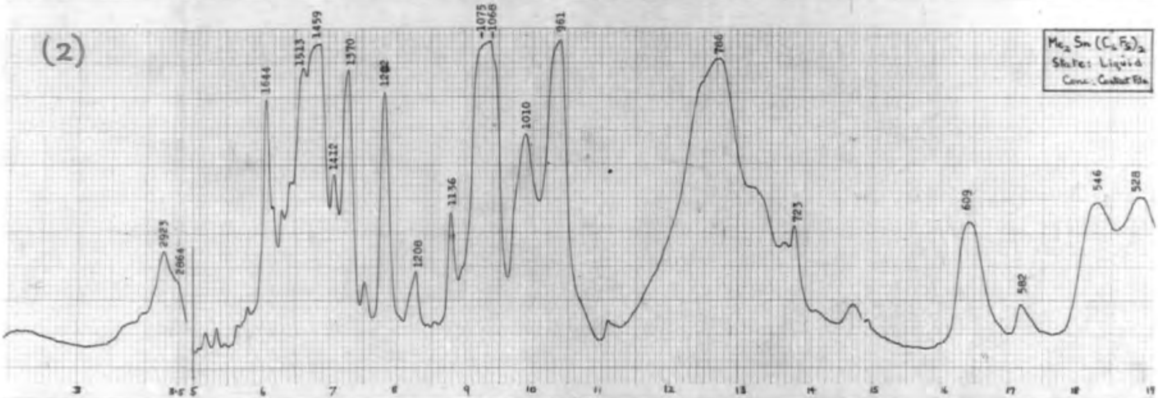
State: Liquid
Conc: Contact Film
2993
2915
1644
1512
1452
1444
1370
1276
1205
1076
1057
1020
1010
962
786
732
605
551
3
2·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19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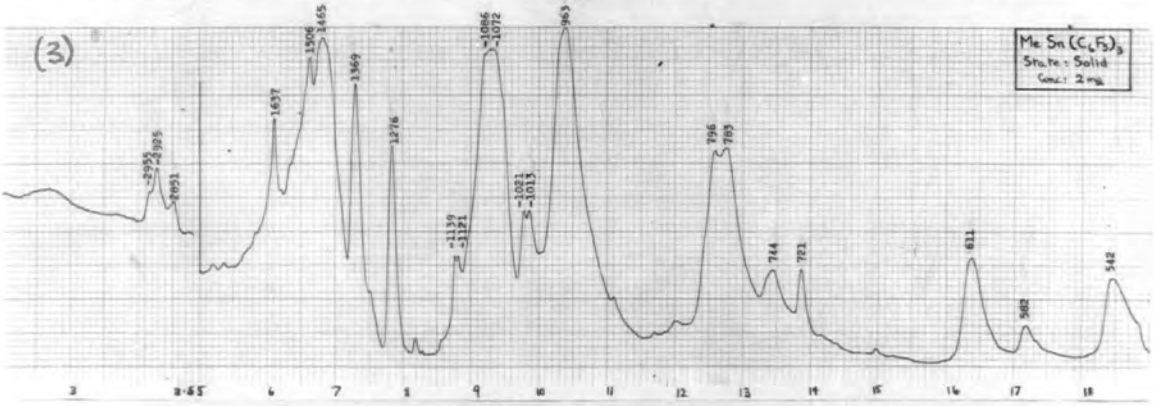
Me$_2$Sn(C$_6$F$_5$)$_2$
State: Liquid
Conc: Contact Film
2923
2864
1644
1513
1459
1412
1370
1282
1208
1136
1075
1068
1010
961
786
725
609
582
546
528
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


