Cleavage reactions of pentafluorophenyl-metal compounds

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CLEAVAGE REACTIONS OF PENTAFLUOROPHENYL-METAL COMPOUNDS

submitted by

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A candidate for the degree of Doctor of Philosophy.

1966.

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1962 and January 1966. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of a publication with Dr. R.D. Chambers in Tetrahedron Letters, 1965, p.2389.

SUMMARY

Cleavage Reactions of Pentafluorophenyl-metal Compounds

Compounds in the series $(CH_3)_3MC_6F_5$, where M = Si, Ge, Sn, Pb, have been prepared using pentafluorophenylmagnesium bromide and the corresponding trimethyl-metal halide, and a halide-ion catalysed hydrolysis of these derivatives has been studied, leading to an order of ease of hydrolysis of pentafluorophenyl from the metal. viz. $\mathrm{Si} \ll \mathrm{Ge} \ll \mathrm{Sn} \ll \mathrm{Pb}$ with a very wide range of reactivity.

Cleavage reactions of methylpentafluorophenylmercury with inorganic halides have been investigated and it has been shown that, whilst chlorides often cause disproportionation of the mercurial, bromides react in absence of solvent to give good yields of pentafluorophenyl derivatives of other elements. In this way pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide have been prepared and these are the first uncomplexed, formally three-covalent, fluorocarbon derivatives of aluminium to be reported. Similar cleavage reactions have led to pentafluorophenyl derivatives of phosphorus, arsenic, and germanium.

Pentafluorophenylaluminium dibromide has been studied and shown to be relatively thermally stable and when decomposition occurs it does so initially by simple disproportionation. Some of the simple organic reactions of this compound indicate that it resembles its hydrocarbon analogue in reactivity, especially towards acyl and aroyl halides, ketones, donor molecules, and alkyl and aryl halides. Preliminary

work with alkenes and alkynes shows that the reactions are often complex but it appears that pentafluorophenylaluminium dibromide forms a very weak but isolable complex with propene, from which the latter can be recovered.

Cleavage reactions involving sulphur dichloride and perfluoroaryl- and bromotetrafluoroaryl-lithium derivatives have led to the synthesis of bis(pentafluorophenyl)sulphide and bis(orthobromotetrafluorophenyl) sulphide respectively and the latter undergoes ring closure via intramolecular coupling in an Ullmann synthesis to yield octafluorodibenzothiophene, and this is the first report of a fully fluorinated, condensed ring compound containing one hetero atom. Octafluorodibenzothiophene has been shown to be remarkably thermally stable and to undergo nucleophilic substitution in the 2 position.

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CHAPTER ONE

INTRODUCTION.

1. Historical Development.

During the last fifteen years interest and work in fluorine chemistry has developed enormously. The study of fluorocarbon systems has grown into a very important area of research and this has been possible because methods have been devised for extensive replacement of hydrogen in hydrocarbon systems by fluorine. Thus new fields of organic and organometallic chemistry have arisen based on fluorocarbon systems and the differences between hydrocarbon and fluorocarbon chemistry are not dominated by stereochemical considerations as are those between hydrocarbons and chlorocarbons. However, steric effects will be involved to some extent in many cases.

Differences do arise from the greater carbon-fluorine bond strength as compared with that for carbon-hydrogen (105 and 98·8 kcals. per mole respectively), the larger size of fluorine and consequent shielding of a carbon chain from attack by reagents, and the difference in electronegativity between hydrogen and fluorine, which leads to entirely different electronic environments for functional groups in fluorocarbon compounds. As expected, the latter often display novel properties and reactions in comparison with those of their hydrocarbon analogues thereby adding to our knowledge of chemistry. Many of these new materials are often of potential commercial application and this is another reason why fluorocarbon chemistry has advanced so rapidly.

Early in the development of fluorocarbon chemistry the synthesis and study of fluorocarbon derivatives of metals and metalloids began. Following the synthesis of perfluoroalkyl iodides, notably trifluoromethyl iodide, perfluoroalkylmercurials were isolated by Emeleus, Haszeldine and their co-workers.[1] Evidence was then obtained for the formation of perfluoroalkyllithium and perfluoroalkyl Grignard reagents and almost immediately it became clear that fluorocarbon derivatives of metals could possess distinctly different properties from those of their hydrocarbon analogues. Bistrifluoromethylmercury was isolated as a white, crystalline, water soluble solid which afforded fluoroform on treatment with alkali whereas dimethylmercury is a liquid which is insoluble in water and hydrolytically stable in conditions which lead to the decomposition of its perfluoro analogue.

Early work led to extensive developments in the fluorocarbon chemistry of metalloids and non-metals and these fields have been reviewed by several authors.[2,3] More recently however, fluorocarbon derivatives of metals have been widely investigated and regularly reported and it can now be said that their study forms an interesting and important sub-division of both fluorocarbon chemistry and organometallic chemistry. Clark,[4] and more recently Stone and Treichel,[5] have reviewed fluorocarbon derivatives of metals; the latter work contains information on perfluoroaryl compounds and this subject itself has been discussed in a very recent article by Chambers and Chivers.[6]

2. Present Work.

The work to be described in this thesis is concerned with polyfluoroaryl compounds of some elements in groups three, four, five and six of the periodic table, namely aluminium, silicon, germanium, tin, lead, phosphorus, arsenic, and sulphur and falls into four categories.

a) The synthesis of some derivatives of group IVB elements, using a Grignard reagent, in order to establish the trend in hydrolytic stability within the group.

b) Investigation of cleavage reactions of methylpentafluorophenylmercury as a route to other, not easily accessible polyfluoroaryl derivatives, particularly those of aluminium.

c) The characterisation of the first stable perfluoro derivatives of tricovalent aluminium and the organic chemistry of these compounds.

d) Preparation of polyfluoroaryl sulphur compounds via the reaction of sulphur dichloride with the corresponding lithio derivatives.

Therefore, the introduction will deal with general methods of preparation of fluorocarbon derivatives of metals and metalloids; the fluorocarbon chemistry of mercury and aluminium; polyfluoroaryl derivatives of silicon, germanium, tin, lead, phosphorus, arsenic and sulphur and be concluded by a brief section dealing with pentafluorophenyl derivatives of other metals and metalloids.

3. General methods of preparation of fluorocarbon derivatives.

a) Perfluoroalkyl derivatives.

(1) Reaction between perfluoroiodoalkanes and metals, metalloids or their derivatives initiated by ultra-violet irradiation or heating.

This method was responsible for the preparation of the first compounds containing a perfluoroalkyl group attached to a metal or metalloid atom.[1]

$$CF_3I + Hg \xrightarrow[150^\circ]{U.V.} CF_3HgI \quad (80\%)$$

The scope is limited by the relatively small number of substances which show reactivity towards the iodides but the route has proved useful in the preparation of derivatives of phosphorus and arsenic. For example trifluoroiodomethane reacts with either red or white phosphorus at 195-230° to yield a mixture of tristrifluoromethylphosphine, iodobistrifluoromethylphosphine, diiodotrifluoromethylphosphine, and phosphorus iodides.

Cleavage of compounds containing a weak covalent bond has also been employed.

$$CF_3I + (CH_3)_3SnSn(CH_3)_3 \xrightarrow{U.V.} CF_3Sn(CH_3)_3 \ (80\%) + (CH_3)_3SnI$$[7]

$$C_2F_5I + (C_6H_5)_3SnSn(C_6H_5)_3 \xrightarrow{220^\circ} C_2F_5Sn(C_6H_5)_3 \ (22\%) + (C_6H_5)_3SnI$$[8]

$$CF_3I + (C_6H_5)_2P\text{-}P(C_6H_5)_2 \longrightarrow (C_6H_5)_2PCF_3{}^{9}$$

In the presence of mercury mixed fluorohydro derivatives can be prepared.

$$CH_3AsI_2 + 2Hg + 2CF_3I \longrightarrow (CF_3)_2AsCH_3 + 2HgI_2{}^{10}$$

(2) Grignard reagents and lithium derivatives.

Several perfluoroalkyl Grignard reagents have been prepared i.e. R_FMgX (X = Br, I). They undergo the types of reaction that are associated with their alkyl analogues, but are thermally unstable and must be prepared and used below room temperature (-78° to 0°)

$$R_FI + Mg \xrightarrow[-30^\circ]{\text{DIETHYL ETHER}} R_FMgI \quad (40 - 80\%)$$

where $R_F = CF_3, C_2F_5, nC_3F_7$.[11,12,13,14] The corresponding bromides are obtained from perfluoroalkylbromides and magnesium amalgam[15] or from perfluoroalkyliodides and phenylmagnesium bromide:-

$$CF_3Br + Mg/Hg \xrightarrow[-20^\circ]{\text{DIETHYL ETHER}} CF_3MgBr \quad (19\%)$$

$$R_FI + C_6H_5MgBr \xrightarrow[-78^\circ]{\text{DIETHYL ETHER}} R_FMgBr\ (40\text{-}85\%) + C_6H_5I.$$

$R_F = C_2F_5, nC_3F_7, iC_3F_7$.[16,17]

The reactions of these reagents are reported to proceed normally but they are unstable above room temperature and the trifluoromethyl compound appears to be particularly unstable.

Few perfluoroalkyl derivatives of lithium have been reported and they have usually been prepared by the application of the familiar halogen-metal exchange reaction to certain perfluoroalkyl iodides:

$$R_FI + RLi \xrightarrow[-78^\circ]{\text{DIETHYL ETHER}} R_FLi + RI$$

where $R_F = CF_3$,[18,19,20,21] nC_3F_7,[20] iC_3F_7,[17] $R = CH_3, nC_4H_9$.

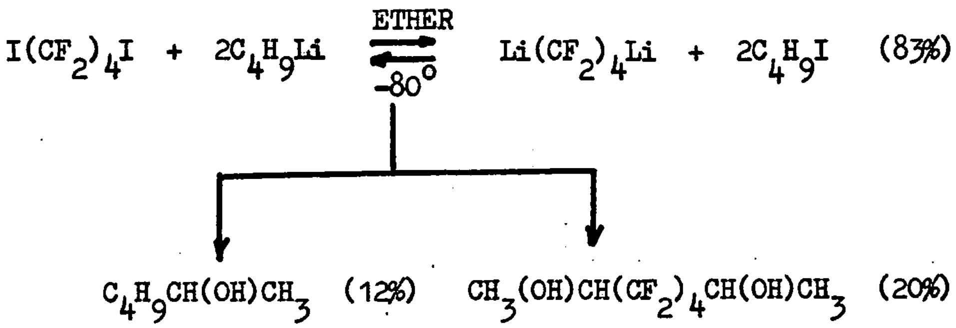
Nevertheless, while perfluoroalkyllithium compounds may be prepared in analogous fashion to alkyllithium compounds, unlike the latter they cannot be utilised easily in syntheses because of their instability. In only a few cases syntheses have been achieved by simultaneous addition procedures, using a low temperature,[21,17]

e.g. $(CF_3)_2CFLi + (CH_3)_3SiCl \xrightarrow[-50^\circ]{\text{DIETHYL ETHER}} (CF_3)_2CFSi(CH_3)_3$ (18%)

or by adding the reactants to magnesium[22]

$$2C_2F_5I + Me_2SnCl_2 \xrightarrow[\text{T.H.F. } 40^\circ]{Mg} Me_2Sn(C_2F_5)_2$$

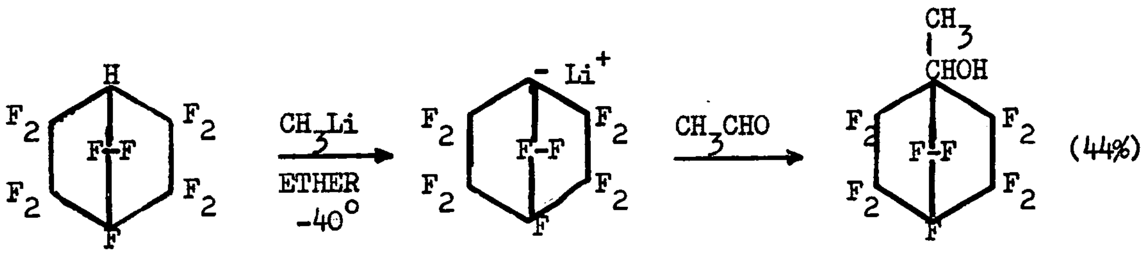
Johncock[23] has recently reported that perfluoro-n-heptyllithium is stable below -90° and can be carbonated at these temperatures and that a fluoroalkyl dilithio compound can be produced at low temperatures.



The instability of fluoroalkyllithium and magnesium compounds is due to the facile migration of fluorine to the metal giving an olefin.[17]

$$(CF_3)_2CFLi \longrightarrow CF_3CF{=}CF_2 + LiF$$

This process is made more difficult in the norbornyl system where a bridged olefin would be produced and the resulting lithio derivative is sufficiently stable for wide synthetic application.[24]



Apart from the latter, polyfluoroalkyl-lithium derivatives are not easily utilised in syntheses.

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

Only limited use has been made of this synthetic route due to the lack of perfluoroalkyl compounds of a convenient degree of activity.

$$2(CH_3)_3M + CF_3I \longrightarrow CF_3M(CH_3)_2 + (CH_3)_4MI \quad {}^{25}$$

$$(M = P,\ As,\ Sb)$$

(4) The reaction of trifluoromethyl radicals with metals.

Bistrifluoromethylditelluride[26] has been prepared by the action of trifluoromethyl radicals, generated by pyrolysis of hexafluoroacetone, on tellurium. The procedure is derived from the classical one used by Paneth[27] to prepare metal alkyls but has not yet found wide application for perfluoroalkyl derivatives.

(5) Direct fluorination of alkyl compounds.

Application of this technique has been restricted to the preparation of derivatives of nitrogen.

$$(C_3H_7)_3N \xrightarrow[N_2\ 300^\circ]{CoF_3} (C_3F_7)_3N \quad {}^{28} \qquad (\ \ 3\%)$$

Most metal-carbon bonds are cleaved by fluorine thus the method is unsuitable for wide application. Even in the case of nitrogen compounds extensive decomposition often occurs.[28]

(6) Electrochemical fluorination.

The method, discovered by Simons,[29] depends on dissolving, or holding in suspension, an organic compound in anhydrous hydrogen fluoride and electrolysing at a voltage lower than that required for the generation of fluorine. Replacement of hydrogen by fluorine occurs by a process which is not understood and multiple bonds and aromatic systems are saturated. Compounds containing polar groups are often soluble in the acid and, whilst fragmentation of carbon skeletons often occurs, functional groups are frequently retained. Derivatives of nitrogen, oxygen and sulphur have been prepared this way.[30]

$$\text{e.g.} \quad n\text{-}C_3H_7COF \xrightarrow[\text{FLUORINATION}]{\text{ELECTROCHEMICAL}} n\text{-}C_3F_7COF \xrightarrow{H_2O} n\text{-}C_3F_7COOH$$

(7) <u>The reaction of fluorides with fluoro-olefins.</u>

The addition of mercuric fluoride to some fluoro-olefins was reported in 1960.[31]

$$HgF_2 + CF_2{=}CF_2 \xrightarrow[\text{AUTOCLAVE} \quad 15 \text{ hrs.}]{AsF_3 \; 100^\circ} Hg(CF_2CF_3)_2 \quad (56\%)$$

$$CF_2{=}CFCl + HgF_2 \xrightarrow[\text{AUTOCLAVE } 10 \text{ hrs.}]{100^\circ} CF_3CFClHgF \quad (24\%)^{32}$$

The authors suggest an ionic mechanism

$$\text{e.g.} \quad \overset{\delta+}{C}F_2{=}\overset{\delta-}{C}FCl \xrightarrow{HgF_2} CF_3CFClHgF$$

with fluoride ion attack on the CF_2 group as in other nucleophilic additions. To date the method has not found wide application.

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

The preparation of perfluorovinylmagnesium iodide was reported by

$$CF_2{=}CFI + Mg \xrightarrow{Et_2O} CF_2{=}CFMgI$$

Park and co-workers in 1956.[33] The iodo compound however was not easily synthesised and other workers[34] used the commercially available bromotrifluoroethylene with success.

$$Me_2SnCl_2 + 2CF_2{=}CFBr \xrightarrow{Mg(CH_2)_4O} Me_2Sn(CF{=}CF_2)_2 + MgBr_2 + MgCl_2 \quad (65\%)$$

The Grignard reagent from the latter was used by Russian authors[34a] to prepare bis-(perfluorovinyl)-mercury and tetrakis-(perfluorovinyl)-silicon. Perfluorovinylboron compounds consequently became available by utilising cleavage reactions between boron trichloride and dimethyl-bis-(perfluorovinyl)-tin.[35]

e.g. $$Me_2Sn(CF{=}CF_2)_2 + 2BCl_3 \xrightarrow[70^\circ]{1\ HOUR} Me_2SnCl_2 + 2CF_2{=}CFBCl_2 \quad (93\%)$$

Many other compounds have been prepared from this reagent.

Trifluorovinyllithium was prepared in an exchange reaction by Tarrant and co-workers,[36] again utilising bromotrifluoroethylene

$$CF_2{=}CFBr + CH_3Li \xrightarrow[0^\circ]{DIETHYL\ ETHER} CF_2{=}CFLi + CH_3Br \quad (73\%)$$

whereas earlier workers[37,38] had used the transmetalation reactions:

$$C_6H_5Sn(CF{=}CF_2)_3 + 3C_6H_5Li \xrightarrow[-35^\circ\ to\ -40^\circ]{DIETHYL\ ETHER} (C_6H_5)_4Sn + 3CF_2{=}CFLi$$

$$n\text{-}C_4H_9Sn(CF{=}CF_2)_3 + 2n\text{-}C_4H_9Li \xrightarrow[-40^\circ]{PENTANE} (n\text{-}C_4H_9)_3SnCF{=}CF_2 + 2CF_2{=}CFLi$$

The stability of the perfluorovinyllithium is markedly affected by temperature and concentration,[36] but it has an advantage over perfluorovinylmagnesium bromide in that it may be used in hydrocarbon solvents.

c) Perfluoroaryl derivatives.

Hexafluorobenzene and its monohydro, chloro, bromo and iodo derivatives are all commercially available[39] and these compounds are the starting materials used for the preparation of pentafluorophenyl-metal compounds.

Pentafluorophenyl Grignard reagents were reported by Tatlow and co-workers[40] in 1959 and shown to react normally. The reagents can be prepared fairly readily from chloro-,[41] bromo-,[40,42] and iodo-[40] pentafluorobenzene. They undergo the standard reactions associated with such reagents and have been used to prepare many pentafluorophenyl derivatives.[4,5,6,43] Reaction between the Grignard reagent and the appropriate metal or metalloid halide to give derivatives of the elements has been widely applied.

e.g. $SiCl_4 + 4C_6F_5MgBr \xrightarrow{\text{DIETHYL ETHER}} (C_6F_5)_4Si + 2MgBr_2 + 2MgCl_2$

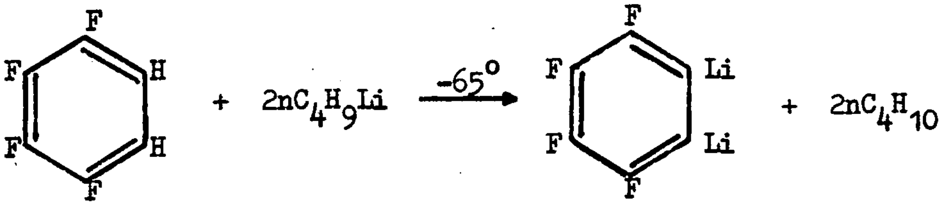
$PCl_3 + 3C_6F_5MgBr \xrightarrow{\text{DIETHYL ETHER}} (C_6F_5)_3P + 3MgClBr.$[44]

The use of n-butyl-lithium in a halogen-metal interchange reaction led to the preparation of pentafluorophenyl-lithium.[45]

$$C_6F_5Br + nBuLi \xrightarrow[-78^{o}]{\text{DIETHYL ETHER}} C_6F_5Li + nBuBr$$

Direct metalation of bromopentafluorobenzene with lithium amalgam at 0° was also successful, giving pentafluorophenyl-lithium in good yield.[45] Tamborski and co-workers[46] showed that hydrogen in polyfluoroaromatic compounds is acidic and prepared mono and dilithio derivatives from pentafluorobenzene and 1,2,3,4-tetrafluorobenzene and n-butyl-lithium.

$$C_6F_5H + nC_4H_9Li \xrightarrow{-65^{o}} C_6F_5Li + nC_4H_{10}$$



The reaction time varies from a few minutes to several hours depending upon the fluoroaromatic compound and the solvent system. The use of pentafluorophenyl-lithium in a hydrocarbon solvent proved particularly advantageous in the preparation of tris(pentafluorophenyl)boron from boron trichloride.[47]

Some derivatives have been made by cleavage of a pentafluorophenyl-metal bond by an inorganic halide.[48]

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

and some of the work to be presented in this thesis involves this type of reaction as a route to pentafluorophenyl derivatives.

A few elements have been shown to react with bispentafluorophenylmercury at elevated temperatures when transmetalation of the perfluoroaryl group occurs.[57]

$$\text{e.g.}\quad (C_6F_5)_2Hg + S \xrightarrow[7\ \text{DAYS}]{250^\circ} (C_6F_5)_2S + Hg$$

Derivatives of sulphur, selenium and tin were isolated in this way, but reactions with aluminium, bismuth, cadmium, chromium, iron, zinc, phosphorus, and titanium gave mainly unreacted starting materials.

In another case, reaction of the sodium salt of a transition metal anion with hexafluorobenzene was successful.[49]

$$[Fe(CO)_2C_5H_5]^-Na^+ + C_6F_6 \longrightarrow C_6F_5Fe(CO)_2C_5H_5 + NaF$$

In view of the well known vulnerability of hexafluorobenzene to nucleophiles this method may find more wide application.

A recent paper by Haszeldine and co-workers[50] describes the preparation of some pentafluorophenyl derivatives of silicon by free radical attack on hexafluorobenzene.

$$(CH_3)_3SiH + C_6F_6 \xrightarrow{\text{U.V.}} (CH_3)_3SiC_6F_5\ (53\%) + \text{OTHER PRODUCTS}$$

The striking differences which separate the properties of perfluoroalkyl metal compounds and their hydrocarbon analogues (e.g. $(CF_3)_2Hg$ and $(CH_3)_2Hg$) are less noticeable in the perfluoroaryl derivatives. The pentafluorophenyl group is readily cleaved by electrophiles, and nucleophiles, from main group elements.[51,52]

Cleavage by electrophiles indicates that the electron density at the metal-bonded carbon atom is not drastically reduced by the presence of the fluorine, and the easy cleavage by nucleophiles probably reflects the polarity of the metal-carbon bond and the overall electronegativity of the group (between that of chlorine and bromine)[53,54] or, more correctly, leaving group ability. Transition metal derivatives seem to be thermally more stable than their hydrocarbon analogues however[55] and this increased stability has mainly been attributed to the high electronegativity of the pentafluorophenyl group[56] leading to stabilisation of transition metal-carbon σ bonds.

At the time of writing pentafluorophenyl derivatives of zinc, mercury, boron, aluminium, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, sulphur and a number of transition metals have been prepared.

4. Fluorocarbon Derivatives of Mercury.

a) Perfluoroalkyl derivatives.

It has already been stated that the first fluorocarbon-metal derivatives to be isolated were compounds of mercury and consequently much research has been devoted to them. This subject has been reviewed regularly[2,3,4,5,6] and this treatment is not intended to be comprehensive.

Perfluoroalkylmercury iodides are obtained either by heating, or by irradiating with ultraviolet light, mixtures of perfluoroalkyl iodides and the metal.[58] The iodides, R_FHgI, are white, crystalline, water soluble solids when $R_F = CF_3$ or C_2F_5 but the compound n-C_3F_7HgI is not appreciably soluble. The perfluoroalkyl groups can be removed by hydrolysis but, like their alkyl analogues, the compounds can be converted to the bases R_FHgOH by treatment with an aqueous suspension of silver oxide. Reaction of the base with the appropriate aqueous acid leads to the compounds R_FHgX (X = F, Cl, Br, NO_3).[58]

Bis(perfluoroalkyl)mercurials can be obtained by treating perfluoroalkylmercury iodides with silver, copper or cadmium amalgam.

$$CF_3HgI \xrightarrow{Cd/Hg\ 120-130^\circ} (CF_3)_2Hg \quad (80-90\%)^{59}$$

and some bis(perfluoroalkyl) derivatives have been obtained by the addition of mercury(II) fluoride to fluoro-olefins. The reactions proceed readily at 50-100° under autogenous pressures in the presence of a solvent.[31]

$$HgF_2 + CF_2{=}CF_2 \xrightarrow[100^\circ\ 14\ HRS.]{AsF_3} (C_2F_5)_2Hg\ (56\%)$$

Reaction with terminally unsaturated fluoro-olefins affords branched chain fluoroalkyl mercurials.[60]

Bis(trifluoromethyl)mercury is also conveniently prepared by the reaction of tris(trifluoromethyl)phosphine and mercuric oxide.[61] It is a white crystalline solid with an irritating odour, soluble in organic solvents and readily sublimable. Like trifluoromethylmercury halides it is soluble in water and can be recovered unchanged from aqueous solution. Above 160° it slowly decomposes[59] in contrast to dimethyl mercury which is only slightly decomposed at 300°.

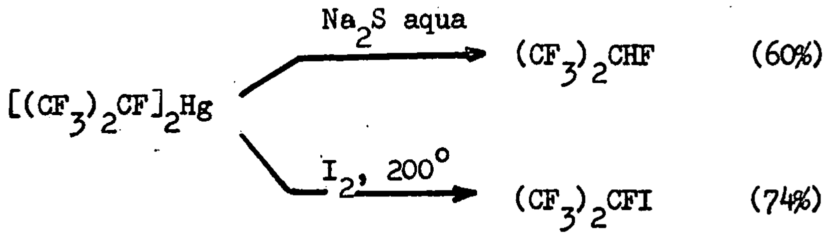
Alkyl mercurials transfer their alkyl groups to other metals or react with certain metal halides but perfluoroalkylmercurials do not function readily in analogous fashion.[59] This has been attributed to the pseudo-halogen character of the perfluoroalkyl groups which causes the perfluoroalkylmercurials to behave like mercury(II) halides rather than organomercurials. The most unusual property of bis(trifluoromethyl)mercury is its solubility in water. This does not occur with the production of Hg^{2+} ions but, because aqueous solutions of $(CF_3)_2Hg$, CF_3HgI or C_3F_7HgI can be conductometrically titrated with potassium halides, it has been suggested that the formation of complex ions $[(CF_3)_2HgX_2]^{2-}$, $[R_FHgIX]^-$ and $[R_FHgIX_2]^{2-}$ ($X = Cl, Br, I$; $R_F = CF_3$, $n\text{-}C_3F_7$)[62] occurs, related to the well-known tetrahalogenomercurate(II) ions. e.g. $(HgI_4)^{2-}$. However more recent work by Downs[63] on the spectroscopy of these solutions failed to support the formation of these complex anions 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. This is further supported by cryoscopic measurements.[64] Complex compounds of the type $(R_F)_2HgL$ and $(R_F)_2HgL_2$ (where R_F = fluoroalkyl or fluoroaryl; L = piperidine, pyridine, triphenylphosphine etc.) have been shown by oscillometric titration to exist in benzene solution.[65]

Bisperfluoroalkylmercurials decompose on pyrolysis or irradiation with U.V. light to yield perfluoroalkyl free radicals.[60,66]

e.g. $$(C_2F_5)_2Hg \xrightarrow{U.V.} Hg + 2C_2F_5^{\bullet} \longrightarrow n\text{-}C_4F_{10} \quad (80\%)$$

$$[(CF_3)_2CF]_2Hg \xrightarrow{498^{\circ}} Hg + 2(CF_3)_2CF^{\bullet} \longrightarrow (CF_3)_2CFCF(CF_3)_2 \quad (57\%)$$

They are reduced to monohydrofluoroalkanes by aqueous sodium stannite and sodium sulphide, and react with halogens under the influence of heat or light to yield perfluoroalkyl halides.[60]



$$[(CF_3)_2CF]_2Hg \xrightarrow{Na_2S\ aqua} (CF_3)_2CHF \quad (60\%)$$

$$[(CF_3)_2CF]_2Hg \xrightarrow{I_2,\ 200^\circ} (CF_3)_2CFI \quad (74\%)$$

Reactions of mercurials containing secondary perfluoroalkyl groups with boiling sulphur provides a general route to perfluorothioketones.

b) Perfluorovinyl Derivatives.

Seyferth and co-workers have used the Grignard reagent to prepare trifluorovinylmercuric halides via perfluorovinyltin compounds,[67] and some unsymmetrical trifluorovinylmercurials have been prepared by the Grignard method in tetrahydrofuran. Bis(trifluorovinyl)mercury can be prepared by the reaction of the Grignard reagent with mercuric chloride in ether at -10° and from the lithio derivative[36] but, unlike bis(trifluoromethyl)mercury, bis(trifluorovinyl)mercury is a liquid[68] and is insoluble in water.

Reactions between unsymmetrical trifluorovinylmercurials and hydrogen chloride and arsenic trichloride have been studied in an attempt to determine the relative ease of cleavage of trifluorovinyl by electrophiles.[69]

$$CF_2{=}CFHgCH{=}CH_2 + HCl \longrightarrow CH_2{=}CHHgCl + CF_2{=}CFH \quad (99\%)$$

$CF_2=CFHgEt + HCl \longrightarrow EtHgCl + CF_2=CFH$ (98%)

$CF_2=CFHgPh + HCl \longrightarrow PhHgCl + CF_2=CFH$ (98%)

These results lead to the following placing of the $CF_2=CF$ group in order of cleavage of organic groups from mercury by hydrogen chloride.

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

Knunyants and co-workers[70] have reported some cleavage reactions of bis(perfluorovinyl)mercury.

e.g. $(CF_2=CF)_2Hg + HgCl_2 \longrightarrow 2CF_2=CFHgCl$ (80%)

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

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

Bis(trifluoromethyl)mercury forms decomposition products in reactions with metal or metalloid halides and thus differs from bis(trifluorovinyl)mercury in this respect.[71]

Bis(trifluorovinyl)mercury reacts with an aluminium hydride trimethylamine complex to give a perfluorovinylaluminium derivative.[72]

$$3(CF_2=CF)_2Hg + 2AlH_3{:}N(CH_3)_3 \xrightarrow[\text{14 HRS.}]{Et_2O,\ -20^{\circ}} 2(CF_2=CF)_3Al{:}N(CH_3)_3 + 3H_2 + 3Hg.$$

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

Pentafluorophenylmercury derivatives are easily prepared in good yield from a perfluoroaryl Grignard reagent and the corresponding mercury(II) halide or organomercury halide.[73]

$$\text{e.g.}\quad HgCl_2 + 2C_6F_5MgBr \xrightarrow[\text{4 HOURS}]{Et_2O\ \text{REFLUX}} (C_6F_5)_2Hg \qquad (73\%)$$

$$CH_3HgI + C_6F_5MgBr \xrightarrow[\text{4 HOURS}]{Et_2O\ \text{REFLUX}} CH_3HgC_6F_5 \qquad (69\%)$$

Bis(pentafluorophenyl)mercury has also been prepared from lithium amalgam and bromopentafluorobenzene[45] and by a decarboxylation of mercury(II) pentafluorobenzoate.[74,74a]

$$(C_6F_5COO)_2Hg \xrightarrow[\text{1 HOUR}]{210\text{-}212^\circ} (C_6F_5)_2Hg + 2CO_2 \qquad (56\%)$$

The action of the pentafluorophenyl radical on mercury also leads to this product.[75] The decarboxylation method can also be used to prepare derivatives of the type $RHgC_6F_5$ but the Grignard method is the more obvious route to these derivatives.

Bis(pentafluorophenyl)mercury displays high chemical and thermal stability. It has been recrystallised from concentrated sulphuric acid and was unchanged after five hours at 250° but is slowly cleaved by halogens.[73]

$$(C_6F_5)_2Hg + Br_2 \xrightarrow[\text{5 DAYS, }60^\circ]{CCl_4} C_6F_5HgBr + C_6F_5Br$$

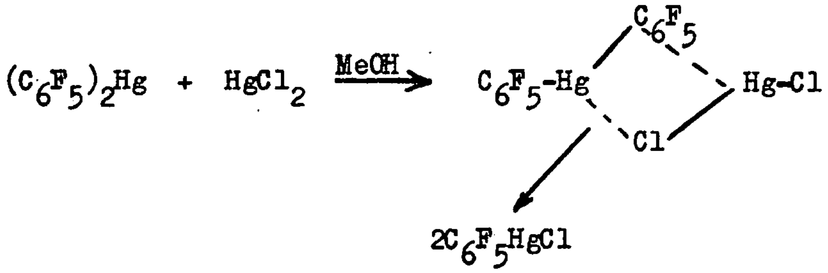
In contrast, with mercury(II) chloride or bromide in methanol, rapid disproportionation occurs, giving the corresponding perfluoroarylmercury halide.

$$(C_6F_5)_2Hg \;+\; HgX_2 \xrightarrow{MeOH} 2C_6F_5HgX \quad (X = Cl,\ Br)$$

Using mercury(II) iodide the equilibrium lies on the side of the biaryl compound and mercury(II) iodide. Some product is formed but attempts to isolate it by recrystallisation result only in the recovery of starting materials.[76]

$$HgI_2 \;+\; (C_6F_5)_2Hg \rightleftharpoons 2C_6F_5HgI$$

Pentafluorophenylmercury iodide is probably unstable, by analogy with trichloro and trifluorovinylmercury iodide.[77] The contrast in the resistance of bis(pentafluorophenyl)mercury to attack by electrophiles like halogens, but reactivity to mercury(II) halides has been attributed to a four-centre mechanism in the latter case.



