THE SYNTHESIS OF PERFLUOROALKYL DERIVATIVES OF SOME METALS AND METALLOIDS

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CONTENTS

SUMMARY

THE SYNTHESIS OF PERFLUOROALKYL DERIVATIVES OF SOME METALS AND METALLOIDS

The original work described in this thesis is divided into four main topics.

(a) The first involves a study of the radical exchange reaction occurring between perfluoroiodoalkanes and trialkyl derivatives of phosphorus, arsenic, and antimony. Two series of reactions were investigated:

(i) Reaction between trimethyl-phosphine, -arsine and -stibine and pentafluoroiodoethane yielded the appropriate dimethylpentafluoroethyl derivative together with the corresponding tetramethyl 'onium iodide.

(ii) Reaction between triethyl-phosphine, -arsine or -stibine and trifluoroiodomethane yielded the appropriate diethyltrifluoromethyl derivative together with the corresponding tetraethyl 'onium iodide and free ethyl iodide.

Possible mechanisms are discussed. The effect of the perfluoroalkyl group is to reduce the availability of the lone electron pair on the Group VB element, this effect being greater in the case of trifluoromethyl than pentafluoroethyl. Vapour pressure-temperature and infra-red

spectral data are presented.

(b) The second part involves the preparation and isolation of alkylperfluoroalkylbismuth compounds. Such compounds were previously unknown. Perfluoroiodoalkanes reacted directly with trialkylbismuth compounds at 100°C forming both dialkylperfluoroalkyl- and alkylbisperfluoroalkyl-bismuthines. These compounds are readily oxidised and may be hydrolysed by aqueous alkali liberating the appropriate fluorocarbon. They act as Lewis acids in forming adducts with the strong base, dimethylamine. Halogens rapidly split off both alkyl and perfluoroalkyl groups. Interconversion of the mixed alkylperfluoroalkyl compounds is readily effected. Vapour pressure-temperature and infra-red spectral data are presented and discussed.

(c) The third section deals with a new potentially general method for the preparation of trifluoromethylated derivatives of metals. The technique involves passing trifluoromethyl radicals, generated from either hexafluoroacetone or hexafluoroethane, over metals and was most successfully applied to the preparation of the new compound bistrifluoromethylditelluride. This compound is hydrolysed by aqueous alkali yielding fluoroform quantitatively and reacts with mercury giving bis(trifluoromethyltelluro)mercury. Evidence was obtained for the

formation of tristrifluoromethylbismuth and tetrakistrifluoromethyl-lead.

(d) In the final section are described reactions used in attempts to prepare perfluoroalkylthallium compounds. The reaction of perfluoroiodoalkanes and trimethylthallium yielded dimethylthallium fluoride, while reactions of the type normally successful for the preparation of trialkylthallium compounds, when modified to permit formation of perfluoroalkylthallium derivatives, did not yield the desired product.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of the author's knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

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CHAPTER I

SOME GENERAL ASPECTS OF THE CHEMISTRY OF ALKYL AND PERFLUOROALKYL DERIVATIVES OF VARIOUS ELEMENTS

1. INTRODUCTION

Organometallic compounds are generally defined as compounds possessing metal-carbon bonds.[1] However it is convenient to include in this definition, compounds which contain bonds between carbon and metalloidal elements[2] and indeed, to extend the definition still further to incorporate compounds like trimethylphosphine and diphenyldiselenide, in which the parent elements are not strictly even metalloids. The reason for using such a broad definition is that in Group VB for example, apart from nitrogen, all the elements form organic derivatives whose properties can be correlated in the form of an approximately graded series, and it is most convenient to refer to such compounds as organometallic.

It is in this general sense that the term "organometallic compound" is used throughout this thesis. Examples of such compounds can be divided into two main categories. The first consists of those compounds in which the metal is bound to a specific carbon atom as in the case of methyl-lithium, triphenylbismuth, tetraethyl-lead, etc. In the second class of compounds there is a generalized bonding of the metal atom to a conjugated ring system as in bis(cyclopentadienyl)titanium dichloride,

dibenzene chromium, etc. The chemistry of compounds belonging to this latter class is not of direct interest to the work described in this thesis and discussion will be limited to compounds of the first type.

Although most of the original work presented in this thesis is concerned with perfluoroalkyl derivatives of various elements, it is of benefit to the discussion to consider firstly some of the most important general features of organometallic compounds and then to consider the special features associated with bonds between elements and a carbon atom of a perfluoroalkyl group. The term "perfluoroalkyl" refers to organic radicals in which there has been total replacement of hydrogen atoms by fluorine.

2. THE NATURE OF CARBON-METAL BONDS

(a) Influence of Electronegativity

Essentially the carbon-metal bonds of organometallic compounds are covalent in nature. However if there is an electronegativity difference between the particular carbon atom and the metal, the bond will possess some degree of ionic character which is proportional to this difference.[3] If this difference is more than 1.7 on the Pauling scale the bonds will

have greater than 50% ionic character and compounds possessing such bonds, e.g. ethylsodium, display many features normally associated with salts. In the majority of organometallic compounds this electronegativity difference is less than the nominal value of 1.7, but the carbon-metal bond may still possess a degree of polarity, the magnitude of which is of great importance in determining the properties of the substance. Since all metals are positive with respect to carbon, the fractional electronic charges formally residing on the bonded atoms may be represented thus:

$$\overset{\delta-}{C}\text{———}\overset{\delta+}{M}$$

If then, the organometallic compound is exposed to a reagent like water, in which the polarity of the hydrogen atoms is positive with respect to oxygen, the relevant fragments of the two molecules will be oriented thus:

$$\overset{\delta-}{C}\text{———}\overset{\delta+}{M}$$

$$\overset{\delta+}{H}\text{———}\overset{\delta-}{OH}$$

Hence an active intermediate is formed which, if the free energy is favorable, will give new bonds depicted as:

$$\begin{array}{cc} C & M \\ | & | \\ H & OH \end{array}$$

The observed products of this hydrolysis reaction will then be the metal hydroxide and a hydrocarbon. Hydrogen halides similarly would produce metal halides and a hydrocarbon.

The electronegativity of alkyl groups decreases with increasing size, i.e. $CH_3 > C_2H_5 > C_3H_7$, etc., with the result that the ionic character of the metal-carbon bond is less in the case when an ethyl group is attached to a particular metal than when a methyl group is attached.

(b) Effects of Size of Organic Groups

As well as the effect on the electronegativity of the carbon atom attached to the metal, an increase in the size of the alkyl group produces changes in the physical and chemical properties of a related series of compounds. For example, the boiling points of the alkyls of silicon increase with increasing size of the ethyl group. There is also a decrease in chemical reactivity with increasing size of the organic radical attached to a particular element. This feature is exemplified by elements of Group V B and in the case of a series of phosphines[4] it is found that, whereas in air trimethylphosphine readily inflames, triethylphosphine

tends to fume, while tri-n-butylphosphine is quite stable.

(c) Effect of Metal

In any particular Group of the periodic table, the properties of analogous derivatives of the elements are graded regularly. For example the boiling points of the tetramethyl derivatives of the elements of Group IVB increase from carbon to lead. The chemical reactivity likewise follows a regular pattern within a particular Group, but the trends are not necessarily in the same direction for all Groups, nor even for the A and B Subgroups of a particular Group. In Groups I, II and III comparable organic derivatives of the A elements have reactivities which increase with increasing atomic number of the parent element, while for the B elements the order of reactivity is reversed. In Groups V, VI and VII these general features are completely the reverse and for the organic derivatives of Group IV elements, chemical reactivities show trends intermediate between those of the elements in the Groups on either side.

3. EXCHANGE REACTIONS

Specific reference to the variety of methods used in the synthesis of organometallic compounds will not be made at this stage, although some important ones

are included in the following discussion of two types of exchange reactions which are of particular importance in organometallic chemistry and of relevance to this study. They are classified as (a) group exchange, and (b) halogen-metal exchange reactions.

(a) Group Exchange Reactions

In a study of some exchange reactions with lead compounds, Calingaert et al.[5] showed, with the aid of radioactive tracers, that at moderate temperatures, in the absence of solvent or catalyst, an equimolar mixture of tetraethyl-lead and triethyl-lead chloride quite rapidly reaches the equilibrium represented thus:

$$(C_2H_5)_4\ Pb^{*} + (C_2H_5)_3\ PbCl \rightleftharpoons (C_2H_5)_3\ Pb^{*}Cl + (C_2H_5)_4\ Pb$$

All four compounds exist in the equilibrium mixture in identical proportions. Similarly when different organic radicals are present in the two lead reactant compounds, the entire range of possible alkyl-lead and alkyl-lead halide compounds appears in the equilibrium mixture. The following reaction[6] is typical and the products found in the equilibrium mixture are those predicted.

$$(CH_3)_4Pb \quad \Big] \rightarrow (CH_3)_4Pb + (CH_3)_3(C_2H_5)Pb + (CH_3)_2(C_2H_5)_2Pb + (CH_3)(C_2H_5)_3Pb + (C_2H_5)_4Pb$$

$$+ \qquad\qquad\qquad\qquad\qquad\qquad +$$

$$(C_2H_5)_3PbCl \quad \Big] \rightarrow (C_2H_5)_3PbCl + (C_2H_5)_2(CH_3)PbCl + (C_2H_5)(CH_3)_2PbCl + (CH_3)_3PbCl$$

This suggested that radical exchange might be possible between two different tetra-alkyl-lead compounds and accordingly it was shown that at moderate temperatures (50-150°C) and using catalytic quantities[7] of an alkyl-lead halide, complete interchange of alkyl radicals occurs, yielding the calculated number of compounds in amounts predicted assuming random distribution of organic radicals.[8,9] The exchange may be represented thus:

$$R_4Pb + R'_4Pb \longrightarrow R_4Pb + R_3R'Pb + R_2R'_2Pb + RR'_3Pb + R'_4Pb.$$

Compounds found to be successful in catalysing such reactions include organometallic compounds like triethyl-lead bromide, triethyltin chloride, etc. and metal halides like aluminium trichloride, zinc fluoride and bismuth trichloride.[8] The latter compounds are capable of forming organometallic halides under the reaction conditions. In the absence of such catalysts,

in most cases the redistribution reaction does not occur. Similar exchange reactions have been found to take place between alkyl and aryl derivatives of a number of other elements including tin, silicon and mercury.[10] In each case all possible combinations of radicals attached to the metals available are found in the equilibrium mixture. The proportion of each product is found to be that calculated from the laws of probability,[11] i.e. that expected for random distribution of organic radicals. The final composition is unaffected by the choice of solvent, catalyst or temperature and only depends on the mole fractions of the organic and metal components. Provided that the same proportion of each different type of radical and metal atom are used for a particular system, the final composition is also independent of the starting material. Thus an equimolar mixture of tetramethyl-lead and tetraethyl-lead, or of trimethylethyl-lead and methyltriethyl-lead; or the single compound dimethyldiethyl-lead, gives the same products in the same proportions.

The action of the catalysts in these reactions is explained knowing that compounds typical of those used in this capacity are capable of the reactions shown

below, the catalysts being underlined.

$$\underline{AlCl_3} + R_4Pb \rightleftharpoons R\,AlCl_2 + R_3PbCl \quad [8]$$

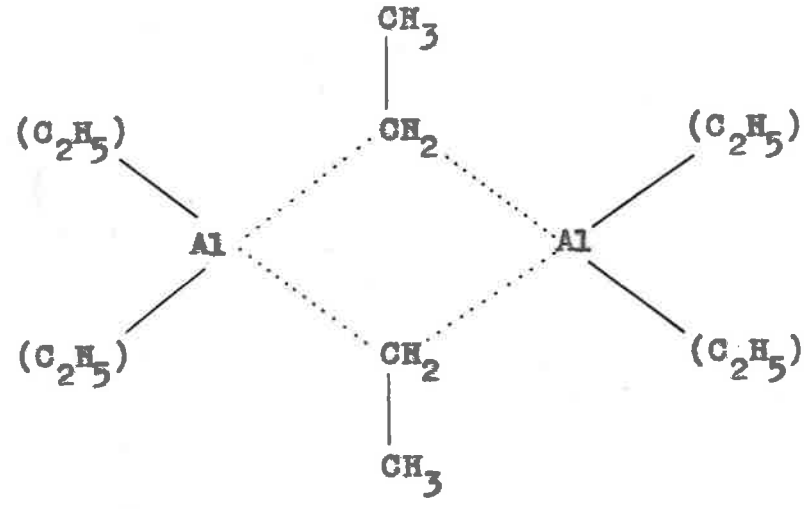
$$\underline{R\,AlCl_2} + R_4Pb \rightleftharpoons R_2AlCl + R_3PbCl \quad [12]$$

$$\underline{R_3PbCl} + R_4Pb^{*} \rightleftharpoons R_3Pb^{*}Cl + R_4Pb \quad [5]$$

The catalysts may then be crudely described as carriers of the groups being interchanged. The mechanism of the redistribution reactions obviously involves radicals and atoms but the low temperatures used and the complete lack of secondary reactions indicates that free atoms and free radicals are not present in the system. It is suggested that there is a reversible formation of a weak complex consisting of the catalyst and one or more molecules of the compound undergoing the redistribution reaction. When the complex breaks up, the constituent molecules, including the catalyst itself, possess the appropriate number of organic groups taken at random from those available on the intermediate. Kinetic studies support the contention that the redistribution reaction is not one of stepwise replacement but of complete, random exchange of groups.[13]

Mixtures of trialkylaluminium compounds are capable of similar redistribution reactions,[14] but the

mechanism is somewhat more clearly defined than for the case of the lead compounds. Most trialkylaluminium compounds exist in associated forms, i.e. as dimers, trimers or polymeric units, and as such belong to the class of "electron deficient" compounds.[15] Although aluminium has only three electrons in the valence shell, it still tends to use all four of its available sp^3 hybrid orbitals. This gives rise to so-called "electron deficient" bonds since the number of two-centre bonds exceeds the number of available electron pairs. Thus the dimeric form of triethylaluminium may be written



In such a compound there is a total of two electrons involved in the linkages Al .... C .... Al, carbon supplying one and the aluminium atoms supplying a total of only one.