(3)
Me Sn(C$_6$F$_5$)$_3$
State: Solid
Conc: 2 mg
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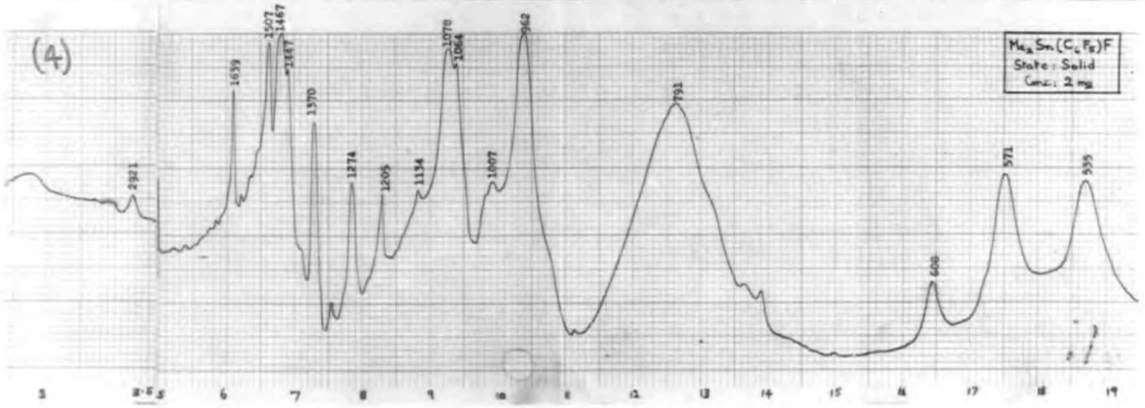
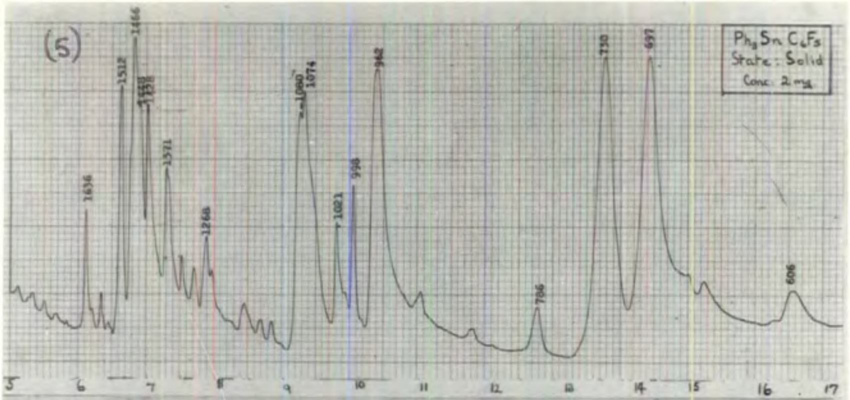
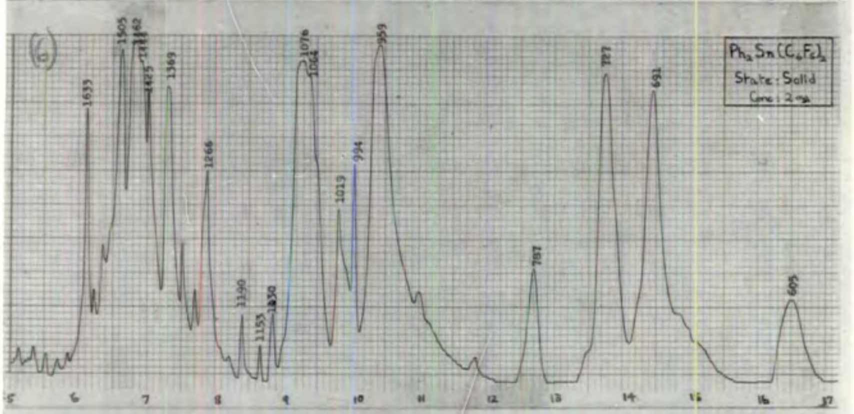
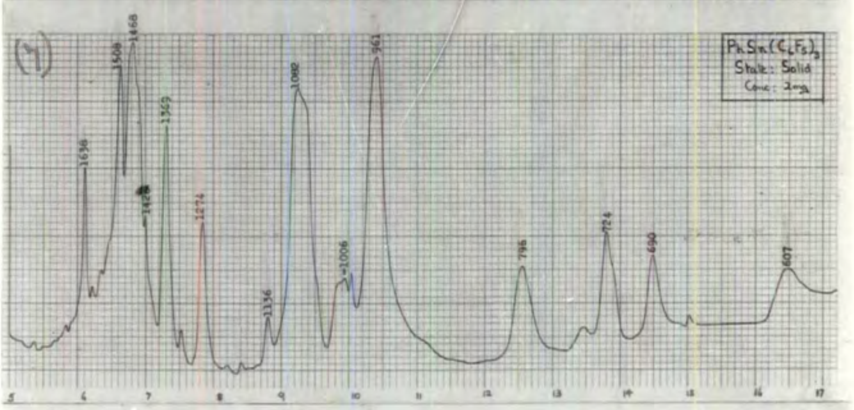
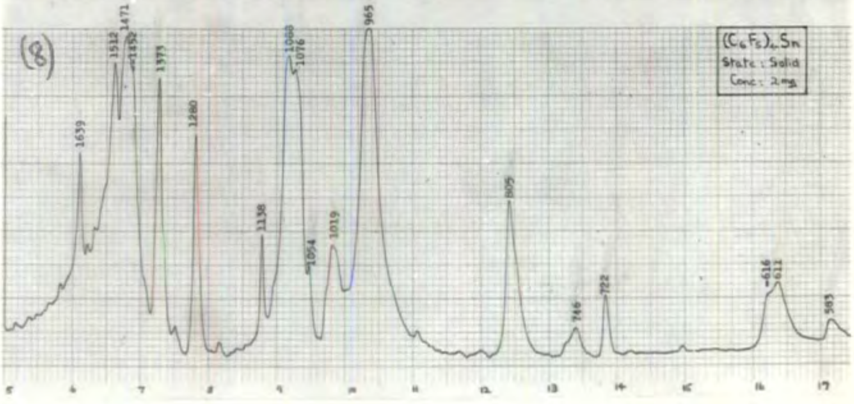
2925
2851
1637
1506
1465
1369
1276
1139
1121
1086
1072
1021
1013
963
796
785
744
721
611
582
542
3
3·65
6
7
8
9
10
11
12
13
14
15
16
17
18


(4)
Me$_2$Sn(C$_6$F$_5$)F
State: Solid
Conc: 2 mg
2921
1659
1507
1467
1447
1370
1274
1205
1134
1078
1064
1007
962
791
608
571
555
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


(5)
Ph$_3$Sn C$_6$F$_5$
State: Solid
Conc: 2 mg
1636
1512
1466
1371
1268
1080
1074
1021
998
962
786
730
697
606
5
6
7
8
9
10
11
12
13
14
15
16
17


(6)
Ph$_2$Sn(C$_6$F$_5$)$_2$
State: Solid
Conc: 2 mg
1635
1505
1462
1425
1369
1266
1190
1153
1130
1076
1064
1013
994
959
787
727
691
605
5
6
7
8
9
10
11
12
13
14
15
16
17


(7)
PhSn(C$_6$F$_5$)$_3$
State: Solid
Conc: 2 mg
1638
1508
1468
1428
1369
1274
1136
1082
1006
961
796
724
690
607
5
6
7
8
9
10
11
12
13
14
15
16
17