An unusual characteristic of bis(pentafluorophenyl)mercury is its ability to co-ordinate donor molecules to form stable complexes.[73] Co-ordination compounds with bipyridyl and with 1,2-[bis(diphenylphosphino)]ethane have been isolated and this was the first report that mercury linked to carbon, other than cyanide, has sufficient electron accepting capacity to enable neutral co-ordination complexes to be isolated.

Unlike diphenylmercury, bis(pentafluorophenyl)mercury does not readily undergo transmetalation reactions. The latter will occur with sulphur, tin and selenium but efforts to prepare derivatives of aluminium, cadmium, iron and several other metals by this route were not successful.[57] For example, sulphur and the mercurial were heated at 250° for seven days in a sealed tube and yielded bis(pentafluorophenyl)sulphide (82%) but there was no reaction with aluminium under similar conditions. Thus, while bis(pentafluorophenyl)mercury is more reactive than are perfluoroalkylmercurials towards other elements, its application in transmetalation reactions is very limited.

The reactions of bis(pentafluorophenyl)mercury with nucleophiles are of particular interest in view of the rapid cleavage of the perfluoroaryl group from main group elements by base to give pentafluorobenzene. Burdon and co-workers[78] have shown that with potassium hydroxide in tertiary butanol or with sodium methoxide in methanol, nucleophilic substitution of fluorine para to mercury occurs.

This orientation follows the general pattern for reactions of compounds of the type C_6F_5X with nucleophilic reagents, in which para substitution most often occurs.[79] It may appear unusual that hydrolytic cleavage of pentafluorophenyl does not occur but it is a general characteristic that mercury-carbon bonds are not easily cleaved by alkali.[80] Reactions with other nucleophiles are less straightforward.

Two unsymmetrical perfluoroaryl compounds of mercury, methylpentafluorophenylmercury and phenylpentafluorophenylmercury have been prepared by the Grignard route[73] and unsymmetrical perfluoroarylmercurials can be made by the decarboxylation method.[74]

$$RHgX + C_6F_5MgBr \longrightarrow RHgC_6F_5 + MgBrX^{73} \quad R = Me,Ph; \quad X = I, Cl.$$

$$p\text{-}MeC_6H_4HgCO_2C_6F_5 \xrightarrow{223\text{-}224^\circ} p\text{-}MeC_6H_4HgC_6F_5{}^{74}$$

Methylpentafluorophenylmercury may also be prepared from bis(pentafluorophenyl)mercury and dimethylmercury and the exchange is dependant on the presence of halide impurities.[73]

Exchange reactions involving bis(trifluoromethyl)mercury and bis(pentafluorophenyl)mercury have been studied by means of F^{19} nuclear magnetic resonance. The formation of the unsymmetrical derivative trifluoromethylpentafluorophenylmercury is indicated.[81]

$$(C_6F_5)_2Hg + (CF_3)_2Hg \xrightarrow{150^{\circ}} 2C_6F_5HgCF_3$$

It was also deduced that a mixture of dimethylmercury and bis-(pentafluorophenyl)mercury rearranged to give 88% of methylpentafluorophenylmercury after one hour at 150°.

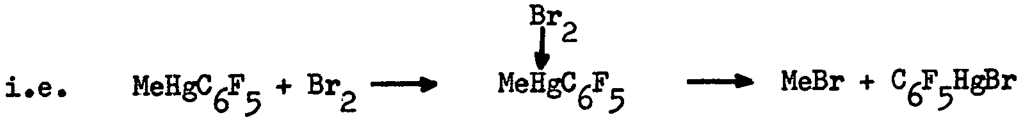
$$(C_6F_5)_2Hg + (CH_3)_2Hg \longrightarrow 2C_6F_5HgCH_3$$

Methylpentafluorophenylmercury undergoes facile electrophilic cleavage of pentafluorophenyl as pentafluorobenzene by anhydrous hydrogen chloride, while a phenyl group is preferentially removed from phenylpentafluorophenylmercury.[73]

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

$$PhHgC_6F_5 + HCl \longrightarrow C_6F_5HgCl + C_6H_6$$

These results are consistent with those obtained for electrophilic attack on pentafluorophenyltin compounds[82] and again reflect the trend in electron density at the metal-bonded carbon atom. Surprisingly, with bromine in decane cleavage of methyl occurs from methylpentafluorophenylmercury, and phenyl and pentafluorophenyl are removed in about equal proportions from phenylpentafluorophenylmercury. It is clear that different mechanisms must obtain for the reactions with bromine and hydrogen chloride. The pentafluorophenyl group is known to influence the acceptor properties of mercury and it has been suggested that the reaction with bromine may involve co-ordination of molecular bromine to mercury.[73]



$$\text{i.e.}\quad MeHgC_6F_5 + Br_2 \longrightarrow \overset{\overset{Br_2}{\downarrow}}{MeHgC_6F_5} \longrightarrow MeBr + C_6F_5HgBr$$

Factors influencing the decomposition of such an intermediate would most probably differ from those involved in determining the course of electrophilic attack by hydrogen chloride.[73]

The cleavage of pentafluorophenyl from methylpentafluorophenylmercury by electrophilic reagents forms a part of the work to be described later. The reaction has been used to obtain derivatives of several other elements.[51,83]

$$MeHgC_6F_5 + SnCl_4 \longrightarrow MeHgCl + C_6F_5SnCl_3 \qquad (51)$$

$$MeHgC_6F_5 + BCl_3 \longrightarrow MeHgCl + C_6F_5BCl_2 \qquad (83)$$

d) Pentachlorophenylorganomercury Compounds.

It would be interesting to compare, in general, the properties of pentachlorophenyl- and pentafluorophenyl- derivatives. The former should be more influenced by steric effects and also by the greater electron withdrawal of the pentachloro group. Dessy and co-workers[84] have prepared some pentachlorophenyl derivatives of mercury including bis(pentachlorophenyl)mercury and methylpentachlorophenylmercury. The former has a very high melting point (383°) c.f. $(C_6F_5)_2Hg$, m.pt. 142° and great thermal stability.[84] Anhydrous hydrogen chloride removes the pentachlorophenyl group from methylpentachlorophenylmercury and the phenyl group from phenylpentachlorophenylmercury. These results are consistent with those obtained for the corresponding pentafluorophenyl-derivatives, and with the conclusion of Dessy and Kim[85] that cleavage occurs preferentially at the carbon carrying the highest electron density.

The following exchange reaction was successful in preparing the phenyl compound only:

$$C_6Cl_5HgCl + R_2Hg \xrightarrow{\text{BENZENE}} RHgCl + C_6Cl_5HgR$$

Attempts to prepare the methyl derivative by this method gave an almost quantitative yield of bis(pentachlorophenyl)mercury, presumably through a second exchange reaction. This is comparable with the disproportionation of methylpentafluorophenylmercury which will be fully discussed in Chapter three.

5. Fluorocarbon Derivatives of Aluminium.

a) Perfluoroalkyl Derivatives.

Little is known about fluorocarbon derivatives of aluminium. By analogy with fluorocarbon boron chemistry the compounds are likely to be inherently unstable unless formation of Al-F bonds can be prevented.

Trifluoromethyl-boron difluoride, the only perfluoroalkyl derivative of three-covalent boron which has been isolated is very unstable, and the decomposition involves migration of fluorine from carbon to boron giving the trifluoride.[86a] This mode of regression is related to the decomposition of perfluoroalkyllithiums and fluorocarbon Grignard reagents, and to the decomposition of trimethyltrifluoromethyltin and perfluoroalkyl transition metal compounds.[86b] When a fluorocarbon group is bonded to a metal having a vacant orbital, transfer of fluorine from the side chain to the metal appears to occur readily, most probably involving little activation energy, and is obviously aided by the relatively high thermodynamic stability of metal fluorine bonds.

Heptafluoro-n-propyl iodide reacts with lithium aluminium hydride as shown.[87]

$$\text{n-}C_3F_7I + LiAlH_4 \longrightarrow Li[C_3F_7AlH_2I] + H_2 \qquad \text{(a)}$$

$$\text{n-}C_3F_7I + Li[C_3F_7AlH_2I] \longrightarrow Li[C_3F_7AlHI_2] + nC_3F_7H \qquad \text{(b)}$$

$$\text{n-}C_3F_7I + Li[C_3F_7AlHI_2] \longrightarrow Li[(C_3F_7)_2AlI_2] + HI \qquad \text{(c)}$$

The reaction is carried out in ethereal solution at -78° and addition of water after stage (a) gives 1H-heptafluoropropane.

$$Li[C_3F_7AlH_2I] + 3H_2O \xrightarrow{0^\circ} C_3F_7H + LiI + Al(OH)_3 + 2H_2$$

After stage (a) further addition of the iodide leads to formation of heptafluoropropane but no additional hydrogen (stage (b)). A third mole of the heptafluoropropyl iodide reacts more slowly, in accordance with reaction (c) and only after addition of three moles of the iodide to one mole of lithium aluminium hydride does the resulting ethereal solution fail to liberate hydrogen on treatment with water.

The stability of $Li[C_3F_7AlH_2I]$ in refluxing ethereal solution has been investigated.[87] Addition of water after a few hours gave only 41% of the expected quantity of hydrogen and 54% of the expected amount of heptafluoropropane. The postulated perfluoropropylaluminium complex decomposes violently to aluminium, lithium iodide, hydrogen and 1H-heptafluoropropane if an attempt to isolate it by removal of ether is made. It has been suggested[88] that anions like $[C_3F_7AlH_2I]^-$ are perhaps stabilised in ether by coordination of the solvent to aluminium so that maximum possible use is made of the metals' orbitals in bonding. Such stabilisation would be similar to that believed to be mainly responsible for the existence of $[CF_3BF_3]^-$.[89]

A reaction involving approximately equimolar amounts of trifluoromethyl iodide and lithium aluminium hydride in diethyl ether at -78° has been represented by the equation[87]

$$CF_3I + LiAlH_4 \longrightarrow Li[CF_3AlH_2I] + H_2$$

Addition of water to the reaction mixture produced several products.

$$2Li[CF_3AlH_2I] \ + \ 3H_2O \longrightarrow CH_4 + CHF_3 + H_2 + Al(OH)_3 + AlF_3 + LiI$$

2H-heptafluoropropane, CF_3CFHCF_3, is obtained by hydrolysis of the product formed in the vigorous reaction of aluminium with bis-(perfluoroisopropyl)mercury, $[(CF_3)_2CF]_2Hg$.[90] This indicates the formation of a perfluoroisopropylaluminium compound, which then decomposes in the presence of water.

b) Perfluorovinyl Derivatives.

Tris(perfluorovinyl)aluminium has been isolated as a trimethylamine adduct in the reaction[72]

$$3(CF_2{:}CF)_2Hg + 2(CH_3)_3N{\cdot}AlH_3 \xrightarrow{\text{DIETHYL ETHER}} 2(CH_3)_3N{\cdot}Al(CF{:}CF_2)_3 + 3H_2 + 3Hg$$

The reactants are mixed at -20°, allowed to warm to room temperature with stirring and then more bis(perfluorovinyl)mercury is added. The reaction is vigorous even at -20° and hydrogen is liberated immediately. The excess mercurial is necessary to effect complete alkylation since the last step of the reaction

$$(CF_2{:}CF)_2AlH{:}NMe_3 \longrightarrow (CF_2{:}CF)_3Al{:}NMe_3$$

is very slow. The final product is a colourless, air sensitive liquid which may be distilled under high vacuum (b.pt. $42{\cdot}5^\circ/10^{-3}$ mm). It may be stored for several weeks at -20°, but at room temperature it becomes viscous and darkens. With water at elevated temperature it releases 80% of its trifluorovinyl groups as trifluoroethylene. Cryoscopic molecular weight studies have shown the compound to be highly associated in cyclohexane solution.

c) Perfluoroaryl Derivatives.

Very little work has been done on fluorocarbon derivatives of aluminium and those derivatives reported in the literature are derived from tetracovalent aluminium.

Recently several authors have described attempts to prepare perfluoroaryl derivatives of aluminium.[57,91,92] Exchange reactions of diarylmercury with aluminium and reaction between triarylboron and triethylaluminium are methods which lead directly to uncomplexed triphenylaluminium.[93] Neither method has been successful in producing perfluoroarylaluminium compounds.[57,92] Activated aluminium failed to react with bis(pentafluorophenyl)mercury[57,92] even after several days. Tris(pentafluorophenyl)boron should react with triethylaluminium according to the following equation,

$$Al(C_2H_5)_3 + (C_6F_5)_3B \xrightarrow{\text{INERT SOLVENT}} (C_6F_5)_3Al + B(C_2H_5)_3$$

but no aluminium derivatives were isolated.[92] Tris(pentafluorophenyl)aluminium etherate, $(C_6F_5)_3Al \cdot O(C_2H_5)_2$, has been prepared from aluminium chloride and bromide and pentafluorophenylmagnesium bromide.[92]

$$3C_6F_5MgBr + AlX_3 \xrightarrow[-20^\circ \text{ to } 0^\circ]{\text{ETHER, TOLUENE}} (C_6F_5)_3Al \cdot O(C_2H_5)_2 \quad (67\%)$$

(X = Cl, Br)

Varied attempts were made to remove the ether but none succeeded. Sublimation in vacuo produced no free ether and rapid heating resulted in violent decompositions. It is reasonable to postulate the formation of Al-F bonds by either intra- or intermolecular abstraction processes, leading to intermediates of fluorobenzyne structure.[92]

Lithium aluminium hydride reacts with bromopentafluorobenzene in tetrahydrofuran at -78° to give lithium tris(pentafluorophenyl)-bromoaluminate, a white, air-sensitive solid, in 30% yield.[91] The product can be recrystallised from boiling cyclohexane but sublimation at 160° under vacuum is accompanied by decomposition. The following reaction stoichiometry is suggested.

$$LiAlH_4 + 2C_6F_5Br \longrightarrow LiAl(C_6F_5)_2Br_2 + 2H_2$$

$$2LiAl(C_6F_5)_2Br_2 \rightleftharpoons LiAl(C_6F_5)_3Br + LiAl(C_6F_5)Br_3$$

6. Fluorocarbon Derivatives of Group IVb Elements.

A great deal of work has been carried out on fluorocarbon derivatives of the elements silicon and tin but derivatives of germanium and lead are relatively obscure. A survey of the methods used to prepare the aliphatic compounds is beyond the scope of this work and indeed would not be relevant. The subject has been reviewed by several authors[3,4] but in spite of Clark's suggestion[94] that further studies of compounds of these group IV elements would be of particular interest, since the elements show a very marked and regular change from non-metal to metal, no-one has yet carried out a comparative study of derivatives within the group.

a) Perfluoroaryl Derivatives of Silicon.

Tetrakis(pentafluorophenyl)silane was one of the first perfluoroaryl derivatives to be isolated.[44]

$$4C_6F_5MgBr + SiCl_4 \xrightarrow[\text{REFLUX}]{\text{DIETHYL ETHER}} (C_6F_5)_4Si$$

The interest in aromatic fluorocarbons as a basis for new thermally stable polymers had led to this work but the product was shown to be thermally less stable than its hydrocarbon analogue. Attempted preparation of bis(pentafluorophenyl)silicon dichloride, the precursor of polybis(pentafluorophenyl)siloxane, from pentafluorophenylmagnesium bromide and silicon tetrachloride (2:1 molar ratio) led to tetrakis-(pentafluorophenyl)silane and unidentified polymeric material.

A brief communication[95] reported a reaction of the Grignard reagent with trimethylchlorosilane which afforded trimethylpentafluorophenylsilane.

$$C_6F_5MgBr + (CH_3)_3SiCl \xrightarrow[\text{REFLUX}]{\text{DIETHYL ETHER}} (CH_3)_3SiC_6F_5$$

Trimethylpentafluorophenylsilane is a stable, colourless liquid b.pt. 172°.

A recent report[50] describes the photochemical reactions of trichlorosilane and trimethylsilane with hexafluorobenzene

$$Cl_3SiH + C_6F_6 \xrightarrow[\text{240 HOURS}]{\text{U.V.}} C_6F_5SiFCl_2 \qquad (61\%)$$

$$(CH_3)_3SiH + C_6F_6 \xrightarrow[\text{240 HOURS}]{\text{U.V.}} C_6F_5Si(CH_3)_3 \quad (53\%)$$

and hydrolysis of dichlorofluoro(pentafluorophenyl)silane with water leads to the white solid polysiloxane, which in turn is decomposed by sodium hydroxide to give pentafluorobenzene.

$$C_6F_5SiFCl_2 \xrightarrow{H_2O} [C_6F_5SiO_{1.5}]_n \xrightarrow[100^{\circ}]{\text{NaOH aqua}} C_6F_5H \qquad (74\%)$$

b) Perfluoroaryl Derivatives of Germanium.

The preparation of tetrakis(pentafluorophenyl)germane and tris(pentafluorophenyl)chlorogermane from germanium tetrachloride and pentafluorophenyl-lithium has been reported.[96] Both products are white, air stable solids.

c) Perfluoroaryl Derivatives of Tin.

Pentafluorophenyl derivatives of tin have been relatively widely studied, partly because of their value as precursors of perfluoroaryl compounds of other elements, e.g. boron. Compounds in the series $Me_{4-x}Sn(C_6F_5)_x$, $Ph_{4-x}Sn(C_6F_5)_x$, (x = 1-4), $(C_6F_5)_{4-x}Sn(p\text{-tolyl})_x$ (x = 1 or 2) have been investigated.[51,53] Some butylpentafluorophenyltin compounds have also been prepared.[97] These products can be obtained from the Grignard reagent and the relevant metal halide in diethyl ether. Reaction times may be relatively long in some cases but good yields can usually be obtained. By using pentafluorophenyllithium reaction times can be readily reduced in a number of cases.[98]

The trifluoromethyl group attached to tin leads to thermal instability in trimethyl(trifluoromethyl)tin[99] because of migration of fluorine to the metal, but this type of instability does not occur in pentafluorophenyl compounds. e.g. trimethylpentafluorophenyltin is stable at 250° but decomposes at 350°.[51]

Perfluoroaryltin compounds are immiscible with water but dissolve readily in aqueous ethanol from which solution they can be recovered intact. They resemble other fluorocarbon tin derivatives in their susceptibility to nucleophilic attack at the metal atom which in this case results in facile cleavage of pentafluorophenyl as pentafluorobenzene. This easy displacement of the perfluoroaryl

$$Me_3SnC_6F_5 \xrightarrow[EtOH]{NaOH} Me_3SnOH + C_6F_5H$$

group is probably due to the high polarity of the tin-carbon bond in these compounds. The hydrolysis has been shown to be catalysed by halide ion.[51] Addition of trace amounts of potassium fluoride to an aqueous alcoholic solution of trimethylpentafluorophenyltin results in the rapid formation of trimethyltin hydroxide and pentafluorobenzene. A study of this phenomenon with respect to the series of compounds $(CH_3)_3MC_6F_5$ (where M = Si, Ge, Sn or Pb) will be discussed in chapter three.

Tetrakis(pentafluorophenyl)tin, whilst being markedly less reactive than tetraphenyltin in reactions with boron halides or bromine will react with sulphur tetrafluoride to yield tris(pentafluorophenyl)tin fluoride.[100]

$$(C_6F_5)_4Sn \; + \; SF_4 \longrightarrow (C_6F_5)_3SnF$$

All three pentafluorophenyltin chlorides have been prepared. Tris(pentafluorophenyl)p-tolyltin reacts with hydrogen chloride at 100° to give tris(pentafluorophenyl)tin chloride in excellent yields.[51]

$$(C_6F_5)_3Sn(\text{p-tolyl}) + HCl \longrightarrow (C_6F_5)_3SnCl \; + \; C_6H_5CH_3$$

The same product can be obtained from the Grignard reagent and stannic chloride.[53] Bis(pentafluorophenyl)tin dichloride and pentafluorophenyltin trichloride are conveniently prepared by cleavage reactions of pentafluorophenyl-metal compounds with stannic chloride.

$$Me_2Sn(C_6F_5)_2 + SnCl_4 \longrightarrow Me_2SnCl_2 + (C_6F_5)_2SnCl_2$$[53]

$$MeHgC_6F_5 + SnCl_4 \longrightarrow MeHgCl + C_6F_5SnCl_3$$[51]

Recently redistribution reactions between tin(IV) chloride and tetrakis(pentafluorophenyl)tin have been reported[101] but reaction times are long and some products were stated to be impure.

$$(C_6F_5)_4Sn + SnCl_4 \xrightarrow[160^\circ]{\text{7 DAYS}} (C_6F_5)_3SnCl$$

$$(C_6F_5)_4Sn + SnCl_4 \xrightarrow[140^\circ]{\text{11 WEEKS}} C_6F_5SnCl_3 \quad \text{(IMPURE)}$$

d) Perfluoroaryl Derivatives of Lead.

Trimethylpentafluorophenyl-lead and pentafluorophenyltriphenyl-lead can be obtained from the Grignard reagent and the appropriate metal halide in diethyl ether.[52] Tetrakis(pentafluorophenyl)lead is produced in low yield when a mixture of lead(II) chloride and an ethereal solution of pentafluorophenylmagnesium bromide is stirred for 24 hours.

$$R_3PbCl + C_6F_5MgBr \longrightarrow R_3PbC_6F_5 \qquad (R = Me, Ph)$$

$$2PbCl_2 + 4C_6F_5MgBr \longrightarrow (C_6F_5)_4Pb + Pb + 2MgBr_2 + 2MgCl_2$$

Trimethylpentafluorophenyl-lead is an air stable, moisture sensitive, colourless liquid b.pt. 50-52° at 10^{-2} mm. while the other two derivatives are air stable, white solids.

The relative ease of hydrolysis of these compounds by water, under vacuum, was found to be

$$Me_3PbC_6F_5 > Ph_3PbC_6F_5 > (C_6F_5)_4Pb$$ [52]

With dry hydrogen chloride, trimethylpentafluorophenyl-lead reacts quantitatively at room temperature giving pentafluorobenzene and trimethyl-lead chloride.

$$Me_3PbC_6F_5 + HCl \longrightarrow Me_3PbCl + C_6F_5H$$

Under similar conditions pentafluorophenyltriphenyl-lead yields benzene and pentafluorobenzene in the approximate ratio 2·5:1. These results are in agreement with those obtained for order of electrophilic cleavage from tin, however, cleavage from lead occurs more easily.

7. Perfluoroaryl Derivatives of Phosphorus and Arsenic.

Pentafluorophenyl derivatives of phosphorus and arsenic have not been widely studied compared with perfluoroalkyl derivatives of these elements. The latter have been the subject of considerable research but their discussion is beyond the framework of this thesis, except where comparisons can be drawn in chapter three.

Using the Grignard reagent the derivatives $(C_6F_5)_3M$ (where M = P, As, Sb) have been obtained.[44,95] The chlorides $C_6F_5PCl_2$ and

$(C_6F_5)_2PCl$ result from reactions between pentafluorophenylmagnesium bromide and phosphorus trichloride in stoichiometric quantities.[102] Hydrolysis of the monochloride yields bis(pentafluorophenyl)phosphinous acid, $(C_6F_5)_2POH$ and similarly the dichloride gives the phosphorous acid $C_6F_5P(OH)_2$. The infrared spectrum of the mono-sodium salt of the latter indicates the structure $C_6F_5PH(OONa)$ rather than $C_6F_5POH(ONa)$ so that the formula of the acid should be $C_6F_5PO_2H_2$. Reaction between bis(pentafluorophenyl)phosphorus chloride and ammonia produces the corresponding amide $(C_6F_5)_2PNH_2$ but, unexpectedly, with dimethylamine it yields $(C_6F_4NMe_2)_2PNMe_2$ by nucleophilic attack on the ring.

8. Perfluoroaryl Derivatives of Sulphur.

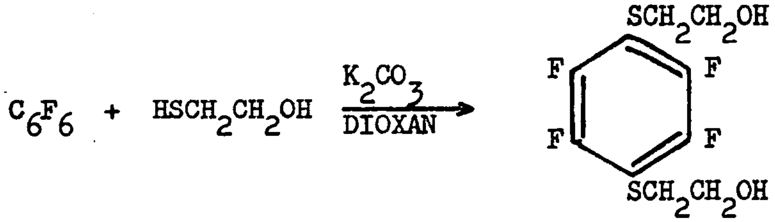
The development of the chemistry of perfluoroaryl and polyfluoroaryl sulphur compounds is relatively recent and the first perfluoroaryl sulphur compounds were reported only six years ago.[103] Pentafluorothiophenol and 2,3,5,6-tetrafluorothiophenol were prepared by the action of sodium hydrogen sulphide in pyridine on hexa- and penta-fluorobenzene respectively.

$$\text{e.g.}\quad C_6F_6 + NaSH \xrightarrow[\text{REFLUX}]{\text{PYRIDINE}} C_6F_5SH + NaF$$

Both fluoro-thiols were obtained as pungent liquids with strongly acidic properties. Several derivatives of the two compounds were also described,[103] and an extension of the work[104] reports the preparation of a series of partly fluorinated aromatic sulphides, the susceptibility of fluoro-aromatic sulphur compounds to nucleophilic attack, pentafluoro-, 2,3,5,6-tetrafluoro-, and 4-acetamido-2,3,5,6-tetrafluorobenzenesulphonyl chloride and a series of derivatives.

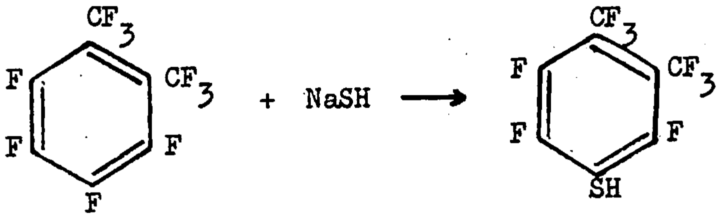
New methods for the preparation of highly fluorinated thiophenols have recently been described.[105] The monolithium derivative of 1,2,3,4-tetrafluorobenzene gave 1,2,3,4-tetrafluorothiophenol with sulphur, plus a small amount of bis(1,2,3,4-tetrafluorophenyl)disulphide.

2-Mercaptoethanol reacts with hexafluorobenzene to give a disubstituted product in good yield even when only one molecular proportion of the nucleophile is used,[106] and in this respect differs from other bifunctional nucleophiles.



Reactions of perfluoro-o- and -p-xylene with sulphur containing nucleophiles have been studied[107] and several new perfluoroaryl sulphur compounds described,

e.g.



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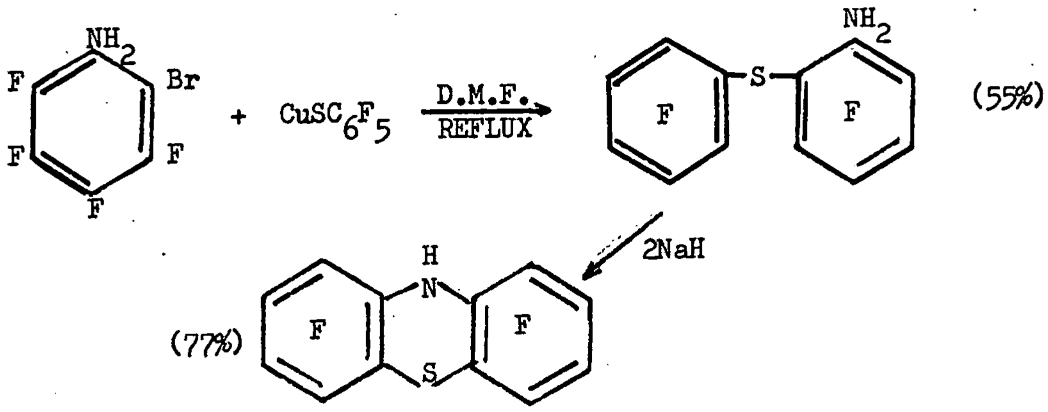
2,5-difluoro-3,6-bistrifluoromethylbenzene-1,4-dithiol was prepared from perfluoro-p-xylene in an analogous reaction[106] and recently tetrafluorobenzene-1,4-dithiol has been isolated from a reaction between 1,4-dilithiotetrafluorobenzene and elemental sulphur.[108]

Bis-(pentafluorophenyl)sulphide is formed in high yield when elemental sulphur and bis-(pentafluorophenyl)mercury are heated in a sealed evacuated tube,[57] though reaction times are long.

$$(C_6F_5)_2Hg \; + \; S \; \xrightarrow[\text{7 DAYS}]{250^{\circ}} \; (C_6F_5)_2S \qquad (82\%)$$

The same product obtains from an analogous reaction between pentafluorophenylmercuric chloride and the element[57] whilst other workers[109] prepared bis-(pentafluorophenyl)sulphide from bromopentafluorobenzene and cuprous pentafluorothiophenoxide in dimethylformamide. The product is a white, crystalline solid (m.pt. 81•5°).

An extension of this reaction has been used to prepare 2-amino-3,4,5,6-tetrafluorophenyl pentafluorophenyl sulphide and this amino-sulphide has been converted into octafluorophenothiazine by treatment with sodium hydride in boiling dioxan.[110]



9. Perfluoroaryl Derivatives of other Metals and Metalloids.

The discussion of the preparation and chemistry of perfluoroaryl derivatives of aluminium necessitates some reference to, and comparison with pentafluorophenyl derivatives of other group III elements and so the latter are briefly described in this section.

Perfluoroaryl derivatives of some transition elements are discussed because of the current interest in the preparation and study of these compounds.

a) Boron.

Perfluoroaryl derivatives of boron have been described in several publications[47,48,83,92,111,112,113,114] and are of interest due to the instability of the corresponding fluoroalkylboron compounds. The only perfluoroalkylboron compound to be isolated, trifluoromethylboron difluoride, is very unstable and decomposes to boron trifluoride via migration of fluorine from carbon to boron. This instability persists in the corresponding perfluorovinyl derivatives, although it is less marked. It has been suggested that this mode of regression is reduced in perfluoroarylboron compounds by absence of fluorine from the α carbon atom and by π-p interaction between the ring and boron. Several routes to pentafluorophenylboron compounds are available. Pentafluorophenylboron dichloride, bis(pentafluorophenyl)boron chloride and pentafluorophenylboron difluoride can be prepared by reacting the appropriate halide with trimethylpentafluorophenyltin,[48,83]

$$Me_3SnC_6F_5 + 2BCl_3 \xrightarrow{25^\circ} C_6F_5BCl_2 + MeBCl_2 + Me_2SnCl_2$$

$$Me_3SnC_6F_5 + 2BF_3 \xrightarrow{CCl_4,\ 25^\circ} C_6F_5BF_2 + Me_3SnBF_4$$

or with dimethylbis(pentafluorophenyl)tin.

$$Me_2Sn(C_6F_5)_2 + BCl_3 \xrightarrow{100^\circ} (C_6F_5)_2BCl + Me_2SnCl_2$$

Cleavage of other perfluoroaryl metal derivatives with boron trichloride also gives pentafluorophenylboron dichloride.

$$MeHgC_6F_5 + BCl_3 \xrightarrow{20^\circ} MeHgCl + C_6F_5BCl_2 \quad {}^{83}$$

$$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2 + 2BCl_3 \xrightarrow{160^\circ} 2C_6F_5BCl_2 + (\pi\text{-}C_5H_5)_2TiCl_2 \quad {}^{115}$$

Both the dichloride and difluoride are colourless, moisture sensitive liquids; they both form a white solid 1:1 complex with pyridine.

Perfluoroarylboron dihalides are unstable with respect to boron trihalides but the reaction involved is simple disproportionation and not migration of fluorine ortho to boron in the perfluoroaryl group thus giving a benzyne.[116]

Tris(pentafluorophenyl)boron can be prepared as an etherate by a reaction between pentafluorophenylmagnesium bromide and boron trichloride in ether-toluene solution. Ether is easily removed under vacuum or at

60°.[92] The same product is readily obtained from pentafluorophenyllithium and boron trichloride in pentane.[47,111]

$$3C_6F_5Li + BCl_3 \xrightarrow[-20^\circ]{\text{PENTANE}} (C_6F_5)_3B + 3LiCl$$

Tris(pentafluorophenyl)boron is a white solid, monomeric in benzene, which is relatively thermally stable but which is cleaved by water to give some pentafluorobenzene.

Hydrolysis of pentafluorophenylboron dihalides yields the corresponding boronic acid[83]

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

and pentafluorophenylboron difluoride forms potassium pentafluorophenyltrifluoroborate when condensed onto an aqueous solution of potassium fluoride.[114]

$$C_6F_5BF_2 + KF \text{ aqua} \longrightarrow K^+[C_6F_5BF_3]^-$$

b) Gallium, Indium and Thallium.

Tris(pentafluorophenyl)gallium may be obtained as an etherate by using the Grignard reagent,

$$3C_6F_5MgBr + GaCl_3 \xrightarrow{\text{ETHER TOLUENE}} (C_6F_5)_3Ga{\cdot}O(C_2H_5)_2$$

and the etherate sublimes unchanged.[92] The corresponding indium derivative is similarly obtained, but when indium tribromide is used the product is bis(pentafluorophenyl)indium bromide, even under forcing conditions.

Perfluoroaryl derivatives of thallium have been the subject of several reports,[92,117,118,119] and indeed are the first known fluorocarbon compounds of that element. Tris(pentafluorophenyl)-thallium,[92] from the Grignard reagent in ether-toluene solution, and compounds of the type $(C_6F_5)_2TlX$ (X = halogen, nitrate etc.), are being investigated. Bis(pentafluorophenyl)thallium bromide, unusually, is very soluble in organic solvents and has been converted to the corresponding fluoride, chloride, sulphate, nitrate, acetate and trifluoroacetate.[118,119]

c) Zinc.