The associated species are quite capable of dissociation.[16]

$$(AlR_3)_2 \rightleftharpoons 2\,Al\,R_3$$

The existence of such equilibria therefore admits the possibility of group exchange in mixtures containing different trialkylaluminium compounds according to the following scheme:

$$R_3Al + R'_3Al \rightleftharpoons R_2Al\begin{matrix}\diagup R \\ \diagdown R'\end{matrix}AlR'_2 \rightleftharpoons R_2AlR' + R\,Al\,R'_2$$

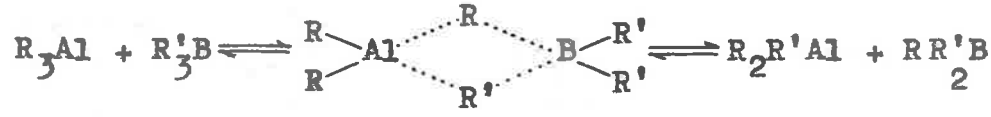
This is found to be the case, since a mixture of tri-iso-butylaluminium and trimethylaluminium has been shown to contain di-iso-butylmethylaluminium,[17] the reaction being represented as:

$$2\,Al(\underline{i}\text{-}C_4H_9)_3 + Al(CH_3)_3 \rightleftharpoons 3\,Al(\underline{i}\text{-}C_4H_9)_2CH_3$$

However, although cryoscopic measurements indicate that this equilibrium is established in the mixture, distillation in this case yields the original pure reactants. This probably indicates that the mixture, whose composition is continually changing due to removal of trimethylaluminium by the distillation, equilibrates sufficiently rapidly for trimethylaluminium to be generated from methyldi-i-butylaluminium as quickly as it is removed. Since distillation of mixtures of different alkyl-lead compounds yields the appropriate pure

components,[6] it appears that the rate at which equilibrium is attained in such cases is much slower than that for the aluminium system described above.

Group exchange reactions also occur when trialkylaluminium and trialkylboron compounds are mixed. Like aluminium, boron forms electron deficient bridge-structured compounds,[15] but unlike aluminium, its alkyl derivatives are not associated due to steric effects. Nevertheless the following type of equilibrium is found to occur:[18]



This fact is used in the preparation of mixed trialkylboron compounds which are obtained by mixing two different trialkylboron compounds in the presence of catalytic amounts of a suitable trialkylaluminium compound.

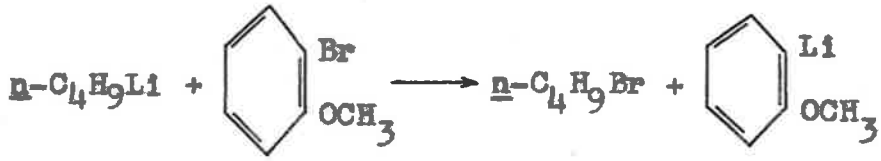
Recent investigations employing the technique of nuclear magnetic resonance showed that group exchange also occurs in mixtures of (i) trimethylaluminium and dimethylcadmium,[19] (ii) dimethylzinc and dimethylcadmium,[19] (iii) trimethyl- and triethyl-thallium.[20]

(b) Halogen-Metal Exchange Reactions

This type of exchange reaction may be represented by the following expression:

$$RM + R'X \longrightarrow RX + R'M$$

where R and R' are different organic groups, M is a metal and X a halogen atom. The formation of o-anisyl-lithium and n-butyl bromide from o-bromo-anisole and n-butyl-lithium was one of the first known reactions of this type.[21,22]



Although lithium[23] is the metal most used in this type of reaction, halogen-metal interconversion reactions have been performed using sodium,[24] magnesium,[25,26] barium[27] and aluminium.[26] An unusual halogen-metal interconversion reaction between aryl iodides and organomercury compounds occurs in the presence of catalytic quantities of an appropriate organolithium compound.[28] The processes occurring are considered to be:

$$R_2Hg + 2\ R'Li \rightleftharpoons 2\ RLi + R'_2Hg$$
$$2R\ Li + 2\ R'I \rightleftharpoons 2R'Li + 2R\ I$$

The addition of these two expressions indicates the

overall observed reaction:

$$R_2Hg + 2R'I \rightleftharpoons R'_2Hg + 2RI$$

The interconversion reactions are most successful when iodides or bromides are used, although chlorides have been used.[29,30] Organic fluorides do not participate in such reactions.[31] Both alkyl and aryl halides can be used in these reactions which are generally carried out in ether solution. The reactions are reversible and therefore in the example chosen below, the equilibrium:

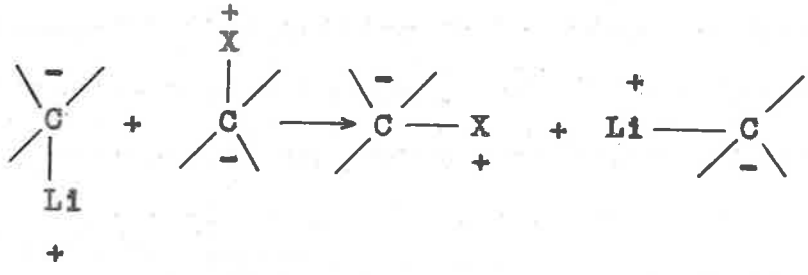
$$\underline{n}\text{-}C_4H_9Li + C_2H_5I \rightleftharpoons \underline{n}\text{-}C_4H_9I + C_2H_5Li$$

is established regardless of the direction from which it is approached.[32] A similar equilibrium mixture is obtained if aryl halides and aryl-lithium compounds are used.

$$C_6H_5Li + \underline{p}\text{-}CH_3.C_6H_4I \rightleftharpoons \underline{p}\text{-}CH_3.C_6H_4Li + C_6H_5I$$

Although the reactions between aryl halides and alkyl-lithium compounds are not reversible, it is suggested that an equilibrium does exist but that it is displaced greatly in favour of the formation of the aryl-lithium and alkyl halide.

The mechanism proposed for the halogen-metal interconversion reaction involves exchange between lithium and an electropositive halogen atom as indicated in the following scheme:



The reason for the differences in behaviour of the halogens in these reactions is then apparent, since the electropositivity of these elements increases with increasing atomic number. The position of the equilibrium will depend largely on the relative electronegativities of the groups R and R' in the system:

$$RLi + R'X \rightleftharpoons R'Li + RX$$

The metal is preferentially attached to the organic group of greater electronegativity and the yield of a desired product will therefore be determined by the selection of such groups.

4. SOME GENERAL FEATURES OF THE PERFLUOROALKYL GROUP

The total replacement of hydrogen by fluorine atoms in an alkyl group gives rise to some completely

new properties in the perfluoroalkyl group. These differences in behaviour between alkyl and perfluoroalkyl groups are very pronounced in the field of organometallic chemistry, and in the following discussion, references are made to the more important features of this kind.

(a) Influence of Electronegativity

As has been indicated previously, the bond character of a metal-carbon bond is governed, to a first approximation, by the electronegativity difference between carbon and the metal. Particularly when the other atoms attached to carbon have electronegativities greatly different from that of carbon itself, consideration of the electronegativity of the organic radical as a whole ensures more accurate explanations for the behaviour of such groups. The following table of electronegativities indicates that the generally accepted value for the trifluoromethyl group lies between those of fluorine and chlorine, with the result that in many instances its behaviour resembles that of the halogens of low atomic number.

Whereas the order of decreasing electronegativity for perfluoroalkyl groups is $CF_3 > C_2F_5 > C_3F_7$, etc., the actual values are all similarly high and

TABLE 1.1

Electronegativities of some atoms and organic groups

Atom (Group)	Electronegativity
F	4.0
CF_3	3.3
Cl	3.0
Br	2.8
C	2.5
H	2.1
CH_3	2.3
I	2.4

accordingly, such groups are generally attached to atoms or radicals of lower electronegativity. The obvious consequence of this fact is that in a perfluoroalkyl compound, the perfluoroalkyl group will be strongly electron-withdrawing. This markedly affects the electron donor-acceptor properties of the element to which it is attached. In compounds containing elements possessing lone electron pairs for example, the effect of the perfluoroalkyl group is to greatly reduce the availability of this electron pair.

(b) Effects of Size of Perfluoroalkyl Groups

The covalent diameter of the trifluoromethyl group is similar to those of pseudo-halogens[33] (Table 1.2) and a close similarity in behaviour might also be anticipated. However, the electronegativities of the pseudo-halogens are decidedly less than those of the perfluoroalkyl groups. Accordingly, due to the relatively large covalent diameter as well as high electronegativity of perfluoroalkyl groups, it is often difficult to predict their properties from knowledge of those of pseudo-halogens.

TABLE 1.2

Covalent Diameters of Some Atoms and Groups

Atom (or Group)	NCS	NCO	CF_3	CH_3	I	CN	Br	Cl	F
Covalent diameter (A^o)	4.3	3.6	3.3	2.8	2.7	2.3	2.3	2.0	1.4

(c) Thermodynamic Effects

Differences in the properties of alkyl (or aryl) groups and those of perfluoroalkyl groups are also expected due to the significant differences in the bond energies of the carbon-hydrogen bond (98.8 $kcal.mole^{-1}$)

and of the carbon-fluorine bond (115 kcal. mole^{-1})[34]. Hence a higher stability and lower reactivity is expected for the fluorocarbon group than for the hydrocarbon group. In addition due to the larger size of fluorine than hydrogen atoms, a greater protection of the carbon skeleton is provided by the attached fluorine atoms. These two facts imply that higher energies of activation are required to break carbon-fluorine bonds and that the mechanisms of attack by reagents at the carbon atoms is severely limited due to the screening of the carbon chain. Such effects will then influence the modes of decomposition of fluorocarbons. It is well known that pyrolysis of hydrocarbons causes loss of hydrogen and the production of unsaturated hydrocarbons or carbon itself but the energy required to break the carbon-fluorine bond is greater than that for the carbon-carbon bond. The result is that in a fluorocarbon, decomposition of the molecule is preferred to removal of fluorine atoms. In compounds like trimethylarsine and tristrifluoromethylarsine[35] similarities in the decompositions exist. From both of these compounds radicals may be generated, the activation energies required for their formation being approximately the same. The decomposition of these radicals does differ however. The following scheme

describes the fate of the methyl radicals derived from trimethylarsine.

$$CH_3\cdot + AsMe_3 \longrightarrow AsMe_2\cdot CH_2\cdot$$

$$2\,CH_3\cdot \longrightarrow C_2H_4 + H_2$$

$$2\,CH_3\cdot \longrightarrow CH_4 + \cdot CH_2\cdot$$

Trifluoromethyl radicals however, may decompose to give fluoride, and the dimer or a higher polymeric form of difluorocarbene. Such is the case in the pyrolysis of tristrifluoromethylstibine,[32] the products being antimony trifluoride, tetrafluoroethylene, perfluorocyclepropane and other unsaturated fluorocarbons.

(d) In Part 1 of this chapter some types of exchange reactions occurring in organometallic chemistry were described. Perfluoroalkyl derivatives of a number of metals are able to undergo exchange reactions, but details of these will be given in the appropriate chapters to follow.

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CHAPTER II

PERFLUOROALKYL DERIVATIVES OF GROUP VB ELEMENTS

The chemistry of the perfluoroalkyl derivatives of the Group VB elements has been investigated in more detail than for any other group of elements. This is due to the relative ease with which, in particular, phosphorus, arsenic and antimony form such derivatives. Although perfluoroalkyl derivatives of nitrogen are known,[1] their properties, like those of compounds of other First Period elements, are frequently dissimilar to those of analogous compounds in the particular Group, and except where particularly relevant, are not discussed in relation to those of phosphorus, arsenic and antimony. Perfluoroalkylbismuth compounds were unknown prior to this work and will be discussed separately in Chapter VI.