(8)
(C$_6$F$_5$)$_4$Sn
State: Solid
Conc: 2 mg
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1512
1471
1452
1373
1280
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1088
1076
1054
1019
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12
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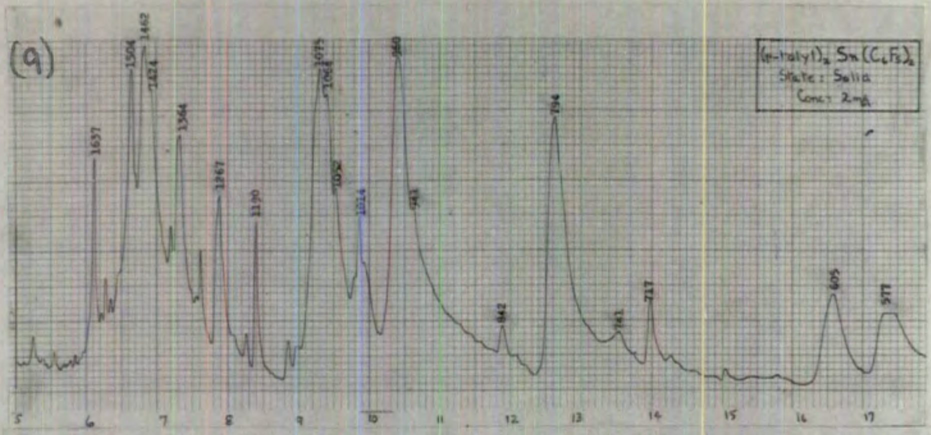
14
15
16
17


(9)
(p-tolyl)2 Sn(C6F5)2
State: Solid
Conc: 2 mg
1637
1504
1462
1424
1364
1267
1190
1075
1064
1032
1014
960
941
842
794
743
717
605
577
5
6
7
8
9
10
11
12
13
14
15
16
17


(10)
p-tolyl Sn(C6F5)3
State: Solid
Conc: 2 mg
1639
1512
1475
1370
1275
1079
1065
1014
1004
961
799
743
718
608
578
5
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13
14
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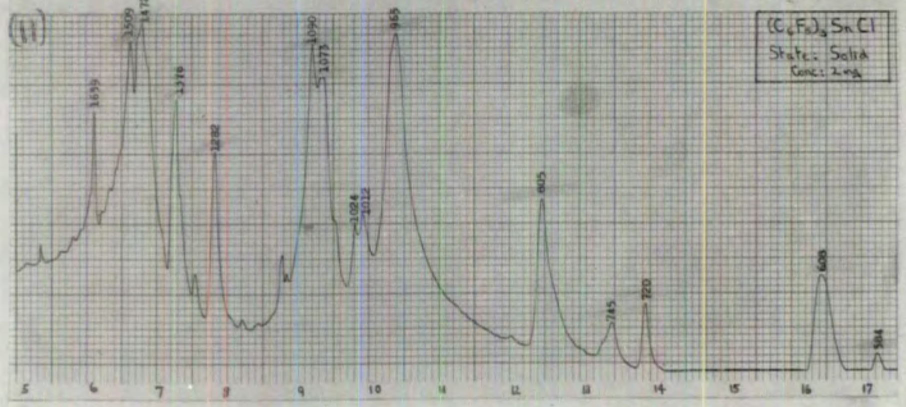
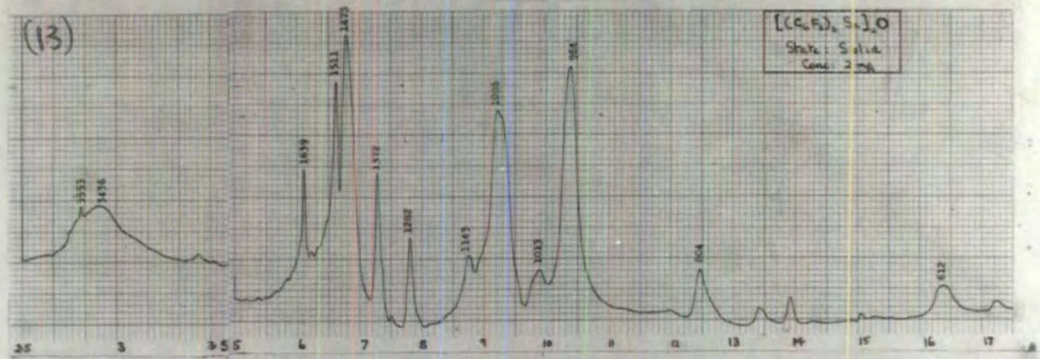
16
17
18

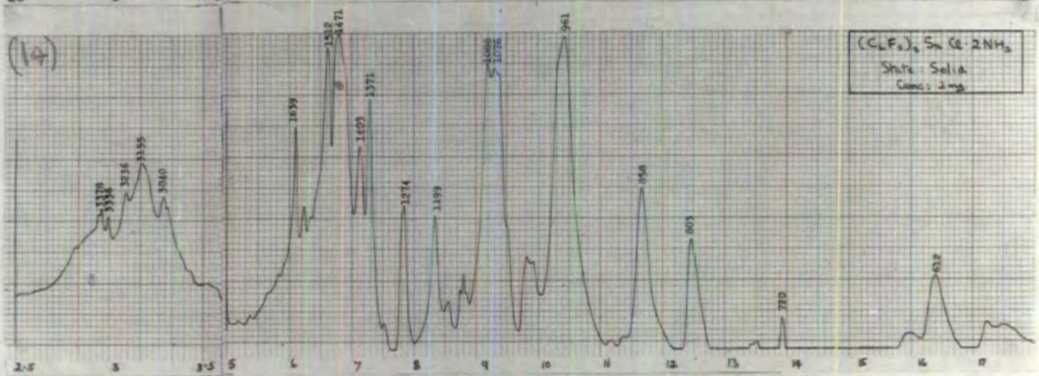

(11)
(C6F5)3 SnCl
State: Solid
Conc: 2 mg
1639
1509
1472
1370
1282
1090
1075
1024
1012
965
805
745
720
608
584
5
6
7
8
9
10
11
12
13
14
15
16
17