Zinc chloride reacts with pentafluorophenylmagnesium bromide in ethereal solution to give bis(pentafluorophenyl)zinc etherate,[120]

$$ZnCl_2 + 2C_6F_5MgBr \xrightarrow{ETHER} (C_6F_5)_2Zn{\cdot}O(C_2H_5)_2 + MgBr_2 + MgCl_2 \quad (15\%)$$

but in this case the ether is removed by vacuum distillation. The product readily forms co-ordination complexes with various oxygen, nitrogen, phosphorus and arsenic containing ligands.

d) Transition Metals.

Research into perfluoroaryl derivatives of transition elements has developed rapidly in the last few years mainly because of the interest in factors responsible for stabilising transition metal to carbon σ bonds. Many pentafluorophenyl transition metal compounds are now known and the subject has been reviewed recently by Stone.[121]

Pentafluorophenyl derivatives of titanium, iron, and manganese were the first perfluoroaryl transition metal compounds to be reported.[115]

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

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

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

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

These substances were shown to be extraordinarily thermally robust for compounds containing organic groups bound to the metal by carbon-metal σ-bonds. e.g. pentafluorophenylmanganese pentacarbonyl was undecomposed after 72 hours in vacuo at 138° but some darkening did occur after 72 hours at 162° when 13% of the carbon monoxide expected for complete decomposition was recovered. Bis(cyclopentadienyl)bis-(pentafluorophenyl)titanium is thermally stable in vacuo at 110°, but pyrolysis at 150° yields small amounts of the compound $(\pi C_5H_5)_2Ti(C_6F_5)F$, a yellow solid formed by migration of fluorine from carbon to the metal. Thus pentafluorophenylmanganese pentacarbonyl and bis(cyclopentadienyl)bis(pentafluorophenyl)titanium are more stable than their respective phenyl analogues which both decompose under the conditions described.

Pentafluorophenyl derivatives of nickel,[122] cobalt,[122] platinum[123] and zirconium[124] have also been reported.

CHAPTER TWO

DISCUSSION OF EXPERIMENTAL WORK

1. Preparation of Compounds of the Type $(CH_3)_3MC_6F_5$ (M = Si,Ge,Sn,Pb).

Pentafluorophenylmagnesium bromide has been used to prepare compounds of the type $(CH_3)_3MC_6F_5$ for the elements silicon, germanium, tin and lead, by reaction of the Grignard reagent with the appropriate trimethyl halo derivative of the element,

e.g. $$(CH_3)_3SiGe + C_6F_5MgBr \xrightarrow[\text{REFLUX}]{Et_2O} (CH_3)_3SiC_6F_5 \qquad (53\%)$$

and table 1 gives the results, boiling points, and yields of the products.

TABLE 1.

Starting Halide	Mole Ratio Grignard. Reagent to Halide	Solvent	Reaction Time	Yield	B.pt.
$(CH_3)_3SiCl$	1:1	Diethyl Ether	72 hours	53%	172°
$(CH_3)_3GeBr$	1:1	Diethyl Ether	36 hours	44%	173°
$(CH_3)_3SnBr$	1:1	Diethyl Ether	48 hours	60%	34-36°/ 10^{-2}mm.
$(CH_3)_3PbCl$	2.8:1	Diethyl Ether + Benzene	48 hours	25%	50-52°/ 10^{-3}mm.

All four products were colourless liquids and whilst the first three compounds were air and water stable after purification by gas chromatography the lead derivative, which was too involatile to be purified in that way, rapidly deposited a white solid on exposure to the atmosphere. This instability was shown to be due to hydrolysis by atmospheric moisture, or by absorbtion of water from glass apparatus giving trimethyl-lead hydroxide, and the perfluoroaryl derivative was unaffected when stored under dry nitrogen in apparatus which had been "baked" for twenty-four hours at 120°.

Cleavage of the Pentafluorophenyl Group from Compounds in the Series $(CH_3)_3MC_6F_5$ (where M = Si,Ge,Sn,Pb).

Pentafluorophenyltin compounds have been shown to undergo an unusual halide- or cyanide-ion catalysed hydrolysis[51] and therefore the synthesis of this series of compounds was carried out to enable a study of ease of cleavage of pentafluorophenyl within the group to be undertaken.

Thus in the series $(CH_3)_3MC_6F_5$ the order of ease of hydrolysis has been found to be

$$(CH_3)_3SiC_6F_5 < (CH_3)_3GeC_6F_5 \ll (CH_3)_3SnC_6F_5 \ll (CH_3)_3PbC_6F_5$$

In the case of the silicon, germanium, and tin derivatives cleavage of pentafluorophenyl as pentafluorobenzene occurs in the aqueous alcoholic solution when halide ion is present and comparison with control experiments showed that the three entities water, alcohol, and halide ion (KF was used) were essential to effect this hydrolysis. Before the experiment was undertaken each compound was purified by gas chromatography to ensure a high state of purity and because it was apparent, especially in the case of tin, that unless the compounds were purified in this way, decomposition occurred on standing in air. Addition of a trace of potassium fluoride to aqueous alcoholic solutions was sufficient to cause hydrolysis and whilst no immediate apparent change occurred in the solutions of the silicon and germanium compounds pentafluorobenzene could be shown to be present (by gas chromatography) in appreciable amounts within 48 hours. With trimethylpentafluorophenyltin immediate precipitation was observed and trimethyltin hydroxide could easily be separated. Trimethylpentafluorophenyl-lead was found to be hydrolytically unstable during the preparation and when one drop of water was added to the ethanolic solution immediate and considerable precipitation occurred to yield pentafluorobenzene and trimethyl-lead hydroxide and this result is in agreement with the results of other workers[52] published after the present work had been carried out, who also found the lead derivative to be unstable to water.

Mechanism of Cleavage.

It is well known that fluorocarbon derivatives of group IVb elements are susceptible to nucleophilic displacement of fluorocarbon groups e.g. fluorocarbon groups in polymeric and non-polymeric silicon compounds are easily removed as fluoroalkanes by dilute aqueous base when fluorine is in an α or β position and nucleophilic attack on silicon is evidently favoured by the electronegative polyfluoroalkyl groups and this behaviour is mirrored in derivatives of germanium, tin, and lead. It is surprising however that hydrolysis is catalysed by halide or cyanide ions and indeed that it appears to be general. Chambers and Chivers[51] and Seyferth and Co-workers[67] have reported this type of hydrolysis and the former have suggested that initial co-ordination of halide ion to the metal must be involved, giving a five covalent species, thus enabling co-ordination of water and finally elimination of pentafluorobenzene.

$$\begin{tikzcd}
\mathrm{Me_3MC_6F_5} + \mathrm{X}^- \arrow[r] & {[\mathrm{Me_3(C_6F_5)MX}]^-} \arrow[d, shift left] \\
\mathrm{Me_3MOH} + \mathrm{C_6F_5H} + \mathrm{X}^- & {[\mathrm{Me_3(C_6F_5)M(OH_2)X}]^-} \arrow[u, shift left] \arrow[l]
\end{tikzcd}$$

Direct displacement of pentafluorophenyl as a carbanion by fluoride ion is unlikely since all the trimethylmetal fluorides would not be readily hydrolysed. Stable complex anions containing fluorocarbon groups have been reported for boron and germanium e.g. $K[C_6F_5BF_3]$[114] and $K_2[CF_3GeF_5]$[125] illustrating the fact that a fluorocarbon group enables the central atom to increase its covalency. Pentafluorophenyl also enhances the acceptor properties of mercury since bis(pentafluorophenyl)-mercury forms some stable co-ordination complexes,[73] but attempts to isolate similar complexes with tetrakis(pentafluorophenyl)tin were unsuccessful.[51]

There is abundant evidence for five-co-ordinate intermediates; several authors[126,127,128] have studied cleavage reactions of hydrocarbon derivatives of group IV elements and concluded that the mechanism involved a five co-ordinate species. Dessy[126] suggests initial co-ordination of halide ion in the acetolysis of tributyltin hydride. Chipperfield and Prince[127] conclude that a similar species is formed in the hydrolysis of the compounds $(CH_3)_3MCl$ (M = Si, Ge) and Kuivila and Levins[128] postulate a five co-ordinate mechanism for the protonolysis of the Sn-H bond.

Factors affecting ease of hydrolysis.

The variation in ease of displacement of the pentafluorophenyl group in a halide-ion catalysed process would depend on the following factors:

(i) The ease with which the central atom expands its covalency.
(ii) The polarity of the metal-carbon bond.
(iii) The size of the central atom.

(i) The availability of empty d orbitals for chemical bonding is of great significance and this allows the occurrence of co-ordination numbers greater than four, in practice five or six, which can be effected by donation of electrons from ligands into these d orbitals. Capability to co-ordinate increases with atomic number both for steric reasons and because $d\pi - p\pi$ bonding decreases rapidly as atomic number increases owing to less effective overlap of orbitals.[129] Beattie[130] has reviewed the acceptor properties of the quadripositive metal derivatives and illustrates the fact that there is considerable disagreement about the exact sequence of electronegativity values to be assigned to silicon, germanium, tin, and lead in the quadripositive state,[131] and reports that the acceptor strength order indicated for tetrahalides is Sn $\gg$ Ge $>$ Si, and whilst the majority of observations refer to 1:2 addition compounds, and can be understood in terms of a co-ordination number of six, it appears that a co-ordination number of five is by no means rare in solution.

(ii) Eaborn and co-workers[132] have studied relative electron releasing effects of the $(CH_3)_3M-$ group (where M = Si, Ge, Sn) and shown that the order of release of electrons is $(CH_3)_3Sn > (CH_3)_3Ge > (CH_3)_3Si$. In the compounds under discussion the metals are bonded to more electronegative species, and as a consequence of increasing electropositivity from silicon to lead, the bonds will become more polar and thus more liable to ionic attack as we move down the group. Table two[129] gives the inter-atomic distances and strengths of bonds between carbon and group IV elements.

TABLE TWO

Element	Covalent Radius Å	M-C Distance Å	M-C Bond Strength K.Cal.
Si	1·13	1·90	60
Ge	1·21	1·98	
Sn	1·41	2·18	54
Pb	1·52	2·29	31

It can be seen that as inter-atomic distance increases bond strength falls off rapidly.

(iii) The atoms of the four elements increase in size from silicon to lead and many differences in properties of their compounds can be attributed to this fact alone. In this order the outer electrons are less firmly held and their increasing freedom lends the element a more metallic character. Thus trialkylmetal hydroxides increase in basicity down the group, and the lead compounds are strongly basic and thus, once formed, would increase the rate of decomposition of fluoroaryl derivatives. Clearly any increase in size of the central metal atom will facilitate nucleophilic attack if steric factors are involved and it has already been stated that atomic size affects the ease with which an atom can expand its covalency, and the polarity of metal-carbon bonds. Therefore all three factors work in the same direction throughout the series and the result is a very marked difference in hydrolytic stability from silicon to lead.

2. Cleavage Reactions of Methylpentafluorophenylmercury with Inorganic Halides.

Methylpentafluorophenylmercury has been shown to react with hydrogen chloride to yield pentafluorobenzene and methylmercury chloride[73] and preliminary investigations[51] showed that reaction with inorganic halides might provide a route to pentafluorophenyl derivatives of some other elements. The particular virtue of the reaction is that soluble perfluoroaryl products are obtained, whilst the only by-product is a methylmercury halide and the latter can readily be removed because of their comparative insolubility. In fact, when the products are liquids, in some cases only a simple filtration is necessary to remove the mercury compound which has been precipitated, whilst petroleum ether has been found to dissolve pentafluorophenyl derivatives but not methylmercury halides.

e.g. $CH_3HgC_6F_5 + GeBr_4 \longrightarrow C_6F_5GeBr_3$(liquid) $+ CH_3HgBr\downarrow$

$CH_3HgC_6F_5 + AlBr_3 \longrightarrow C_6F_5AlBr_2$ (a solid soluble in petroleum) $+ CH_3HgBr$

In this way reactions of methylpentafluorophenylmercury with many inorganic halides have been studied and several new compounds have been isolated. Results obtained using bromides are shown in table three.

TABLE THREE

Halide	Mole Ratio Mercurial: Halide	Time and Temp.	Product	Yield
PBr_3	1:1	2 weeks at 60°	$C_6F_5PBr_2$	84%
$AsBr_3$	1:1	2 weeks at 60°	$C_6F_5AsBr_2$	83%
$GeBr_4$	1:1	2 weeks at 60°	$C_6F_5GeBr_3$	67%
$AlBr_3$	1:1·1	120 hours at 70°	$C_6F_5AlBr_2$	100%
$C_6F_5AlBr_2$	1·8:1	96 hours at 45°	$(C_6F_5)_2AlBr$	80%

All of the reactions were contained in sealed, evacuated tubes which were heated by total immersion in an oilbath, and with the exception of the reaction between pentafluorophenylaluminium dibromide and the mercurial, they were carried out in absence of solvent. In the excepted case petroleum ether was used to promote better mixing of the reactants. It will be noted that reaction times were long and, in cases where reaction had not gone to completion, difficulties arose in trying to obtain pure products. These difficulties were the greater because the products were moisture sensitive, whilst the aluminium derivatives were also oxygen sensitive.

Reaction with Chlorides.

Similar reactions were investigated using inorganic chlorides and in particular reactions between sulphur dichloride and methylpentafluorophenylmercury were studied in the hope that they might lead to perfluoroarylsulphur compounds, but they were not successful. Reactions with chlorides are summarized in the following table. (page 56).

As before the reactions were contained in sealed, evacuated tubes and it can be seen immediately that there is a considerable difference in the reactivity of the mercurial towards different halides and also that, in general, by comparison of tables three and four it can be said that chlorides react less readily than do bromides.

TABLE FOUR

Halide	Mole Ratio Mercurial: Halide	Time and Temp.	Main Product	Yield
BCl_3*	1:1		$C_6F_5BCl_2$	84%
$SiCl_4$	1:1	Several Days 160°	No reaction	
$GeCl_4$	1:1	Several Days 160°	No reaction	
$SnCl_4$*	1:1		$C_6F_5SnCl_3$	80%
PCl_3	1:1	Several Days 100°	$C_6F_5PCl_2$	50%
$AsCl_3$	1:1	Two days 74°	$(C_6F_5)_2Hg$	Almost Quantitative
SCl_2	1:1	Several Days 70°	$(C_6F_5)_2Hg$	60%
	2:1		$(C_6F_5)_2Hg$	Almost Quantitative
$SOCl_2$	1:1	5 Days 74°	$(C_6F_5)_2Hg$	70%

* Ref. 83.

a) Reaction with Aluminium Halides.

The Preparation of Pentafluorophenylaluminium Dibromide and Bis(pentafluorophenyl)aluminium Bromide.

Cleavage reactions of methylpentafluorophenylmercury with aluminium tribromide proceed readily in absence of solvent to give good yields of pentafluorophenylaluminium dibromide.

$$CH_3HgC_6F_5 + AlBr_3 \longrightarrow C_6F_5AlBr_2 + CH_3HgBr$$

Reaction begins immediately at room temperature and is complete after a few days at 60-100°. Extraction with 40° petroleum, filtration to remove methylmercury bromide and removal of solvent by vacuum transfer leaves the aluminium compound in quantitative yield as a colourless, viscous, liquid which slowly solidifies on pumping. In practice a slight excess of aluminium tribromide (ca. 10%) is used and has been found to give a cleaner product, free from any unreacted mercurial, which is readily soluble in petroleum. However the mercurial can be removed from the product by prolonged pumping under high vacuum, when it is quite volatile.

Pentafluorophenylaluminium dibromide is a, translucent, crystalline, solid (m.pt. 69-71°) which is extremely sensitive to moisture and oxygen and the properties and reactions of the compound are discussed in section three of this chapter.

Reaction of a further mole of methylpentafluorophenylmercury with pentafluorophenylaluminium dibromide in petroleum yields bis(pentafluorophenyl)aluminium bromide as a viscous liquid, which again solidifies on prolonged pumping, after isolation in the same manner.

$$CH_3HgC_6F_5 \; + \; C_6F_5AlBr_2 \xrightarrow{\text{PETROLEUM}} (C_6F_5)_2AlBr + CH_3HgBr\downarrow$$

Again the product is extremely sensitive to oxygen and moisture and its characterisation is discussed in the next section of this chapter.

When two moles of the mercurial were reacted with aluminium tribromide a mixture of pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide was obtained.

$$2CH_3HgC_6F_5 \; + \; AlBr_3 \; \xcancel{\longrightarrow} \; (C_6F_5)_2AlBr \; + \; 2CH_3HgBr$$

Even after long periods the same result was obtained, whether neat or in a solvent, and therefore the method was not pursued. A reaction between methylpentafluorophenylmercury and aluminium trichloride gave a small amount of a brown, viscous liquid which appeared, by comparison of infrared data, to be pentafluorophenylaluminium dichloride, but the product was not fully characterised. Reaction was much slower than with the bromide and a higher temperature was required.

b) Reaction with Group IV Halides.

Group IV metal tetrahalides display a wide range of reactivity towards methylpentafluorophenylmercury and this has been demonstrated by studying reactions of chlorides and bromides. Thus silicon tetrachloride and germanium(IV) chloride both failed to react with the mercurial even on prolonged heating at 160°, whilst germanium(IV) bromide reacted rather slowly at 60° to yield pentafluorophenyltribromogermane as a colourless, moisture sensitive liquid which boiled at 51-52° under a "sticking" vacuum.

$$GeBr_4 + CH_3HgC_6F_5 \longrightarrow C_6F_5GeBr_3 + CH_3HgBr\downarrow$$

Tin tetrahalides (i.e. chloride and bromide) have been shown[51] to react readily with one mole of methylpentafluorophenylmercury but reaction with a second mole is very slow. Therefore the order of reactivity is $SiCl_4$, $GeCl_4 < GeBr_4 \ll SnCl_4 < SnBr_4$. The acceptor properties of these halides decrease in the series Sn > Ge > Si[130] and this is partly due to a decrease in size of the central metal atom and decrease in the availability of d orbitals. It can be seen that acceptor strength, or more correctly electrophilic strength of the halide has a great influence on its reactivity towards the mercurial.

The reaction would have been particularly valuable as a route to the pentafluorophenylsilicon halides and indeed it may be possible in the future to effect reaction between methylpentafluorophenylmercury and silicon tetrabromide.

c) <u>Reaction with Group V Halides.</u>

Phosphorus and arsenic tribromides have been shown to react with methylpentafluorophenylmercury to yield pentafluorophenylphosphorus dibromide and pentafluorophenylarsenic dibromide respectively.

$$CH_3HgC_6F_5 + PBr_3 \longrightarrow C_6F_5PBr_2 + CH_3HgBr \downarrow$$

Again reactions were quite slow and apparently endothermic and difficulty was experienced in obtaining pure products, and this seemed to be due to the slight solubility of methylmercury bromide in the products. Both the phosphorus and arsenic compounds were obtained as colourless liquids which fumed in moist air. Corresponding reactions with the trichlorides were even slower, and with arsenic trichloride the main product was bis(pentafluorophenyl)mercury formed by disproportionation of the starting material. While this work was in progress pentafluorophenylphosphorus chlorides where reported[102] and some of their reactions discussed and therefore no further investigation of these compounds was undertaken.

d) <u>Reactions with Sulphur Dichloride.</u>

When it became apparent that methylpentafluorophenylmercury reacted with quite a wide variety of inorganic halides reactions with sulphur dichloride were investigated in the hope that the then unknown bis(pentafluorophenyl)sulphide might be obtained.

$$2CH_3HgC_6F_5 + SCl_2 \xcancel{\longrightarrow} (C_6F_5)_2S + 2CH_3HgCl$$

Unfortunately the sulphur compound was not sufficiently reactive and in fact disproportionation of the mercurial occurred. A similar result was observed when an equimolar reaction was investigated.

$$CH_3HgC_6F_5 + SCl_2 \not\longrightarrow C_6F_5SCl + CH_3HgCl$$

In the latter case a small amount of yellow, viscous liquid was obtained and this could have been pentafluorophenylsulphur chloride (infrared) but the great majority of the mercurial had undergone disproportionation.

<u>Methylpentafluorophenylmercury.</u>

A discussion of the properties of this compound is relevant here because they are of central importance to these reactions. Methylpentafluorophenylmercury is a white, crystalline, low-melting (36°), volatile solid which can be sublimed easily at room temperature under high vacuum. It is insoluble in water but extremely soluble in organic solvents and like many unsymmetrical organomercury derivatives it can be induced to rearrange to the symmetrical compounds, but under normal conditions the equilibrium

$$2CH_3HgC_6F_5 \rightleftharpoons (CH_3)_2Hg + (C_6F_5)_2Hg$$

lies to the left.[81]

$$\text{i.e.} \quad 2CH_3HgC_6F_5 \leftrightharpoons (CH_3)_2Hg + (C_6F_5)_2Hg$$

However, disproportionation into dimethylmercury and bis(pentafluorophenyl)mercury can occur under certain circumstances as a result of removing either one of the symmetrical rearrangement products from the system. Thus disproportionation is encouraged by the precipitation of bis(pentafluorophenyl)mercury from the reaction medium or by evaporation of the volatile dimethylmercury (b.pt. 96°) thereby moving the equilibrium to the right. Care must be taken to prevent disproportionation due to slow evaporation of dimethylmercury during storage and also to ensure that only pure methylpentafluorophenylmercury is used in cleavage reactions, because the presence of bis(pentafluorophenyl)mercury and its subsequent precipitation from the reaction medium may cause complete disproportionation of the methylpentafluorophenylmercury present. Methylmercury halides must also be rigorously eliminated when methylpentafluorophenylmercury is purified because they can act as rearrangement catalysts.[132]

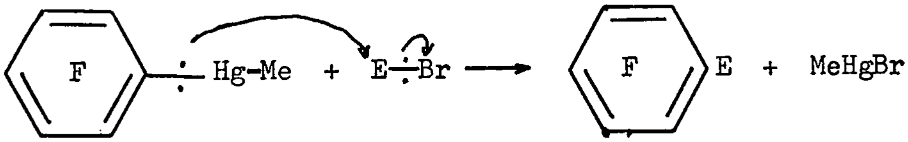
Bis(pentafluorophenyl)mercury.

It is interesting to compare the reactivities of methyl- and bis(pentafluorophenyl)mercury. The latter is much more stable and comparatively inert and whilst it has been used in transmetalation reactions[57] the application was very limited. With aluminium tribromide reaction did occur at 180° but a mixture of aluminium derivatives was obtained and use of methylpentafluorophenylmercury was more convenient. This is in marked contrast to the wide use of diphenylmercury as a phenylating agent.

Mechanism of Cleavage of Methylpentafluorophenylmercury with Inorganic Halides.

Reactions between inorganic halides and methylpentafluorophenylmercury are all electrophilic aromatic substitutions with the inorganic halide, e.g. aluminium tribromide acting as the electrophile and methylmercury being the leaving group.

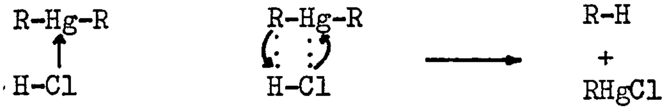
i.e.



The results obtained can be accounted for in terms of increased electrophilic strength of the halides. Bromides are much more effective than chlorides and this can be emphasised by comparing the reactions of germanium(IV) bromide and chloride. The former reacts at 60° to give pentafluorophenyltribromogermane whilst the latter does not react even after prolonged heating at 160°. Furthermore, the strongest electrophile used, aluminium tribromide, produced the best results in the shortest time. The greater Lewis acid characteristics of bromides over chlorides is probably the deciding factor in explaining their greater activity, and this is substantiated by the fact that the higher reactivity of aluminium tribromide over the trichloride, which has been known for a long time, has been shown to be due to the greater acceptor strength of the bromide.[133]

There is a considerable amount of work in the literature concerned with reactions of electrophiles with alkyl- and aryl-mercury compounds, and several authors conclude that four-centre processes are important, with nucleophilic attack at mercury occurring at the same time as electrophilic attack at carbon bonded to mercury.

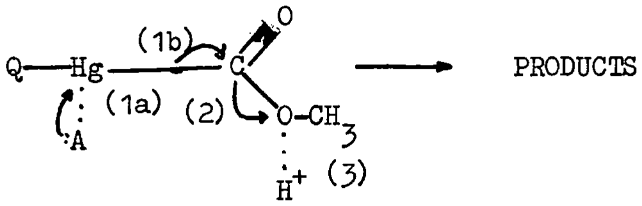
Dessy and co-workers[134,135] have studied the cleavage of organomercury compounds with hydrogen chloride and concluded that attack by chloride ion on mercury and by proton on carbon bonded to mercury combine in a four-centre type mechanism.



Whether the hydrogen chloride is in the form of ion pairs or unionized molecules is immaterial. The important point is that both nucleophilic attack and electrophilic attack occur together, and this conclusion is in agreement with similar proposals by Winstein,[136] based on the reaction of bis-organomercury compounds with mercury(II) chloride, and also supports the supposition of Kaufman and Corwin[137] that unionised hydrogen chloride may be the attacking species in this type of cleavage reaction.

That the concept of electronegativity of groups is very meaningful in the cleavage of aryl-metal bonds has been discounted by several authors.[138,8,85] Eaborn and co-workers have shown that substituent effects on the rate of cleavage of aryl-metal bonds by acids can be explained in terms of ease of attack at the metal-bonded carbon atom. Dessy concludes that electron availability at the metal-bonded carbon atom is more important than electronegativity of the leaving group and uses the term "assistance"[135] to describe the mechanism which he defines as a process including increased reactivity in an adjacent part of the molecule by a co-ordination step.

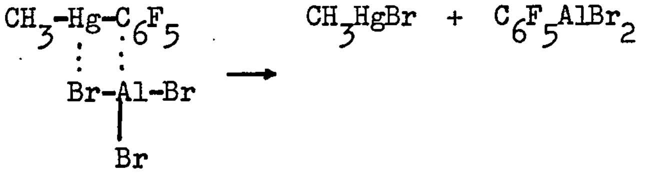
e.g.



The sequence 1a, 1b, 2, 3 is suggested as assisting attack by proton, and the geometry of the molecules may also be important in determining whether multicentre pathways occur.[135]

It has alrady been suggested that cleavage of methylpentafluorophenyl mercury by hydrogen chloride proceeds via a four-centre type mechanism[73] and it is reasonable to propose that cleavage involving inorganic halides is similar.

e.g.



$$\underset{\underset{\displaystyle Br}{|}}{\underset{\vdots\quad\vdots}{CH_3\text{-}Hg\text{-}C_6F_5}} \quad \underset{\text{Br-Al-Br}}{} \longrightarrow CH_3HgBr + C_6F_5AlBr_2$$

If this is so, the course of a particular reaction will also depend on the ability of the inorganic halide to attack the mercurial in this way. In this process we would expect bromides to be more reactive than chlorides because interaction of halogen with mercury occurs at greatest internuclear distances with the larger halogen atoms i.e. I > Br > Cl > F where Hg-X becomes more ionic from iodine to fluorine.[139] Consequently nucleophilic attack by bromine on mercury in a four-centre transition state will be more effective than that by chlorine and this is substantiated by the results obtained.

i.e. order of reactivity for group IV halides

$$SnBr_4 \geqslant SnCl_4 > GeBr_4 > GeCl_4 \sim SiCl_4.$$

When reporting work on pentachlorophenylmercury compounds Dessy and co-workers[84] suggested that in reactions where methylmercury chloride was formed the driving force was the precipitation of that substance from the reaction medium.

e.g. $$ClHgCOOCH_3 + R_2Hg \xrightarrow{SOLVENT} RHgCl\downarrow + RHgCOOCH_3$$

This is in agreement with results obtained in the present work but it must be noted that precipitation of bis(pentafluorophenyl)mercury can also be a directing influence in reactions of methylpentafluorophenylmercury, and it is interesting to note that an attempted exchange between dimethylmercury and pentachlorophenylmercury chloride gave a quantitative yield of bis(pentachlorophenyl)mercury.[84]

The general conclusions which can be drawn from this study of cleavage reactions of methylpentafluorophenylmercury with inorganic halides are that with halides of sufficient electrophilic character, pentafluorophenyl derivatives of other elements can be obtained, and that the reactions can be readily explained on the basis of electrophilic aromatic substitution via a four-centre type mechanism.

Attempted Preparation of Tris(pentafluorophenyl)aluminium.

When cleavage reactions of methylpentafluorophenylmercury with aluminium tribromide led to the isolation of pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide, it was of great interest to try to synthesise tris(pentafluorophenyl)aluminium and this has been attempted in several ways.

Reactions between large excesses of the mercurial and aluminium tribromide produce mixtures which are difficult to separate and replacement of a second bromine on aluminium seems to be slow. Thus three moles of the mercurial with aluminium tribromide did not yield tris(pentafluorophenyl)aluminium,

$$3MeHgC_6F_5 + AlBr_3 \nrightarrow (C_6F_5)_3Al + 3MeHgBr$$

and neither did a reaction between pentafluorophenylaluminium dibromide and two moles of methylpentafluorophenylmercury, and a reaction between bis(pentafluorophenyl)aluminium bromide and one equivalent of methylpentafluorophenylmercury also failed. In most cases starting materials or mixtures of perfluoroarylaluminium bromides were recovered.

When reactions of the above type failed to yield the desired product other routes to tris(pentafluorophenyl)aluminium were investigated. It has been shown recently by other workers[92] that use of pentafluorophenylmagnesium bromide in ether leads to the isolation of an etherate[92] from which solvent cannot be removed. Reactions of pentafluorophenyllithium with aluminium halides were studied in various solvents. When ether was present, etherates were isolated and again solvent could not be removed under vacuum, whilst in hydrocarbon solvents no soluble pentafluorophenyl derivatives could be isolated and this indicates the formation of salts of the type reported by Dickson.[91]

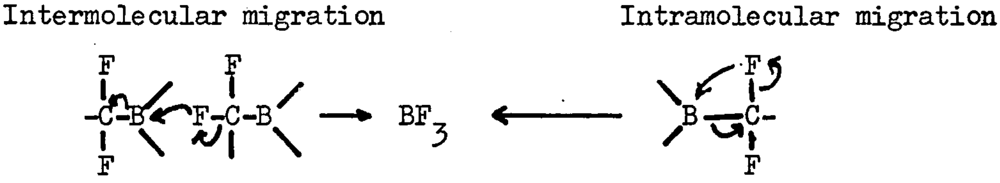
$$\text{i.e.}\quad C_6F_5Li + AlBr_3 \longrightarrow Li[C_6F_5AlBr_3]$$

$$\text{excess}\quad C_6F_5Li + AlBr_3 \longrightarrow Li[(C_6F_5)_3AlBr]\quad \text{etc.}$$

It must be noted however that extraction of the white solids obtained, which had been shown to contain the pentafluorophenyl group (infrared), failed to yield any products, even with benzene. Thus it seems that these reactions are not suitable routes to uncomplexed tris(pentafluorophenyl)aluminium, whilst in the next section (see thermal stability of $C_6F_5AlBr_2$) it will be seen that it may eventually be possible to prepare this compound by controlled disproportionation of pentafluorophenylaluminium halides.

3. The Properties and Reactions of Pentafluorophenylaluminium Dibromide and some Properties of Bis(pentafluorophenyl)aluminium bromide.

Prior to this work, no fluorocarbon derivatives of tricovalent aluminium had been isolated, and the tendancy of fluoroalkyl- and fluorovinyl-boron compounds to decompose, giving boron trifluoride, by migration of fluorine from carbon to boron suggests that the isolation of fluoroalkyl derivatives of tricovalent aluminium will almost certainly be prevented by analogous instability. Recent work by Lagowski[140] supports this conclusion.



However, perfluoroaryl derivatives of tricovalent boron are quite stable, and this has been attributed partly to p-π interaction between boron and the ring, and to the absence of fluorine on carbon α to boron. Therefore it was thought that perfluoroaryl derivatives of tricovalent aluminium might also be sufficiently stable for isolation, and the cleavage reactions already described led to the synthesis of the first derivatives of this type to be reported.

The object of this study of perfluoroarylaluminium compounds, in addition to the intrinsic interest in understanding the factors leading to the stabilisation of these species, was to study the organic chemistry of the compounds, and in particular to investigate their ability to undergo insertion reactions with olefins, in the hope that they may, eventually, be useful in polymerising fluoro-olefins.

Characterisation of Perfluoroarylaluminium Derivatives.

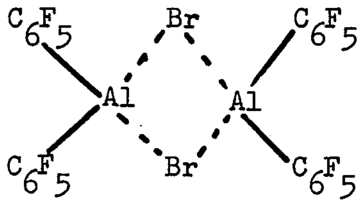
The characterisation of perfluoroarylaluminium compounds posed several problems. Because the derivatives were extremely sensitive to moisture and oxygen, normal handling was impossible and most of the work was carried out using a drybox. (See section on techniques and photograph 1). Both pentafluorophenylaluminium dibromide and bis-(pentafluorophenyl)aluminium bromide were initially isolated as liquids and indeed were investigated as such for some time. When the preparative methods were perfected however, the former was readily obtained as a crystalline solid, whilst the latter usually solidified on prolonged pumping under high vacuum.

Carbon analyses could not be obtained by the method used in this department because violent explosions occurred when the derivatives were ignited in oxygen. Aluminium was determined gravimetrically and bromine could be estimated by standard micro-analytical methods, whilst carefully controlled, low temperature hydrolyses gave pentafluorobenzene, which could be weighed as a gas.

Molecular Weight Determinations.