1. PHOSPHORUS

(a) Haloperfluoroalkylphosphines

The reaction between white or red phosphorus and trifluoroiodomethane at high temperatures yields tristrifluoromethylphosphine, iodobistrifluoromethylphosphine and di-iodotrifluoromethylphosphine, together with small quantities of phosphorus iodides.[2,3]

$$P + CF_3I \xrightarrow{200\text{-}220^\circ} (CF_3)_3P + (CF_3)_2PI + CF_3PI_2 + P_2I_4 + PI_3$$

Since trifluoroiodomethane can be prepared by heating together a mixture of silver trifluoroacetate and iodine,[4]

$$CF_3COOAg + I_2 \xrightarrow{heat} CF_3I + CO_2 + AgI$$

it is not surprising to find that if phosphorus is included in such a reaction mixture, compounds of the form $(CF_3)_nPI_{3-n}$ are produced.[5]

$$CF_3COOAg + P + I_2 \longrightarrow (CF_3)_3P + (CF_3)_2PI + CF_3PI_2 + POF_3 + CO_2 + AgI$$

When phosphorus and heptafluoroiodopropane are heated together, only iodobisheptafluoropropylphosphine and di-iodoheptafluoropropylphosphine are formed and no trisheptafluoropropylphosphine.[6]

$$C_3F_7I + P \longrightarrow (C_3F_7)_2PI + C_3F_7PI_2$$

Unlike the analogous reaction between alkyl halides, e.g. ethyl iodide, and phosphorus, which give the appropriate tetra-alkyl 'onium halide,[7] no quaternary compound results from reactions of perfluoroalkyl iodides and phosphorus. The mechanism of the latter reaction,

although not fully understood, is considered to involve homolytic fission of the C-I bond of the perfluoroalkyl iodide and attack of the perfluoroalkyl and iodine radicals on the "metal-metal" bonds of the tetra-atomic phosphorus molecules.[8]

Equilibrium reactions similar to those thought to occur during the reaction of phosphorus with perfluoroalkyl iodides have been observed when a mixture, either of tristrifluoromethylphosphine and iodine, or of tristrifluoromethylphosphine, iodobistrifluoromethylphosphine and di-iodotrifluoromethylphosphine is heated.[3] The reactions occurring are represented below.

$$(CF_3)_3P + I_2 \rightleftharpoons (CF_3)_2PI + CF_3I$$

$$2(CF_3)_2PI \rightleftharpoons (CF_3)_3P + CF_3PI_2$$

$$2\ CF_3PI_2 \rightleftharpoons (CF_3)_2PI + PI_3$$

$$2\ PI_3 \rightleftharpoons P_2I_4 + I_2$$

Neither iodotrifluoromethylphosphine has a hydrocarbon analogue[9] but, as expected from comparison with known haloalkylphosphines, they are both air reactive as is tristrifluoromethylphosphine.[3] All the compounds having the general formula $(CF_3)_nPI_{3-n}$ are readily

hydrolysed by aqueous alkali, liberating fluoroform quantitatively.

$$(CF_3)_3P \xrightarrow{NaOH} 3\ CHF_3$$

$$(CF_3)_2PI \xrightarrow{NaOH} 2\ CHF_3$$

$$CF_3PI_2 \xrightarrow{NaOH} CHF_3$$

In this respect they are markedly different from haloalkylphosphines which, although readily hydrolysed, do not undergo phosphorus-carbon fission reactions under these conditions.[10] In addition, although tristrifluoromethylphosphine is not affected by water at room temperature, iodobistrifluoromethylphosphine is attacked by this reagent and liberates one molecule of fluoroform, while di-iodotrifluoromethylphosphine is also attacked but does not liberate any fluoroform.[3]

The iodotrifluoromethylphosphines are of great importance synthetically for they undergo reactions to give a variety of new compounds. Their treatment with silver halides (and pseudo-halides) yields the appropriate new halides[3] according to the following equations:

$$(CF_3)_2PI + AgCl \xrightarrow{20^\circ} (CF_3)_2PCl + AgI$$

$$CF_3PI_2 + 2\ AgCl \xrightarrow{20\text{-}100^\circ} CF_3PCl_2 + 2\ AgI$$

$$(CF_3)_2PI + AgCN \xrightarrow{20^\circ} (CF_3)_2PCN + AgI$$

Fluorobistrifluoromethylphosphine results from the reaction of iodobistrifluoromethylphosphine with antimony trifluoride.[11]

(b) Halophosphoranes

The reaction of chlorine with excess tristrifluoromethylphosphine at low temperatures yields the pentavalent phosphorus compound tristrifluoromethyl-phosphorus dichloride.[12]

$$(CF_3)_3P + Cl_2 \xrightarrow{-40^\circ C} (CF_3)_3PCl_2$$

This compound, when dissolved in acetonitrile, shows electrolytic behaviour similar to that of phosphorus pentachloride which is known to dissociate[13] according to the following scheme:

$$2\ PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

The dissociation of tristrifluoromethylphosphorus dichloride into ions proceeds similarly.

$$(CF_3)_3 PCl_2 \rightleftharpoons (CF_3)_3 PCl^+ + (CF_3)_3 PCl_3^-$$

The other trifluoromethylphosphorus chloride known, namely bistrifluoromethylphosphorus trichloride,[14] behaves as a non-conductor under these conditions.

In the removal of trifluoromethyl groups from trifluoromethylphosphines using bromine, there is some evidence for the formation of intermediate phosphoranes[15] of the form $(CF_3)_n PBr_{5-n}$. However there is a tendency for phosphorus to acquire bromine at the expense of trifluoromethyl groups under conditions considered suitable for the formation of the appropriate phosphoranes. Thus bromine reacts with bromobistrifluoromethylphosphine, initially yielding bistrifluoromethylphosphorus tribromide quantitatively.

$$(CF_3)_2 PBr + Br_2 \longrightarrow (CF_3)_2 PBr_3$$

Slow spontaneous decomposition of this product occurs to give the compounds shown in the equation:

$$2(CF_3)_2PBr_3 \longrightarrow (CF_3)_2PBr + 2CF_3Br + PBr_3$$

The proposed mechanism for this process involves as intermediates, the phosphoranes, tristrifluoromethylphosphorus dibromide and trifluoromethylphosphorus tetrabromide.

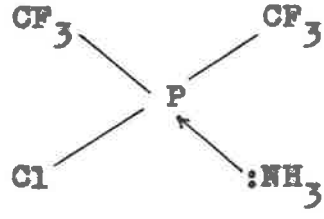
No iodotrifluoromethylphosphoranes have been characterized and they are thought to exist only at low temperatures, if at all.

(c) Aminophosphines

Chlorobistrifluoromethylphosphine reacts readily with a number of amines to yield the appropriate aminophosphine.[16] The reaction of the phosphine with ammonia is typical.

$$(CF_3)_2\,PCl + 2NH_3 \longrightarrow (CF_3)_2\,PNH_2 + NH_4Cl$$

Since it is not possible to replace more than one hydrogen of the amine by $(CF_3)_2P$ to give compounds like $(CF_3)_2PNH\,P(CF_3)_2$, the intermediate involved is considered to be of the form:



Loss of hydrogen chloride then accounts for the observed products. The other known aminophosphines in this class are $(CF_3)_2\,PNHCH_3$; $(CF_3)_2PN(CH_3)_2$; $(CF_3)_2PNHPh$.

(d) Diphosphines

The reaction of iodobistrifluoromethylphosphine with mercury at room temperature yields tetrakistrifluoromethyldiphosphine[3] almost quantitatively.

$$2\,(CF_3)_2\,PI + Hg \longrightarrow (CF_3)_2P - P(CF_3)_2 + HgI_2$$

When this reaction is performed in the presence of a protic solvent[17] e.g. hydrogen chloride, trifluoroacetic acid, etc., a good yield of bistrifluoromethylphosphine results. It is also observed that, after the tetrakistrifluoromethyldiphosphine (94%) is removed from the products of the reaction performed in the absence of acid, addition of hydrogen chloride to the involatile residue causes the liberation of the missing CF_3P groups as bistrifluoromethylphosphine. From this evidence it appears that the initial reaction involves the formation of a phosphorus-mercury bond. The suggested intermediate[17] is $(CF_3)_2PHg_2I$ which is thought to react, either with the acid to give bistrifluoromethylphosphine, or with a molecule of unchanged iodobistrifluoromethylphosphine to give tetrakistrifluoromethyldiphosphine. In this latter compound the electronegative trifluoromethyl groups stabilize the phosphorus-phosphorus linkage by enhancing the -type

bonds involving the phosphorus lone pair of electrons from one phosphorus atom with the 3d orbitals of the neighbouring one.[18] Tetrakistrifluoromethyldiphosphine reacts with trifluoroiodomethane, giving tristrifluoromethylphosphine and iodobistrifluoromethylphosphine.[19]

$$(CF_3)_2P - P(CF_3)_2 + CF_3I \xrightarrow{70^\circ} (CF_3)_3P + (CF_3)_2PI$$

A similar, but slower reaction occurs with methyl iodide and yields methylbistrifluoromethylphosphine and iodobistrifluoromethylphosphine.

$$(CF_3)_2P - P(CF_3)_2 + CH_3I \xrightarrow{150^\circ} (CF_3)_2P\,CH_3 + (CF_3)_2PI$$

The reaction of the diphosphine with iodine causes the quantitative release of trifluoromethyl groups as trifluoroiodomethane.[3]

$$(CF_3)_2P - P(CF_3)_2 \xrightarrow{I_2} 4\ CF_3I$$

Alkaline hydrolysis of the diphosphine, although causing degradation, only produces three molecules of fluoroform from the four trifluoromethyl groups available.[3] The remaining group breaks down giving fluoride, carbonate and a trifluoromethyl phosphorus acid. Separate experiments indicate that this reaction involves initial

fission of the phosphorus-phosphorus link, with the formation of bistrifluoromethylphosphine and bistrifluoromethylphosphinous acid.[20]

$$(CF_3)_2P - P(CF_3)_2 \xrightarrow[H_2O]{NaOH} (CF_3)_2PH + (CF_3)_2POH$$

Subsequent reaction of the acid with aqueous alkali produces two molecules of fluoroform, while the phosphine liberates only one molecule, together with fluoride, carbonate and a trifluoromethyl phosphorus acid.

$$(CF_3)_2POH \xrightarrow[H_2O]{NaOH} 2\ CHF_3$$

$$(CF_3)_2PH \xrightarrow[H_2O]{NaOH} CHF_3 + F^- + CO_3^= + CF_3\text{-P-acid}$$

If hydrolysis is effected using water only, the phosphinous acid still produces two molecules of fluoroform but bistrifluoromethylphosphine only partly decomposes and produces trifluoromethylphosphine, fluoride and carbon dioxide thus:

$$(CF_3)_2\ PH \longrightarrow CF_3PH_2 + F^- + CO_3^=$$

The symmetrical compound, 1,2-bistrifluoromethyldiphosphine, is prepared by the aqueous hydrolysis of

either tetrakistrifluoromethylcyclotetraphosphine or pentakistrifluoromethylcyclopentaphosphine,[21] the details of which are presented below, together with the general chemistry of these latter compounds. Hydrolysis of 1,2-bistrifluoromethyldiphosphine causes the liberation of half the available trifluoromethyl groups as fluoroform suggesting that the mechanism is similar to that proposed for the hydrolysis of tetrakistrifluoromethyldiphosphine.[20] At temperatures greater than 250°C the former diphosphine decomposes, producing mainly trifluoromethylphosphine and tetrakistrifluoromethylcyclotetraphosphine.[21]

$$(CF_3PH)_2 \longrightarrow CF_3PH_2 + (CF_3P)_4$$

A hybrid diphosphine, 1,1-dimethyl-2,2-bistrifluoromethyldiphosphine has been obtained from the low temperature reaction between dimethylphosphine and chlorobistrifluoromethylphosphine.[22]

$$(CH_3)_2PH + (CF_3)_2P\,Cl \xrightarrow{-78^\circ} (CH_3)_2P - P(CF_3)_2$$

This compound, unlike either the fully methylated or fully trifluoromethylated derivatives, is very reactive. It forms adducts with diborane and with trimethylamine and readily undergoes protolytic cleavage giving high yields of bistrifluoromethylphosphine. In the presence

of methyl iodide, the diphosphine dispropertionates into diphosphines possessing only one type of organic group per molecule.

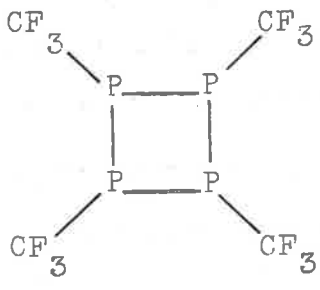
$$2\,(CF_3)_2P - P(CH_3)_2 + CH_3I \longrightarrow (CF_3)_2P - P(CF_3)_2 + (CH_3)_2P - P(CH_3)_3I$$

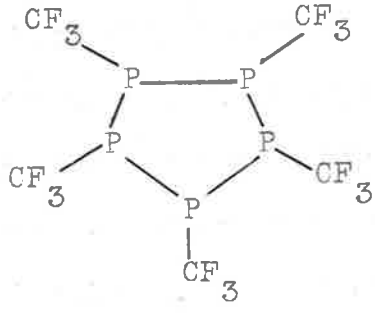
(e) Cyclic Polyphosphines

Di-iodotrifluoromethylphosphine, like iodobistrifluoromethylphosphine, reacts with mercury to give compounds containing phosphorus-phosphorus bonds, but instead of yielding a diphosphine, it undergoes almost complete conversion to a mixture of two cyclic compounds, tetrakistrifluoromethylcyclotetraphosphine and pentakistrifluoromethylcyclopentaphosphine.[18]

$$(CF_3PI_2) + Hg \xrightarrow{R.T.} (CF_3P)_4(60\%) + (CF_3P)_5(40\%)$$

The structures[23,24] of these compounds may be represented thus:





Pyrolysis of bistrifluoromethylphosphine[18] and of tetrakistrifluoromethyldiphosphine[21] also yields these two compounds together with higher cyclic polymers $(CF_3P)_x$ (where $x > 5$)

$$(CF_3)_2PH \xrightarrow{350^\circ} (CF_3P)_4 + (CF_3P)_5 + (CF_3P)_x + CHF_3$$

$$(CF_3)_2P-P(CF_3)_2 \xrightarrow{350^\circ} (CF_3P)_4 + (CF_3P)_5 + (CF_3P)_x$$

The more stable tetramer may also be generated by heating the pentamer in an inert fluorocarbon solvent.

$$(CF_3P)_5 \xrightarrow[F/C]{\text{Heat}} (CF_3P)_4$$

The cyclic polymers are converted quantitativel to di-iodotrifluoromethylphosphine by the action of iodine.[21]

$$(CF_3P)_n + n\ I_2 \longrightarrow n\ CF_3PI_2$$

where $n = 4, 5, x$

Excess chlorine also breaks the phosphorus-phosphorus bonds forming trifluoromethylphosphorus tetrachloride which can be converted to the trivalent phosphorus compound, dichlorotrifluoromethylphosphine, by contact with mercury.

$$(CF_3P)_4 + 2n\,Cl_2 \longrightarrow n\,CF_3PCl_4$$

$$CF_3PCl_4 \xrightarrow{Hg} CF_3PCl_2$$

The cyclic compounds possess a high degree of stability, particularly the tetramer which is not affected by (i) hydrogen chloride or boron trifluoride at temperatures below 300°C, (ii) diborane in the temperature range 25-70°C, or (iii) concentrated sulphuric acid at 100°C, from which it may be recrystallized unchanged. This extraordinary stability is attributed to a supplementation of the σ-bonding in the phosphorus-phosphorus bonds by π-bonds involving interaction of the lone electron pairs on the phosphorus atoms with 3d orbitals on neighbouring phosphorus atoms as in the case of the diphosphines.