(12)
C6F5 SnCl3
State: Liquid
Conc:
1639
1513
1491
1464
1387
1289
1091
1078
1017
1006
970
805
719
610
5
6
7
8
9
10
11
12
13
14
15
16
17

(13)


$[(C_6F_5)_3Sn]_2O$
State: Solid
Conc: 2 mg
3553
3436
1639
1511
1475
1372
1282
1145
1088
1033
964
804
612
2.5
3
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18

(14)


$(C_6F_5)_3SnCl\cdot 2NH_3$
State: Solid
Conc: 2 mg
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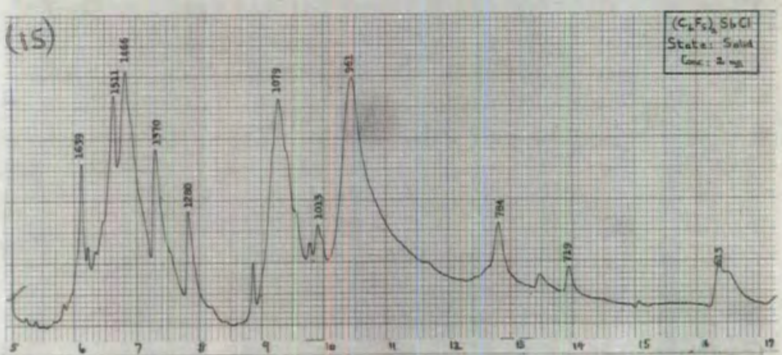
3338
3236
3155
3060
1639
1512
1471
1405
1371
1274
1199
1086
1076
961
856
805
720
612
2.5
3
3.5
5
6
7
8
9
10
11
12
13
14
15
16
17

(15)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State: Solid
Conc: 2 mg
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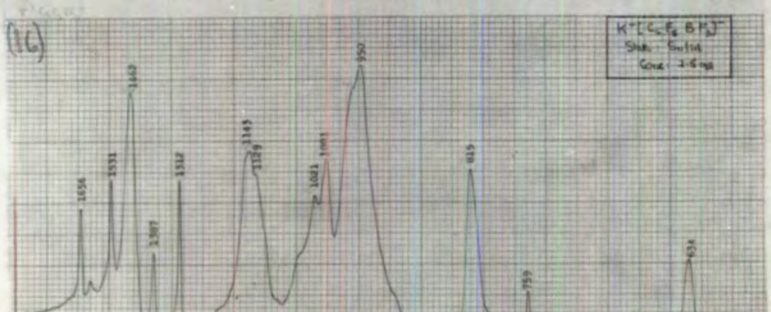
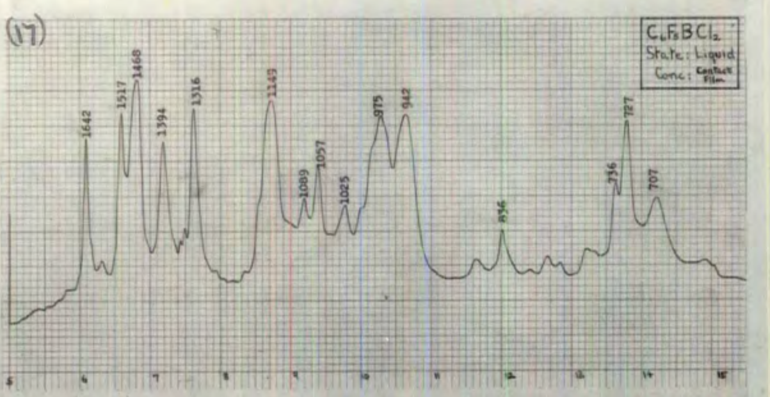
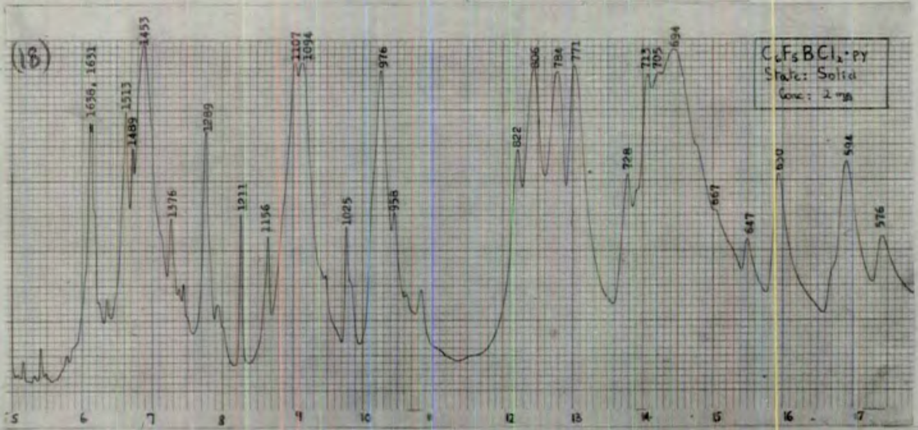
1511
1466
1370
1280
1079
1015
961
784
719
615
5
6
7
8
9
10
11
12
13
14
15
16
17