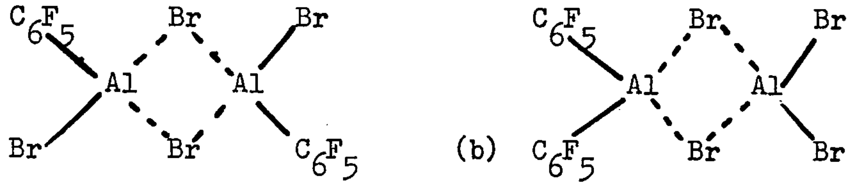
Freezing point determinations showed that both perfluoroaryl-aluminium derivatives were dimeric in benzene solution and it is reasonable to postulate bridging through bromine in the following structures.

(i)



$(C_6F_5)_2AlBr.$

(ii)



(a)

(b)

$C_6F_5AlBr_2$

More possibilities arise in (ii) but the two structures shown are probably the most important and it is unlikely that bridging would occur via fluorine in the ring. Similar structures have been postulated by Mole,[141] and Perkins and Twentyman,[142] for phenylaluminium chlorides, and the last mentioned authors suggest that in no case does the organic group perform the bridging function, although this conclusion is not easily reached. The bridge structures shown are examples of those typically formed by electron deficient molecules and they allow aluminium to become co-ordinatively saturated.

Thermal Stability.

Careful heating of an analytically pure sample of pentafluorophenylaluminium dibromide to 140° under a 'sticking' vacuum produced a pure white sublimate, which appeared from infrared evidence to be unchanged starting material, but the product had a lower melting point and a slightly higher bromine analysis than the original substance. No decomposition occurred, and it was apparent that pentafluorophenylaluminium dibromide had sublimed, with very slight disproportionation, to give some aluminium tribromide, and bis(pentafluorophenyl)aluminium bromide, which was left as a trace of viscous residue.

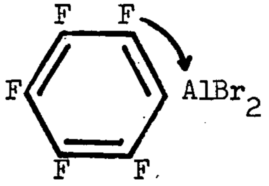
$$2C_6F_5AlBr_2 \longrightarrow (C_6F_5)_2AlBr + AlBr_3$$

$$3C_6F_5AlBr_2 \longrightarrow (C_6F_5)_3Al + 2AlBr_3$$

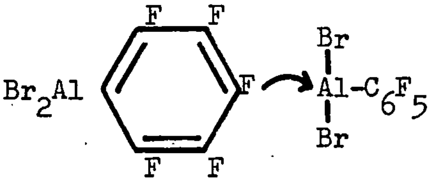
This experiment was repeated carefully several times but on each occasion slight disproportionation occurred, whilst the majority of the starting material was recovered unchanged.

When another sample of the same compound was slowly heated to 160° in a sealed, evacuated tube, a dark red, viscous liquid was formed and this remained unaltered at this temperature for twenty-four hours, before finally decomposing, after the temperature had been raised to 180°, to give carbon. Rapid heating of pentafluorophenylaluminium dibromide again in a sealed evacuated tube, ended after two hours in a violent explosion, when the temperature had reached 195°.

Since evidence exists for the disproportion of pentafluorophenylaluminium dibromide, it is reasonable to conclude that decomposition does not occur via inter- or intramolecular migration of fluorine from carbon to aluminium as shown,



or

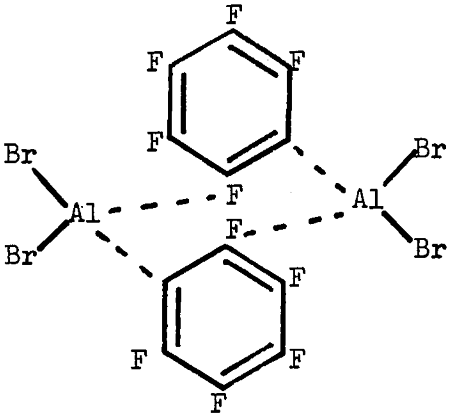


but rather via disproportionation to give tris(pentafluorophenyl)-aluminium

$$3C_6F_5AlBr_2 \longrightarrow (C_6F_5)_3Al + 2AlBr_3$$

which then decomposes in the above fashion giving a tetrafluorobenzyne.[45] This comparative thermal stability of pentafluorophenylaluminium dibromide is probably largely due to the dimeric nature of the compound and the absence of fluorine on carbon α to the metal atom and if the above mode of decomposition is correct it would seem that the already unlikely fluorine bridging in the dimer

viz.



is ruled out, since this type of structure would facilitate the formation of aluminium-fluorine bonds. However, if tris(pentafluorophenyl)aluminium is formed, dimerization through bromine bridging would not be possible and both the monomer and a fluorine bridged dimer would be likely to decompose via migration of fluorine from carbon to aluminium. Recently Brinckmann[92] has suggested that tris-(pentafluorophenyl)aluminium etherate decomposes in this way, either by inter- or intra-molecular fluorine abstraction.

There is further evidence to suggest the formation of tris(pentafluorophenyl)aluminium by disproportionation of pentafluorophenylaluminium bromides. On several occasions the latter appeared to have decomposed slightly after standing for several weeks under nitrogen in a drybox, and when the compounds were extracted with petroleum, insoluble, white, solid residues were obtained and at first these were assumed to be aluminium hydroxide. When the residue was discarded into a sink however, an explosion occurred, flames were observed, and carbon was deposited. Subsequently these residues were shown to be pentafluorophenyl derivatives (infrared) and it may be that slow disproportionation had occurred to give small amounts of tris(pentafluorophenyl)aluminium, which may eventually be isolated by a controlled disproportionation of this kind.

Reactions of Pentafluorophenylaluminium Dibromide.

Since this is a new fluorocarbon system and the chemistry of it is unknown, reactions of pentafluorophenylaluminium dibromide with various types of compound have been studied and where possible a comparison has been drawn with phenylaluminium halides. A summary of the study is shown in figure 1, whilst figure 2 illustrates the reactions of the analogous hydrocarbon compounds.

Figure 1.

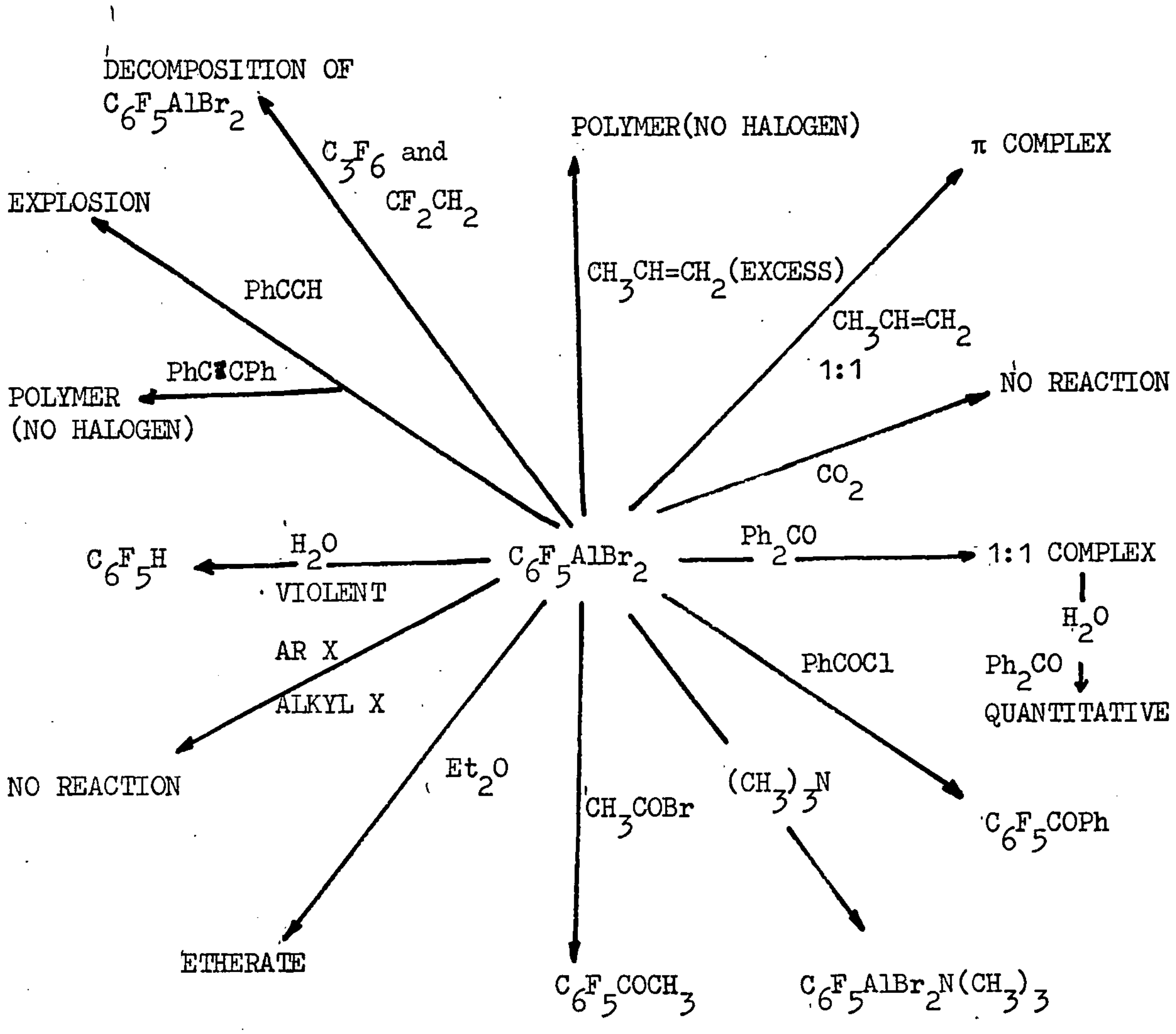
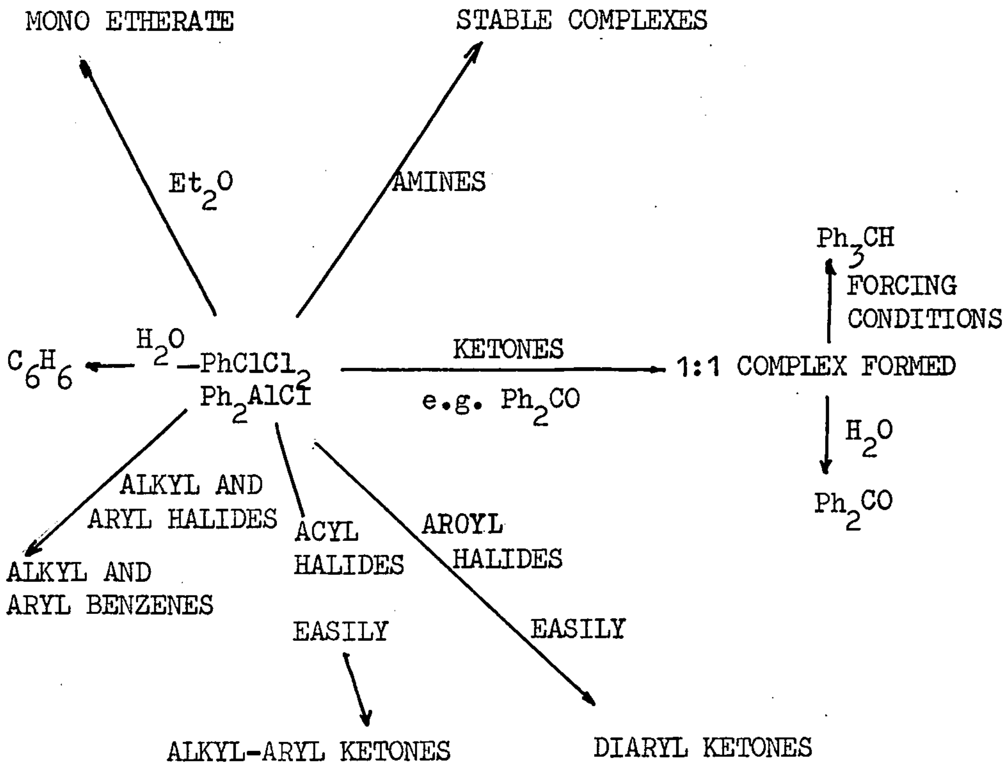
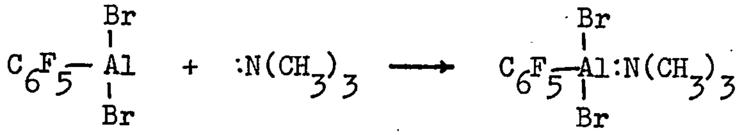


Figure 2.



Reaction with Donor Molecules.

The aluminium atom in pentafluorophenylaluminium dibromide has two electrons fewer than an octet and thus the compound is a Lewis acid. As expected, electron donors e.g. trimethylamine are easily complexed with pentafluorophenylaluminium dibromide, with the nitrogen lone pair completing the octet.

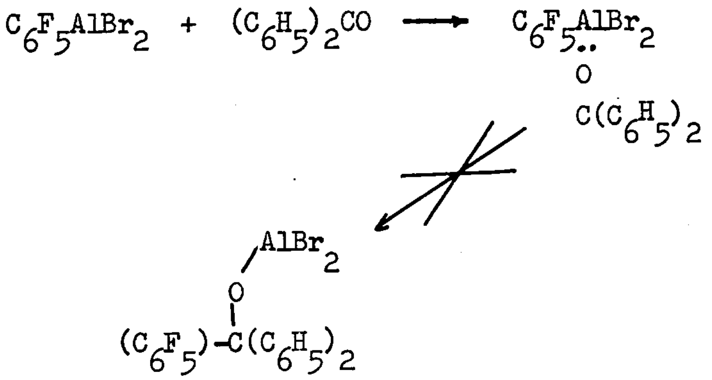


$$C_6F_5-\overset{Br}{\underset{Br}{Al}} + :N(CH_3)_3 \longrightarrow C_6F_5-\overset{Br}{\underset{Br}{Al}}:N(CH_3)_3$$

Thus the aluminium compound and the amine react exothermically at room temperature giving a 1:1 complex which melts at 42° with loss of trimethylamine, and which is air and moisture sensitive. The 1:1 composition was established by bromine and aluminium analyses, and by hydrolysing a known weight of the complex to give a mixture of pentafluorobenzene and trimethylamine, which was weighed. When a solvent was used the complex was obtained as an oil which solidified on pumping under vacuum. Pyridine also gave an oil when added to the aluminium compound in toluene, but this liquid could not be crystallised. Phenylaluminium halides also form 1:1 complexes with donor molecules,[93] and with diethyl-ether. Whilst no attempt was made to isolate the latter type of complex with pentafluorophenylaluminium dibromide, the chemical shifts in the ^{19}F nuclear magnetic resonance spectrum of the compound in diethyl-ether differed from those observed in petroleum, indicating complex formation in the ether. (See later).

Reaction with Benzophenone.

Pentafluorophenylaluminium dibromide forms a 1:1 complex with benzophenone from which the ketone can be recovered unchanged on hydrolysis, even after several days at 100° in a sealed, evacuated tube.

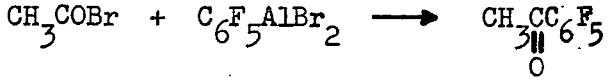


More drastic conditions were not investigated, but it seems probable that complex formation, and stabilisation, is aided by the electron withdrawing properties of the fluorinated ring increasing the acceptor capacity of aluminium, and hence stabilising the adduct.

The phenylation of ketones by phenylaluminium halides is not easily accomplished and does not always yield the expected products. With benzophenone in refluxing benzene, monomeric 1:1 complexes are obtained from which the ketone can be recovered unchanged on hydrolysis. More drastic conditions however, lead to the formation of triphenylmethane in 15% yield.[143] Mole[144] suggests that by virtue of their strong Lewis acidities, phenylaluminium halides tend to form stable complexes with benzophenone which do not readily rearrange by migration of a phenyl group to the carbonyl carbon atom. Results obtained in the present work are in obvious agreement with this, and one would expect pentafluorophenylaluminium dibromide to have greater Lewis acid characteristics than its phenyl analogue, and hence form even more stable adducts.

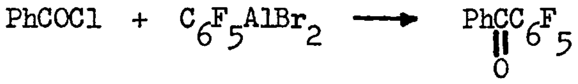
Reaction with Acyl and Aroyl Halides.

Acyl and aroyl halides react quite readily with pentafluorophenylaluminium dibromide to give good yields of the corresponding alkyl-pentafluorophenyl and aryl-pentafluorophenyl ketones. Acetyl bromide and pentafluorophenylaluminium dibromide in refluxing hexane gave an 80% yield of pentafluoroacetophenone on hydrolysis,



$$CH_3COBr + C_6F_5AlBr_2 \longrightarrow CH_3\underset{\underset{O}{\|}}{C}C_6F_5$$

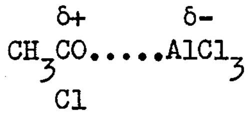
whilst benzoyl chloride and pentafluorophenylaluminium dibromide gave a 70% yield of pentafluorobenzophenone after being heated to 80^o for a few days in a sealed, evacuated tube.



$$PhCOCl + C_6F_5AlBr_2 \longrightarrow Ph\underset{\underset{O}{\|}}{C}C_6F_5$$

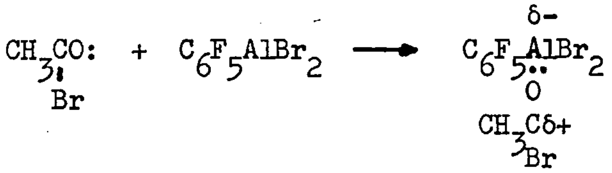
Phenylaluminium halides react in analogous fashion to give good yields of the ketones[145,146] and the reactions are said to proceed most readily in benzene or toluene solution.

The presence of two functional groups in an acyl or aroyl halide, the carbonyl donor group and the ionisable halogen atom, suggests that two types of intermediate may be possible in the interaction of these halides with Lewis acid type compounds. The acetyl chloride-aluminium trichloride system has recently been discussed on the basis of infrared spectroscopic data by Cook,[147] who differentiated between the ionic salt $CH_3CO^+ AlCl_4^-$ and the polarised donor-acceptor complex,



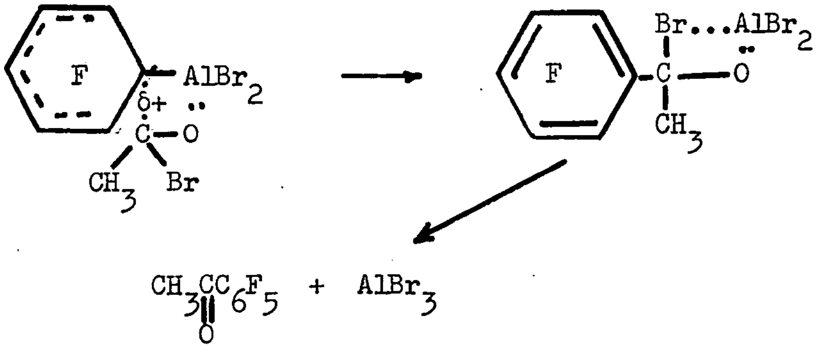
$$\underset{Cl}{\overset{\delta+}{CH_3CO}}\cdots\cdots\overset{\delta-}{AlCl_3}$$

In reactions of acyl or aroyl halides with pentafluorophenylaluminium dibromide the first step will probably involve co-ordination of the organic molecule to aluminium through oxygen, as with ketones.



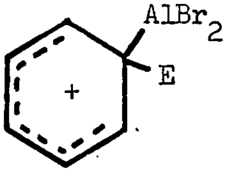
$$\underset{Br}{CH_3CO:} + C_6F_5AlBr_2 \longrightarrow \begin{array}{c}\delta-\\ C_6F_5\ddot{A}lBr_2\\ O\\ CH_3C\delta+\\ Br\end{array}$$

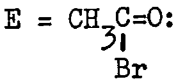
This then breaks down to give a ketone plus an aluminium trihalide via attack by the carbonium ion at the metal-bonded carbon in the aromatic ring, and attack by bromine on aluminium.



These processes may occur together in a four-centre type mechanism and it is interesting to note that whilst benzophenone can form a complex with the aluminium compound, this breaks down to give starting materials. The main difference in the two reactions is the lack of concerted attack in the case of the ketone, that is, whilst oxygen donates to aluminium and positive carbon attacks at the ring, there is no halide ion to attack the aluminium atom. Obviously the polarisation of the acyl halide molecule due to the halogen atom is very important.

Again the reaction is essentially one of electrophilic aromatic substitution with $AlBr_2$ being the leaving group, and the acylium or oxocarbonium ion being the attacking species. Pentafluorophenylaluminium dibromide can be viewed as acting as its own Friedel-Crafts type catalyst for the process, with the formation of an intermediate σ complex,

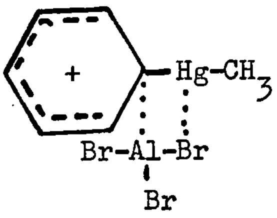




$$E = \underset{\displaystyle Br}{CH_3\underset{|}{C}}=O:$$

with the electrophile also donating via the carbonyl group to the molecule being attacked. Thus attack by acyl halide on pentafluorophenylaluminium dibromide is very similar to attack on methylpentafluorophenylmercury by aluminium tribromide, which was postulated as a four-centre type reaction.

i.e.



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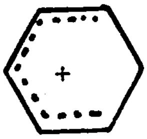


= C_6F_5)

Both processes can be viewed as Friedel-Crafts type electrophilic aromatic substitution.

Reaction with Alkyl and Aryl Halides.

Alkyl and aryl halides failed to react with pentafluorophenylaluminium dibromide even after several days at 100° in sealed, evacuated tubes. No solvents were used so that the opportunity for Friedel-Crafts attack on them was eliminated.

Phenylaluminium halides react with alkyl and aryl halides under forcing conditions with elimination of aluminium trihalide. Thus alkyl benzenes were obtained by the condensation of alkyl halides with phenylaluminium dichloride and di-iodide.[148] Bromobenzene and the di-iodide were heated in benzene for one hour at 250° and yielded a mixture containing bi-, ter-, quater-, and quinquephenyl, and a free-radical mechanism involving thermal cleavage of the aluminium compound has been suggested.[149]

Pentafluorophenylaluminium dibromide shows no great increase in reactivity compared with its phenyl analogue and since a free-radical mechanism is proposed one must conclude that like the phenyl compounds, pentafluorophenylaluminium derivatives will only react with alkyl and aryl halides at temperatures at which the aluminium compounds are thermally unstable. In view of previous evidence it would seem that complications would arise due to disproportionation of perfluoroarylaluminium compounds.

Reaction with Carbon Dioxide.

When pentafluorophenylaluminium dibromide was treated with gaseous carbon dioxide no reaction occurred, even in refluxing benzene, and hydrolysis invariably yielded pentafluorobenzene. The failure of this reaction was probably due to the inability to form an intermediate in which co-ordination to aluminium, with resulting elimination of a trivalent aluminium compound, could assist attack by electrophilic carbon at the metal-bonded carbon atom in the ring. This reflects the results of reactions of alkyl and aryl halides, and benzophenone with pentafluorophenylaluminium dibromide, when again there was no possibility for a four-centre type mechanism.

No reference to reactions of phenylaluminium halides with carbon dioxide could be found in the literature and tri-p-tolylaluminium only reacted with the gas on treatment in boiling xylene for two hours.[150]

Reaction with Olefins.

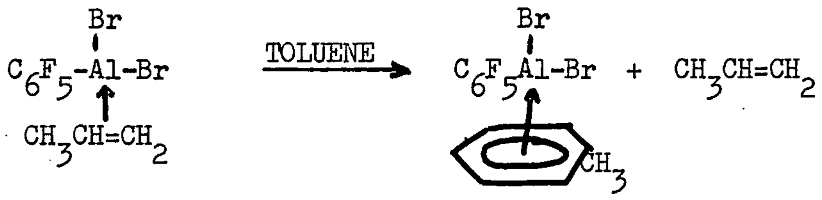
The interaction of aluminium alkyls with olefins and acetylenes has received a great deal of attention,[151] but in contrast little has been done on the corresponding reactions of aluminium aryls. A recent patent[152] however, states that the well-known "growth" reaction of aluminium alkyls also occurs with aryls and aralkyls, and mixtures of long-chain phenylalkanes may be produced by the action of ethylene, at raised temperatures and pressures, on triphenyl, tribenzyl, or triphenylethylaluminium.

When pentafluorophenylaluminium dibromide and excess propene were allowed to react at room temperature in a sealed, evacuated tube an extremely exothermic reaction occurred and the olefin polymerised almost instantaneously, to give a completely involatile, viscous polymer. No propene was recovered and micro-analyses failed to detect any halogen in the product, although carbon and hydrogen analyses accounted for only 96% of the material.

To determine where insertion occurred, an attempt was made to moderate the reaction by adding an equimolar amount of the olefin to the aluminium compound in a solvent, petroleum ether. Quite inadvertently insufficient solvent was added to dissolve all of the aluminium compound but when the olefin was added, all of the pentafluorophenyl derivative went into solution. After two days at 50° removal of solvent left a brown solid plus some polymer, and the latter was shown to contain almost 10% of fluorine, but no bromine, indicating that insertion had occurred mainly between the fluorinated ring and aluminium.

Hydrolysis of the solid product gave a mixture of two volatile components of which one, which was in large excess, was shown to be pentafluorobenzene by gas chromatography and infrared analysis. The second component, which was not separated, was volatile at room temperature and could be observed to bubble out of the mixture. It was not detected by gas chromatography, presumably because of its volatility, and comparison of retention times showed that propyl bromides were not present in the mixture, which only gave a peak corresponding to pentafluorobenzene. An infrared spectrum of the mixture showed strong carbon-hydrogen bands in the short order, whilst the remainder of the spectrum was virtually identical to that of pentafluorobenzene. The solid material, which also had strong carbon-hydrogen peaks in its infrared spectrum, was subjected to prolonged pumping under high vacuum, but subsequent hydrolysis produced the same result. Investigation of the mixture of volatiles by mass spectroscopy, and comparison of the spectrum with that of pure pentafluorobenzene, and background, indicated the presence of a species of mass forty-two, and the cracking pattern observed was consistent with that expected for propene.

Solution of the solid reaction product in benzene or toluene caused slow evolution of a gas, and this material was collected, with excess of toluene, and again examined by mass spectroscopy. Again comparison of spectra of identical intensity showed a definite increase at masses forty-two, forty-one, and twenty-seven, corresponding to the cracking pattern of propene. Whilst this evidence is by no means conclusive, it appears that pentafluorophenylaluminium dibromide forms a weak, but isolable complex with propene, from which the latter can be recovered.



It must be noted however that whilst slight differences in chemical shift were observed when the ^{19}F nuclear magnetic resonance spectrum of the aluminium compound, measured in diethyl ether, was compared with that measured in petroleum, the proposed propene complex gave identical chemical shifts to those observed for pentafluorophenylaluminium dibromide in petroleum. This can be explained however when one considers that a propene π complex of the type postulated would hardly be as strong as an etherate, and also, the product from the propene reaction almost certainly contained excess pentafluorophenylaluminium dibromide, since some olefin was polymerised.

This is the first known report of an aluminium compound forming a π complex, and also the first report of an insertion reaction in a fluorocarbon system.

Fluoro-olefins.

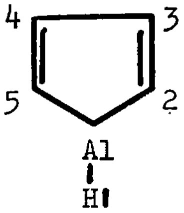
Similar reactions were attempted with vinylidene fluoride and hexafluoropropene, but no polymerisation was observed. In the presence of fluoro-olefins pentafluorophenylaluminium dibromide turned black and appeared to decompose, and the unsaturated compounds were recovered in quantitative yield.

It may eventually be possible however, to incorporate pentafluorophenylaluminium dibromide into a Ziegler type catalyst which will be able to polymerise fluoro-olefins, and investigations along these lines will continue.

Reaction with Acetylenes.

Several reports have appeared recently concerning reaction of phenylaluminium[153,154] and phenylboron derivatives[155] with acetylenes and some very interesting results have been obtained. Eisch and Kaska[153] added triphenylaluminium across a triple bond and cyclised the resulting unsaturated aluminium derivatives to give the heterocyclic aluminole system.

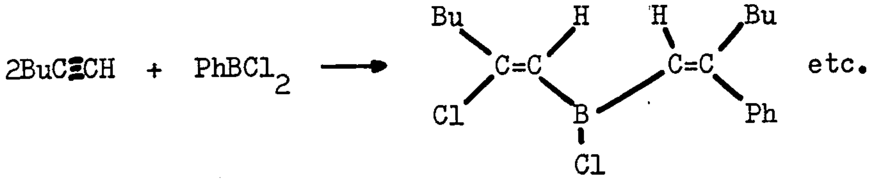
i.e.



The aluminole nucleus.

The same authors[154] described the facile metalation of terminal alkynes by triphenylaluminium, whilst Lappert and Prokai[155] described the haloboration and phenylboration of acetylenes.

e.g.



Preliminary reactions between acetylenes and pentafluorophenylaluminium dibromide have produced complex results. When phenylacetylene was added to the aluminium compound under nitrogen, at room temperature, an immediate explosion occurred and carbon was deposited. Obviously no real conclusion can be drawn from this result, except to say that an extremely vigorous reaction, or a highly unstable species, occurs.

Reactions between diphenylacetylene and pentafluorophenylaluminium dibromide were exothermic at room temperature, but not violent, and the product on hydrolysis, was a green material which turned black on heating, and which appeared to be polymeric. No halogen could be detected by micro-analyses on this substance.

These reactions need further investigation and this work will be continued in the future. It will be interesting to determine the course of reactions, and if possible to discover whether metalation occurs with acetylenes containing acidic hydrogen, and also, if substituted olefins are formed, whether pentafluorophenyl or halogen migrates first.

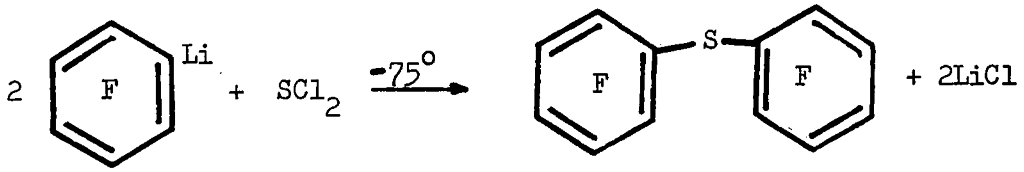
One can conclude from the previous discussion that in many respects pentafluorophenylaluminium dibromide resembles its phenyl analogue, or, more correctly, phenylaluminium dichloride, since only one reference to phenylaluminium dibromide[156] could be found in the literature. Reactions of the former with donor molecules, ketones, and acyl and aroyl halides all follow the same course as do those with phenylaluminium halides, and a general conclusion is that reactions proceed most readily with polarised species which can form intermediates in which electrophilic attack on the carbon bonded to aluminium is accompanied by nucleophilic attack on the metal itself. Complex results occur when the perfluoroarylaluminium compound reacts with alkenes and alkynes and this area needs further study.

4. Reactions of Polyfluoroaryl-lithium Derivatives with Sulphur Dichloride, and the Preparation and some Reactions of Octafluorodibenzothiophene.

a) The Preparation of Bis(pentafluorophenyl)sulphide and Bis-(orthobromotetrafluorophenyl)sulphide.

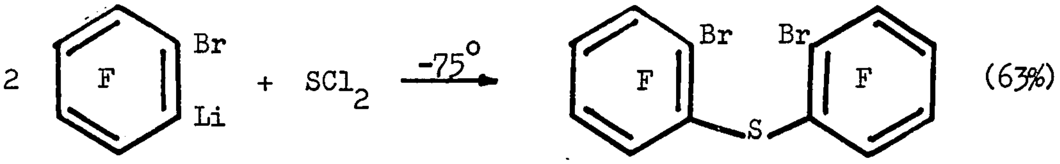
Cleavage reactions of methylpentafluorophenylmercury with inorganic halides had proved successful in several cases, (see section two of this chapter) and it was decided to explore the reaction of the mercurial with sulphur dichloride, in an attempt to prepare the then unknown bis(pentafluorophenyl)sulphide. Unfortunately these reactions were unsuccessful and rearrangement of the mercurial occurred, and the same result was obtained with thionyl chloride.

Interest in perfluoroaryl sulphur derivatives was thus developed and preliminary investigations[157] indicated that it might be possible to prepare sulphur derivatives by reacting sulphur halides with perfluoroaryl-lithium compounds. In the event this route proved to be quick, simple, and effective, and good yields of products were obtained. Thus when sulphur dichloride in diethyl ether was added to two equivalents of pentafluorophenyl-lithium in hexane-ether solution at -75°, bis(pentafluorophenyl)sulphide was obtained in 60% yield, as a white crystalline solid. The compound was characterised by carbon and fluorine analyses



and by nuclear magnetic resonance spectroscopy, and in the course of this work was reported in the literature.[57,109]

An extension of the method led to the isolation of bis(orthobromotetrafluorophenyl)sulphide when the monolithio derivative from 1,2-dibromotetrafluorobenzene was reacted with half an equivalent of sulphur dichloride.



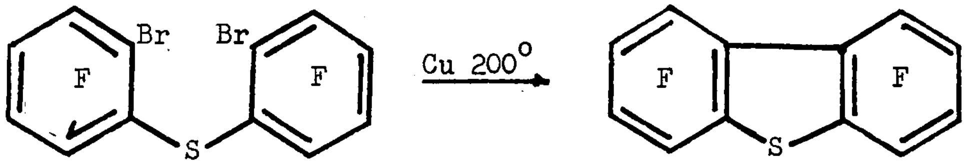
Again the reaction was carried out in hexane-ether solution and whilst the aryl-lithium, which was prepared from the dibromo compound and n-butyl-lithium, took longer to form than in ether, better yields of the sulphur compound were obtained.