The reaction of tetrakistrifluoromethylcyclotetraphosphine with water produces fluoroform, trifluoromethylphosphine and 1,2-bistrifluoromethyldiphosphine together with some polymeric materials in which it is thought that cross-linking occurs.[21]

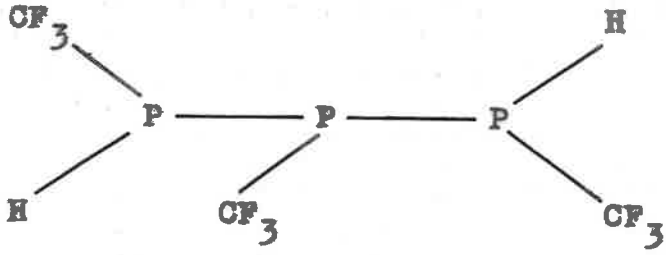
$$(CF_3P)_4 \xrightarrow[140°]{H_2O} H_3PO_3 + CHF_3 + CF_3PH_2 + CF_3\!\!>\!\!P\!-\!P\!<\!\!CF_3 + \text{polymers}$$

Pentakistrifluoromethylcyclopentaphosphine reacts with

water in poly-ether solvents in a similar manner but yielding, in addition to the hydrolysis products of the tetramer, a triphosphine formulated as $(CF_3P)_3H_2$.

$$(CF_3P)_5 \xrightarrow[\text{solvent}]{H_2O/50^\circ} CF_3PH_2 + (CF_3PH)_2 + (CF_3P)_3H_2$$

The triphosphine is not cyclic but has the structure shown below:



This compound decomposes on active nickel giving trifluoromethylphosphine and the cyclic tetramer and pentamer.

$$(CF_3P)_3H_2 \xrightarrow{Ni/25^\circ} CF_3PH_2 + (CF_3P)_4 + (CF_3P)_5$$

The basic hydrolysis of tetrakistrifluoromethylcyclotetraphosphine, pentakistrifluoromethylcyclopentaphosphine and 1,2-bistrifluoromethyldiphosphine causes half the trifluoromethyl groups to be liberated as fluoroform, while 1,2,3-tristrifluoromethyltriphosphine gives only one molecule of fluoroform.

(f) Alkylperfluoroalkylphosphines

The direct reaction between trialkylphosphines and a perfluoroiodoalkane is a convenient route to mixed alkylperfluoroalkylphosphines.[25]

$$R_fI + 2R_3P \longrightarrow R_fPR_2 + R_4PI$$

Thus the reaction between trifluoroiodomethane and trimethylphosphine gives dimethyltrifluoromethylphosphine and tetramethylphosphonium iodide. However, although the above equation represents the major reaction occurring, it has recently been found that the volatile quaternary compound dimethylbistrifluoromethylphosphonium iodide is also formed.[26] Di-n-butyltrifluoromethylphosphine is prepared from tri-n-butylphosphine and trifluoroiodomethane.[27] The mechanism for this type of reaction is thought to involve a pentavalent state of phosphorus and is discussed in detail in Chapter III.

Treatment of dimethyltrifluoromethylphosphine with further trifluoroiodomethane does not yield methylbistrifluoromethylphosphine which however, can be prepared easily by the action of methyl iodide on tristrifluoromethylphosphine.[28]

$$(CF_3)_3P + CH_3I \xrightarrow{240^\circ} CH_3P(CF_3)_2 + CF_3I$$

Further reaction with methyliodide produces dimethyltrifluoromethylphosphine and then trimethyltrifluoromethylphosphonium iodide. These reactions are conveniently represented by the following sequence:

$$(CF_3)_3P \xrightarrow[240^\circ]{CH_3I} (CF_3)_2P\,CH_3 \xrightarrow[240^\circ]{CH_3I} CF_3P(CH_3)_2 \xrightarrow[Fast]{CH_3I} [CF_3P(CH_3)_3]^+ I^-$$

$$CF_3P(CH_3)_2 \xrightarrow[20^\circ]{CF_3I} (CH_3)_3P$$

Alternatively alkylperfluoroalkylphosphines may be prepared by the reaction of an alkyl halide with a perfluoroalkyldiphosphine.[19]

$$(CF_3)_2P-P(CF_3)_2 \xrightarrow[150^\circ]{CH_3I} (CF_3)_2P\,CH_3 + (CF_3)_2PI$$

Although each of the trifluoromethylphosphines yields fluoroform when treated with aqueous sodium hydroxide, only tristrifluoromethylphosphine does so quantitatively at room temperature. The methyltrifluoromethylphosphines require prolonged heating with alkali and even then they are most reluctant to break down completely.[25]

The effect of the highly electronegative trifluoromethyl groups in reducing the availability of the lone pair of electrons on the phosphorus atom is exemplified by reactions of the trifluoromethylphosphines

with Lewis acids. It is found that the stability of complexes with platinous chloride and with boron trifluoride decreases with increasing number of trifluoromethyl groups attached to phosphorus, as is shown by the following sequences[26]

$$\left[(CH_3)_3P\right]_2PtCl_2 < \left[(CH_3)_2PCF_3\right]_2PtCl_2 > \left[CH_3P(CF_3)_2\right]_2PtCl_2 >$$

$$\underbrace{\left[(CF_3)_3P\right]_2PtCl_2}_{\text{Not formed}}$$

$$(CH_3)_3P.BF_3 > (CH_3)_2PCF_3.BF_3 > \underbrace{CH_3P(CF_3)_2.BF_3 > (CF_3)_3P.BF_3}_{\text{Not formed}}$$

The apparent anomaly in the order of stability of the platinous chloride complexes is attributed to the existence of a π-bond whose electrons originate from the platinum. Such a bond is strengthened in those complexes in which trifluoromethyl groups are attached to phosphorus. Of course there is an even greater weakening of the σ-bond accompanying this and if there are more than two trifluoromethyl groups attached to phosphorus, the bond is not sufficiently strong to permit the existence of a complex. The low basicity of the trifluoromethylphosphines is also demonstrated by their reluctance for form adducts with a number of

other compounds known to complex with trimethylphosphine. Thus no compounds of the form $(CF_3)_n P(CH_3)_{3-n}$ give complexes with carbon disulphide or mercuric halides and only dimethyltrifluoromethylphosphine forms one with silver iodide.[25]

(g) Arylperfluoroalkylphosphines

Diphenyltrifluoromethylphosphine is most conveniently prepared by a reaction involving cleavage of a phosphorus-phosphorus bond.[29] This occurs when tetraphenyldiphosphine and trifluoroiodomethane are allowed to react under conditions suitable for free radical formation.

$$Ph_2P - P\,Ph_2 + CF_3I \xrightarrow[\text{or U.V.}]{185\text{-}200^\circ} Ph_2PCF_3 + Ph_2PI$$

The reaction of trifluoroiodomethane with triphenylphosphine at 185-200°C or with diphenylchlorophosphine in the presence of mercury also yields diphenyltrifluoromethylphosphine, together with a number of by-products.

$$Ph_3P + CF_3I \xrightarrow{185\text{-}200^\circ} Ph_2PCF_3 + Ph_2PI + PhCF_3$$

$$Ph_2PCl + CF_3I \xrightarrow{Hg} Ph_2PCF_3 + Ph_2PI + Ph_2PCl + PhCF_3 + CF_3Cl$$

Diphenyltrifluoromethylphosphine is very stable thermally and is not affected by water or dilute acid at 150°C. There is only slight hydrolysis by aqueous sodium hydroxide at 100°C. With bromine and iodine it forms the pentavalent derivatives, diphenyltrifluoromethyl-phosphorus dibromide and di-iodide respectively. These compounds are stable to air and water at 200°C but are hydrolysed by aqueous alkali, giving fluoroform quantitatively. Although diphenyltrifluoromethyl-phosphine does not react with trifluoroiodomethane, its reaction with methyl iodide yields a quaternary compound which is readily hydrolysed by water to fluoroform and diphenylmethylphosphine oxide.

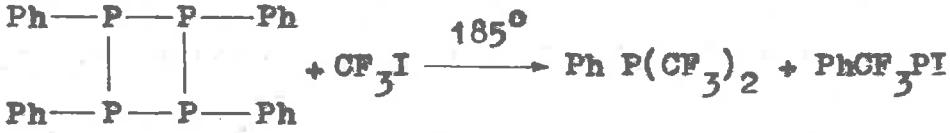
$$Ph_2PCF_3 + CH_3I \longrightarrow [Ph_2CH_3PCF_3]^+ I \xrightarrow{H_2O}$$

$$Ph_2CH_3PO + CHF_3 + HI$$

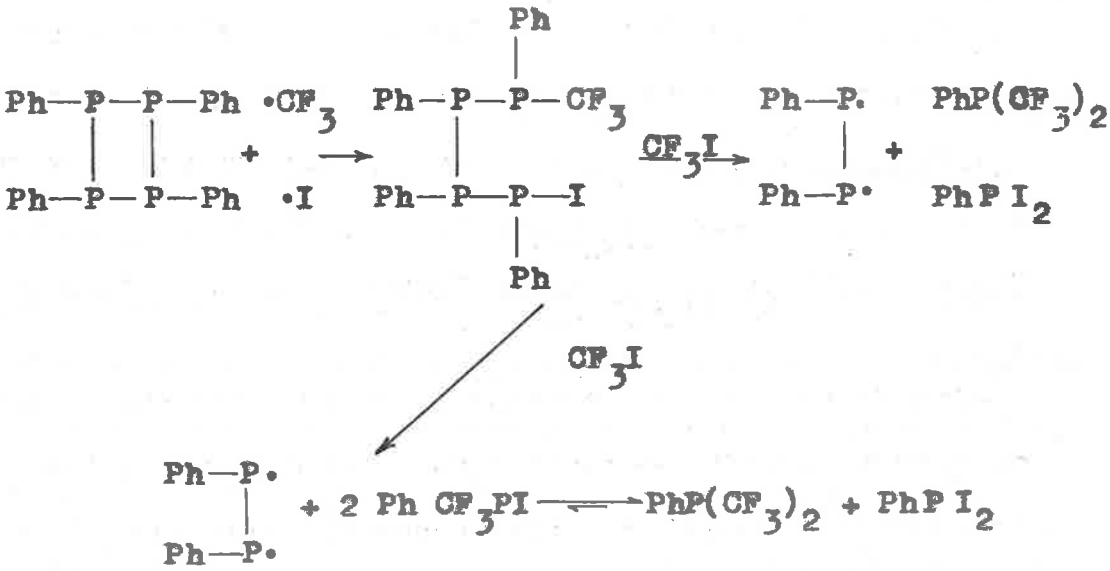
A study of the decomposition of phosphonium hydroxides has shown that the most electron withdrawing groups are most easily eliminated, leaving the other three groups to form the phosphine oxide.[30] This is in agreement with the mode of decomposition of the quaternary compound discussed above.

Phenylbistrifluoromethylphosphine is readily prepared by reacting tetraphenylcyclotetraphosphine with

trifluoroiodomethane at 185° or in the presence of ultraviolet light.[31]



Iodophenyltrifluoromethylphosphine is a major reaction product and traces of fluoroform and hexafluoroethane also form. A free radical mechanism involving stepwise fission of the phosphorus-phosphorus bonds is thought to operate.



Phenyliodotrifluoromethylphosphine is thermally very stable, resistant to attack by water or dilute acids but hydrolysed at 80°C by aqueous alkali liberating fluoroform. It reacts with iodine only at high temperatures with the result that trifluoromethyl groups are cleaved as trifluoroiodomethane.

$$PhP(CF_3)_2 + 2\,I_2 \xrightarrow{185^\circ} PhPI_2 + 2\,CF_3I$$

Reaction of phenylbistrifluoromethylphosphine occurs with bromine at much lower temperatures (ca. 20°C) yielding the pentavalent dibromide. This compound reacts slowly with water at 100°C and is hydrolysed by aqueous alkali at 80°C according to the following scheme:

$$Ph(CF_3)_2PBr_2 \xrightarrow[NaOH]{H_2O} Ph(CF_3)P(O)OH + CHF_3$$

Like their methyl analogues,[26] diphenyltrifluoromethylphosphine and phenylbistrifluoromethylphosphine form complexes with platinous chloride,[29] but only the former does so with boron trifluoride.

2. ARSENIC

As is to be expected much of the chemistry of perfluoroalkylarsines has been studied concurrently with that of the corresponding phosphines. In general the properties of analogous compounds are similar, the differences being mainly a result of the relative positions of phosphorus and arsenic in the Periodic Table. However there are some features of perfluoroalkylarsines which apparently have no parallel in phosphorus chemistry and special reference will be made to these in the following discussion.

(a) Haloperfluoroalkylarsines

Iodoperfluoroalkylarsines are prepared by heating together perfluoroiodoalkanes and finely divided arsenic. When trifluoroiodomethane is used in such a reaction at 220°C, as well as the iodotrifluoromethylarsines, tristrifluoromethylarsine is formed.[32,33] The following equilibria are considered to exist in this reaction system:

$$2\,(CF_3)_2AsI \rightleftharpoons (CF_3)_3As + CF_3AsI_2$$

$$2\,CF_3AsI_2 \rightleftharpoons (CF_3)_2AsI + AsI_3$$

$$(CF_3)_3As + AsI_3 \rightleftharpoons (CF_3)_2AsI + CF_3AsI_2 + CF_3I + As$$

Unlike the comparable reaction of arsenic with methyl iodide which gives methyliodoarsines and tetramethylarsonium iodide,[34]

$$CH_3I + As \longrightarrow (CH_3)_4AsI + (CH_3)_xAsI_{3-x}$$

there is no evidence for the formation of quaternary compounds from tristrifluoromethylarsine.