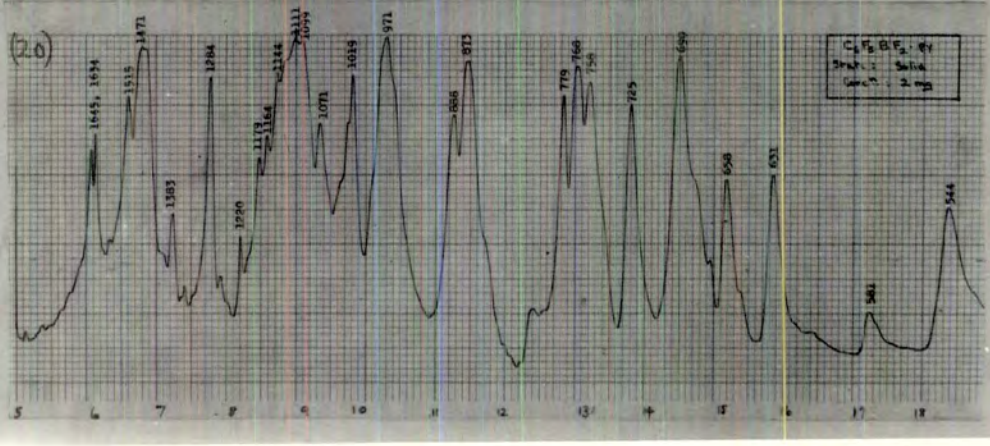
(16)


$K^+[C_6F_5BF_3]^-$
State: Solid
Conc: 2.5 mg
1656
1531
1463
1307
1312
1145
1129
1021
1001
950
819
759
634
5
6
7
8
9
10
11
12
13
14
15
16

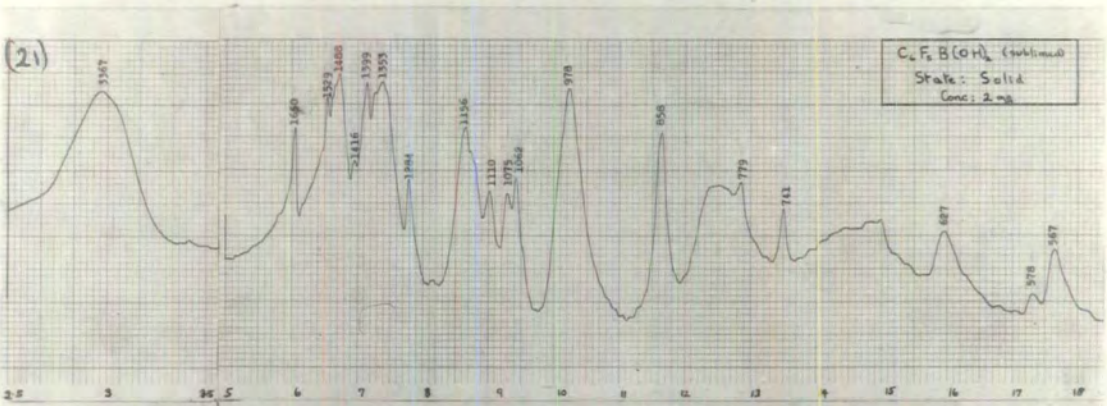

(17)
$C_6F_5BCl_2$
State: Liquid
Conc: Contact Film
1642
1517
1468
1394
1316
1149
1089
1057
1025
975
942
856
736
727
707
5
6
7
8
9
10
11
12
13
14
15


(18)
$C_6F_5BCl_2 \cdot PY$
State: Solid
Conc: 2 mg
1658, 1631
1513
1489
1453
1376
1289
1211
1156
1107
1094
1025
976
958
822
806
784
771
728
715
705
694
667
647
630
594
576
5
6
7
8
9
10
11
12
13
14
15
16
17


(19)
$C_6F_5BF_2$
State: Gas
Conc: 7 mm
1661
1499
1431
1377
1355
1274
1255
1093
995
909
867
831
753
691
605
572


(20)
$C_6F_5BF_2 \cdot PY$
State: Solid
Concn.: 2 mg
1645, 1634
1515
1471
1383
1284
1220
1179
1164
1144
1111
1099
1071
1019
971
888
873
779
768
758
725
690
658
631
581
544
5
6
7
8
9
10
11
12
13
14
15
16
17
18