When this reaction was initially carried out, in ether solution, mixtures containing several components were obtained, and separation was very difficult. Mass spectroscopy identified one component as a species of molecular weight 517, and the cracking pattern indicated the presence of three bromine atoms in the molecule,[158] and this suggests the formula $C_{12}F_7Br_3$. This species must have been formed by attack of orthobromotetrafluorophenyl-lithium on unreacted 1,2-dibromotetrafluorobenzene. Experiments with different solvents were investigated and results showed that whilst reactions were slower, good yields of a pure product could be obtained by using a mixture of hexane and ether as solvent. The product, a white crystalline solid with a rather unpleasant, pungent odour, melted sharply at 100° after resublimation at 80° under high vacuum, and was characterised by carbon and halogen analyses, and by mass spectroscopy.

b) The Preparation of Octafluorodibenzothiophene.

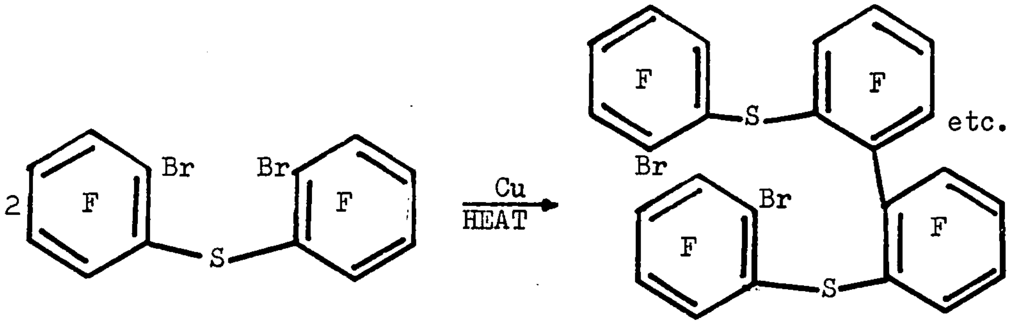
The Ullmann Reaction of Bis(orthobromotetrafluorophenyl)sulphide.

When bis(orthobromotetrafluorophenyl)sulphide had been characterised it was of interest to determine whether ring closure could be effected by application of the well-known Ullmann Synthesis,[159] and accordingly the reaction was investigated. In several experiments the sulphur compound and excess copper powder were heated to temperatures ranging from 90° to 180° in dimethylformamide, both under reflux, and in sealed tubes. Below 160° no reaction occurred, and starting material could easily be recovered, and whilst above this temperature reaction did take place, it appeared to involve the solvent, because hydrogen containing products were isolated. However, when bis(orthobromotetrafluorophenyl)sulphide and excess copper powder alone were heated to 200°, for several days, in a sealed evacuated tube, octafluorodibenzothiophene was obtained in virtually quantitative yield.



The product sublimed straight from the reaction mixture as a white, crystalline solid which melted at 99-100° and which was characterised by carbon and fluorine analyses, mass spectroscopy, and its nuclear magnetic resonance spectrum, and by reduction to the known 2,2'-dihydro-octafluorobiphenyl. This is the first report of a fully fluorinated condensed-ring compound containing one hetero atom, although a related compound, octafluorophenothiazine, has been described,[110] and so has octachlorodibenzothiophene.[160] Lower temperatures and shorter reaction times give mixtures of the starting material and product, and in one reaction, where good mixing of the copper and the dibromo compound was not effected, two less volatile products were produced in minor quantities, and these substances were probably the result of inter-, rather than intra-molecular coupling.

e.g.

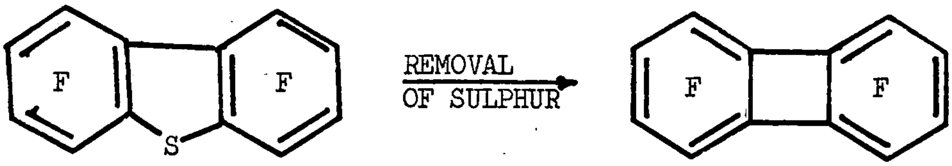


In another experiment bis(orthobromotetrafluorophenyl)sulphide was heated to 300° in the presence of copper, and whilst some octafluorodibenzothiophene was obtained, quite a large proportion of starting material decomposed.

c) Some Properties and Reactions of Octafluorodibenzothiophene.

Octafluorodibenzothiophene is remarkably thermally stable. Interest lay in trying to remove sulphur from the molecule, in the hope that intra-molecular ring closure would occur giving octafluorobiphenylene.

i.e.



Accordingly, octafluorodibenzothiophene was heated, with copper, in sealed evacuated tubes at high temperatures for several days, but even after five days at 480° only starting material was recovered, although in this case some decomposition had occurred. At lower temperatures almost quantitative recovery of the sulphur compound was achieved in most cases. Experiments using copper in the presence of solvents e.g. quinoline will be investigated in the future, but these results cannot be included in the present work. Kharasch reports that octachlorodibenzothiophene is also a very stable substance[160] (m.pt. 302°), and dibenzothiophene itself has exactly the same melting point (99-100°) as its perfluoro analogue,[161] whilst the ultra-violet spectra of the fluorocarbon and its hydro analogue also appear to be very similar. Badger and Christie[162] report three major absorption regions for dibenzothiophene at 235, 275-285, and 305-330 mµ and the spectrum of the perfluoro derivative shows three major regions of similar form at 220-235, 250-275, and 305-330 mμ.

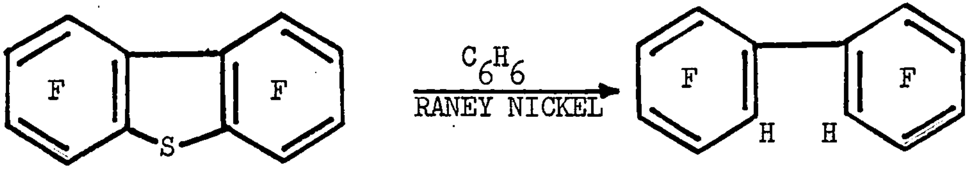
Reaction with Raney Nickel.

The extrusion of sulphur from organic sulphur containing compounds has been reviewed by Loudon,[163] and another article[164] published recently, contains a section on the reductive coupling of organic sulphur compounds. A series of papers by Djerassi and co-workers[165] contains many references to desulphurisations, mainly by using Raney nickel, and Mozingo and co-workers[166] showed that active Raney nickel, in a solvent at moderate temperatures, removes either reduced or oxidised sulphur by cleavage from the molecule, and, that of the two possible types of product,

viz.
$$\begin{tikzcd} & \text{(a)} \quad R\text{-}R + R'\text{-}R' + R\text{-}R' \\ R\text{-}S\text{-}R' \; + \; Ni(H) \arrow[ur] \arrow[dr] & \\ & \text{(b)} \quad RH + RH' \end{tikzcd}$$

using aliphatic or aromatic sulphides, disulphides, sulphoxides or sulphones, only reaction (b) was observed. However, more recent work by Badger and Sasse,[167] and Djerassi and co-workers[165] has shown that Raney nickel can be used to remove sulphur without substituting hydrogen in the molecule, and with this work in mind, various attempts were made to remove sulphur from octafluorodibenzothiophene by treatment with Raney nickel.

When octafluorodibenzothiophene and Raney nickel were stirred in ethanol at room temperature for a few hours under an atmosphere of nitrogen virtually no reaction occurred. After refluxing the same mixture, the product obtained was 2,2'-dihydro-octafluorobiphenyl, which was recognised by comparison with an authentic sample of that compound. Raney nickel which had been washed ten times with dry benzene and a little of the solution distilled azeotropically, gave the same product with octafluorodibenzothiophene.

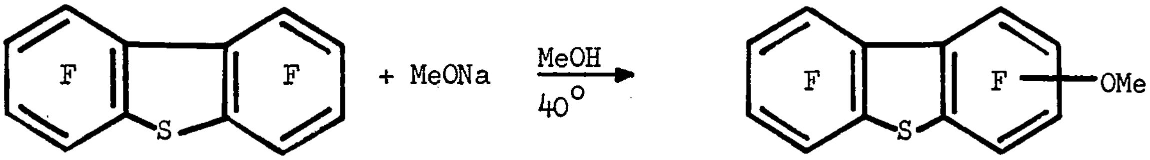


Even when the catalyst had been washed several times with dry ether, vacuum dried, and pumped under vacuum with agitation, for two days, the same product was obtained, and when nickel treated in this way and octafluorodibenzothiophene were heated together in a sealed, evacuated tube, a very complex mixture of at least six products was obtained, and mass spectroscopy results indicated that perfluorobiphenylene was not present.

These results showed that straightforward reactions between Raney nickel and the sulphur compound seem unlikely to yield perfluorobiphenylene, and whilst investigations are by no means exhausted, further discussion is beyond the scope of this thesis.

Reaction with Nucleophiles.

Octafluorodibenzothiophene reacted smoothly with sodium methoxide in methanol, and after 24 hours at 40° an 83% yield of a white, solid monomethoxyheptafluorodibenzothiophene was obtained, and a small amount of a mixture of starting material and a dimethoxy derivative, was also recovered.

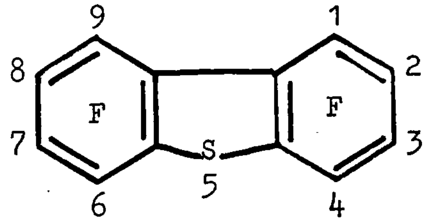


A similar reaction gave only a 50% yield of the mono-ether after six hours at the same temperature, and these results can be compared with those for hexafluorobenzene, when high yields of the monomethoxide can be obtained after one hour at reflux. Monomethoxyheptafluorodibenzothiophene is an air stable, white solid m.pt. 105-107°, which was characterised by elemental analyses and mass spectroscopy, and which can be reduced with Raney nickel in benzene to give 2,2'-dihydromonomethoxyheptafluorobiphenyl.

Ammonia reacts with octafluorodibenzothiophene in ethereal solution to give mainly a monoamino derivative, but again some disubstitution occurs. Thus after 170 hours at 128°, in a sealed tube, a 56.5% yield of monoaminoheptafluorodibenzothiophene was obtained, and 20% of the octafluorodibenzothiophene was recovered. The mono-amine resublimed as a white solid, but quickly darkened on standing in air, and melted with decomposition at 142°. Mass spectroscopy confirmed the molecular weight as 325, and a correct carbon analysis was obtained, but several attempts to obtain an accurate fluorine analysis produced inconsistent results and, after consultation,[168] the matter was not pursued.

Orientation in Derivatives of Octafluorodibenzothiophene.

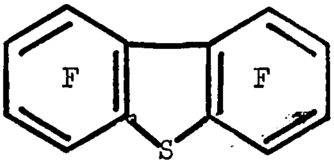
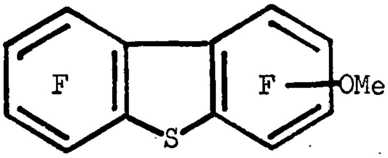
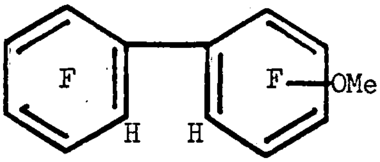
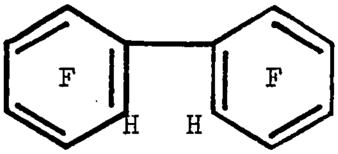
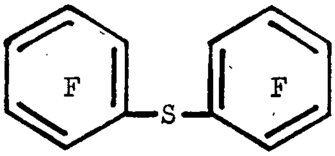
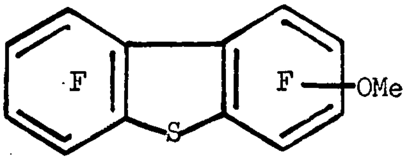
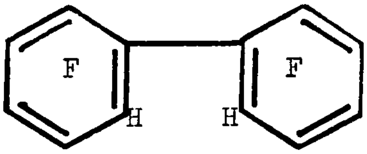
By studying the ^{19}F and 'H nuclear magnetic resonance spectra of octafluorodibenzothiophene and some of its derivatives, the orientation of the first substituent has been assigned to position 2.



Where applicable ^{19}F and 'H spectra were obtained for the compounds, octafluorodibenzothiophene, monomethoxyheptafluorodibenzothiophene, 2,2'-dihydromonomethoxyheptafluorobiphenyl, 2,2'-dihydro-octafluorobiphenyl, and bis(pentafluorophenyl)sulphide, and the details of these spectra are recorded in table five.

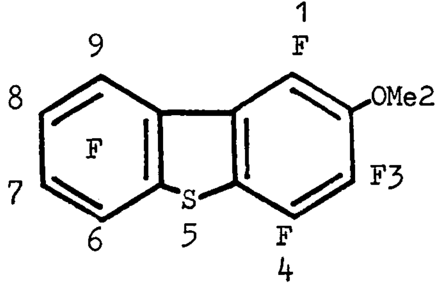
Examination of the proton spectrum of monomethoxyheptafluorodibenzothiophene showed it to be a pair of doublets which were almost symmetrical, and this indicated that the methyl group was coupling equally with two ortho fluorine atoms, and since this could only occur

TABLE FIVE

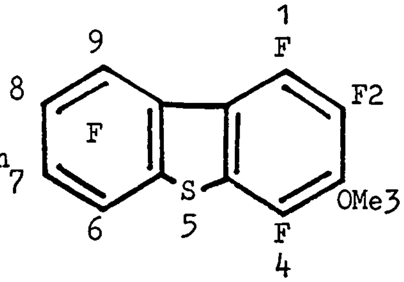
COMPOUND	SPECTRUM	NUMBER OF PEAKS	REFERENCE	SHIFTS, p.p.m.
	^{19}F	4	$CFCl_3$	134, 141, 156, 158
	^{19}F	6(1 x 2)	$CFCl_3$	134(X2), 136, 141, 153, 156, 158
	^{19}F	5(2 x 2)	$CFCl_3$	134, 140(X2), 142, 151, 155(X2)
	^{19}F	2	$CFCl_3$	140, 156
	^{19}F	3(2 x 2)	$CFCl_3$	133(X2), 151, 161(X2)
	'H	2(pair of doublets)	$(CH_3)_4Si$	6·05 (CH_3-) ((CH_3)$_4$S 10)
	'H	1	$(CH_3)_4Si$	2·9 ((CH_3)$_4$Si 10)

with the substituent in position 2 or 3, positions 1 and 4 could be eliminated immediately.

i.e. for position 2

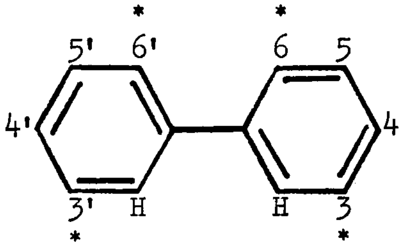


for position 3



The spectrum of 2,2'-dihydro-octafluorobiphenyl shows only two peaks, which must be two sets of two overlapping peaks unresolved, and the spectrum can be rationalised by comparison of ortho shifts, due to hydrogen, with those observed in pentafluorobenzene,[169] and 2-hydrononafluorobiphenyl.[170]

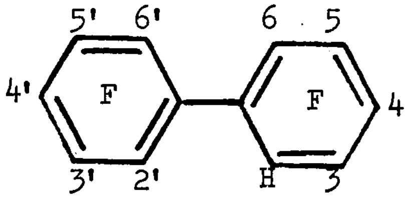
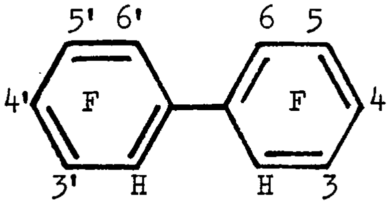
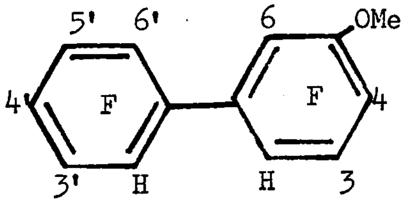
It is known that the resonance due to the fluorine atoms ortho to the group X in C_6F_5X always occurs at lower field than that due to the meta or para fluorine atoms, and in pentafluorobenzene[169] and 2 hydro-nonafluorobiphenyl[170] the effect of hydrogen, on the fluorine ortho to it, has resulted in shifts of 23 and 24 p.p.m. respectively to lower field. Thus a comparison of the observed shifts in the ^{19}F n.m.r. spectra of 2 hydro-nonafluorobiphenyl and 2,2' dihydro-octafluorobiphenyl (table six) leads to the assignment shown,



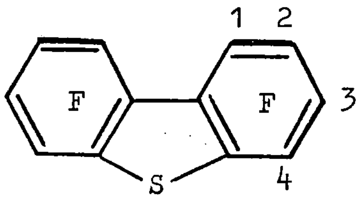
* Low field peaks.

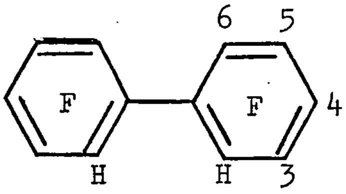
remembering that the spectrum contained only two, complex peaks.

TABLE SIX

COMPOUND	SHIFTS ($CFCl_3$) p.p.m.								
	3,	4,	5,	6,	2',	3',	4',	5',	6' POSITION
	138	152	152	137	140	162	154	162	140
	140	156	156	140	SYMMETRICAL				
	142	151		134		140	156	156	140

When the ^{19}F spectrum of methoxy-2,2' dihydroheptafluorobiphenyl is compared with that of 2,2' dihydro-octafluorobiphenyl (table six), two shifts to low field (5 and 6 p.p.m.), and one to high field (2 p.p.m.), are observed, and these can be attributed to two ortho shifts due to a methoxyl substituent and one meta shift by the same substituent, again showing that the methoxyl must have two ortho fluorine neighbours, and therefore must be in position 2 or 3 in octafluorodibenzothiophene, which are equivalent to positions 5 and 4 respectively in the biphenyl.





The largest shifts due to methoxyl in pentafluoroanisole (4 p.p.m. downfield) affect the fluorines ortho to the substituent,[169] whilst meta and para shifts are upfield (2 p.p.m.), and the same effects are found in methoxy 2,2' heptafluorobiphenyl, and methoxyheptafluorodibenzothiophene, where shifts of the same order have been observed, whilst similar results have been noted in tetrafluoronaphthalene.[171]

Octafluorodibenzothiophene gives the expected ^{19}F spectrum of four peaks of equal intensity, two of which are at low field (134 and 141 p.p.m.), and two at high field (156 and 158 p.p.m.). Comparison of these shifts with those observed in the spectra of perfluorobiphenyl,[172] bis(pentafluorophenyl)sulphide, and the two hydropolyfluorobiphenyls already discussed, leads to the assignment of the lowest field peak to position 4, i.e. ortho to sulphur. In bis(pentafluorophenyl)sulphide there is a significant shift (5 p.p.m.) to lower field of the fluorines ortho to sulphur, compared with the shifts of the ortho fluorines in perfluorobiphenyl, and by analogy, this effect should be repeated in the heterocyclic compound, thus affecting the 4 position. Again by analogy with the biphenyls, the second lowest field peak has been assigned to position 1, i.e. ortho to the carbon-carbon ring link.

Shifts in methoxyheptafluorodibenzothiophene can be accounted for as two shifts due to an ortho methoxyl (5 and 7 p.p.m. downfield), and one shift due to a meta methoxyl substituent (2 p.p.m. upfield), and on the basis of the above observations and assignments, the shifts expected for methoxyl in position 2 and position 3 in methoxyheptafluorodibenzothiophene have been calculated, and it can be seen, in table seven, that the observed shifts agree only with those calculated for position 2.

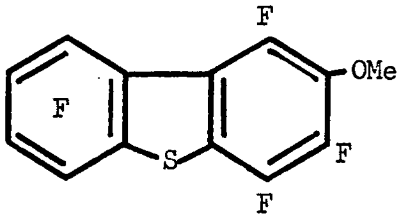
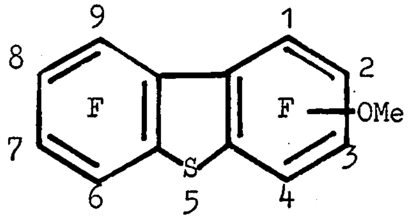
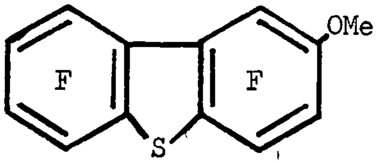
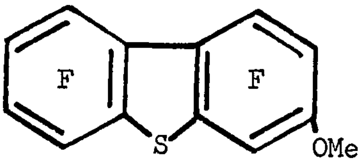


TABLE SEVEN

COMPOUND	SHIFTS ($CFCl_3$) p.p.m.							
	6	1	4	9	3	8	7	POSITION
	134	134	136	141	153	156	158	Observed
	134	135	136	141	152	156	158	Calculated
	128	134	141	143	150	156	158	Calculated

Nuclear Magnetic Resonance Data

The fluorine chemical shift for para fluorine in pentafluorophenyl derivatives has been suggested as a possible probe for indicating dπ-pπ interaction between pentafluorophenyl and metal atoms,[51] since it has been shown that the ^{19}F shift is sensitive to resonance interaction of a para-substituted group with the aromatic ring, both in fluorobenzenes[173] and pentafluorobenzenes.[174] e.g. A shift of 10 p.p.m. occurs between $Me_3SnC_6F_5$ and $C_6F_5SnCl_3$. Chambers and Chivers[83] have measured the relevant shifts in three- and four-covalent pentafluorophenylboron compounds and shown that there is a significant shift, (10 p.p.m.) to low field, for the para fluorine, from the four- to the three-covalent state, and this relative deshielding is attributed to p-π interaction. Therefore it was of interest to investigate trends in the para shift in derivatives of the type $(CH_3)_3MC_6F_5$ (M = Si, Ge, Sn) and the ^{19}F chemical shifts for these compounds are shown in table eight.

TABLE EIGHT

COMPOUND	SHIFT ($CFCl_3$) p.p.m.		
	o	m	p
$(CH_3)_3SiC_6F_5$	127•9	162•4	153•2
$(CH_3)_3GeC_6F_5$	128•0	162•0	156•1
$(CH_3)_3SnC_6F_5$	122•4	161•4	153•9

The small differences in para shift are not sufficient to warrant discussion in the terms outlined above because factors which can lead to small shifts, e.g. solvent effects, are not properly understood.

A similar comparison to that for boron compounds was made for pentafluorophenylaluminium dibromide as a dimer in petroleum, and in a donor solvent, ether.

TABLE NINE

COMPOUND	SHIFT (C_6F_6) p.p.m.		
	o	m	p
$(C_6F_5AlBr_2)_2$	41	2•8	15•1
$C_6F_5AlBr_2 \cdot OEt_2$	41	1•3	10•8
$(C_6F_5)_2AlBr$	41	2•6	13•8

Thus whilst the four-covalent etherate shows a difference in para-shift, the change (5 p.p.m.), is less than that observed in the change from a three- to a four-covalent boron compound, and this can be attributed to partial saturation of the fourth covalency of aluminium in the dimer through bromine bridging.

CHAPTER THREE

EXPERIMENTAL WORK

EXPERIMENTAL

1. Starting Materials.

Pentafluorobenzene, bromopentafluorobenzene and 1,2-dibromotetrafluorobenzene were obtained from the Imperial Smelting Corporation.

Preparation of Starting Materials.

Tetramethylgermane.[173]

Methyl iodide (90 g., 0·64 moles) in di-n-butyl ether (200 ml.) was added dropwise to magnesium (20 g., 0·82 moles) in di-n-butyl ether (300 ml.) in a 1 litre, three-neck flask fitted with a mercury seal stirrer, dropping funnel and reflux condenser. The reaction was initiated with ethylene dibromide and the apparatus was purged with dry nitrogen. After refluxing for 3 hours, germanium(IV) chloride (17 g., 0·08 moles) was carefully added, with stirring, at room temperature. Further refluxing for 3 hours was followed by distillation of the mixture and the fraction boiling between 90° - 130° was collected. Fractionation of this mixture using a glass helices column yielded tetramethylgermane (7·0 g., 66%) b.pt. 40° - 42°.

Trimethylbromgermane.[173]

Tetramethylgermane (7·0 g., 0·05 moles) and bromine (8·0 g., 0·05 moles) were condensed into a constricted carius tube using standard vacuum techniques and the tube was sealed under vacuum. After 1 week at 100° the tube was cooled, opened into a vacuum system and allowed to warm to room temperature when ca. 3 g. of a volatile liquid, which was shown to be mainly methyl bromide (infrared spectrum), was collected. The remaining liquid was fractionated to yield trimethylbromgermane (9·0 g., 87%) as a colourless liquid (b.pt. 113-115°).

Tetramethyltin.

This compound was prepared by a method similar to that described for tetramethylgermane.[174]

Trimethyltinbromide.

Trimethyltinbromide was obtained from the redistribution reaction between tetramethyltin and tin(IV) bromide.[175]

Tetramethyl-lead.[176]

Methyl iodide (45 g., 0·32 moles) in di-ethyl ether (100 ml.) was added dropwise to magnesium (9·6 g., 0·4 moles) in di-ethyl ether (100 ml.) under dry nitrogen in a 500 ml. three-neck flask fitted with a dropping funnel, mercury seal stirrer, and reflux condenser. Ethylene dibromide was used to initiate the reaction which was gently refluxed for 2 hours after complete addition of methyl iodide. Lead(II) iodide (46 g., 0·1 moles) in diethyl ether (50 ml.) containing methyl iodide (16 g., 0·12 moles) was added slowly as a slurry at room temperature. The reaction mixture was refluxed for 2 hours, cooled, and hydrolysed (dil. HCl) and finally the ether layer was separated and dried ($MgSO_4$). Tetramethyl-lead was not isolated but used in dry ethereal solution to prepare trimethyl-lead chloride.

Trimethyl-lead Chloride.[177]

A dry ethereal solution of tetramethyl-lead was cooled to 0° in an ice bath and saturated with dry hydrogen chloride gas (1½ hours). On slowly warming to room temperature white needles of trimethyl-lead chloride precipitated. These crystals were filtered, washed with dry ether, and finally, vacuum dried.

Yield = 8 g., 28% (based on PbI_2 used to prepare $(CH_3)_4Pb$).

Methylmercury Iodide.

Methyl iodide (120 g., 0·84 moles) and mercury (85 g., 0·43 moles) were poured into a Carius tube which was cooled, evacuated and sealed. After rotation and irradiation with ultra-violet light for 3 days the tube was opened and the solid product recrystallised from benzene to give methylmercury iodide (110 g., 76%).

Methylpentafluorophenylmercury.[73]

Bromopentafluorobenzene (49·4 g., 0·2 moles) in di-ethyl ether (100 ml.) was added dropwise to magnesium (4·8 g., 0·2 moles) in di-ethyl ether (100 ml.) under dry nitrogen in a 500 ml. three-neck flask fitted with a mercury seal stirrer, dropping funnel, and reflux condenser. The mixture was refluxed for 2 hours after complete addition of the bromo compound. Methylmercury iodide (48 g., 0·14 moles) in ether (100 ml.) was added as a suspension and the mixture was again refluxed, for about 8 hours. After cooling to room temperature the mixture was filtered under dry nitrogen through glass wool and a coarse sinter, before being hydrolysed with distilled water, to prevent reduction of the product by residual, highly active magnesium. The ethereal layer was separated and dried ($MgSO_4$) and solvent removed under vacuum. The solid residue was taken up in the minimum of 40° petroleum ether, filtered, and solvent removed as before. Finally the solid product was resublimed at room temperature to yield methylpentafluorophenylmercury (36 g., 66%). (m.pt. 36°).

Sulphur Dichloride.

Before being used this compound, which was available in the laboratory, was freshly redistilled in the presence of a few drops of phosphorus trichloride.[178]

Inorganic Halides.

Solid trihalides, e.g. aluminium tribromide, were resublimed immediately before use and manipulated under dry nitrogen (see later). Liquids, e.g. phosphorus tribromide, were redistilled and handled in the same way.

Solvents.

All non-halogenated solvents were dried over sodium wire, redistilled from sodium in an atmosphere of dry nitrogen and stored in three-neck flasks over clean sodium wire, again in a nitrogen atmosphere. Quantities of solvent were removed by using a long needled syringe inserted through the bore of a gas tap, whilst dry nitrogen was flushed through the vessel.

2. Preparation of Compounds of the type $(CH_3)_3MC_6F_5$. (M = Si, Ge, Sn, Pb).

Trimethylpentafluorophenylsilane.

Bromopentafluorobenzene (20 g., 0·08 moles) in di-ethyl ether (100 ml.) was added dropwise to magnesium (2·0 g., 0·08 moles) in diethyl ether (100 ml.), in a 500 ml., three-neck flask fitted with a mercury seal stirrer, reflux condenser, and dropping funnel. The rate of addition was sufficient to maintain a gentle reaction and the experiment was carried out in an atmosphere of dry nitrogen. When addition was complete the mixture was refluxed for 2 hours and then cooled to room temperature when trimethylchlorosilane (9·0 g., 0·08 moles) in di-ethyl ether (100 ml.) was slowly added. This was followed by refluxing for 72 hours, hydrolysis (distilled water), separation of the organic layer and drying of the latter ($MgSO_4$). Removal of the ether under vacuum left a light brown oil which was fractionated to yield a colourless liquid which was further purified by gas chromatography. The product was re-distilled from phosphorus pentoxide and boiled at 172° at atmospheric pressure, giving trimethylpentafluorophenylsilane (8 g., 53%). (Found: F, 39·2; C, 45·0. $C_9H_9F_5Si$ requires F, 39·6; C, 45·0%). This compound was later reported by other workers.[95]

Trimethylpentafluorophenylgermane.

Trimethylbromgermane (8·0 g., 0·04 moles) in diethyl ether (100 ml.)

and pentafluorophenylmagnesium bromide (0·04 moles) in diethyl ether (200 ml.) were heated under reflux for 36 hours in the apparatus described above. Work-up and purification in the same way as for trimethylpentafluorophenylsilane yielded trimethylpentafluorophenylgermane (5·0 g., 44%) which boiled at 173° at atmospheric pressure. (Found: F, 33·7; C, 37·8. $C_9H_9F_5Ge$ requires F, 33·3; C, 37·9%).

Trimethylpentafluorophenyltin.

Trimethyltin bromide (14 g., 0·058 moles) in diethyl ether (100 ml.) and pentafluorophenylmagnesium bromide (0·06 moles) in diethyl ether (200 ml.) were heated under reflux for 48 hours and after hydrolysis and purification as described above yielded trimethylpentafluorophenyltin (11·5 g., 60%) which boiled at 34-36°C at 10^{-2} mm. (Found: F, 28·2; Sn, 35·6. Calc. for $C_9H_9F_5Sn$: F, 28·7; Sn, 35·9%).

Trimethylpentafluorophenyl-lead.

Trimethyl-lead chloride (8·5 g., 0·029 moles) in warm benzene (150 ml.) was added to pentafluorophenylmagnesium bromide (0·08 moles) in di-ethyl ether (150 ml.) and the mixture was refluxed for 48 hours under dry nitrogen. Benzene was used to allow a higher reaction temperature to be employed. After hydrolysis (distilled water) and drying ($MgSO_4$) the organic layer was fractionated under nitrogen at reduced pressure to yield trimethylpentafluorophenyl-lead (3 g., 25%) which boiled at 50-52° at 10^{-3} mm. and which decomposed on standing in air.

(Found: F, 22•5; C, 26•6. $C_9H_9F_5Pb$ requires F, 22•7; C, 25•8%).

A communication by other workers[52] confirmed these results.

Reaction of compounds of the type $(CH_3)_3MC_6F_5$ with Aqueous-alcoholic Potassium Fluoride (where M = Si, Ge, Sn, Pb).

Procedure:-

Each of the compounds $(CH_3)_3MC_6F_5$ in turn was treated in the following way. Approximately 0•5 ml. of the substance was dissolved in the minimum quantity of ethanol and sufficient water to just cause separation into two layers was added. The solution was made homogeneous again by adding ethanol dropwise, and then divided into two equal portions, in separate specimen bottles. To one half of the solution a crystal of potassium fluoride was added and then the vessels were stoppered and labelled.

The silicon and germanium solutions showed no apparent change even after several days, but examination of the mixtures by gas chromatography demonstrated the presence of pentafluorobenzene in the solutions which contained potassium fluoride, whilst no change was observed in the composition of the aqueous alcoholic solutions.

Addition of potassium fluoride to the aqueous alcoholic solution of trimethylpentafluorophenyltin caused an immediate white precipitate, and gas chromatography again showed that the solution contained pentafluorobenzene, whilst the other half of the solution was unaltered.

Addition of water to the alcoholic solution of trimethylpentafluorophenyl-lead produced an immediate white precipitate and again pentafluorobenzene was shown to be present by gas chromatography. Therefore only the lead compound is cleaved by aqueous alcohol whilst the other three derivatives were cleaved by varying amounts, only by aqueous alcoholic potassium fluoride.

3. Cleavage of Methylpentafluorophenylmercury by Inorganic Halides.

a) Reaction of Aluminium Tribromide with Methylpentafluorophenylmercury.

(i) The Preparation of Pentafluorophenylaluminium Dibromide.