Arsenic reacts with pentafluoroiodoethane at 220°C to form trispentafluoroethylarsine and iodobispentafluoroethylarsine,[35] and with heptafluoroiodopropane

at 200-220°C but in this case the products have not been identified.[6]

Dichloropentafluoroethylarsine has been prepared by the direct reaction of tetrafluoroethylene with arsenic trichloride.[36]

$$3\,CF_2{=}{=}CF_2 + 2\,AsCl_3 \xrightarrow[70\text{-}100^\circ]{AlCl_3} 2\,CF_3CF_2AsCl_2 + CF_2{=}{=}CCl_2$$

All the compounds of the form $(R_f)_n AsX_{3-n}$ are hydrolysed rapidly by aqueous alkali liberating the appropriate fluorocarbon quantitatively. It appears that the more negative is the group attached to arsenic, the more susceptible the compound is to hydrolysis and resistant to oxidation.[33]

Replacement of the iodotrifluoromethylarsines by other halogens or pseudo-halogens is readily effected by reaction with the appropriate silver salt. Reduction of the iodo-compounds with a zinc/hydrochloric acid mixture or with lithiumaluminium hydride produces trifluoromethylarsine and bistrifluoromethylarsine.

(b) Pentavalent Trifluoromethylarsines

When tristrifluoromethylarsine is allowed to react, even at very low temperatures with fluorine diluted with nitrogen, complete degradation occurs and

the only products obtained are carbon tetrafluoride and arsenic trifluoride. However tristrifluoromethylarsenic difluoride can be prepared by the room temperature reaction of silver fluoride with tristrifluoromethylarsenic dichloride.[37] In the liquid phase tristrifluoromethylarsine reacts with chlorine to form tristrifluoromethylarsenic dichloride which on standing, is slowly converted to bistrifluoromethylarsenic trichloride.

$$(CF_3)_3As + Cl_2 \longrightarrow (CF_3)_3 Cl_2 \longrightarrow (CF_3)_2 As Cl_3$$

The reaction of bromine with tristrifluoromethylarsine, even at low temperatures, does not yield a pentavalent arsenic derivative. Instead arsenic tribromide is deposited and trifluorobromomethane, bromobistrifluoromethylarsine and dibromotrifluoromethylarsine are formed. Reaction of tristrifluoromethylarsine with iodine only occurs at temperatures above 100°C and the products obtained are analogous to those obtained from the reaction with bromine.[37]

(c) Aminoarsines

Like the analogous phosphorus compound, chlorobistrifluoromethylarsine reacts with ammonia and primary and secondary amines to give aminoarsines.[38]

$$(CF_3)_2AsCl + 2NHRR' \longrightarrow (CF_3)_2AsNRR' + RR'NH_2Cl$$

With the phosphine it is impossible to replace more than one hydrogen of ammonia by $(CF_3)_2P$ but the low temperature reaction of ammonia with chlorobistrifluoromethylarsine proceeds according to the following equation:

$$2\,(CF_3)_2AsCl + 3NH_3 \longrightarrow \left[(CF_3)_2As\right]_2NH + 2\,NH_4Cl$$

At room temperature, in the gas phase, the reaction also yields the aminobistrifluoromethylarsine.

$$(CF_3)_2AsCl \xrightarrow{NH_3} \left[(CF_3)_2As\right]_2NH + (CF_3)_2AsNH_2$$

Tristrifluoromethylarsine does not react with ammonia in the gas phase, but in liquid ammonia at 20°C almost complete solvolysis occurs and fluoroform is liberated. At -64°C this system produces the two aminoarsines previously discussed.

The ammonolysis of tetrakistrifluoromethyldiarsine closely resembles the hydrolysis of this compound[39] and fission of the arsenic-arsenic bond is considered to be the first stage of the reaction.

$$(CF_3)_2As - As(CF_3)_2 \xrightarrow{NH_3} (CF_3)_2AsNH_2 + (CF_3)_2AsH$$

The independent reactions of aminobistrifluoromethylarsine and of bistrifluoromethylarsine with ammonia yields a total amount of fluoroform equal to that obtained by the direct reaction of ammonia with the diarsine. Thus the proposed mechanism appears to be valid.

(d) Diarsines

The reaction of iodobistrifluoromethylarsine with mercury at room temperature gives tetrakistrifluoromethyldiarsine in good yield.[33]

$$2\,(CF_3)_2AsI \xrightarrow{Hg} (CF_3)_2As-As(CF_3)_2$$

This compound, although stable to water, is hydrolysed by aqueous alkali giving fluoroform (83%), the remaining fluorine present being converted to fluoride (17%).[37] The hydrolysis occurs via the initial fission of the arsenic-arsenic bond.

$$(CF_3)_2As-As(CF_3)_2 \xrightarrow[NaOH]{H_2O} (CF_3)_2AsOH + (CF_3)_2AsH$$

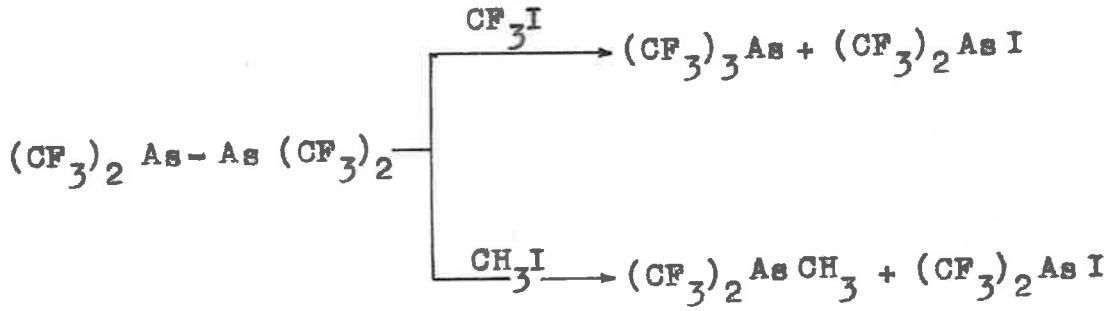
$$\downarrow \qquad\qquad \downarrow$$

$$2\,CHF_3 \qquad CHF_3 + F^- + CO_3^{=}$$

The separate hydrolysis of a sample of bistrifluoromethylarsine gives 66% of the available fluorine as fluoroform and the remaining 34% as fluoride. This then supports the mechanism proposed for the hydrolysis of

the diarsine since the total quantity of fluoroform is obviously made up of 50% from bistrifluoromethylarsonous acid and 33% ($\frac{1}{2}$ x 66%) from the bistrifluoromethylarsine.

Trifluoroiodomethane reacts with the diarsine at 75°C, rupturing the arsenic-arsenic bond and producing tristrifluoromethylarsine and iodobistrifluoromethylarsine.[19] Methyl iodide reacts similarly, but less readily, to give methylbistrifluoromethylarsine and iodobistrifluoromethylarsine.



There is no evidence for the existence of arsenic analogues of the cyclic trifluoromethylphosphines.

(e) Alkylperfluoroalkylarsines

A number of different methods are available for the preparation of alkylperfluoroalkylarsines.

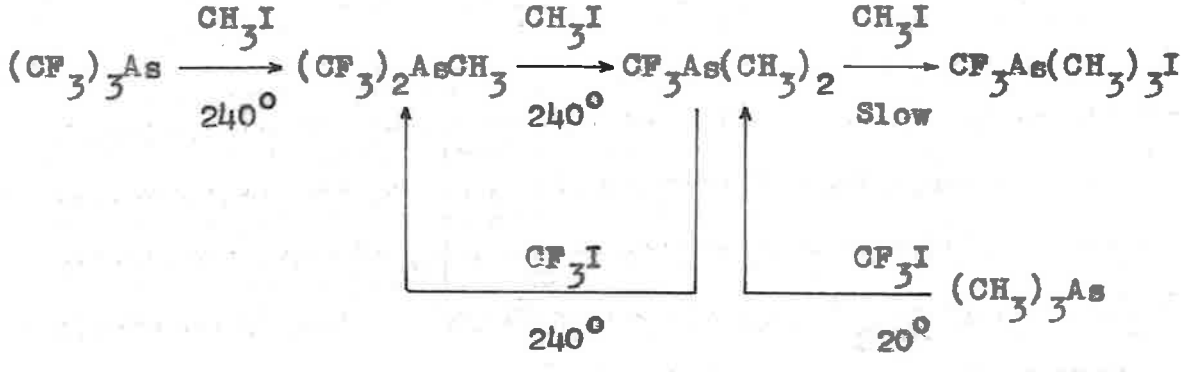
(i) They may be prepared in a manner identical with that used for the formation of the corresponding

phosphorus compounds. The reaction between a perfluoroiodoalkane and a trialkylarsine therefore gives the appropriate dialkylperfluoroalkylarsine and the tetraalkylarsonium iodide.[25,27]

$$R_3As + R_fI \longrightarrow R_2AsR_f + R_4AsI$$

where R = CH_3, C_2H_5, n - C_4H_9 and R_f = CF_3, C_3F_7

In dimethyltrifluoromethylarsine and diethyltrifluoromethylarsine, unlike their phosphorus analogues, it is possible to replace a further alkyl group with a trifluoromethyl. Even so the yields are generally very low. A more successful preparation of methylbistrifluoromethylarsine involves treatment of tristrifluoromethylarsine with methyl iodide. The exchange of methyl and trifluoromethyl groups which are possible in tertiary arsines are represented as follows:



(ii) A method which has little general application and appears to be successful only for the preparation of arsenic derivatives involves the decarboxylation of an acetoxy compound.[40] Dimethyltrifluoroacetoxyarsine is prepared by the reaction of chlorodimethylarsine with silver trifluoroacetate and is decarboxylated at 205°C giving dimethyltrifluoromethylarsine.

$$(CH_3)_2AsCl + AgOOC.CF_3 \longrightarrow (CH_3)_2AsOOC.CF_3 + AgCl$$

$$(CH_3)_2AsOOC.CF_3 \xrightarrow{205^\circ C} (CH_3)_2AsCF_3$$

(iii) The reaction of the Grignard reagent, methylmagnesium iodide, with iodobistrifluoromethylarsine[37] and with di-iodotrifluoromethylarsine[41] gives methylbistrifluoromethylarsine and dimethyltrifluoromethylarsine respectively.

$$(CF_3)_2AsI \xrightarrow{CH_3MgI} (CF_3)_2AsCH_3$$

$$CF_3AsI_2 \xrightarrow{CH_3MgI} CF_3As(CH_3)_2 + (CF_3)(CH_3)AsI$$

(iv) A very convenient synthetic method involves the elimination of iodine from a mixture of an alkyliodoarsine and a perfluoroiodoalkane using mercury as the halogen acceptor.[19]

$$(CH_3)_2AsI + R_fI + Hg \longrightarrow (CH_3)_2AsR_f + HgI_2$$

where $R_f = CF_3$ or C_3F_7

$$CH_3AsI_2 + 2Hg + 2CF_3I \longrightarrow CH_3As(CF_3)_2 + 2HgI_2$$

The reaction of diethyliodoarsine with trifluoroiodomethane in the presence of mercury produces mainly ethylbistrifluoromethylarsine, the reason for which is not known.[42]

(v) The formation of alkylperfluoroalkylarsines from diarsines has already been discussed in Part (d) of this Chapter.

Although very little quantitative work has been done to determine the basic strengths of alkylperfluoroalkylarsines, it is apparent that such compounds show even less tendency to react with Lewis acids than do their phosphorus analogues. This is demonstrated by the inability of all but dimethyltrifluoromethylarsine to

form quaternary 'onium compounds with methyl iodide[27] or to form adducts with silver iodide.[25]

The reaction of these arsines with aqueous alkali produces fluoroform at a rate which is extremely slow in the case of methyl derivatives, but noticeably faster for ethylarsines.[27]

(f) Arylperfluoroalkylarsines

A very convenient route to arylperfluoroalkylarsines is the room temperature reaction of an aryliodoarsine with a perfluoroiodoalkane in the presence of mercury. Only trifluoroiodomethane[43] and heptafluoroiodopropane[42] have so far been used in such reactions. The formation of diphenyltrifluoromethylarsine from diphenyliodoarsine and of phenylbistrifluoromethylarsine from phenyldi-iodoarsine are typical of these reactions.

$$Ph_2AsI + CF_3I \xrightarrow{Hg} Ph_2AsCF_3$$

$$PhAsI_2 + 2C_3F_7I \xrightarrow{Hg} PhAs(C_3F_7)_2$$

Of interest is the fact that this synthetic method has been used for the preparation of both alkyl- and arylperfluoroalkylarsines and can also be used to prepare alkylarylperfluoroalkylarsines, e.g. phenyldimethylheptafluoropropylarsine.

$$Ph(CH_3)AsI + C_3F_7I \xrightarrow{Hg} Ph(CH_3)AsC_3F_7$$

Whereas triphenylphosphine reacts with trifluoroiodomethane to give diphenyltrifluoromethylphosphine, the analogous reaction does not occur with triphenylarsine.[43] Instead a mixture of fluoroform, benzotrifluoride, benzene and arsenic tri-iodide is formed. Nor can radical exchange reactions be used to prepare aryl-perfluoroalkylarsines, for it is found that even at 240°C tristrifluoromethylarsine and iodobenzene do not react, while triphenylarsine and trifluoroiodomethane at 210°C give degradation products only.

All the phenyltrifluoromethylarsines are liquidswhich are stable to both air and moisture at ordinary temperatures.

Diphenyltrifluoromethylarsine is stable to concentrated hydrochloric acid at 85°C and only slowly attacked by 10% sodium hydroxide at 85°C to give fluoroform. Phenylbistrifluoromethylarsine is attacked by alkali more readily. Similar rates of ammonolysis occur when these compounds are treated with liquid ammonia.

With halogens only diphenyltrifluoromethylarsine gives a pentavalent derivative.

$$Ph_2AsCF_3 + Br_2 \xrightarrow{CCl_4} Ph_2AsCF_3.Br_2$$

Phenylbistrifluoromethylarsine is decomposed by halogens.