(21)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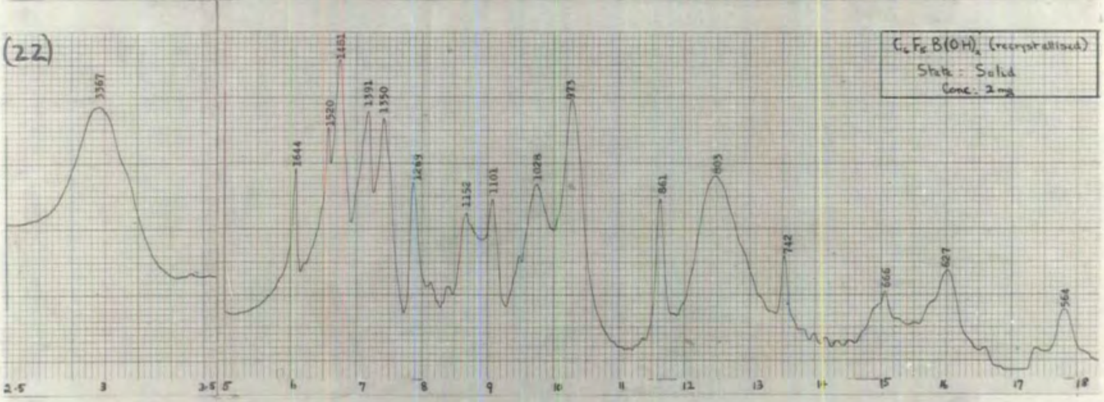
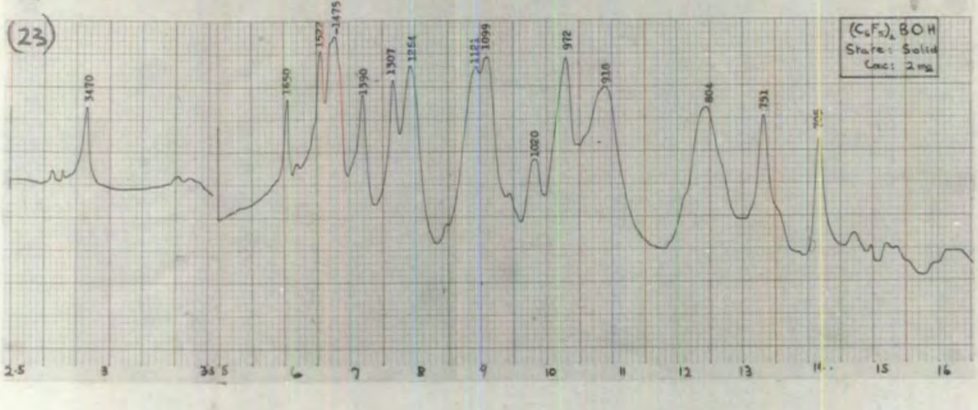
1650
1529
1488
1416
1399
1353
1284
1156
1110
1075
1062
978
858
779
741
627
578
567
C₆F₅B(OH)₂ (sublimed)
State: Solid
Conc: 2 mg
2·5
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18

(22)


3367
1644
1520
1481
1391
1350
1269
1152
1101
1028
975
861
805
742
666
627
564
C₆F₅B(OH)₂ (recrystallised)
State: Solid
Conc: 2 mg
2·5
3
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17
18

(23)


3470
1650
1527
1475
1390
1307
1254
1121
1099
1020
972
916
804
751
(C₆F₅)₂BOH
State: Solid
Conc: 2 mg
2·5
3
3·5
5
6
7
8
9
10
11
12
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15
16

ULTRA-VIOLET SPECTRA.

Ultra-violet spectra were recorded with an Optica, model CF4DR, ratio-recording instrument. Solvents were spectrosol grade, and solutions (approximately 10^{-5} molar) were made up by dissolving a known weight of compound in a known volume of solvent. Two main bands occur, at 210 and 260 mµ, and the former band is about ten times as intense as the latter. The positions and extinction coefficients of the 260 mµ for some pentafluorophenyl-tin and -mercury compounds are tabulated below.

	Cyclohexane		Methanol	
Compound	λ max;(mµ)	ε	λmax:(mµ)	ε
$Me_3SnC_6F_5$	263	600	262.5	1270
$Me_2Sn(C_6F_5)_2$	265	1540	261.5	1140
$MeSn(C_6F_5)_3$	266.5	2880	263	1990
$Ph_3SnC_6F_5$	253	1120	254	2030
	259.5	1590	260	2390
	265	1520	264	2340
			253*	2020
			269*	1980

$Ph_2Sn(C_6F_5)_2$	260	2130	259	2630
	264.5	2300	264	2740
			268*	2400
$PhSn(C_6F_5)_3$	265	3050	263	3100
$(C_6F_5)_4Sn$	267	3890	265	3090
$(C_6F_5)_3SnCl$	270	3680	262	1830
$MeHgC_6F_5$	267	740	262	500
$PhHgC_6F_5$	255	950	254	820
	261	1130	260	990
	267	1070	265.5	880
$(C_6F_5)_2Hg$	269	1820	263	1360
C_6F_5HgBr	267	900	261	650

* = inflection.

The positions and extinction coefficients of the 210 mμ band are shown below.

	Cyclohexane		Methanol	
Compound	λmax:(mμ)	ε	λmax:(mμ)	ε
$Me_3SnC_6F_5$	208	11090	210	19050
$Me_2Sn(C_6F_5)_2$	211	19200	205	11980
$MeSn(C_6F_5)_3$	212	21900	208	22400
$Ph_3SnC_6F_5$	213	42290	204.5	68750
$Ph_2Sn(C_6F_5)_2$	212	41750	206-212	58500
$PhSn(C_6F_5)_3$	212	37790	211	43200
$(C_6F_5)_4Sn$	213	37200	212	21400
$(C_6F_5)_3SnCl$	216	-	208	-
$MeHgC_6F_5$	214	18850	208	9230
$PhHgC_6F_5$	210	19910	208	24720
$(C_6F_5)_2Hg$	229	21050	214	22020
C_6F_5HgBr	218	13830	208	10970

Discussion of Ultra-violet Spectra.