Methylpentafluorophenylmercury (6·6 g., 17 m.moles) was melted into a previously constricted Carius tube using a very narrow funnel and the tube was evacuated and introduced into a drybox. (See section on handling techniques p. 158). Freshly resublimed aluminium tribromide (5·3 g., 20 m.moles) was weighed, ground-up, and carefully added to the mercurial in the tube. A rigid stainless steel wire prevented blocking of the constriction and assisted addition. After removal from the drybox the tube was immediately connected to a high vacuum system by means of a double cone device with a vacuum tap between the cones. (See later). Nitrogen was pumped from the vessel and then any adhering aluminium tribromide was carefully sublimed from the constriction before the tap was closed and the tube was cooled in liquid air and sealed under a "sticking" vacuum. On warming to room temperature the mercurial melted, and the mixture became a viscous white mass. The reaction vessel was immersed in an oil bath and heated to 70° for 5 days, cooled, cleaned, and reintroduced to the drybox, when the mixture was a hard, white, crystalline aggregate. Extraction with several small volumes (ca. 20 ml.) dry, 40° petroleum (total volume ca. 100 ml.) followed, and the combined extracts were filtered through a coarse sinter into a dry, weighed, two-neck 250 ml. flask, which was removed from the drybox and connected to the vacuum system by a double cone device similar to that already mentioned, but also containing a sinter to prevent splashing from the flask when under vacuum. (See p. 157). Solvent was removed by vacuum transfer to leave a colourless, viscous liquid, which was pumped to remove methylpentafluorophenylmercury and which solidified after several hours under high vacuum to give a translucent, crystalline solid and then the apparatus was returned to the drybox and reweighed. The yield of pentafluorophenylaluminium dibromide was virtually quantitative (5·8 g., 97%) and the solid melted at 69-71°. The residue after extraction and filtration was shown to be methylmercury bromide (6·0 g., 100%) by infrared analysis. (Found: Br, 45·6; Al, 7·7. $C_6F_5Br_2Al$ requires Br, 45·2; Al, 7·6%).

(ii) Reaction of Aluminium Tribromide with Methylpentafluorophenyl- in Petroleum Ether.

Methylpentafluorophenylmercury (5·5 g., 14 m.moles) in 40°

petroleum (ca. 10 ml.) and aluminium tribromide (3·8 g., 14 m.moles) were heated to 60° for 5 days in a sealed, evacuated tube. Work-up by the method described above yielded pentafluorophenylaluminium dibromide (1·7 g., 33%) recognised by its infrared spectrum. The residue (4·6 g.) contained methylmercury bromide and bis(pentafluorophenyl)mercury. Unreacted methylpentafluorophenylmercury was removed from the product by prolonged pumping.

(iii) Reaction of Aluminium Tribromide (1 mole) with Methylpentafluorophenylmercury (2 moles).

Methylpentafluorophenylmercury (9·0 g., 24 m.moles) and aluminium tribromide (3·13 g., 12 m.moles) were heated to 70° for 7 days in a sealed, evacuated tube. The experiment yielded pentafluorophenylaluminium dibromide, bis(pentafluorophenyl)mercury, and methylmercury bromide, recognised by their infrared spectra, and a fourth product, associated with the aluminium derivative, which was later shown to be bis(pentafluorophenyl)aluminium bromide. Because the mixture was difficult to separate the route was not pursued.

(iv) Reaction of Aluminium Tribromide (1 mole) with Methylpentafluorophenylmercury (2 moles) in Petroleum Ether.

Methylpentafluorophenylmercury (7·5 g., 20 m.moles) in 40° petroleum ether (10 ml.) and aluminium tribromide (2·3 g., 9 m.moles) were heated to 60° for 5 days in a sealed evacuated tube. After work-up by the method described the main product was shown to be pentafluorophenylaluminium dibromide (Infrared) which was contaminated by a viscous light-brown oil later shown to be bis(pentafluorophenyl)aluminium bromide. The residue was shown to be methylmercury bromide by infrared analysis.

b) Reaction of Germanium Tetrabromide with Methylpentafluorophenylmercury.

Methylpentafluorophenylmercury (3·88 g., 10 m.moles) and germanium tetrabromide (4·34 g., 11 m.moles) were put into a Carius tube which was then evacuated and sealed. At room temperature a colourless liquid mixture formed, heat was absorbed, and slow precipitation of colourless "plates" was observed. After 2 days at 60° a substantial amount of solid was present and this temperature was maintained for 2 weeks. Extraction of the mixture in a drybox with 40° petroleum and removal of solvent by vacuum transfer, followed by prolonged pumping to remove methylpentafluorophenylmercury and distillation under reduced pressure gave pentafluorophenyltribromogermane (3·5 g., 67%) which boiled at 51-52° under a sticking vacuum. A small amount of germanium(IV) bromide remained after distillation and the residue after extraction was shown to be methylmercury bromide by infrared. (Found: F, 20·4; Br, 49·2; C, 15·2. $C_6F_5Br_3Ge$ requires F, 19·8; Br, 50·0; C, 15·0%).

c) Reaction of Phosphorus Tribromide with Methylpentafluorophenylmercury.

Methylpentafluorophenylmercury (3·83 g., 10 m.moles) and phosphorus tribromide (2·71 g., 10 m.moles) were mixed in a Carius tube which was evacuated and then sealed. Slow precipitation, and an apparently endothermic reaction, began after about 1 hour at room temperature and the deposit was substantial after 2 days at 60°. This temperature was maintained for 2 weeks when the tube was introduced into a drybox and the contents extracted with 40° petroleum ether. Removal of solvent by vacuum transfer gave pentafluorophenylphosphorus dibromide (3·0 g., 84%).

(Found: Br, 45·1; C, 20·0. $C_6F_5Br_2P$ requires Br, 44·7; C, 20·1%).

Difficulty was experienced in trying to obtain a product free from methylmercury bromide which was apparently slightly soluble in the phosphorus compound.

d) Reaction of Arsenic Tribromide with Methylpentafluorophenylmercury.

Methylpentafluorophenylmercury (11·5 g., 30 m.moles) and arsenic tribromide (9·5 g., 30 m.moles) were put into a Carius tube which was then evacuated and sealed. Heat was absorbed and after 1 day at room temperature very slow precipitation had begun and the rate of deposition was markedly increased after 48 hours at 60°. This temperature was maintained for 2 weeks and then the reaction was worked up as described previously to yield pentafluorophenylarsenic dibromide (10 g., 83%) which boiled at 60° under a sticking vacuum. The residue was shown to be methylmercury bromide by infrared analysis.

(Found: C, 17·6; $C_6F_5Br_2As$ requires C, 17·9%).

Again the apparent solubility of methylmercury bromide in the product caused difficulty when analytically pure samples were required.

e) Reaction of Phosphorus Trichloride with Methylpentafluorophenylmercury.

Phosphorus trichloride (0·9 g., 6·5 m.moles) and methylpentafluorophenylmercury (2·5 g., 6·5 m.moles) were heated to 70° for 144 hours in a sealed, evacuated tube then to 100° for a further 144 hours. When the tube was opened into a vacuum system phosphorus trichloride (0·3 g., 33%) was recovered from a trap cooled in liquid air. Extraction of the residue in the tube with 40° petroleum and removal of solvent gave a colourless liquid (1 g.) which boiled at 160° under atmospheric pressure, which fumed in air and which appeared from its infrared spectrum to be pentafluorophenylphosphorus dichloride (c.f. that of $C_6F_5PBr_2$). Solid remaining in the tube was shown to be mainly methylmercury chloride by infrared analysis but some disproportionation to bis(pentafluorophenyl)mercury had occurred.

f) Reaction of Arsenic Trichloride with Methylpentafluorophenylmercury.

Arsenic trichloride (1·4 g., 7·7 m.moles) and methylpentafluorophenylmercury (3·0 g., 7·8 m.moles) were heated to 74° for 48 hours in a sealed, evacuated tube and the mixture became dark brown. Extraction with 40° petroleum ether gave methylpentafluorophenylmercury (1·0 g., 33%) mixed with arsenic trichloride and the residue was shown to be bis(pentafluorophenyl)mercury by infrared analysis. No pentafluorophenylarsenic derivatives were isolated.

g) Reaction of Acetyl Bromide with Methylpentafluorophenylmercury in presence of Aluminium Trichloride.

Acetyl bromide (0·6 g., 4·9 m.moles) in petroleum ether (5 ml.) was added to aluminium trichloride (0·65 g., 4·9 m.moles) in petroleum ether (5 ml.) in a 25 ml., two-neck flask fitted with a dropping funnel and a reflux condenser carrying a drying tube and the mixture was magnetically stirred until the chloride had dissolved. Methylpentafluorophenylmercury (1·9 g., 4·95 m.moles) in petroleum ether (5 ml.) was added dropwise with stirring and the reaction was allowed to stand overnight at room temperature before being hydrolysed with water. When the organic layer had been separated and dried ($MgSO_4$) solvent was removed by vacuum transfer but no residue remained. The presence of pentafluorobenzene in the solvent was confirmed by comparison of retention time on a gas chromatogram and sublimation of the precipitate formed on hydrolysis yielded methylmercury bromide, recognised by its infrared spectrum. No 2,3,4,5,6-pentafluoroacetophenone was isolated.

Similar reactions in pentane and methylene chloride were also unsuccessful.

h) Reaction of Thionyl Chloride with Methylpentafluorophenylmercury.

Thionyl chloride (1·0 g., 8·4 m.moles) and methylpentafluorophenylmercury (3·4 g., 8·9 m.moles) were heated to 74° for 120 hours in a sealed evacuated tube. When the tube was opened into a vacuum system thionyl chloride (0·75 g., 75%) was collected in a weighed trap cooled in liquid air. Extraction of the solid residue with 40° petroleum and removal of solvent under vacuum gave methylpentafluorophenylmercury (1·0 g., 30%), recognised by its infrared spectrum. The remaining solid (ca. 1·8 g.) was shown to be bis(pentafluorophenyl)-mercury again by infrared analysis.

i) Reaction of Sulphur Dichloride with Methylpentafluorophenylmercury.

(i) Sulphur dichloride (1·0 g., 10 m.moles) and methylpentafluorophenylmercury (8·0 g., 21 m.moles) were heated to 70° for 240 hours in a sealed evacuated tube when the initial red solution had become pale yellow and a considerable amount of precipitation had occurred. Extraction with 40° petroleum ether and removal of solvent left a mixture of unreacted methylpentafluorophenylmercury and sulphur dichloride, whilst the solid residue (4·8g.) was shown to be bis-(pentafluorophenyl)mercury by infrared analysis.

(ii) A reaction between sulphur dichloride and methylpentafluorophenylmercury in equimolar proportions also resulted in disproportionation of the mercurial.

j) Reaction of Silicon Tetrachloride with Methylpentafluorophenylmercury in presence of Aluminium Tribromide.

(i) Methylpentafluorophenylmercury (3·8 g., 10 m.moles) was melted into a constricted Carius tube which was evacuated and introduced into a drybox where aluminium tribromide (2·67 g., 10 m.moles) was added and when the tube had been removed to a vacuum system and evacuated, silicon tetrachloride (1·7 g., 10 m.moles), was condensed into it and the tube was sealed and heated to 100° for 240 hours. When the Carius tube was opened into a vacuum system silicon tetrachloride (1·7 g., 100%), recognised by its infrared spectrum was collected in a weighed trap cooled in liquid air and therefore no further investigation was carried out on the residue.

(ii) The reaction was repeated at 100° for 3 weeks when free mercury was observed in the tube. Volatile material recovered contained ethane and silicon tetrachloride, recognised by their infrared spectra, and a third component b.pt. 90-92° which could not be identified. Extraction of the residue in the tube with 40° petroleum yielded pentafluorophenylaluminium dibromide and left methylmercury bromide and mercury.

k) Reaction of Pentafluorophenylaluminium Dibromide with Methylpentafluorophenylmercury.

The Preparation of Bis(pentafluorophenyl)aluminium Bromide.

A solution of methylpentafluorophenylmercury (5·7 g., 15 m.moles)

in petroleum ether (ca. 10 ml.) was made up in a Carius tube in a drybox and pentafluorophenylaluminium dibromide (3·0 g., 8 m.moles) was added. When the tube had been removed to a vacuum system, cooled, evacuated, and sealed, the mixture was heated to 45° for 96 hours by complete immersion in a magnetically stirred oilbath. After cooling, the reaction vessel was returned to a drybox, opened, and filtered through a coarse sinter into a weighed 100 ml. two-neck flask, and the residue was extracted with five 10 ml. portions of the solvent and these extracts were also filtered into the flask, which was then removed to a vacuum system. Solvent was removed by vacuum transfer to leave a light brown viscous liquid which was pumped under a 'sticking' vacuum for 8 hours to remove any excess methylpentafluorophenylmercury. The flask was returned to the drybox and reweighed to yield bis(pentafluorophenyl)aluminium bromide (2·8 g., 80%) as a viscous liquid which slowly crystallised on standing.
(Found: Br, 18·1; Al, 6·2. $C_{12}F_{10}BrAl$ requires Br, 18·1; Al, 6·1%).

1) Reaction of Aluminium Tribromide with Bis(pentafluorophenyl)mercury.

Aluminium tribromide (1·87 g., 7 m.moles) and bis(pentafluorophenyl)mercury (3·8 g., 7 m.moles) were put into a Carius tube in a drybox and the tube was then evacuated and sealed. No reaction occurred at room temperature and after 7 hours at 55° little change was apparent and the mixture was then heated to 180° for 12 hours, when the contents had become dark brown and completely solid. Extraction with 40° petroleum in a drybox yielded a dark brown, viscous liquid (ca. 1·5 g.) which appeared from infrared evidence to be a mixture of pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide. A grey solid residue (3·7 g.) was shown to be a mixture of mercury(II) bromide, pentafluorophenylmercury bromide and free mercury.

4. Characterisation of Bis(pentafluorophenyl)aluminium Bromide.

Because of the extreme difficulty experienced in the manipulation of this compound (e.g. several explosions occurred in attempts to analyse the substance) only very limited investigation was attempted. Indeed it was extremely difficult to obtain and maintain the compound in a sufficient state of purity to enable acceptable analyses to be obtained.

a) Hydrolysis.

Bis(pentafluorophenyl)aluminium bromide (1·53 g., 3·5 m.moles) was weighed into a 250 ml. two-neck flask in a drybox and the flask was removed to a vacuum system. Water (excess) was condensed into the flask using standard vacuum techniques and carefully controlled low temperature hydrolysis was allowed to occur. Volatile material was vacuum transferred to a vessel containing phosphorus pentoxide, dried at room temperature and finally transferred to a weighed bulb to yield pentafluorobenzene (0·94 g., 83%) recognised by its infrared spectrum and shown to be pure by gas chromatography.

b) Molecular Weight.

Molecular weight determinations were carried out as for pentafluorophenylaluminium dibromide (see page 124) and bis(pentafluorophenyl)aluminium bromide was shown to be dimeric in benzene solution.

c) Aluminium Analyses.

A gravimetric method was employed for aluminium analyses and the technique is described on this page.

5. Reactions of Pentafluorophenylaluminium Dibromide.

a) Characterisation.

(i) Aluminium Analyses.

A gravimetric method was used for the determination of aluminium. A long-necked silica flask (150 ml.) was heated strongly for one hour in a bunsen flame and cooled in a desiccator (P_2O_5). Platinum wire was fixed around the neck of the flask for suspension both from the balance and for heating. After one hour, the flask was introduced into a drybox, weighed, the aluminium compound added, and then reweighed. After being unstoppered, the vessel was removed into air when the derivative began to decompose. Half an hour later distilled water (ca. 1 ml.) was cautiously added dropwise to effect hydrolysis and this was followed by a mixture of analar, concentrated sulphuric and nitric acids (1 ml.). Gentle warming was commenced and gradually the temperature was increased to fume off all volatile material, and finally the flask was ignited for one hour using two roaring bunsens. After cooling in a desiccator for one hour the flask was transferred to the drybox and the aluminium oxide weighed.

(ii) Hydrolysis.

Pentafluorophenylaluminium dibromide (0·64 g., 1·8 m.moles) was weighed out into a 200 ml. flask in a drybox, transferred to a vacuum system, and water (0·14 g., 8 m.moles) was condensed on to it. Vigorous hydrolysis began as the flask was allowed to warm to room temperature, and, when this was complete, all volatile material was vacuum transferred to a second flask containing phosphorus pentoxide. Dry, volatile products were collected in a weighed, evacuated bulb and after reweighing the gas was shown to be pentafluorobenzene (0·299 g., 99%) by its infrared spectrum, and by gas chromatography.

(iii) Molecular Weight.

Molecular weight determinations were carried out using a cryoscopic technique adapted to facilitate the use of air and moisture senstive compounds. A Beckmann thermometer apparatus was used and pentafluorophenylaluminium dibromide was shown to be dimeric in benzene solution.

(iv) Thermal Stability.

(a) Pentafluorophenylaluminium dibromide (2·0 g., 5·6 m.moles) was slowly heated under vacuum to 140° during three hours. The compound melted at 69° and slowly sublimed on to a cold finger (CO_2) as a white solid, which appeared to be starting material from its infrared spectrum, but which melted at 59-60°. A bromine analysis showed that the percentage of that element present was slightly too high for the solid to be pentafluorophenylaluminium dibromide, and it was concluded that some slight disproportionation had occurred, to give aluminium tribromide and bis(pentafluorophenyl)aluminium bromide. A small amount of colourless liquid remained, but there was insufficient material to investigate.

(b) Pentafluorophenylaluminium dibromide (1·5 g., 4·2 m.moles) was slowly heated to 100° for 12 hours in a sealed, evacuated tube and on cooling no apparent change had occurred. After further heating to 160° for 24 hours the liquid had become dark red-brown and when, finally, the temperature was increased to 180°, after 30 minutes the compound decomposed, filling the tube with carbon.

(c) In a sealed, evacuated tube, pentafluorophenylaluminium dibromide (1·3 g., 3·6 m.moles) was quickly heated. The compound melted at 69-71° and above 160° the liquid became dark red and began to bump. Decomposition occurred with extreme violence at 195° and the Carius tube exploded.

b) Reaction with Donor Molecules.

(i) Trimethylamine

Pentafluorophenylaluminium dibromide (3·0 g., 8·4 m.moles) was put into a two-neck, 250 ml. flask in a drybox and then the flask was removed to a vacuum system. Trimethylamine (2·0 g., 34 m.moles) was condensed on to the aluminium compound and an exothermic reaction took place at room temperature. After several hours excess amine was removed by pumping to leave pentafluorophenylaluminium dibromide trimethylamine $C_6F_5AlBr_2 \cdot N(CH_3)_3$ (3·55 g., 100%) which melted at 42° with loss of trimethylamine.

(Found: Br, 38·4; Al, 6·2. $C_9H_9AlBr_2N$ requires Br, 38·8; Al, 6·5%).

(ii) Trimethylamine in Petroleum Ether.

Trimethylamine (excess) mixed with dry nitrogen was bubbled into a solution of pentafluorophenylaluminium dibromide (3·0 g., 8·4 m.moles) in 40° petroleum ether (ca. 20 ml.) in a two neck, 250 ml. flask which was fitted with a reflux condenser. An exothermic reaction took place and an oil was quickly precipitated. Removal of solvent and excess amine by vacuum transfer left a viscous liquid which slowly crystallised on prolonged pumping to yield pentafluorophenylaluminium dibromide trimethylamine complex, recognised by its infrared spectrum and melting point.

(iii) Pyridine in Toluene.

Pyridine (0·22 g., 2·8 m.moles) in toluene (ca. 5 ml.) was added dropwise to pentafluorophenylaluminium dibromide (1·0 g., 2·8 m.moles) in toluene (ca. 10 ml.) in a Schlenk apparatus purged with nitrogen. During addition, and for several hours the mixture was stirred with a teflon covered magnet but no precipitate was observed. Concentration of the solution caused the precipitation of an oil which could not be recrystallised even on cooling to -78°C. The product had an infrared spectrum consistent with that expected for a pyridine adduct but was not investigated any further.

c) Reaction with Ketones.

(i) Benzophenone.

(a) A mixture of pentafluorophenylaluminium dibromide (1·45 g., 4 m.moles) in hexane (ca. 25 ml.) and benzophenone (0·73 g., 4 m.moles) was magnetically stirred for 12 hours under dry nitrogen in a two-neck, 100 ml. flask, fitted with a nitrogen inlet and a reflux condenser topped by a drying tube ($CaCl_2$). Removal of solvent by vacuum transfer gave a viscous, dark brown oil which was warmed to 70° for 2 hours and finally pumped under high vacuum to yield a brown, crystalline mass (needles). Hydrolysis with distilled water gave pentafluorobenzene, recognised by its infrared spectrum, and unchanged benzophenone in quantitative yield.

(b) Pentafluorophenylaluminium dibromide (1·5 g., 4 m.moles) and benzophenone (0·75 g., 4 m.moles) were heated to 45° for 16 hours in a sealed evacuated tube which had been charged in a drybox. On cooling a viscous oil was observed and the tube was reheated to 100° for 96 hours and slowly allowed to come to room temperature when long, dark brown, crystalline needles formed. An infrared spectrum of this solid was virtually identical with that of a mixture of the two compounds thus indicating formation of a stable coordination complex. Hydrolysis with water gave a quantitative recovery of the ketone.

d) Reaction with Acyl and Aroyl Halides.

(i) Acetyl Bromide.

A solution of acetyl bromide (1·0 g., 8 m.moles) in hexane (ca. 5 ml.) was added dropwise to pentafluorophenylaluminium dibromide (1·0 g., 3 m.moles) in hexane (20 ml.) under nitrogen, in a two-neck, 100 ml. flask fitted with a dropping funnel and a reflux condenser carrying a drying tube ($CaCl_2$). The mixture turned red immediately, and, after refluxing for 15 minutes, was hydrolysed with ice-water and the organic layer separated and dried ($MgSO_4$). Removal of solvent gave pentafluoroacetophenone (0·5 g., 80%) shown by infrared to be identical with an authentic sample prepared from pentafluorophenylmagnesium bromide and acetyl chloride.

(Found: F, 45·5; C, 46·0; H, 1·4. Calc. for $C_8H_3F_5O$: F, 45·2; C, 45·7; H, 1·4%).

(ii) Benzoyl Chloride.

(a) Pentafluorophenylaluminium dibromide (2·5 g., 7 m.moles) in benzene (20 ml.) and benzoyl chloride (1·0 g., 7 m.moles) gave a red solution which was refluxed under nitrogen for 1 hour in a two-neck, 100 ml. flask fitted with a dropping funnel and a condenser carrying a drying tube. After standing overnight the mixture was hydrolysed with water and dilute sodium bicarbonate solution was added before the organic layer was separated and dried ($MgSO_4$). Removal of solvent by distillation left a small amount of unreacted benzoyl chloride recognised by its infrared spectrum.

(b) In a sealed, evacuated tube benzoyl chloride (0·88 g., 6 m.moles) and pentafluorophenylaluminium dibromide (2·2 g., 6 m.moles) were heated to 80° for 96 hours. When the reactants were mixed a red colour appeared and on heating darkening occurred. The contents of the tube, a thick, brown liquid, was poured into ice-water and sodium bicarbonate was added with warming. Extraction with several small volumes (ca. 20 ml.) of ether followed and when the solution had been dried ($MgSO_4$) solvent was removed by vacuum transfer to give a dark brown, viscous liquid which yielded 2,3,4,5,6-pentafluorobenzophenone (1·2 g., 70%) as a white crystalline solid on room temperature sublimation under high vacuum. The product had melting point 33·5° (lit. 33-34°).

(Found: C, 57·2; H, 2·1. Calc. for $C_{13}H_5F_5O$: C, 57·4; H, 1·9%).

e) Reaction with Alkyl and Aryl Halides.

(i) Ethyl Bromide.

Ethyl bromide (0·66 g., 6·0 m.moles) and pentafluorophenylaluminium dibromide (2·34 g., 6·6 m.moles) were put into a Carius tube in a drybox and the tube was evacuated and sealed. On mixing the two compounds an orange colour appeared and this changed to red on warming. After 72 hours at 80° the tube was cooled, opened and the contents hydrolysed with ice-water. Extraction with ether in several small volumes was followed by drying of the combined organic extracts and removal of solvent by vacuum transfer to give a small amount of a viscous dark red semi solid which could not be identified. Ethyl bromide and pentafluorobenzene were shown to be present in the solvent by comparing retention times on a gas chromatograph.

(ii) Chlorobenzene.

(a) Chlorobenzene (0·48 g., 4·2 m.moles) and pentafluorophenylaluminium dibromide (1·49 g., 4·2 m.moles) were heated to 80° for 72 hours in a sealed evacuated Carius tube. Mixing of the two reactants produced a red colour which darkened on heating. Hydrolysis with ice-water and extraction with ether gave chlorobenzene and pentafluorobenzene recognised by their retention times on a gas chromatograph.

(b) Chlorobenzene (0·51 g., 4·5 m.moles) and pentafluorophenylaluminium dibromide (1·62 g., 4·6 m.moles) were heated to 102° for 168 hours in a sealed, evacuated tube. A red colour was observed immediately on mixing the reactants. Hydrolysis with ice-water was followed by ether extraction, drying of the organic solution ($MgSO_4$) and removal of solvent by distillation to yield ca. 0·5 g. of a liquid mixture which was shown to contain only chlorobenzene and pentafluorobenzene by gas chromatography.

f) Reactions with Carbon Dioxide.

(i) In Hexane Solution.

A hexane solution of pentafluorophenylaluminium dibromide (1·0 g., 3 m.moles) was saturated with pure, dry carbon dioxide gas at room temperature during 0·5 hours. The experiment was carried out in a 100 ml. two-neck flask fitted with a reflux condenser, which carried a drying tube, and a carbon dioxide inlet dipping below the surface of the solution, the whole being initially purged with dry nitrogen. Subsequent hydrolysis (ice-water), acidification with dilute hydrochloric acid, and ether extraction gave only pentafluorobenzene, recognised by its retention time on a gas chromatogram. No pentafluorobenzoic acid was isolated.

This experiment was repeated in diethyl ether and refluxing benzene but hydrolysis gave pentafluorobenzene only.

g) Reaction with Olefins.

(i) Propene.

(a) Propene (2·34 g., 56 m.moles) i.e. in excess, was condensed into a Carius tube containing pentafluorophenylaluminium dibromide (1·36 g., 3·8 m.moles) which was evacuated and sealed. At room temperature the mixture became extremely viscous, turned yellow, and considerable heat was evolved, and the olefin could be seen to polymerise. After a few minutes reaction appeared to be complete although the aluminium compound seemed unaffected and when the tube was opened into a vacuum system no volatile material was recovered. Hydrolysis with ice-water gave a gas identified as pentafluorobenzene by its infrared spectrum. Extraction with hexane and drying of the solution ($MgSO_4$) was followed by removal of solvent by vacuum transfer to yield an extremely viscous yellow oil with a very simple infrared spectrum which indicated the presence of carbon and hydrogen only. This substance could not be distilled when heated to 200° at 0·005 mm. and micro analyses detected carbon and hydrogen but no halogen. (Found: C, 84·5; H, 11·4%).

(b) Propene in Petroleum Ether.

Pentafluorophenylaluminium dibromide (3·1 g., 8·8 m.moles) and petroleum ether (ca. 10 ml.) were put into a Carius tube in a drybox and it was noticed that not all of the aluminium derivative dissolved.

After removal from the drybox and connection to a vacuum system the vessel was cooled in liquid air, evacuated, and propene (0·37 g., 8·8 m.moles) was introduced using standard vacuum techniques. The tube was sealed under vacuum, and when the contents had warmed to room temperature a homogeneous solution was formed and heat was evolved, and then the mixture was heated to 50° for 48 hours, cooled, and the tube returned to the drybox where it was opened and the contents poured into a weighed 100 ml. two-neck flask. No evolution of propene was observed and the flask was removed to a vacuum system where solvent was transferred to another vessel leaving a dark-brown crystalline solid and some viscous liquid (total weight = 3·45 g.) which later became completely solid after several weeks in a drybox. This substance was shown to contain strong C-H bonds and also the C_6F_5 group by infrared analysis, and was investigated in the following ways.

(i) A sample of the solid was hydrolysed with water, in a vacuum system, and volatiles were collected by vacuum transfer, and dried (P_2O_5). Infrared analysis indicated the presence of pentafluorobenzene and a hydrocarbon compound, and at room temperature the volatile material gave off bubbles of a gas. Comparison of retention times on a gas chromatogram, which showed a single peak, confirmed the main component as pentafluorobenzene. Volatile material from a second hydrolysis was immediately studied by mass spectroscopy, and comparison with a spectrum of pure pentafluorobenzene of the same intensity showed definite increases in intensity at masses 42, 41 and 27 corresponding to the cracking pattern of propene, whilst no extra peaks were observed above mass 42.

(ii) Nuclear magnetic resonance measurements were carried out on the solid product and the chemical shifts observed in the ^{19}F spectrum were identical with those observed for pentafluorophenylaluminium dibromide, whilst those of the latter in diethyl ether showed small shifts.

(iii) Another sample of the solid product was treated with toluene in a vacuum system and a gas was evolved, and collected, with excess of toluene, by vacuum transfer. Mass spectroscopy measurements, as before, again showed definite increases in intensity at masses 42, 41, and 27.

(iv) The polymer produced in this reaction was recovered by extraction of the residue after hydrolysis and shown to contain almost 10% of fluorine, and no bromine, by micro-analysis, and infrared data indicated the presence of the pentafluorophenyl group.

(ii) Vinylidene Fluoride.

Vinylidene fluoride (3·58 g., 56 m.moles) was condensed into a Carius tube containing pentafluorophenylaluminium dibromide (1·0 g., 2·8 m.moles) using standard vacuum techniques and when the tube had been sealed and was allowed to attain room temperature the aluminium derivative began to darken and in a few minutes it was completely black. On opening into a vacuum system after 48 hours at 75° vinylidene fluoride (3·4 g., 95%), recognised by its infrared spectrum, was recovered together with a trace of pentafluorobenzene recognised in similar fashion. Extraction of the black solid residue yielded a trace of unchanged pentafluorophenylaluminium dibromide but the remaining black material could not be identified.

(iii) Hexafluoropropene.

(a) Hexafluoropropene (4·75 g., 32 m.moles) was condensed into a Carius tube containing pentafluorophenylaluminium dibromide (0·5 g., 1·4 m.moles) using standard vacuum techniques. When the tube was sealed and allowed to attain room temperature the aluminium compound turned black and no polymerisation was observed. After several days at room temperature the olefin was recovered quantitatively.

(b) Hexafluoropropene in Petroleum Ether. Hexafluoropropene (5·0 g., 33 m.moles) was condensed into a Carius tube containing a solution of pentafluorophenylaluminium dibromide (1·0 g., 2·8 m.moles) in petroleum ether (5 ml.). At room temperature blackening of the aluminium compound occurred and after several days only unchanged olefin, recognised by its infrared spectrum, was identified.

h) Reaction with Acetylenes.

(i) Phenylacetylene.

Phenylacetylene (2·8 g., 28 m.moles) was cautiously added dropwise to pentafluorophenylaluminium dibromide (4·8 g., 14 m.moles) in a two-neck, 100 ml. flask in a drybox. Addition of the first drop of the acetylene caused violent decomposition and carbon was deposited.

(ii) Diphenylacetylene.

(a) Diphenylacetylene (0·46 g., 2·6 m.moles) was cautiously added to pentafluorophenylaluminium dibromide (1·3 g., 3·7 m.moles) in a 50 ml. two-neck flask in a drybox and a reaction began immediately with evolution of heat and the mixture became dark green. After removal of the flask to a vacuum system, evacuation, and warming to 60° for 2 hours the mixture was allowed to stand overnight before being hydrolysed with glacial acetic acid in methylated spirits. A precipitate was formed, and filtered, and the organic layer was evaporated to leave a green-yellow solid which could not be sublimed and which appeared to contain only carbon and hydrogen (Infrared). Micro-analyses could detect no halogen in this material.

(b) Pentafluorophenylaluminium dibromide (1·6 g., 5 m.moles) and diphenylacetylene (0·8 g., 5 m.moles) were heated to 80° for

96 hours in a sealed evacuated tube which had been loaded in a drybox. The mixture turned dark green immediately and after heating, a tarry, viscous product was hydrolysed with glacial acetic acid in hexane. After filtration, removal of solvent by vacuum transfer left a dark green solid, which was not significantly affected by decolourising charcoal, and which contained no halogen detectable in micro analyses. Infrared analysis indicated the presence of carbon and hydrogen only, and the substance could not be sublimed or recrystallised and appeared to be polymeric.

(Found: C, 88 ; H, 5·5 %).

6. Reaction of Pentafluorophenyl-lithium with Inorganic Halides.

(a) Arsenic Tribromide.

(i) In Hexane-Ether Solution.

n-Butyl-lithium (6 m.moles in hexane) was added dropwise during 0·25 hours to a solution of pentafluorobenzene (1·0 g., 6 m.moles) in diethyl ether (5 ml.) cooled to -65° and magnetically stirred in a 100 ml., two-neck flask fitted with a dropping funnel and nitrogen inlet tap and purged with dry nitrogen. After a further 10 minutes, arsenic tribromide (1·86 g., 6 m.moles) in ether (20 ml.) was added dropwise and the mixture was allowed to attain room temperature after 1 hour. The solution was filtered to remove lithium bromide and solvent was removed by vacuum transfer to yield a buff coloured solid which could not be identified and seemed to be polymeric. An infrared spectrum indicated that the substance was a polyphenylene.

(ii) In Hexane Solution.

Pentafluorobenzene (1·0 g., 6 m.moles) in hexane (10 ml.) was cooled to -65° and a hexane solution of n-butyl-lithium (6 m.moles) in hexane (5 ml.) was added dropwise to it in a 100 ml., two-neck flask fitted with a dropping funnel and nitrogen inlet tap. Nitrogen passed out through the side arm of an adaptor between the flask and the funnel. After 0·5 hours arsenic tribromide (1·86 g., 6 m.moles) in hexane (30 ml.) was added and the mixture was magnetically stirred for a further half hour before being allowed to come to room temperature. Lithium bromide was removed by filtration and solvent by vacuum transfer to yield pentafluorophenyl arsenic dibromide (1·0 g., 42%), recognised by comparing its infrared spectrum with that of a sample made by cleavage of methylpentafluorophenylmercury. A small amount of a pale yellow crystalline solid settled out of the product and was shown to be a pentafluorophenyl derivative by its infrared spectrum and this substance was possibly bis(pentafluorophenyl)arsenic bromide or tris(pentafluorophenyl)arsine.