The basic strengths of arylperfluoroalkylarsines have not been studied in detail but it is known that these compounds neither form 'onium derivatives with methyl iodide nor adducts with e.g. mercuric halides.

3. ANTIMONY

The chemistry of the perfluoroalkyl derivatives of antimony has not been examined to the same extent as that of the corresponding phosphorus and arsenic compounds. However, from the limited information available, two important features appear. The first is the pronounced difference between some of the properties of the stibines compared to those of the phosphines and arsines, brought about by the progressive weakening of the carbon-metal bond. It has been established that the strength of these bonds decreases with increasing atomic number of the Group V B element.[44] The second is the tendency for perfluoroalkylstibines to act as electron acceptors.[45]

(a) Haloperfluoroalkylstibines

The temperature at which reaction between trifluoroiodomethane and antimony occurs to produce iodotrifluoromethylstibines and tristrifluoromethylstibine[45] is 165-170°C.

$$CF_3I + Sb \longrightarrow (CF_3)_3Sb + (CF_3)_2SbI + CF_3SbI_2$$

If the reaction temperature is higher than 170°C the major products are fluorocarbons and antimony trifluoride which probably result from the pyrolysis of first formed tristrifluoromethylstibine. The mechanism proposed for this reaction involves the initial formation of tetrafluoroethylene, followed by polymerization initiated by trifluoromethyl radicals arising from homolytic fission of the Sb—CF_3 bond. These facts are summarized as follows:

$$(CF_3)_3Sb \longrightarrow (CF_3)_2Sb^{\bullet} + CF_3^{\bullet}$$

$$(CF_3)_3Sb \longrightarrow C_2F_4 + CF_3SbF_2 \longrightarrow SbF_3, \text{ etc.}$$

$$(CF_3)_3Sb \longrightarrow {}^{\bullet}CF_2{}^{\bullet} + (CF_3)_2SbF \cdots\cdots\rightarrow {}^{\bullet}CF_2{}^{\bullet} + SbF_3$$

$$CF_3^{\bullet} + C_2F_4 \longrightarrow CF_3CF_2CF_2{}^{\bullet} \cdots\cdots\rightarrow CF_3(CF_2)_nCF_3$$

$$CF_3^{\bullet} + {}^{\bullet}CF_2{}^{\bullet} \longrightarrow CF_3CF_2{}^{\bullet} \cdots\cdots\rightarrow CF_3(CF_2)_nCF_3$$

In this regard the stibine differs markedly from its phosphorus and arsenic analogues which yield trifluoromethyl radicals when pyrolysed.[35] During the formation of the iodotrifluoromethylstibines disproportionation reactions are thought to occur:

$$(CF_3)_3Sb + CF_3SbI_2 \rightleftharpoons (CF_3)_2SbI$$

$$(CF_3)_2SbI + SbI_3 \rightleftharpoons 2\,CF_3SbI_2$$

$$(CF_3)_3Sb + SbI_3 \rightleftharpoons (CF_3)_2SbI + CF_3SbI_2$$

Hydrolysis of the iodotrifluoromethylstibines is rapid and causes fluoroform to be liberated quantitatively. The iodo compounds may be converted by the action of silver chloride into the appropriate chloro derivatives.

(b) Pentavalent Antimony

Tristrifluoromethylstibine reacts with chlorine at -45°C giving tristrifluoromethylantimony dichloride. This compound forms 1:1 adducts with water and with pyridine[46] and in so doing demonstrates the pseudo-halogen character of the trifluoromethyl group, since antimony pentachloride is known to form similar adducts.[47] Tristrifluoromethylantimony dichloride can be converted

to the trivalent antimony derivative by treatment with mercury.

$$(CF_3)_3SbCl_2 \xrightarrow{Hg} (CF_3)_3Sb$$

Pentavalent trifluoromethylantimony bromides can also be formed at low temperatures but at room temperature, the reaction between bromine and tristrifluoromethylstibine gives iodobistrifluoromethylstibine, di-iodotrifluoromethylstibine and antimony tribromide.[45] Iodine does not react with tristrifluoromethylstibine at low temperatures, but at 20°C it removes a trifluoromethyl group as trifluoroiodomethane and leaves iodobistrifluoromethylstibine which may react further to give di-iodotrifluoromethylstibine and antimony tri-iodide.

(c) Reactions with Amines

The antimony analogues of amino-phosphines and -arsines are not known. Tristrifluoromethylstibine is decomposed quantitatively by liquid ammonia giving fluoroform and antimony nitride.[38] Almost complete decomposition also occurs with dimethylamine.

(d) Distibines

Tetrakistrifluoromethyldistibine is prepared by treating iodobistrifluoromethylstibine with mercury

or zinc.[45]

$$2\,(CF_3)_2\,Sb\,I \xrightarrow{Hg\ (Zn)} (CF_3)_2\,Sb - Sb\,(CF_3)_2$$

Chlorine reacts at -78°C with the distibine forming bistrifluoromethylantimony trichloride.

$$(CF_3)_2\,Sb - Sb\,(CF_3)_2 \xrightarrow{Cl_2} 2\,(CF_3)_2\,Sb\,Cl_3$$

Bromine and iodine react at moderate temperatures causing complete decomposition of the distibine and producing the appropriate trifluorohalomethane and antimony trihalide.

Unlike the phosphorus and arsenic analogues, tetrakistrifluoromethyldistibine liberates almost the whole of its fluorine as fluoroform (99%) when treated with aqueous alkali.

(e) <u>Alkylperfluoroalkylstibines</u>

Dimethyltrifluoromethylstibine is the only alkylperfluoroalkylstibine so far reported[25] and is prepared, together with tetramethylstibonium iodide by reacting trimethylstibine with trifluoroiodomethane at room temperature.

$$CF_3I + 2\,(CH_3)_3\,Sb \longrightarrow CF_3\,Sb\,(CH_3)_2 + Sb\,(CH_3)_4\,I$$

Hydrolysis of the stibine with aqueous alkali causes fluoroform to be liberated quantitatively and quickly.

No basic character is exhibited by trifluoromethylstibines[45] and in fact, in the case of tristrifluoromethylstibine, the strongly electronegative trifluoromethyl groups completely overcome any electron donating properties. Thus whereas trimethylstibine forms complexes[48] with platinous chloride and with palladium dichloride, tristrifluoromethylstibine does not. Instead it acts as an electron acceptor and as such, forms a 1:1 adduct with pyridine.[45]

No arylperfluoroalkylstibines have been reported as yet.

4. BISMUTH

No perfluoroalkyl derivatives of bismuth were known prior to the investigations described in this thesis. The compounds prepared and their relation to comparable derivatives of the other elements within Group V B are described in Chapter VI.

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CHAPTER III

REACTIONS OF GROUP V B ORGANOMETALLIC COMPOUNDS WITH HALOALKANES

Since the preparation of the new alkylperfluoroalkyl compounds prepared in this study involves reaction of trialkyl derivatives of the Group V B elements with perfluoroiodoathanes, it is relevant to the discussion to describe briefly the nature of the reactions of Group V B organometallic compounds with different haloalkanes.

1. REACTIONS WITH MONOHALOALKANES

The reaction between organic derivatives of Group V B elements and alkyl (or aryl) halides to form the appropriate 'onium halide compound is well known and can be represented thus,

$$R_3M + R'X \longrightarrow (R_3 MR')X$$

where M=N, P, As or Sb; R, R' = CH_3, C_2H_5, C_6H_5, etc.; R and R' can be the same or different and R groups attached to M may be the same or different. The ease of reaction varies both with the parent element and the nature of the alkyl or aryl groups. The elements of lower atomic number generally give quaternary compounds and reaction is more easily accomplished when the alkyl groups are small. An anomaly appears in the reaction of

alkyl halides with the triaryl derivatives of this group of elements since, whereas both triphenylphosphine and triphenylarsine give quaternary compounds, triphenylamine does not react.[1] Stibines containing more than one aromatic group fail to give quaternary compounds with methyl iodide,[2] but at elevated temperatures reaction between triphenylstibine and methyl iodide gives triphenylantimony di-iodide, iodobenzene and ethane.[3]

Bismuth is normally incapable of quaternary compound formation[4] and only at high temperatures can any reaction be induced with alkyl halides. It is found that at 200°C, trimethylbismuth and methyl iodide react to give di-iodomethylbismuth and ethane.[5]

$$(CH_3)_3Bi \xrightarrow{200^\circ C} CH_3BI_2 + C_2H_6$$

This reaction shows marked similarities to that occurring between triphenylstibine and methyl iodide under comparable conditions and closely related mechanisms probably operate in each case.

Examples of radical exchange reactions have been found to occur in the quaternization of trialkylamines. Such is the case when ethyl-n-propyl-i-butylamine is treated with methyl iodide since, instead of producing the expected methylethyl-n-propyl-i-butyl

ammonium iodide, the reaction proceeds according to the following equation,[6]

$$(C_2H_5)(\underline{n}\text{-}C_3H_7)(\underline{i}\text{-}C_4H_9)N + 2\,CH_3I \longrightarrow C_2H_5I + [(CH_3)_2(\underline{n}\text{-}C_3H_7)(\underline{i}\text{-}C_4H_9)N]\,I$$

2. REACTION WITH DIHALOALKANES

Methylene dibromide (and ethylene dibromide) react with trimethylamine forming a monoquaternary compound initially and then a diquaternary salt.[7,8]

$$CH_2Br_2 + (CH_3)_3N \longrightarrow [(CH_3)_3N\,CH_2\,Br]\,Br$$

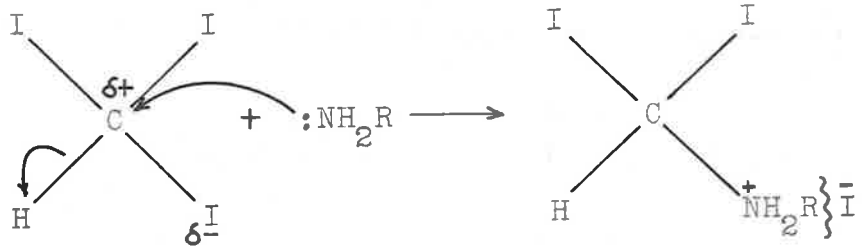
$$CH_2Br_2 + 2(CH_3)_3N \longrightarrow [(CH_3)_3N\,CH_2N\,(CH_3)_3]\,Br_2$$

A similar reaction occurs between ethylene dibromide and phenyldimethylphosphine[9] to yield $[C_6H_5(CH_3)_2P(CH_2)_2Br]\,Br$ and $[C_6H_5(CH_3)_2P(CH_2)_2P(CH_3)_2\,C_6H_5]\,Br_2$. From the reaction between triphenylphosphine and ethylene dibromide however, only the diquaternary compound $[(C_6H_5)_3P(CH_2)_2P(C_6H_5)_3]\,Br_2$ is obtained.[10]

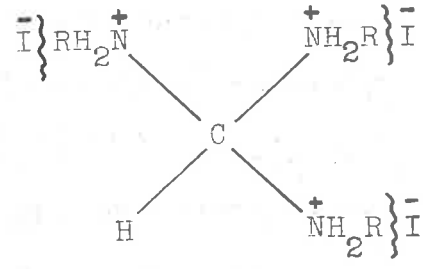
3. REACTIONS WITH TRIHALOALKANES

Iodoform is capable of forming a number of

different adducts with a particular amine,[11] e.g. $RNH_2.CHI_3$; $(RNH_2)_2.CHI_3$; $(RNH_2)_3.CHI_3$. Such compounds were described as comparable with hydrated salts due to their "instability", and the ability of the more complex to yield less complex ones on treatment with hot solvents known to be effective dehydrating agents. However the production of hydrogen iodide, formic acid and the salts of the appropriate bases with these two acids on hydrolysis suggests the structures shown in the proposed mechanism illustrated below:



This process, if repeated on each new product, ultimately gives the compound



Whereas bromoform reacts with trimethylamine and triethylamine to give the appropriate trialkylammonium bromide,[12] no such reaction occurs with chloroform. Bromoform also reacts with triphenylphosphine

under conditions favorable for free radical formation, yielding triphenyldibromomethylphosphonium bromide.[13] The mechanism proposed involves a chain process in which the following steps are thought to occur:

$$CHBr_3 \longrightarrow \cdot CHBr_2 + Br$$

$$(C_6H_5)_3P + \cdot CHBr_2 \longrightarrow (C_6H_5)_3\dot{P}\,CHBr_2$$

$$(C_6H_5)_3\dot{P}\,CHBr_2 + BrCHBr_2 \longrightarrow [(C_6H_5)_3P\,CHBr_2]Br + \cdot CHBr_2$$

4. REACTIONS WITH PERHALOALKANES

Many aliphatic and aromatic nitrogen-containing compounds form molecular complexes with perhaloalkanes.[14] The following examples illustrate the variety of such complexes formed with carbon tetrabromide.

$$\text{Quinoline} + CBr_4 \longrightarrow C_9H_7N.CBr_4$$

$$\text{Pyridine} + 2CBr_4 \longrightarrow C_5H_5N.(CBr_4)_2$$

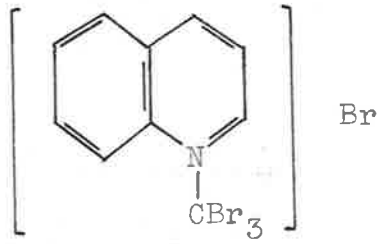
$$4\,\text{Ethylamine} + CBr_4 \longrightarrow (C_2H_5NH_2)_4.CBr_4$$

These compounds hydrolyse readily in the presence of

water, giving the hydrobromide of the appropriate base, e.g.

$$C_5H_5N.(CBr_4)_2 + 2H_2O \longrightarrow C_5H_5N.HBr + 3HBr + CBr_4 + CO_2$$

The structures suggested[14] for these complexes involve pentacovalent nitrogen which is now regarded as being inadmissable. Alternatively, in the case of the complex consisting of equimolar quantities of quinoline and carbon tetrabromide, a structure based on a quaternary ammonium salt seems feasible.