Dessy[146] has recorded the ultra-violet spectra of some arylmercury compounds and he found that non-coordinating solvemts e.g. cyclohexane result in bathochromic shifts in the 210 mμ band which would be expected if diphenylmercury is more planar, and is therefore capable of exhibiting more phenylmercury resonance interaction, in such solvents when compared to methanol. The 260 mμ band is attributable to the B band of benzene,[147] while the 210 mμ band is apparently associated with both the ring and covalently bonded mercury. The 260 mμ band is not shifted in wavelength, apparently because the rings are operating independently of the mercury atom. Ultra-violet spectra indicate that in alcohol the resonance interaction of the phenyl groups is negligible, as previously pointed out by Gowenlock.[148]

The ultra-violet spectra of pentafluorophenyl-tin and -mercury compounds were recorded in a coordinating solvent (methanol) and in a non-coordinating solvent (cyclohexane) in an attempt to detect $d_\pi - p_\pi$ interaction between the pentafluorophenyl group and the metal atom. The shifts in the 260 mμ band are small, and no significance can be attached to them. However, a bathochromic shift of 8 mμ in the 260 mμ band of tris(pentafluorophenyl)tin chloride is probably indicative of $d_\pi - p_\pi$ interaction between the ring and the metal atom. This is further supported by the hyperchromic effect observed for this compound in a non-coordinating solvent (for the B-band, $\varepsilon = 3680$ in cyclohexane, $\varepsilon = 1830$ in methanol). The suggestion that $d_\pi - p_\pi$ interaction between the ring and the metal atom is greatest in pentafluorophenyltin chlorides is supported by N.M.R. data (next SECTION)

It is interesting to note that the vibrational fine structures observed for the B-band of tetraphenyltin[148a] are absent in the spectrum of tetrakis(pentafluorophenyl)tin, and, instead, there is one sharp band in this region of the spectrum.

N.M.R. SPECTRA.

Several reports of studies of the N.M.R. spectra of pentafluorophenyl-metal or -metalloidal derivatives have a appeared in the last year.[149,150,151] Randall and coworkers[149] showed that ^{19}F chemical shifts of the θ-fluorine atoms in C_6F_5X compounds depend markedly upon the nature of X. δ(ortho) shifts to lower field when, in a given group of the Periodic Table the atomic number of X increases, or when the pentafluorophenyl group is bonded to a transition metal rather than to a main-group metal. These differences have been attributed to paramagnetic contributions to the chemical shifts, which are greatest at the fluorine atoms closest to X. For main-group atoms of high atomic number, the excitation energies are smaller than for lighter atoms, and larger paramagnetic shifts are expected in the former cases. Even smaller energies, and consequently larger paramagnetic shifts, should occur in the transition metal compounds.

The same author has also studied the proton magnetic resonance spectra of some pentafluorophenyltin compounds.[152] The electron-withdrawing power of the pentafluorophenyl group in these tin compounds was estimated by measuring the internal chemical shift (Δ) between CH_3 and CH_2 protons in ethyl compounds of the type $(C_2H_5)_2SnX_2$ (where X = Cl, C_6F_5, Br and C_2H_5)[153]. The position of pentafluorophenyl in the electron withdrawing sequence is

$$Cl > C_6F_5 > Br > C_2H_5$$

Theory of N.M.R. Chemical Shifts in Conjugated Fluorine Compounds.

An equation for ^{19}F shielding in conjugated fluorine compounds has been derived by Goodman and Prosser[154] from molecular orbital theory. Their treatment was based upon changes in the π-electron distribution throughout the molecule (a constant σ-bond framework is assumed). The basic equation derived is the following:

in p.p.m, $$\int_{X_o}^{X} = 488\Delta E^{-1}\left[11.9\Delta q\ (F_z) + 3.9\Delta p(F_zC_z) + 0.1\Delta q(C_z)\right]$$

Where, $\int_{X_o}^{X}$ = the shielding parameter for the general conjugated fluorocarbon relative to that for the standard of comparison, X_o.

$\Delta q(F_z)$ = the difference in the fluorine π electron charge density (of the conjugating Z orbital) between X and X_o.

$\Delta p(F_zC_z)$ = the difference in the fluorine-carbon π electron bond order.

$\Delta q(C_z)$ = the difference in the carbon π electron charge density.

ΔE = an adjustable parameter, having units of electron volts.

The terms $\Delta p(F_zC_z)$ and $\Delta q(F_z)$ are opposite in sign and they tend to cancel each other to a substantial degree.

This analysis of fluorine shielding together with molecular orbital calculations of π charge densities[155] for models of p-substituted fluorobenzenes, permit the conclusion that in this special case the ^{19}F shielding can be interpreted as a linear function of the π charge density of the fluorine atom (or of its bonded carbon atom). Similarly, it has been shown that the para ^{19}F chemical shift in C_6F_5X is sensitive to resonance interaction of the group X with the ring.[156]

Experimental Results.

The N.M.R. spectra of some pentafluorophenyl derivatives of mercury, tin and boron have been recorded and the ^{19}F chemical shifts of the fluorine atoms have been measured as shown in Tables I and II.

TABLE I

	^{19}F Chemical Shifts*		
Compound‡	δ(ortho)	δ(meta)	δ (para)
C_6F_5HgMe	122.2	160.7	154.3
C_6F_5HgPh	119.75	161.7	156.2
$(C_6F_5)_2Hg$	119.75	161.7	155.1
C_6F_5H	138.9	162.1	153.5
$C_6F_5SnMe_3$	122.2	161.4	153.9
$(C_6F_5)_2SnMe_2$	122.15	160.25	151.4
$(C_6F_5)_3SnMe$	122.1	159.0	148.9
$C_6F_5SnPh_3$	118.5	160.0	151.7
$(C_6F_5)_2SnPh_2$	119.7	159.5	150.2
$(C_6F_5)_3SnPh$	121.0	159.0	148.8
$(C_6F_5)_4Sn$	121.4	159.4	148.8
$(C_6F_5)_3$Snp-tolyl	120.6	158.75	148.7
$(C_6F_5)_3SnCl$	122.5	157.8	145.75
$C_6F_5SnCl_3$	121.65	156.75	143.1

* Measured in p.p.m. ($\pm$0.1) relative to CCL_3F as internal standard.