(b) Aluminium Tribromide. Attempted Preparation of Tris(pentafluorophenyl)aluminium.

(i) In Hexane-Ether Solution.

Aluminium tribromide (1•6 g., 6 m.moles) in ether (10 ml.) was added to a cooled, -65°, solution of pentafluorophenyl-lithium (18 m.moles) formed from a hexane solution of n-butyl-lithium (6 ml., 18 m.moles) and pentafluorobenzene (3•0 g., 18 m.moles) in hexane (20 ml.) in a 100 ml., two-neck flask purged with dry nitrogen. After being magnetically stirred for half an hour the mixture was allowed to attain room temperature. Filtration in a drybox and removal of solvent by vacuum transfer left a small amount (ca. 1 ml.) of a viscous orange liquid which appeared to be a pentafluorophenyl derivative and also to contain ether (Infrared). Solvent could not be removed even after several hours under high vacuum, and the liquid, which was air sensitive was not characterised, but was probably a mixture of pentafluorophenyl derivatives of aluminium complexed with ether. Brinckmann and co-workers[92] obtained tris(pentafluorophenyl)-aluminium as a etherate and also found that solvent could not be eliminated from the product.

(ii) In Hexane Solution.

Aluminium tribromide (1•6 g., 6 m.moles) suspended in hexane (15 ml.) was added to a solution of pentafluorophenyl-lithium (6 m.moles) in hexane (20 ml.) at -65°, formed from n-butyl-lithium

(2 ml., 6 m.moles) and pentafluorobenzene (1·0 g., 6 m.moles), in a 100 ml. two-neck flask purged with nitrogen. After half an hour at -65° the mixture was allowed to attain room temperature, the precipitate was filtered in a drybox, and solvent removed by vacuum transfer to leave a viscous yellow oil which did not contain any pentafluorophenyl (Infrared). Extraction of the solid residue with benzene, and petroleum ether also failed to isolate a pentafluorophenyl derivative and so it seemed that no soluble pentafluorophenyl compounds had been formed and this may have been due to the formation of a lithium-aluminium salt.

(iii) The experiment was repeated in hexane-benzene solution but the desired product could not be isolated.

(c) Reaction of Pentafluorophenyl-lithium with Sulphur Dichloride. The Preparation of Bis(pentafluorophenyl)sulphide.

Pentafluorobenzene (8·4 g., 50 m.moles) in hexane-ether solution (20:30 ml.) was cooled to -70° in a four-neck, 250 ml. flask fitted with a mercury seal stirrer, dropping funnel, nitrogen inlet, and drikold condenser and n-butyl-lithium (22 ml. of a hexane solution, 50 m.moles) in hexane (20 ml.) was added dropwise over half an hour. The mixture was stirred at this temperature for 3 hours and then sulphur dichloride (2·58 g., 25 m.moles) in ether (10 ml.) was slowly added dropwise (0·5 hour), and, after a further 2 hours at

-70°, the reaction was allowed to come slowly to room temperature. Hydrolysis (H_2O) was followed by separation of the organic layer, which was dried ($MgSO_4$), and removal of solvent by vacuum transfer to yield bis(pentafluorophenyl)sulphide (5·5 g., 60%) as a white crystalline solid which melted at 81-82°.

(Found: C, 39·4; F, 51·5 after resublimation at 70° and 10^{-3} cm. Calc. for $C_{12}F_{10}S$: C, 39·3; F, 51·9%).

This compound has since been reported by other workers.[57,109]

(d) Reaction of σ-Bromotetrafluorophenyl-lithium with Sulphur Dichloride. The Preparation of Bis(orthobromotetrafluorophenyl)sulphide.

σ-Dibromotetrafluorobenzene (9·2 g., 30 m.moles) in hexane-ether solution (30:20 ml.) was cooled to -75° in a 250 ml., four-neck flask fitted with a mercury seal stirrer, dropping funnel, nitrogen inlet, and drikold condenser, and purged with dry nitrogen, and n-butyl-lithium (12·8 ml. of a hexane solution, 30 m.moles) in hexane (20 ml.) was added dropwise over half an hour. The mixture was stirred for 3 hours at -75° and then sulphur dichloride (1·55 g., 15 m.moles) in ether (10 ml.) was slowly added over half an hour. After a further 1·5 hours at -75° the reaction was allowed to warm to room temperature, hydrolysed (H_2O), the organic layer separated and dried ($MgSO_4$), and solvent removed under vacuum to yield a yellow solid plus some yellow oil (7·7 g.). The solid product was carefully washed on a sintered funnel with several small volumes (ca. 5 ml.) of 40° petroleum ether and air dried before being resublimed at 80° and 10^{-3} mm. to yield bis(orthobromotetrafluorophenyl)sulphide (4·5 g., 63%) as a white, crystalline solid which melted at 100°.

(Found: C, 29·4; F, 31·2; Br, 32·7. $C_{12}F_8Br_2S$ requires C, 29·5; F, 31·1; Br, 32·8%).

7. Reactions of Bis(orthobromotetrafluorophenyl)sulphide with Copper.

(a) Reaction of Bis(orthobromotetrafluorophenyl)sulphide with Copper Powder in Dimethyl Formamide.

(i) Bis(orthobromotetrafluorophenyl)sulphide (1·1 g., 2·3 m.moles) and copper powder (0·6 g., 9·5 m.moles) in dimethylformamide (10 ml.) were heated to 90° under reflux in a 20 ml. flask for 24 hours. Copper was removed by filtration and the metal was washed several times with dry amide before the combined organic solution was poured into water to yield starting material, which was recovered quantitatively.

(ii) The above experiment was repeated at the following temperatures but only starting material was recovered: 100°, 120°, 150°.

(iii) Bis(orthobromotetrafluorophenyl)sulphide (1·35 g., 2·8 m.moles), copper powder (2·5 g., 40 m.moles), and dimethylformamide (8 ml.) were heated to 172° for 24 hours in a sealed, evacuated tube. Treatment as before yielded a "fluffy" white precipitate which was dried and resublimed at 130° and 10^{-3} mm. to yield a white solid which contained strong carbon-hydrogen bands in its infrared spectrum.

This product was not investigated further since infrared evidence indicated that reaction with the solvent had occurred and this was verified by mass spectrometry.

(b) Reaction of Bis(orthobromotetrafluorophenyl)sulphide with Copper Powder. The Preparation of Octafluorodibenzothiophene.

(i) Bis(orthobromotetrafluorophenyl)sulphide (0·8 g., 1·6 m.moles) and copper powder (2·0 g., 31 m.moles) were heated to 160° for 48 hours in a sealed, evacuated Carius tube. The contents of the tube were emptied into a sublimation apparatus and starting material (0·7 g., 88%) was recovered after sublimation at 80° and 10^{-3} mm.

(ii) Bis(orthobromotetrafluorophenyl)sulphide (0·5 g., 1 m.mole) and copper powder (0·3 g., 4·8 m.moles) were heated to 180° for 96 hours in a sealed, evacuated Carius tube. The contents of the tube were extracted with ether and excess copper was removed by filtration before solvent was removed by vacuum transfer to leave a white solid which resublimed at 90° and 10^{-3} mm. to yield octafluorodibenzothiophene (0·2 g., 66%) which melted at 99-100°.

(Found: C, 43·8; F, 46·3. $C_{12}F_8S$ requires C, 43·9; F, 46·3%).

(iii) Bis(orthobromotetrafluorophenyl)sulphide (3·0 g., 6 m.moles) and copper powder (1·8 g., 29 m.moles) were heated to 200° for 120 hours in a sealed, evacuated Carius tube and yielded octafluorodibenzothiophene (1·9 g., 100%) recognised by its infrared spectrum and melting point.

8. Reactions of Octafluorodibenzothiophene.

(a) Reaction with Nucleophiles.

(i) Sodium Methoxide.

A solution of sodium (0·033 g., 1·47 m.moles) in dry methanol (20 ml.) was added dropwise during 1 hour to a magnetically stirred solution of octafluorodibenzothiophene (0·46 g., 1·4 m.moles) in methanol (30 ml.) in a 100 ml., two-neck flask fitted with a reflux condenser carrying a drying tube, and a dropping funnel. After 24 hours at 40° the mixture was allowed to cool to room temperature when a white precipitate appeared. Water (50 ml.) was added and the solution extracted with methylene chloride, the combined extracts being dried ($MgSO_4$) before solvent was removed by vacuum transfer to yield 0·6 g. of a white solid which was shown to contain three components by gas chromatography. Fractional sublimation yielded octafluorodibenzothiophene (ca. 0·05 g.), monomethoxyheptafluorodibenzothiophene (0·4 g., 83%) and a residue (ca. 0·1 g.) which was shown to be a mixture of mono and di-methoxy derivatives by gas chromatography and mass spectrometry. Heptafluoromethoxydibenzothiophene was obtained as a white, crystalline solid, m.pt. 105-107°. (Found: C, 45·9; H, 1·00; F, 38·6. $C_{13}H_3F_7SO$ requires C, 45·9; H, 0·9; F, 39·1%).

(ii) Ammonia

Octafluorodibenzothiophene (0·5 g., 1·6 m.moles) in ether (10 ml.)

and ammonia gas (3·2 m.moles), which had been accurately measured in a vacuum system, were heated to 128° for 170 hours in a sealed, evacuated tube. When the tube had cooled a precipitate was observed and, after removal of solvent by vacuum transfer, the solid was washed with distilled water, taken up in ether, and, after the solution had been dried, ($MgSO_4$) solvent was again removed under vacuum to yield a cream coloured solid (0·6 g.). Fractional sublimation yielded heptafluoroaminodibenzothiophene (0·3 g., 56·5%) as a white solid, which turned cream on standing in air, and which melted at 142° with decomposition. A small amount of octafluorodibenzothiophene (0·1 g., 20%) was also recovered and some brown tarry residue remained.

(Found: C, 44·0; H, 0·7; F, 41·8 . $C_{12}H_2F_7SN$ requires C, 44·3; H, 0·6; F, 40·9%).

(b) Reaction with Raney Nickel.

(i) Raney Nickel in Ethanol.

Octafluorodibenzothiophene (0·14 g., 0·43 m.moles) and Raney nickel (ca. 0·4 g.) in ethanol (20 ml.) were stirred at room temperature for 4 hours in a 100 ml., two-neck flask fitted with a reflux condenser, leading to a gas bubbler, and a nitrogen inlet. After filtration to remove nickel, and washing of the metal with ethanol, solvent was removed by distillation to leave a white solid (0·1 g.) which sublimed easily at 80° and 10^{-2} mm. and which was shown to be a mixture of starting material and 2,2'-dihydro-octafluorobiphenyl by comparison of retention times on a gas chromatograph and infrared spectra, after separation of the latter by room temperature, fractional sublimation.

(ii) Raney Nickel in Benzene.

Raney nickel (three spatulas full) was washed ten times with dry benzene under nitrogen to remove ethanol and a small amount of solvent was distilled[165] before octafluorodibenzothiophene (0·3 g., 0·91 m.moles) in benzene (10 ml.) was added to it in a 100 ml., two-neck flask, flushed with nitrogen and fitted with a reflux condenser connected to a gas bubbler, and a nitrogen inlet. After 24 hours under reflux nickel was removed by filtration and washed several times with methylene chloride and the washings plus the benzene solution were distilled to leave a pale yellow oil, which crystallised on cooling to room temperature. The solid product sublimed readily at 60° and 0·05 mm. to yield a white crystalline solid (0·2 g.). Gas chromatography showed the solid to be largely a single component contaminated with an impurity (ca. 10%) of higher volatility and the former, after separation by fractional sublimation was identified as 2,2'-dihydro-octafluorobiphenyl by its infrared and N.M.R. spectra. The second component appeared, from its mass spectrograph, to contain three hydrogen atoms in the molecule but was not characterised.

(iii) Raney Nickel in a Sealed Tube.

Raney nickel was washed six times with dry ether under nitrogen and then pumped dry under high vacuum for 30 hours, before excess of it with octafluorodibenzothiophene (0·2 g., 0·61 m.moles) was heated to 85° for 48 hours in a sealed, evacuated Carius tube which was filled in a drybox. Extraction with methylene chloride yielded perfluorodibenzothiophene (0·18 g., 90%) after removal of solvent by vacuum transfer. Gas chromatography showed the presence of a trace (5%) of a more volatile component but there was not sufficient material to investigate.

(iv) Raney Nickel in a Sealed Tube.

Octafluorodibenzothiophene (0·29 g., 0·9 m.moles) and excess Raney nickel (treated as above) were heated to 290° for 72 hours in a sealed, evacuated tube which had been filled in a drybox. Work-up as before yielded a complex mixture of at least six products and no starting material was recovered. Infrared spectroscopy showed the presence of carbon-hydrogen bonds in the products and mass spectrometry showed that perfluorobiphenylene was not present and therefore they were not investigated any further.

(c) Reactions with Copper.

(i) Octafluorodibenzothiophene (0·2 g., 0·61 m.moles) and copper powder (0·5 g., 7·9 m.moles) were heated to 280° for 120 hours in a sealed, evacuated Carius tube. The contents of the tube were emptied into a sublimation apparatus and a white, crystalline solid which resublimed at 80° and 10^{-2} mm. was shown to be octafluorodibenzothiophene (0·2 g., 100%) by its infrared spectrum and melting point.

(ii) Octafluorodibenzothiophene (0·2 g., 0·61 m.moles) and copper powder (1·5 g., 23·7 m.moles) were heated to 420° for 96 hours in a sealed, evacuated Carius tube and after sublimation as above only starting material (0·18 g., 90%) was recovered.

(iii) Octafluorodibenzothiophene (0·22 g., 0·67 m.moles) and copper powder (1·5 g., 23·7 m.moles) were heated to 480° for 72 hours in a sealed, evacuated Carius tube and it was noticed that quite considerable blackening of the copper had occurred but only octafluorodibenzothiophene (0·13 g., 60%) was recovered. The black residue and etching of the glass tube indicated decomposition of the compound.

(d) Reaction with Cuprous Oxide.

Cuprous oxide (1·0 g., 7 m.moles) and octafluorodibenzothiophene (0·2 g., 0·61 m.moles) were heated to 350° for 48 hours in a sealed, evacuated Carius tube. When the reaction mixture was emptied into a sublimation apparatus and heated under vacuum only octafluorodibenzothiophene was recovered.

Reaction of Monomethoxyheptafluorodibenzothiophene with Raney Nickel in Benzene.

Raney nickel (excess) was washed ten times with dry benzene under nitrogen before being added to monomethoxyheptafluorodibenzothiophene (0·06 g., 0·18 m.moles) in benzene (30 ml.) in a 100 ml., two-neck flask fitted with a reflux condenser connected to a gas bubbler, and a nitrogen inlet. When the mixture had been refluxed for 24 hours, nickel was removed by filtration and washed several times with hot methylene chloride and the combined washings and benzene solution distilled, to leave a white solid which sublimed at 40° and 0·005 mm. to give long needles of a white crystalline solid, which was shown to be a single component by gas chromatography. Mass spectrometry showed this compound to have a molecular weight of 310 and since sulphur was shown to be absent from the molecule by analysis it was concluded that, by analogy with octafluorodibenzothiophene, the compound was 2,2'-dihydromonomethoxybiphenyl.

9. Manipulation of Air and Moisture Sensitive Compounds.

All manipulations of pentafluorophenylaluminium dibromide, bis(pentafluorophenyl)aluminium bromide and several other derivatives were carried out in the drybox shown in photograph one. (page 154).

1. The Drybox.

(a) Specifications.

A steel box 100 cm. wide, 75 cm. high and 65 cm. from front to back, which had a perspex roof and front which contained two ports used for armholes, was obtained from Lintott Engineering Ltd., Horsham, Sussex. The perspex windows were fitted with rubber airtight seals and neoprene arm-length gloves were used on the front ports. At one side of the box was a cylindrical transfer tube 43 cm. long and 25 cm. diameter which opened into the drybox by means of a screw-in port and which similarly opened to the air at the other end. A strip-light was mounted outside the perspex roof and electricity was carried into the box which contained a recirculating pump and an electrical balance. Behind the transfer tube were four, 1 cm. diameter tubes leading through the side of the apparatus and closed inside and out by 4 mm. glass high vacuum taps, whilst the floor was covered with a sheet of black plastic material.

(b) Maintenance of an Inert Atmosphere.

The nitrogen atmosphere in the drybox was kept free from oxygen and moisture in the following way. The pump, which could completely recycle the atmosphere in the box in ten hours, passed nitrogen out through a 4 mm. tap, through a trap 18 inches deep cooled in liquid air, over copper wire packed in two silica towers at 400°, through a second trap similarly cooled, and back through another 4 mm. tap into the box. This process was maintained whenever the drybox was not being used for experiments and the oxygen content of the atmosphere was measured as 190 p.p.m. using an Engelhard Hersch Mark II oxygen meter. Copper towers and liquid air traps were connected to the drybox by p.v.c. and silicone tubing and normally the pressure in the box was maintained slightly above atmospheric. Nitrogen from the bench supply could be introduced into the system via the copper towers and liquid air cooled traps, and a flow diagram is shown on page 155 (diagram one). A relay was incorporated into the electrical supply to the pump and attached to a U tube containing mercury. One limb of the tube was open to air and the other connected to the box through a 4 mm. tap. When the pressure inside the box fell to a certain level the pump was cut off to prevent the gloves "sucking" into the box as the pressure went down.

(c) Movement into and out of the Drybox.

Whenever possible all apparatus introduced into the drybox was dried by "baking" for at least twenty-four hours in an oven at 120°. Items being moved into the system were placed in the transfer tube which had an inlet tap connected to the nitrogen system of the drybox, and nitrogen from the bench supply was flushed through via the copper towers and liquid air traps, and passed out of the transfer chamber via a gas bubbler into the air. When the transfer tube had been purged for at least one hour the apparatus could be moved into the drybox. In practice times varied between one and three hours and whilst the atmosphere in the transfer tube could be displaced every five minutes a long slow purge was found to be most effective. After use apparatus could be returned to the transfer chamber immediately and thence back into air.

2. Isolation of Pentafluorophenyl Derivatives.

Most perfluoroaryl derivatives prepared in the present work, and particularly those of aluminium, had to be isolated in the drybox and the work-up procedure involved filtration to remove insoluble methylmercury halides. The apparatus used is shown in diagram two. A two-neck, 250 ml. flask was normally used and in one neck was placed a filter tube having a coarse sinter (porosity 2) whilst the other neck was connected by means of a gas lead and rubber tubing to a rubber bulb having a non-return valve at one end. When the bulb was squeezed nitrogen was drawn out of the flask and the solution passed through the sinter leaving the insoluble methylmercury halide behind.

The flask was connected to a vacuum system as shown in diagram three. The vessel was fitted with high vacuum taps so that it could be transferred from the drybox to the vacuum system and back with impunity. The double cone device shown served two purposes. Firstly it allowed attachment to a vacuum system and secondly the sinter allowed evaporation of solvent but prevented bumping and subsequent contamination of the product by grease etc.

3. Filling of Carius Tubes with Methylpentafluorophenylmercury and Aluminium Tribromide.

Methylpentafluorophenylmercury (m.pt. 36°) was melted into a constricted Carius tube as shown in diagram four. A drawn out glass tube was placed in the constriction as shown and the mercurial could thus be added without touching the walls of the Carius tube. When the latter had been introduced into the drybox crushed aluminium tribromide was added as shown in four (b). The stainless steel rod was moved up and down and the powdered solid fell into the tube without blocking the constriction. If these procedures were not followed and the two compounds came into contact in the neck of the Carius tube reaction began and on heating decomposition occurred and a good seal could not be obtained. Aluminium tribromide was readily sublimed from the constriction by gentle "flaming" under vacuum.

PLAN VIEW OF FLOW

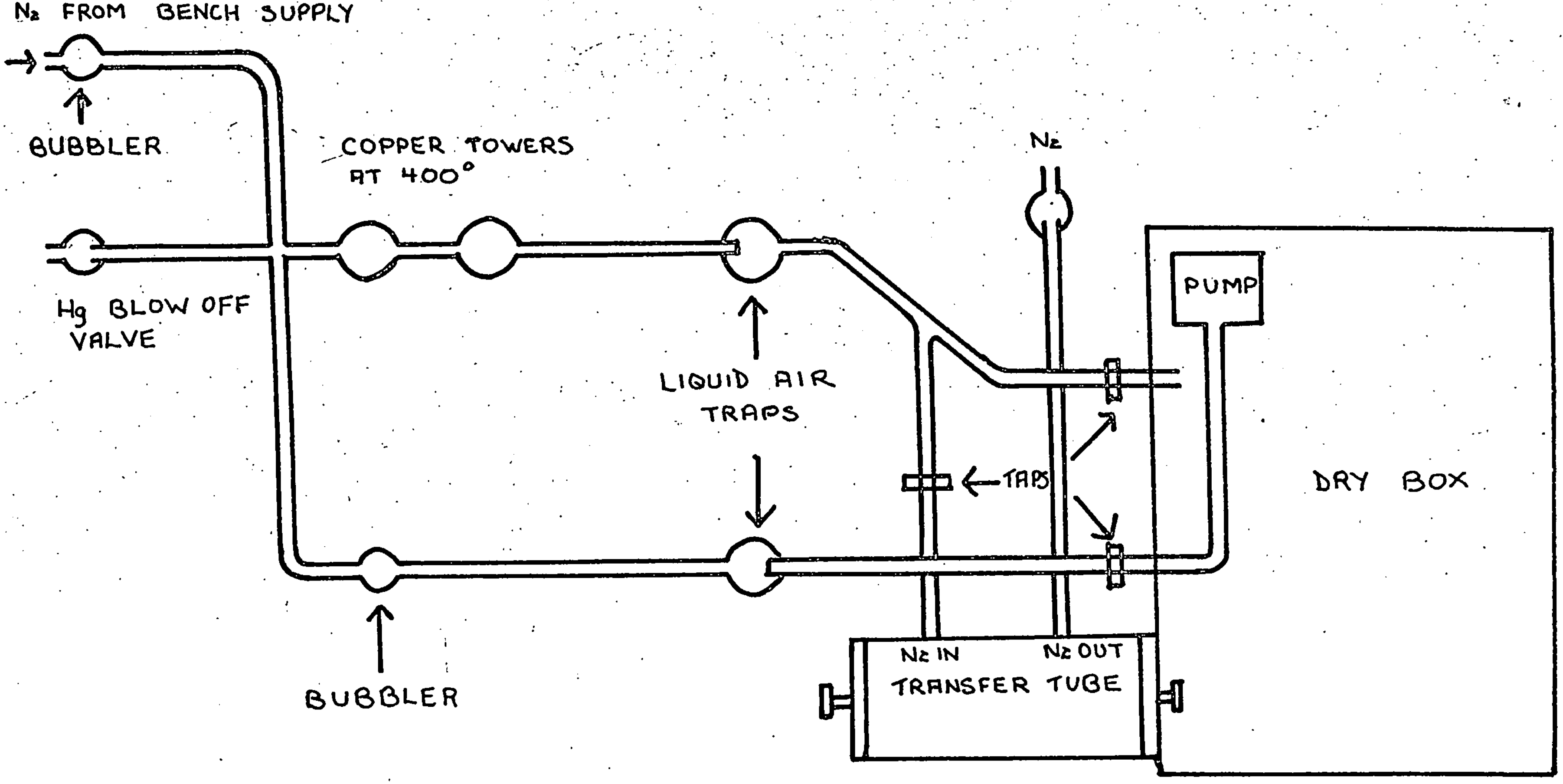
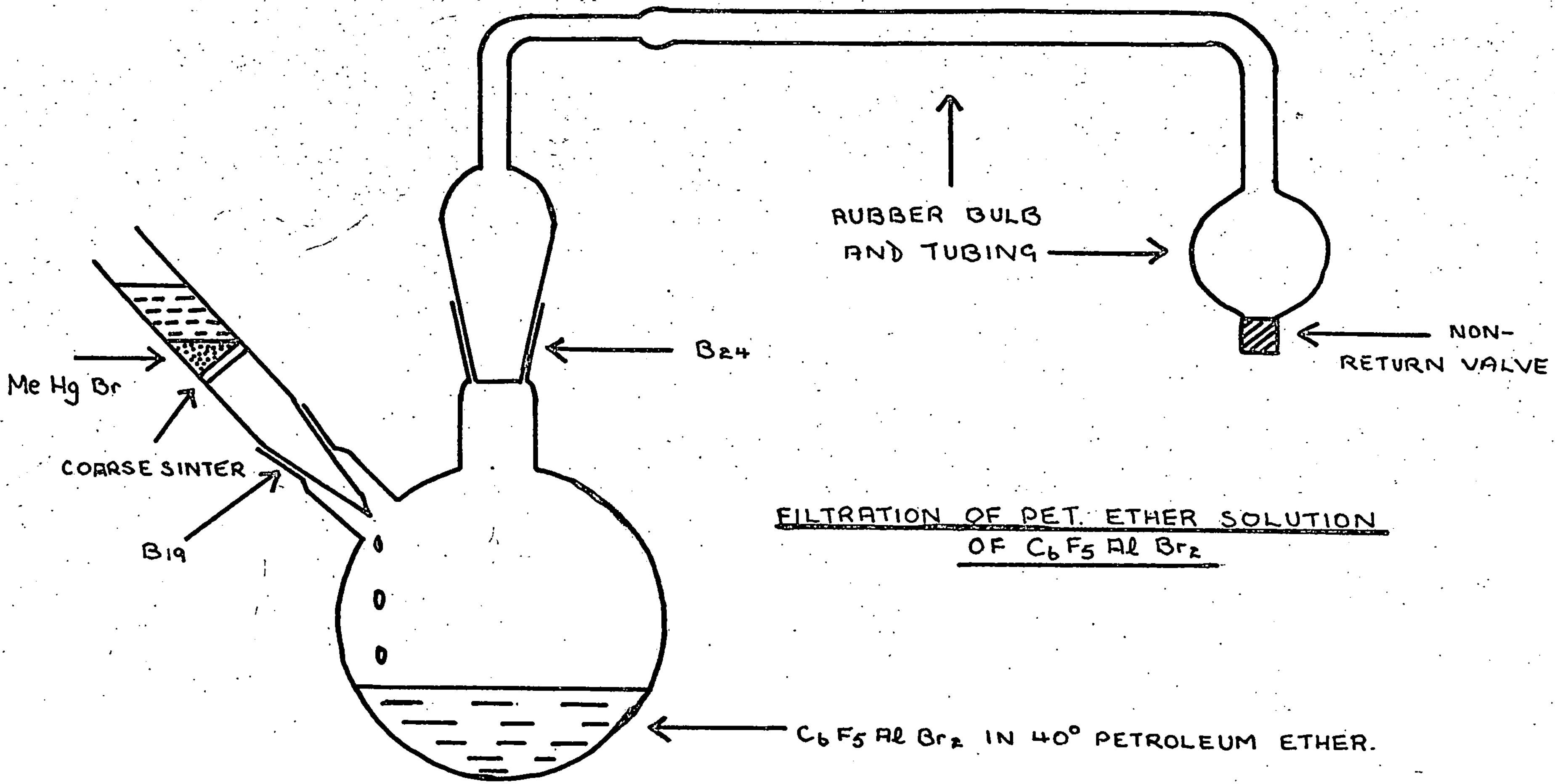


DIAGRAM ONE.



FILTRATION OF PET. ETHER SOLUTION OF $C_6F_5AlBr_2$

DIAGRAM TWO

REMOVAL OF SOLVENT UNDER VACUUM

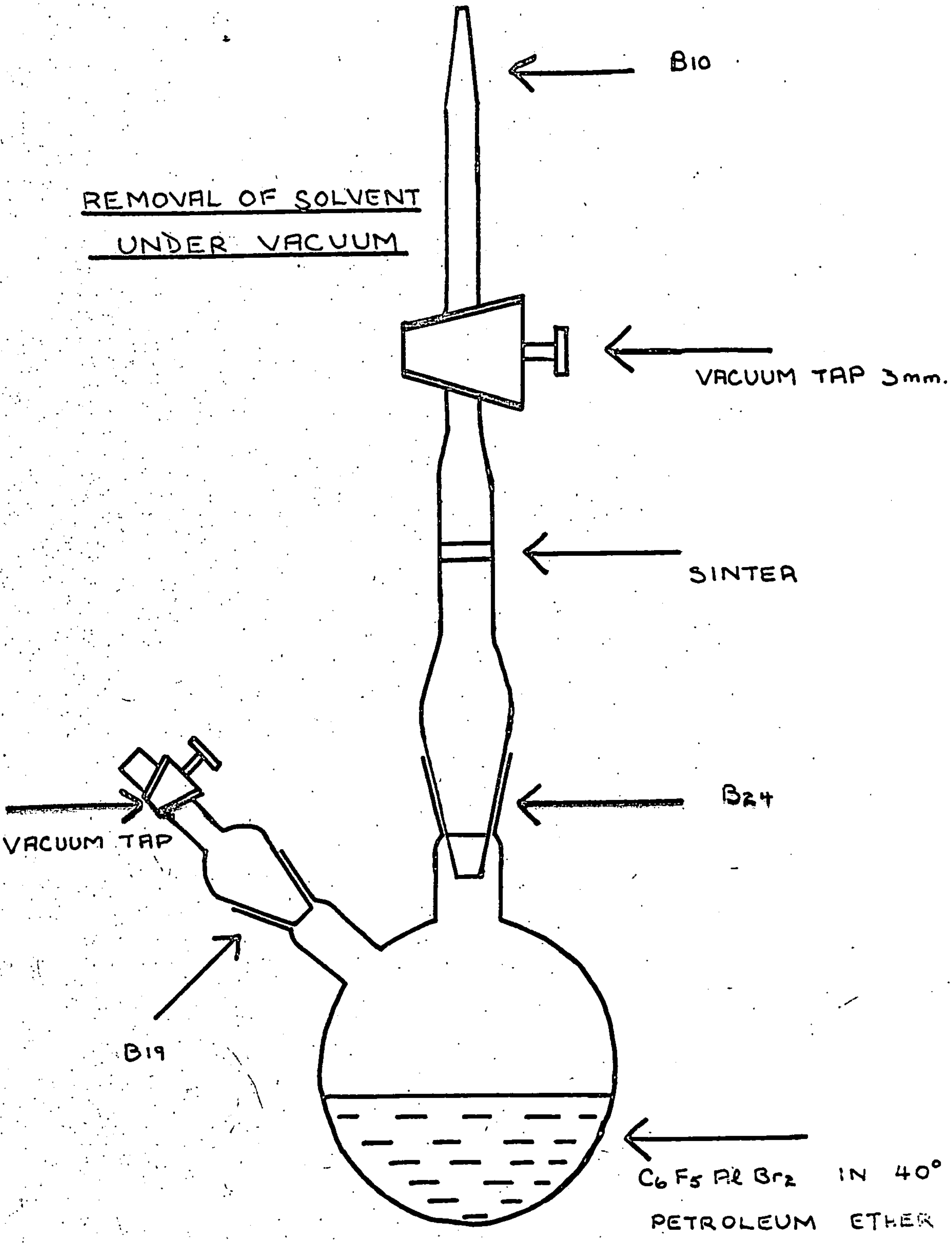


DIAGRAM THREE

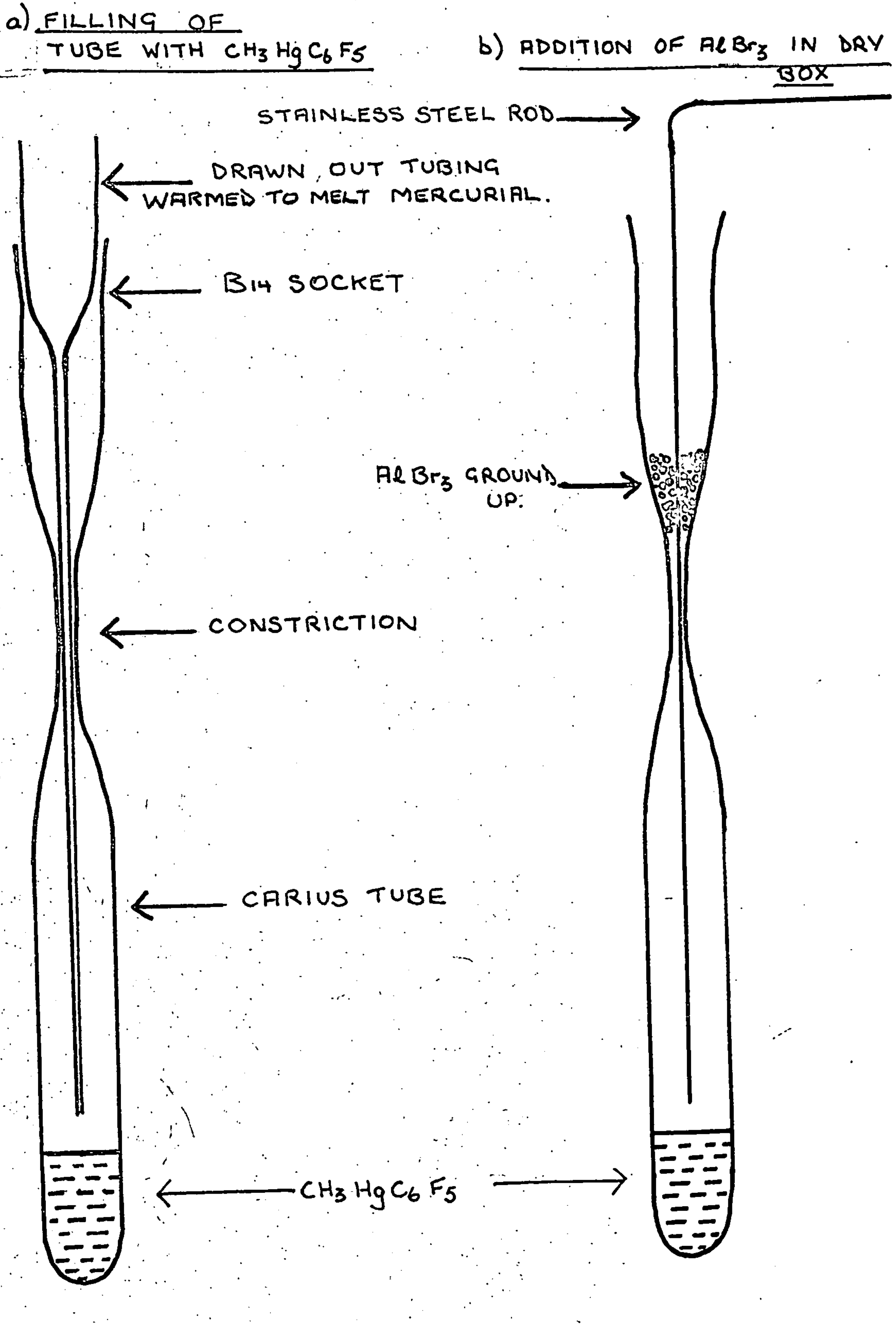
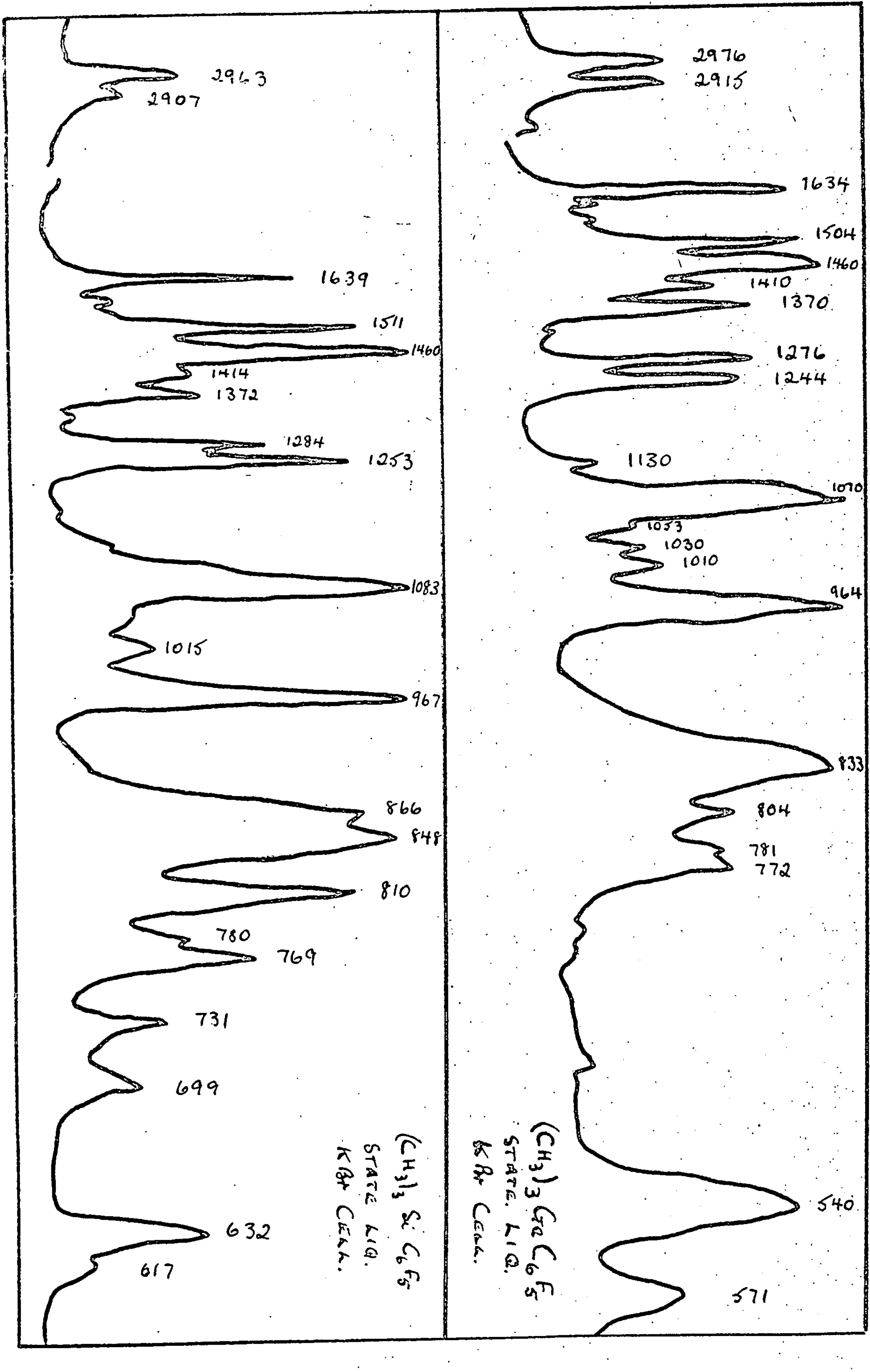