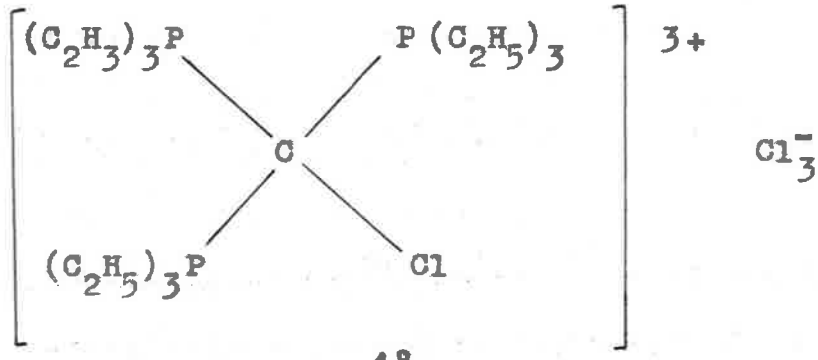


This type of explanation for the structure is not obviously applicable to the complex $C_5H_5N.(CBr_4)_2$.

Carbon tetrachloride does not normally react at room temperature (or lower) with amines, phosphines and arsines,[15] but at higher temperatures (ca. 150-200°C) polymeric substances result. A notable exception to this observation is the rather violent reaction which occurs with triethylphosphine and carbon tetrachloride.[16]

$$3(C_2H_5)_3P + CCl_4 \longrightarrow [(C_2H_5)_3P]_3 . CCl_4$$

The material is considered to have the structure[17]



Pullman and West[18] have shown that trichloroiodomethane reacts with a number of alkyl and aryl compounds of Group V B elements forming 1:1 adducts. The stability of these compounds, to a first approximation, increases with increasing co-ordinating ability of the parent element of the organometallic compound used. Conductivity measurements indicate that the adducts are not ionised in solution. Their formulation as quaternary compounds, either $[R_3M\,I]^+\,C\,Cl_3^-$ or $[R_3M\,C\,Cl_3]^+\,I^-$ can therefore be discounted. Bonding is considered to exist between the Group V B element and the iodine of trichloroiodomethane. The fact that triphenylphosphine forms a very stable adduct while triphenylamine does not form one at all, seems likely to be due to the existence of $p_\pi - d_\pi$ bonding[19] between iodine and phosphorus in addition to the ordinary P→I coordination. Nitrogen is unable to participate in bonds of this type since it does not possess any suitable

vacant orbitals to receive electrons from iodine. This, together with the fact that triphenylamine normally displays very little basic character, accounts for its inability to form an adduct with trichloroiodomethane. The few adducts of triphenylamine that are known[20] involve strong Lewis acids like the boron halides, although recently complexes of the amine with silver perchlorate and silver tetrafluoroborate have been reported.[21]

Partial displacement of the base (R_3M) from its adduct with trichloroiodomethane occurs when another base (R'_3M), also capable of forming a similar adduct, is present.[15] The general equilibrium for this type of reaction may be represented as:

$$R_3M \cdot CCl_3I + R'_3M \rightleftharpoons R'_3M \cdot CCl_3I + R_3M$$

(if $R = R'$, $M \neq M'$ and if $M = M'$, $R \neq R'$).

The compounds whose reactions with trichloroiodomethane were studied are listed in Table 2.1.

TABLE 2.1

Reactions of Trichloroiodomethane with Group V B Organometallic Compounds

Class of compound	Adduct formed	No Reaction
Amines	$(CH_3)_2NH$	NH_3
	$(CH_3)_3N$	CH_3NH_2
	$(C_2H_5)_3N$	$(C_6H_5)_3N$
Phosphines	$(CH_3)_3P$	
	$(C_6H_5)_3P$	
Arsines	$(CH_3)_3As$	
	$(C_6H_5)_3As$	
Stibines	$(CH_3)_3Sb$	$(C_6H_5)_3Sb$

In some circumstances trifluoroiodomethane undergoes reactions similar to those of trichloroiodomethane. For example each compound reacts with mercury in the presence of ultra-violet light giving trifluoromethylmercuric iodide[22] and trichloromethylmercuric iodide[23] respectively. However in their reactions with organic derivatives of Group V B elements, these haloalkanes

show marked differences. Instead of adduct formation, reaction of trimethyl-phosphine, -arsine and -stibine with trifluoroiodomethane yields the appropriate dimethyltrifluoromethyl derivative together with the corresponding tetramethyl 'onium iodide and a trace of fluoroform.[24,25] The corresponding reaction with trimethylamine does not give dimethyltrifluoromethylamine but gives some tetramethylammonium iodide, fluoroform in greater than 70% yield, and an unidentified solid. A mechanism has been proposed for this radical exchange reaction and involves an intermediate quaternary compound of the type $[(CH_3)_3M\,CF_3]^+ I^-$. In the case where the metal is phosphorus, it is possible to prepare the mixed alkylperfluoroalkyl 'onium compound independently.

$$CH_3I + (CH_3)_2P\,CF_3 \longrightarrow [(CH_3)_3P\,CF_3]\,I$$

This quaternary compound is stable at room temperature. The fact that such a compound is not detected in the products of the reaction between the trialkyl compounds and trifluoroiodomethane means that subsequent steps in the reaction mechanism must provide for complete removal of the quaternary compound. The following observations are relevant to the choice of mechanism.[24]

(a) Both trimethyltrifluoromethylphosphonium iodide and tetramethylphosphonium iodide are obtained from the reaction between trimethylphosphine and trifluoroiodomethane in carbon tetrachloride. This indicates that reaction to give the mixed quaternary compound can occur in a solvent. The inability of trimethyltrifluoromethylphosphonium iodide to react further in this case is attributed to its insolubility in the solvent used.

(b) Trimethyltrifluoromethylphosphonium iodide is soluble in, and can be recovered unchanged from trifluoroiodomethane. Thus there is no direct reaction between the quaternary compound and trifluoroiodomethane.

(c) Tetramethylphosphonium iodide is soluble in trifluoroiodomethane from which it can be recovered unchanged.

(d) Trimethyltrifluoromethylphosphonium iodide is almost insoluble in trimethylphosphine and not even traces of tetramethylphosphonium iodide are formed unless ethanol is added.

It therefore appears that solvent effects are important in this reaction and that trifluoroiodomethane can be regarded as the solvent, for its reaction with trimethylphosphine. The ready solubility of trimethyltrifluoromethylphosphonium iodide in this solvent

explains why the reaction proceeds to completion in trifluoroiodomethane but not in carbon tetrachloride. The proposed mechanisms by which trimethyltrifluoromethylphosphonium iodide may be removed and the observed reaction products formed, are closely related:[24]

(a) The mixed quaternary iodide may dissociate to dimethyltrifluoromethylphosphine and methyl iodide, the latter then reacting with trimethylphosphine to form tetramethylphosphonium iodide.

$$\left[(CH_3)_3P\,CF_3\right]I \longrightarrow (CH_3)_2P\,CF_3 + CH_3I$$

$$CH_3I + (CH_3)_3P \longrightarrow \left[(CH_3)_4P\right]I$$

(b) Alternatively, the conditions are favorable for nucleophilic attack of trimethylphosphine on a methyl group of the quaternary compound:

$$(CH_3)_3P: + CH_3 - \overset{CH_3}{\underset{CH_3}{P^+}} - CF_3 \longrightarrow (CH_3)_4P^+ + (CH_3)_2P\,CF_3$$

In just the same way in which nucleophilic attack of hydroxide ions on trifluoroiodomethane occurs to give fluoroform:[26]

$$OH^- + I - CF_3 \longrightarrow HOI + CF_3^-$$

$$CF_3^- + \text{solvent} \longrightarrow CHF_3$$

the formation of the mixed quaternary compound may result from nucleophilic attack of trimethylphosphine on the relatively positive iodine of trifluoroiodomethane:[24]

$$(CH_3)_3P: \overset{\delta+}{\frown} I \overset{\delta-}{\frown} CF_3 \longrightarrow \left[(CH_3)_3P\,I\right]^+ CF_3^-$$

Rearrangement of the positive iodine complex via a pentacovalent state then gives trimethyltrifluoromethylphosphonium iodide. The small amount of fluoroform produced in the reactions between trifluoroiodomethane and the compounds $(CH_3)_3M$ (where M = P, As, Sb) is attributed to a side reaction in which the trifluoromethyl anion of $\left[(CH_3)_3M\,I\right]^+ CF_3^-$ attacks a neighbouring molecule, abstracting hydrogen. The fact that the yield of fluoroform is so low indicates that the conversion:

$$\left[(CH_3)_3M\,I\right]^+ CF_3^- \rightarrow \left[\begin{array}{c} CH_3 \\ CH_3 \quad P \quad I \\ CH_3 \quad CF_3 \end{array}\right] \rightarrow \left[(CH_3)_3P\,CF_3\right]^+ I^-$$

is rapid.

Both trimethylarsine and trimethylstibine react in a manner identical with that of trimethylphosphine with trifluoroiodomethane and since both arsenic and antimony can exist in pentacovalent states the operating mechanism is considered to be the same in each case.

In the case of the reaction of trimethylamine with trifluoroiodomethane however, the yield of fluoroform is very high and is attributed to the inability of nitrogen to form more than four covalent bonds. Thus, the positive iodine complex $[(CH_3)_3N\,I]^+\,CF_3^-$ cannot rearrange to $[(CH_3)_3N\,CF_3]^+\,I^-$ via a pentacovalent state and all the trifluoromethyl anions are available for hydrogen abstraction, giving fluoroform as the major reaction product. The exchange reaction to give dimethyltrifluoromethylamine then cannot occur.

The available evidence as to the existence of cations of the type $R_3M\,I^+$ (where M is N, P, As, Sb), at first sight appears to be conflicting. Trimethylamine dibromide[27] and the analogous di-iodide[28] have been known for a long time and the formulation of these compounds[29] as $[(CH_3)_3N\,X]^+\;X^-$ has been supported by conductivity measurements.[30] The solid state structure

determinations of such compounds indicate that the halogen molecule is attached by a covalent bond[31] to the nitrogen atom and that the linear arrangement N - X - X exists.[32] However, in solutions possessing favorable dielectric properties, it is apparent from conductimetric measurements that heterolysis of the halogen-halogen link can readily occur to produce ionic species.[18,33]

It has similarly been shown that tertiary phosphine di-iodides[34] and tertiary arsenic dibromides and di-iodides[33] have conductances similar to those of 1:1 electrolytes in polar solvents like nitrobenzene and methyl cyanide.

A similar bond fission in CF_3 —— I can readily be considered knowing that the trifluoromethyl group is known to behave in some circumstances as a pseudo-halogen.[35] The higher electronegativity of the trifluoromethyl group (3.3) than iodine (2.4) indicates that the products of the bond fission envisaged, are I^+ and CF_3^-. The existence of quaternary cations of the type $\left[R_3M\,I\right]^+$ as intermediates in the reactions between trialkyl derivatives of Group V B elements and trifluoroiodomethane, therefore appears feasible.

The original work on a number of new perfluoroalkyl derivatives of phosphorus, arsenic and antimony is described in Chapter IV.

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CHAPTER IV

MIXED ALKYLPERFLUOROALKYL DERIVATIVES OF GROUP VB ELEMENTS

1. INTRODUCTION

Although the reaction of trifluoroiodomethane with the trimethyl derivatives of nitrogen, phosphorus, aresenic and antimony had been studied previously,[1,2] prior to this present study, no work had been done to determine the influence of larger alkyl or perfluoroalkyl groups on the course of the reaction. It was the aim in this programme to make such a study and to determine the trends in behaviour of the products of reactions between higher molecular weight perfluoroiodoalkanes and trialkyl derivatives of the Group V B elements. After this investigation was started, Cullen[3] published the results of some exchange reactions similar to those to be described in this Chapter. The only reaction which has been duplicated is that between triethylarsine and trifluoroiodomethane and the results of both workers are the same.

The overall reaction between trimethyl-phosphine, -arsine or -stibine and trifluoroiodomethane was originally stated to give as products, the appropriate dimethyltrifluoromethyl derivative (50%) and the

corresponding tetramethyl 'onium iodide (50%).

$$2\,(CH_3)_3M + CF_3I \longrightarrow (CH_3)_2M\,CF_3 + [(CH_3)_4M]\,I$$

However a closer examination of the reaction involving trimethylphosphine indicated that, in addition to these two products, dimethylbistrifluoromethylphosphonium iodide was formed.[4] This was very surprising since neither the reaction of trifluoroiodomethane with dimethyltrifluoromethylphosphine nor that of methyl iodide with methylbistrifluoromethylphosphine yielded such a quaternary compound. Another anomaly appeared when diethyliodoarsine reacted with trifluoroiodomethane in the presence of mercury giving predominantly ethylbis-trifluoromethylarsine.[5] In all other cases tried, the products anticipated were obtained from this type of reaction which may be expressed in the general form:

$$R_xAsI_{3-x} + R_fI \xrightarrow{Hg} R_xAs(R_f)_{3-x}$$

Subsequent investigations revealed that the formation of ethylbistrifluoromethylarsine was not due in the above instance to reaction of trifluoroiodomethane with the initial product, diethyltrifluoromethylarsine, since these two compounds did not react under the conditions employed in such a reaction.[3]

Thus it was apparent that the chemistry of the perfluoroalkyl derivatives of the Group V B elements was more complicated than was once thought.