‡ CCl_3F (approx. 10%) was added to liquid samples, and solid samples which were not sufficiently soluble in CCl_3F were dissolved in the minimum amount of acetone.

TABLE II

		^{19}F Chemical Shifts‡		
Compound	Solvent	δ(ortho)	δ(meta)	δ(para)
$C_6F_5BCl_2$	None	129.2	161.0	145.0
	CCl_4*	128.25	160.7	145.3
$C_6F_5BCl_2.C_5H_5N$	$CHCl_3$	133.5	163.3	155.7
	Me_2CO	133.1	164.1	157.2
$C_6F_5BF_2$	CCl_4*	127.75	160.4	143.0
$C_6F_5BF_2.C_5H_5N$	Me_2CO	132.9	163.1	155.6
$K^+(C_6F_5BF_3)^-$	Me_2CO	134.25	164.2	159.9
$C_6F_5B(OH)_2$	Me_2CO	132.9	164.1	155.4
$(C_6F_5)_2BCl$	None	129.5	161.3	145.35

* At infinite dilution.

‡ Measured in p.p.m. (± 0.1) relative to CCl_3F as internal standard.

Discussion of N.M.R. Spectra.

a) Pentafluorophenyltin Compounds.

The shifts of para fluorine resonance are probably most significant in the above series of pentafluorophenyl compounds, since it has been shown that the para ^{19}F chemical shift in C_6F_5X is sensitive to resonance interaction of the group X with the ring[156]. Evidence for $d_\pi - p_\pi$ bonding in tin aryls has been presented, based on calculation of the overlap integrals,[157] comparison of bond lengths,[158] and the thermodynamic dissociation constants of p-carboxyphenyltin compounds.[159] However, it was emphasised that the amount of π-bonding will be greatly dependent on the electron-attracting or -releasing effects of substituents attached to the benzene nucleus or to the tin atom.

It was of interest to study the variation of para ^{19}F chemical shift in pentafluorophenyl while other groups attached to tin were varied, since this may have reflected d_π-p_π interaction of pentafluorophenyl with tin. Two points of significance arise from the para ^{19}F chemical shifts observed for the series of pentafluorophenyltin compounds shown in Table I. Firstly a shift to low field of 10 p.p.m. is observed when the substituent on pentafluorophenyl is changed from Me_3Sn. to $Cl_3Sn^\bullet$. This is a large effect bearing in mind that the substituent being changed is two bonds distant from the aromatic ring. Secondly the para ^{19}F shift in trimethylpentafluorophenyltin is approximately the same as that in pentafluorobenzene (i.e. in a compound in which the substituent on pentafluorophenyl does not interact with the ring). These two observations indicate that d_{π}- p_{π} interaction of tin with pentafluorophenyl is significant in pentafluorophenyltin chlorides, and this is supported by ultra-violet data.

b) Pentafluorophenylboron Compounds.

Many organoboron compounds possess properties which suggest the presence in these compounds of carbon-boron π-bonding, and the relatively high stability of perfluorovinylboron compounds has been attributed to a contribution of the π electrons of the perfluorovinyl group to the p_{π}-orbital of the boron atom.[75] Also, dipole moment measurements of phenylboron dichloride indicate strong resonance involving carbon-boron π-bonded structures.[160]

With the exception of pentafluorophenylboronic acid, it was found that the para ^{19}F chemical shifts in compounds where boron is three covalent was about 10 p.p.m. to low field compared with the para ^{19}F chemical shifts in compounds where boron is coordinatively saturated. This shift to low field in three covalent boron compounds can be interpreted in terms of interaction of the π-electrons of the aromatic ring with the p_π-orbital of the boron atom. The spectrum of pentafluorophenylboronic acid was recorded in a coordinating solvent (acetone), and this probably accounts for the small para ^{19}F chemical shift observed for this compound.

The spectrum of pentafluorophenylboron dichloride was recorded both as a neat liquid and in carbon tetrachloride solution. The solvent effect was very small. However, bigger solvent effects are to be expected in coordinating solvents, and a more detailed investigation of the N.M.R. spectra of this series of pentafluorophenylboron compounds is in progress.

The ^{19}F chemical shift of BF_2 fluorine atoms in pentafluorophenylboron difluoride was 55 p.p.m. to low field relative to boron trifluoride. It is interesting to compare this value with the values obtained by Stone[161] for some organoboron difluorides (Table III).

TABLE III

Compound	^{19}F Chemical Shift (p.p.m.)
BF_3	0
$PhBF_2$	-35
$CH_2=CHBF_2$	-38
$CF_2=CFBF_2$	-40
$EtBF_2$	-52
$CH_2=CH-CH_2BF_2$	-52
n-$PrBF_2$	-54
$BuBF_2$	-54

The shifts to low field (from BF_3) are smaller for aryl- and vinyl-boron difluorides than for alkylboron difluorides. This fact was interpreted by Stone as indicative of interaction between the π orbitals of the organic group and the p_π orbital of the boron atom. The value observed for pentafluorophenylboron difluoride is close to that observed for alkylboron difluorides, but this does not necessarily indicate lack of interaction between the organic group and the boron atom in the case of pentafluorophenylboron difluoride, since the effect of the o-fluorine atoms on the BF_2 group must be taken into consideration.

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