DIAGRAM FOUR

INFRARED SPECTRA

INFRARED SPECTRA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1511
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1414
1372
1284
1253
1083
1015
967
866
848
810
780
769
731
699
632
617
(CH$_3$)$_3$ Si C$_6$F$_5$
STATE LIQ.
KBr CELL.
2976
2915
1634
1504
1460
1410
1370
1276
1244
1130
1070
1053
1030
1010
964
833
804
781
772
540
571
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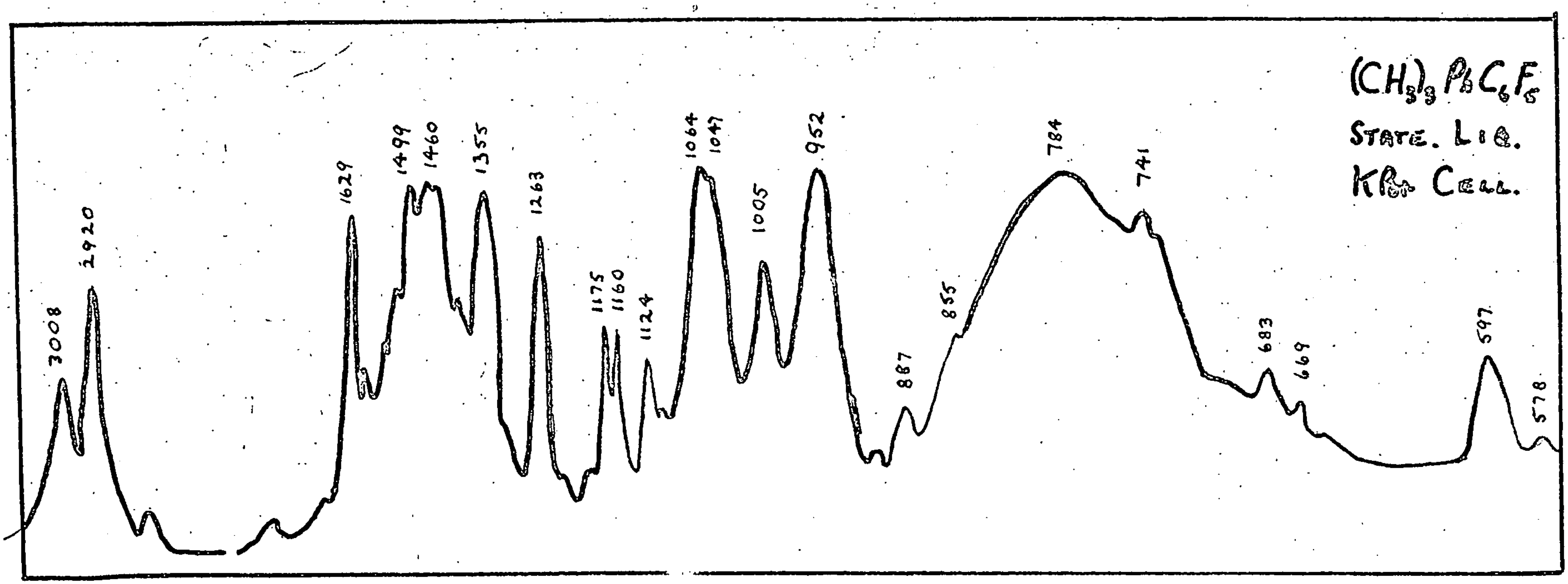
STATE. LIQ.
KBr CELL.

A

B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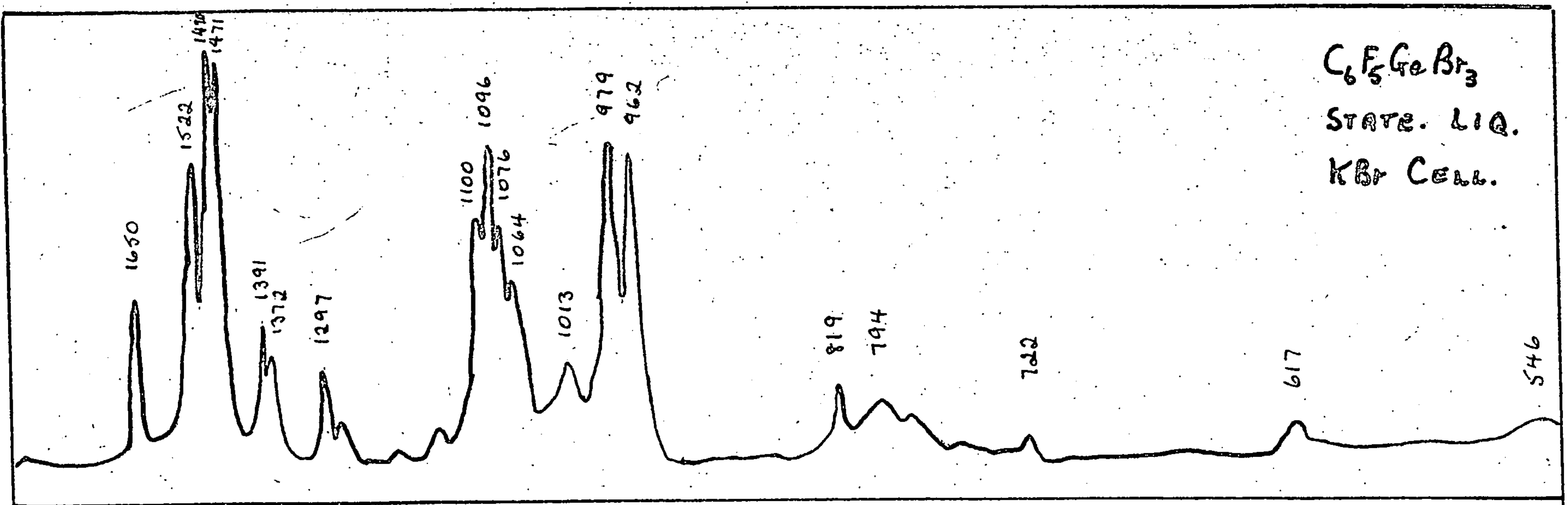
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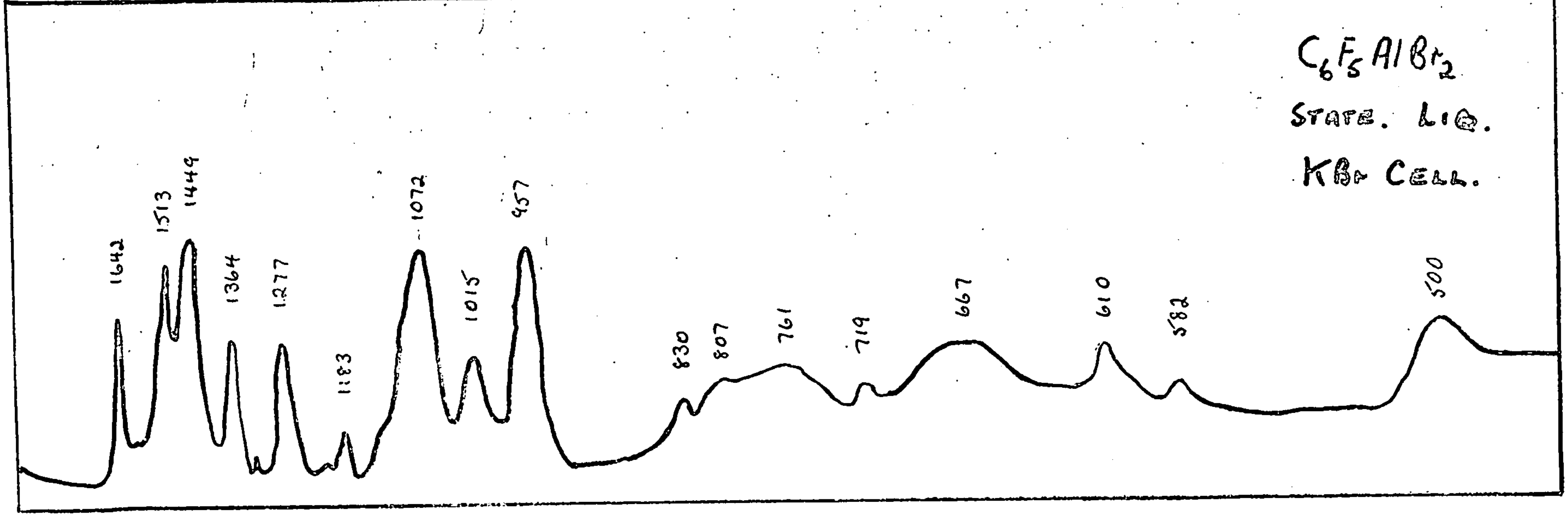
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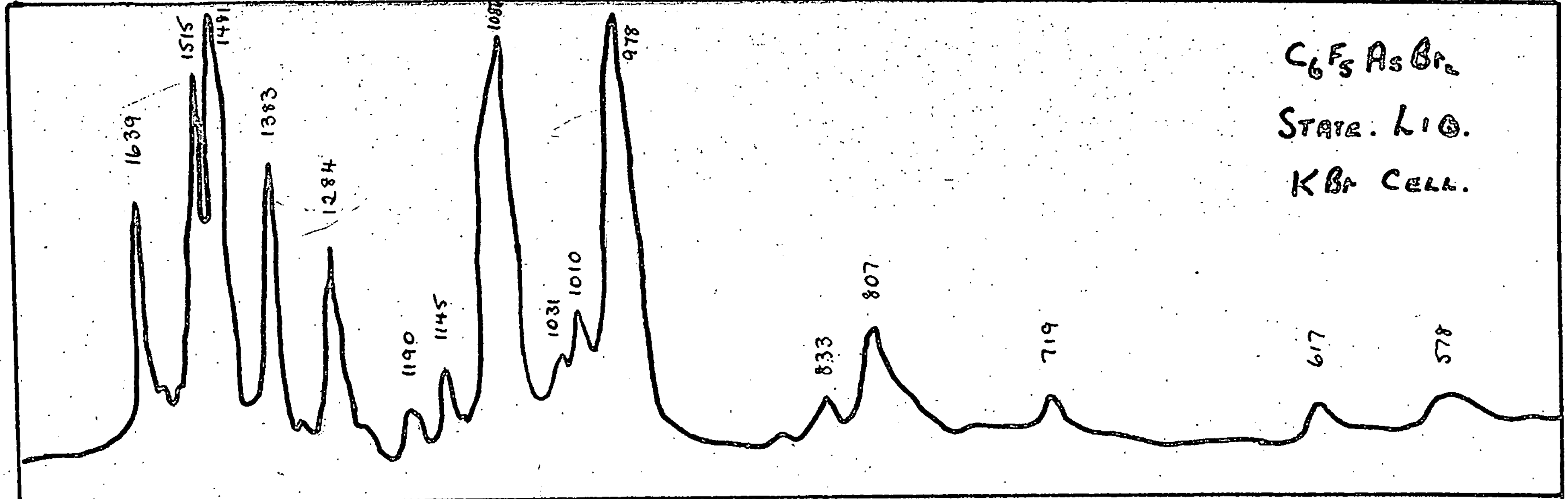
500

A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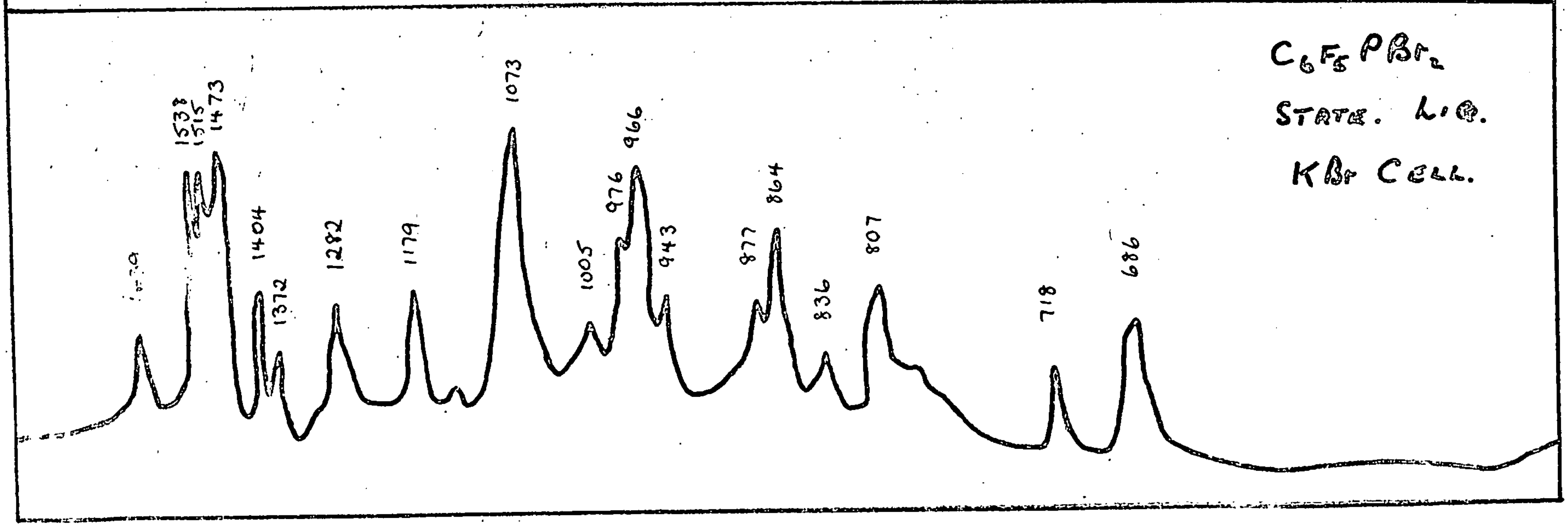
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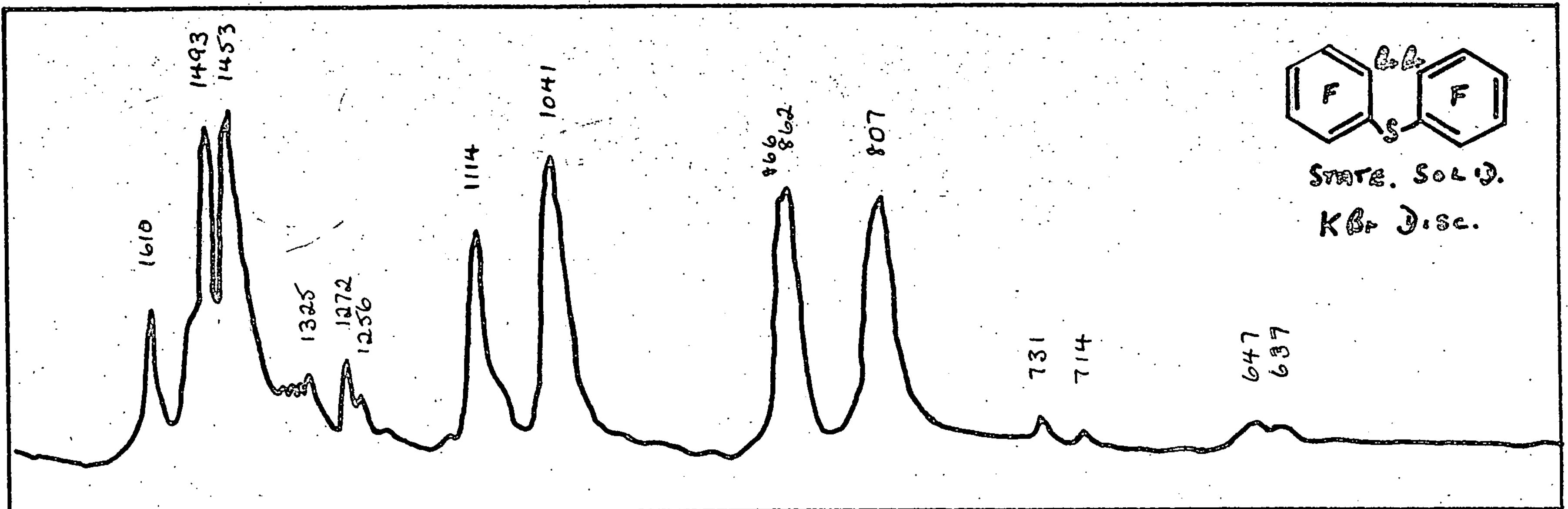
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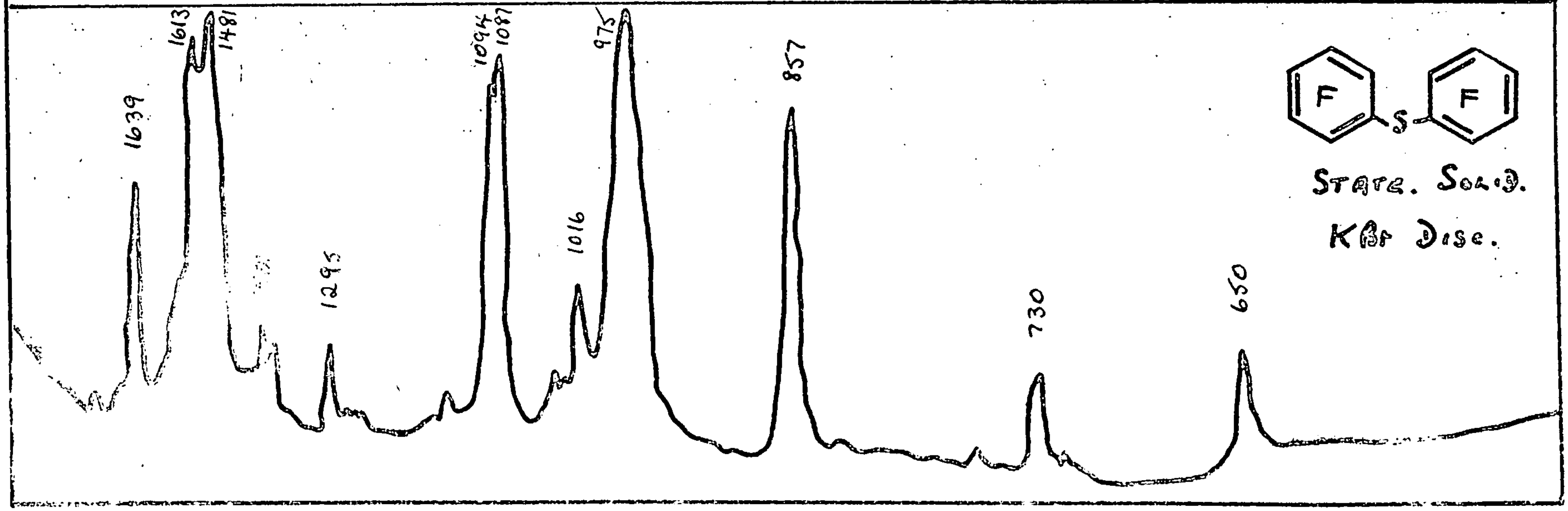
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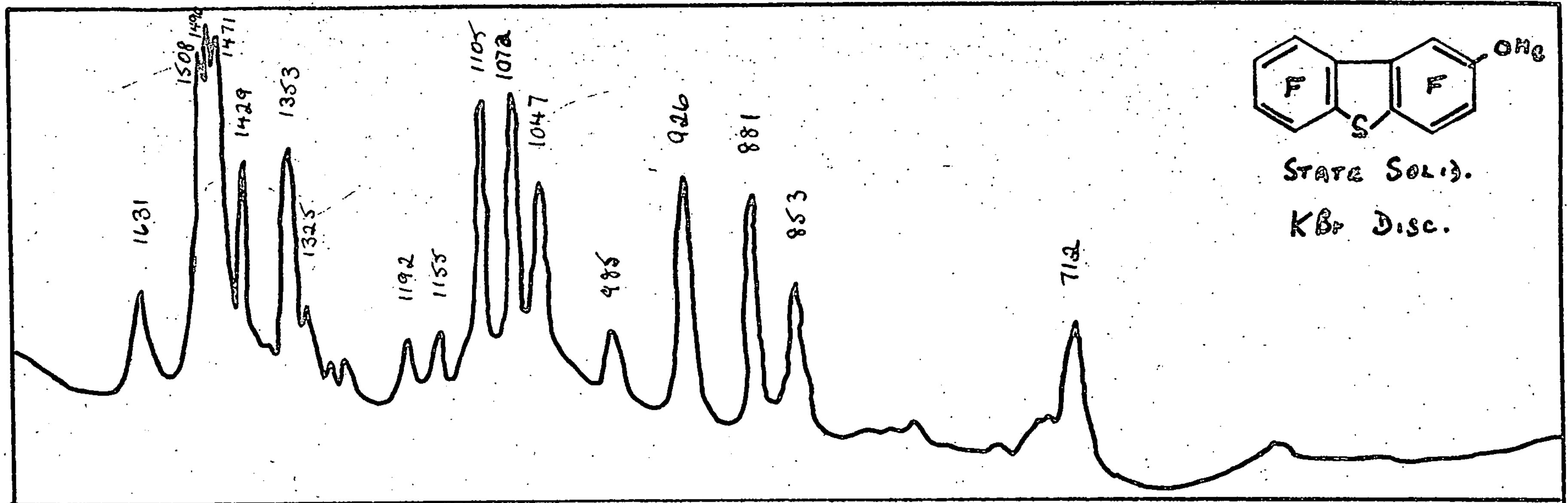
L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KBr DISC.
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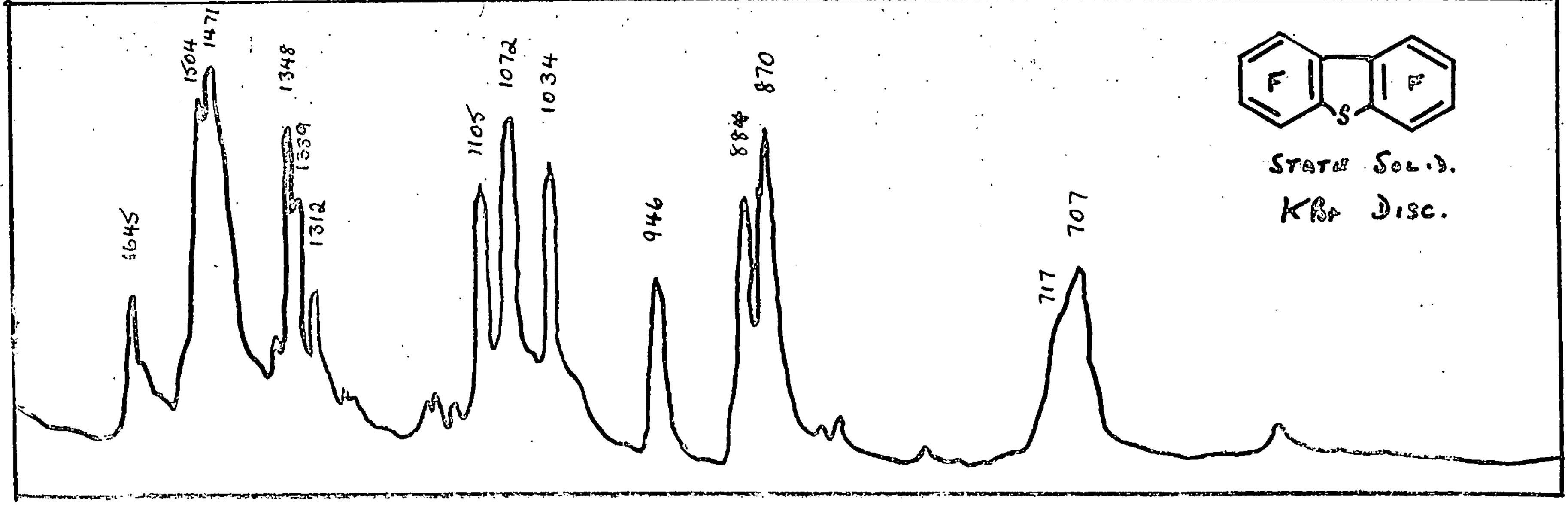
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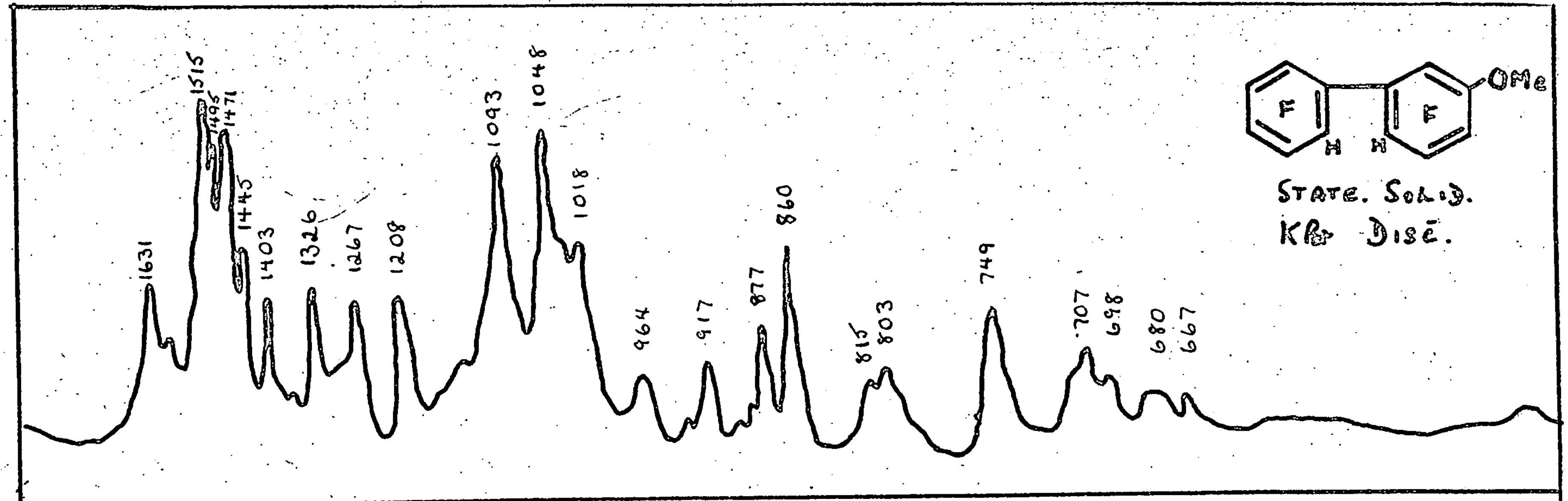
5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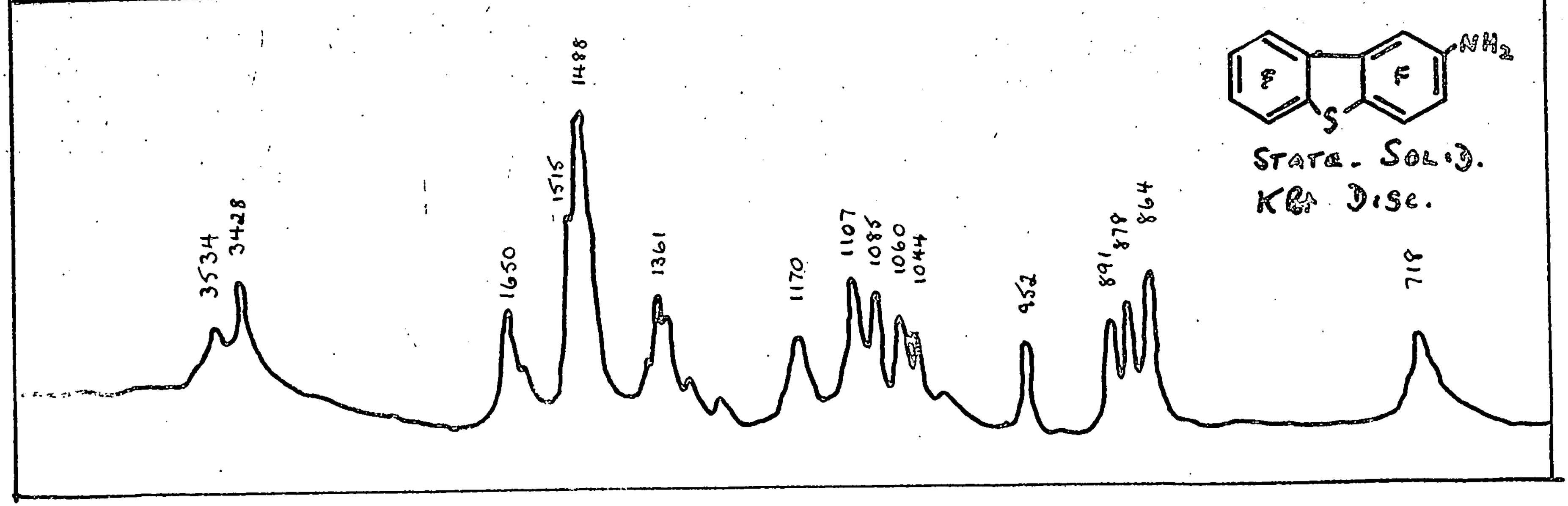
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952
891
878
864
718

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