2. THE REACTION OF TRIFLUOROIODOMETHANE WITH TRIETHYL-PHOSPHINE, -ARSINE AND - STIBINE

Trifluoroiodomethane was found to react with triethyl-phosphine, -arsine and -stibine giving the appropriate diethyltrifluoromethyl derivative together with the corresponding tetraethyl 'onium iodide. It was necessary to heat the reaction mixture containing the arsine to 100°C to induce significant reaction, but with the phosphine and stibine, adequate quantities of products were formed at room temperature. Qualitatively, the rate of reaction of trifluoroiodomethane with triethyl compounds was slower than with their trimethyl analogues,[1] as shown by longer time required for the first deposition of solid tetraethyl 'onium iodides. In all three cases, even though a large excess of trifluoroiodomethane was used, the reaction mixtures reached an equilibrium position when only 20-30% of the organometallic compound had reacted, and it was found that the yields of the various products were unchanged even after periods as long as six months. However the yields were greatly improved by removing all the

volatile constituents of the equilibrated mixtures from the solid quaternary compounds formed in each case and allowing new equilibria to be established. By repeating these procedures several times, it was possible to obtain yields of the appropriate diethyltrifluoromethyl derivatives as high as 80%.

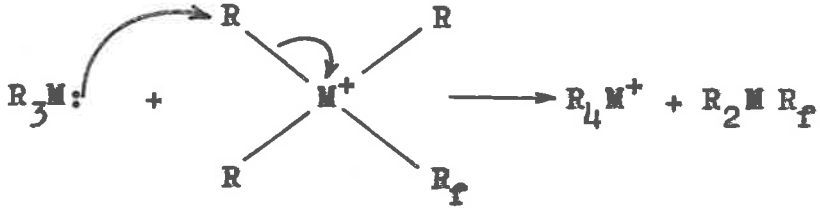
In the reactions of trimethyl derivatives of phosphorus, arsenic and antimony, there was almost quantitative conversion of the trimethyl compounds to an equimolar mixture of the dimethyltrifluoromethyl derivative and the tetramethyl 'onium iodide.[1] There was no evidence for the formation of compounds of the form $CH_3M(CF_3)_2$ in any of these reactions.

Also important was the fact that in the present work, great difficulty was experienced in separating unreacted trifluoroiodomethane from the mixture of triethyl and diethyltrifluoromethyl derivatives. A similar observation for comparable systems was made by Cullen[3] who attributed the fact to the formation of moderately stable 'onium complexes with trifluoroiodomethane. This problem was overcome in the present study by using vapour phase chromatography. With careful choice of conditions, complete separation of the various

components of the reaction mixtures was readily achieved. This technique not only enabled the compounds present to be obtained in a pure form, but also indicated the presence of another component which would probably have remained undetected if other separation methods had been used. This compound was produced in each of the reactions studied and was found to be ethyl iodide. This was very surprising since some unchanged triethyl compound was also present in the systems. Normally of course, ethyl iodide and triethyl derivatives of Group V B elements react to form tetraethyl 'onium iodides. The fact that these two materials could co-exist as such, was not due to the fact that they had insufficient time to react, since as was previously stated, the reaction mixtures were on occasions allowed to stand for six months. The explanation provided for this apparent anomaly requires a closer study of the overall mechanism of the reactions.

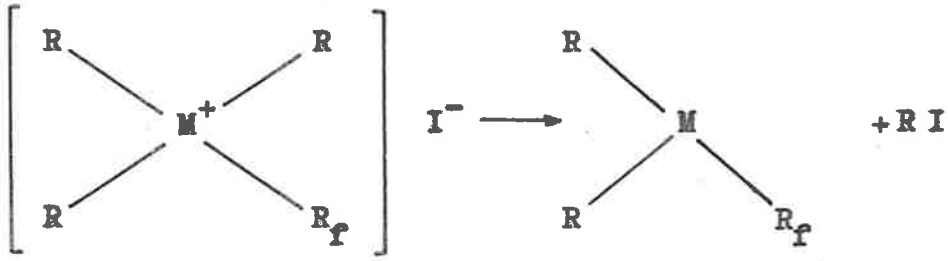
The two closely related mechanisms proposed by Haszeldine and West for the reaction of trimethyl-phosphine, -arsine and -stibine with trifluoroiodo-methane involved the formation of an intermediate quaternary compound $[(CH_3)_3M\,R_f]^+\,I^-$. One assumed that a subsequent step was the nucleophilic attack of a further molecule of the original trimethyl compound on

a methyl group in the mixed quaternary compound, thus:



where R = CH_3 and R_f = CF_3.

This implied direct formation of the tetramethyl 'onium iodide from the intermediate and did not permit even the transient existence of free alkyl iodide. The other mechanism involved dissociation of the intermediate quaternary compound thus:



Reaction of the liberated methyl iodide with a molecule of the original trimethyl compound then, accounted for the appearance of the tetramethyl 'onium iodide observed as a major reaction product. The fact that free ethyl iodide remained after reaction between trifluoroiodomethane and the triethyl compounds was no doubt related to the slower rate of reaction found for ethyl iodide with triethyl derivatives of phosphorus, arsenic and

antimony, compared with that of methyl iodide and the analogous trimethyl derivatives. Thus in the systems under consideration, the dilution by the newly formed alkylperfluoroalkyl compound plus the excess perfluoroalkyl iodide was probably sufficient to retard the formation of tetraethyl quaternary compounds under the mild thermal conditions used. It appeared that the relative proportions of ethyl iodide and tetraethyl 'onium iodide were quite variable and probably depended on factors such as the quantity of perfluoroiodoalkane used (and therefore the extent of dilution) and the size of the reaction vessel.

An important result of the fact that not all of the liberated ethyl iodide reacted with the triethyl compound, was that obviously more of the latter was then available to react with trifluoroiodomethane. Therefore the overall yields of the diethyltrifluoromethyl derivatives were found to be much higher (80%) than when trimethyl compounds were used (35-50%).

An alternate explanation for the existence of free ethyl iodide as a reaction product in the systems under consideration admits the possibility of either one of the reaction mechanisms postulated. It was considered that the tetraethyl 'onium iodide may have

formed and irrespective of the route by which this happened, partial dissociation occurred in the solvent, trifluoroiodomethane, giving free ethyl iodide and the triethyl compound. Immediate recombination of the two species would be retarded by the presence of trifluoroiodomethane due to its ability to form either a reasonably stable 'onium compound with the triethyl derivative, as was suggested previously, or simply a type of molecular compound with the base, and similar to that known to occur when trifluoroiodomethane is dissolved in some basic solvents.[6] This would be protected to some extent by an atmosphere of trifluoroiodomethane molecules which would hinder the close approach of the relatively minor quantities of ethyl iodide. It was significant that when most of the excess trifluoroiodomethane was removed, further deposition of the tetraethyl 'onium iodide invariably occurred. Therefore, although the triethyl compound was probably still present at this stage in the form of the complex with trifluoroiodomethane, the degree of protection of such a complex was greatly reduced and the competition for the reaction with the triethyl compound was then changed in favour of ethyl iodide.

As will be shown in Chapter VI, the reaction of perfluoroiodoalkanes with trialkyl derivatives of

bismuth invariably produced the appropriate alkyl iodide as one reaction product, but since bismuth is normally incapable of forming quaternary compounds, this fact does little to support either reason given for the appearance of ethyl iodide in the above reaction mixtures.

In Table 4.1 are listed with the compounds prepared in this series, the conditions under which they were formed, the yields and also the extrapolated boiling points.

TABLE 4.1

Diethyltrifluoromethyl Derivatives of Group V B Elements

Compound	Extrapolated Boiling Point	Reaction Conditions	No. of times treated	Overall Yield (%)
$(C_2H_5)_2P\,CF_3$	97	20°/72 hr.	5	80
$(C_2H_5)_2As\,CF_3$	110	100°/24 hr.	2	60
$(C_2H_5)_2Sb\,CF_3$	136	20°/48 hr.	2	70

All the new alkylperfluoroalkyl compounds prepared in this series exhibited properties comparable with those of their dimethyltrifluoromethyl analogues.

They were very reactive towards air and tended to fume strongly when exposed to it. The electron donating power of the Group V B elements in these compounds was reduced in a manner expected, due to the presence of the strongly electronegative trifluoromethyl groups.

(a) Reaction of Diethyltrifluoromethyl Compounds with Silver Iodide

In the reaction with silver iodide, diethyltrifluoromethylphosphine was found to possess a much lower basicity than triethylphosphine. The adduct formed by triethylphosphine with silver iodide is sufficiently stable to be used in the preparation of the phosphine as a means of isolating it from the other reaction products. The analogous complex derived from diethyltrifluoromethylphosphine was much less stable and was found to undergo considerable dissociation even at room temperature. It has been established that the basicity of trialkyl derivatives of the Group V B elements follows the sequence[7] $P > As > Sb$. The stability of the silver iodide complexes of the diethyltrifluoromethyl derivatives of these elements follows the same order. Thus it was found that diethyltrifluoromethylarsine formed an adduct which was even less stable than that formed by the analogous phosphine, while the stibine did not form one at all. Of course the availability of

the lone pair of electrons on the parent element is progressively reduced as more alkyl groups are replaced by perfluoroalkyl. For example, Beg and Clark[4] showed that the stability of the complexes formed by methyltrifluoromethylphosphines with the strong Lewis acids, boron trifluoride and platinous chloride, decreases in the order:

$$(CH_3)_3P > (CH_3)_2P\,CF_3 > CH_3P(CF_3)_2 > P(CF_3)_3.$$

(b) Reaction of Diethyltrifluoromethyl Compounds with Ethyl Iodide

In the reactions with ethyl iodide the diethyltrifluoromethyl compounds of the three elements showed basicities markedly lower than those of the corresponding triethyl compounds. Whereas the latter readily reacted,[8] the compounds containing trifluoromethyl groups did so only after heating the appropriate mixtures at 75°C for quite long periods of time. The products were so unstable that on contact with air, they rapidly decomposed, giving highly coloured oils. The original products were tentatively formulated as triethyltrifluoromethyl 'onium iodides having the general formula $[(C_2H_5)_3M\,C_2F_5]I$.

(c) Hydrolysis of Diethyltrifluoromethyl Compounds

All the diethyltrifluoromethyl compounds prepared were found to liberate fluoroform when treated with hot 20% aqueous alkali. The rate of hydrolysis increased with increasing atomic number of the parent element and, although complete hydrolysis was not accomplished each time, all the fluorine derived from the liberated trifluoromethyl group appeared as fluoroform. The results were consistent with the mechanism proposed by Haszeldine and West,[2] who suggested that the hydrolysis was initiated by the nucleophilic attack of hydroxyl groups on the central parent element. Thus any increase in the electropositive character of the metals, such as that occurring with increasing atomic number, facilitated the hydrolysis. Attachment of more than one trifluoromethyl group to the parent element rendered the resulting compound even more susceptible to such attack. Accordingly it has been found that the rate of hydrolysis of the trifluoromethyl derivatives of a particular element increased with increasing number of attached trifluoromethyl groups.[2]

Hydrolysis of the diethyltrifluoromethyl compounds with aqueous sodium hydroxide caused fluoroform to be liberated. Although no fluoride was produced,

the hydrolysis was incomplete in the case of the phosphine and arsine and only for the stibine was fluoroform produced quantitatively.

3. THE REACTION OF PENTAFLUOROIODOETHANE WITH TRIMETHYL-PHOSPHINE, -ARSINE AND -STIBINE

Pentafluoroiodoethane was found to react with trimethyl-phosphine, - arsine and -stibine, giving the appropriate dimethylpentafluoroethyl derivative together with the corresponding tetramethyl 'onium iodide. The reactions were performed at room temperature and appeared to proceed at a rate comparable with that observed when trifluoroiodomethane reacted with these same organometallic compounds and certainly more rapidly than the reactions of trifluoroiodomethane with the analogous triethyl derivatives. Here again, removal of the volatile products and unchanged reactants from the solid quaternary iodide deposited, enabled the yields of the dimethylpentafluoroethyl derivatives to be significantly increased. However, as was to be expected, no free methyl iodide was found in these reaction mixtures and there were no obvious differences in the mode of reaction from that observed for the analogous ones with trifluoroiodomethane.

Table 4.2 contains a list of the compounds prepared in this series, their extrapolated boiling points and a summary of the reaction conditions.

TABLE 4.2

Dimethylpentafluoroethyl Derivatives of Group VB Elements

Compound	Extrapolated Boiling Point	Reaction Conditions	No. of times treated	Overall Yield (%)
$(CH_3)_2P\,C_2F_5$	57	20°/14 hr.	3	38
$(CH_3)_2As\,C_2F_5$	67	20°/24 hr.	2	39
$(CH_3)_2Sb\,C_2F_5$	79	20°/72 hr.	4	43

These new compounds possessed properties more closely related to those of their dimethyltrifluoromethyl analogues than of the comparable diethyltrifluoromethyl derivatives. This was particularly noticeable when they were exposed to air in which they tended to ignite. The powerful electron attracting properties of the pentafluoroethyl group were demonstrated in the reactions with silver iodide, with which only dimethylpentafluoroethylphosphine formed a complex. Even this complex was so unstable that, at room temperature, there was considerable dissociation into the component molecules.

Both the phosphine and the arsine reacted with methyl iodide forming compounds which rapidly decomposed when exposed to air, giving highly coloured oils. The compounds themselves were tentatively formulated as quaternary type derivatives of the form $[(CH_3)_3M\,C_2F_5]$ I. Alkaline hydrolysis of the dimethylpentafluoroethyl compounds caused pentafluoroethyl groups to be liberated as pentafluoroethane, but the quantitative liberation of these groups only occurred in the case of the stibine.

4. INFRA-RED SPECTRA

The infra-red spectra of the dimethylpentafluoroethyl and diethyltrifluoromethyl derivatives of phosphorus, arsenic and antimony were recorded and compared with those of related compounds. Tentative vibrational assignments were made generally only for those frequencies associated with C-H and C-F vibrations in the frequency range 700-4000 cm.$^{-1}$

(a) Dimethylpentafluoroethyl Compounds

The observed frequencies and tentative assignments are listed in Table 4.3.

TABLE 4.3

Vibrational Frequencies for Dimethylpentafluoroethyl Compounds

$(CH_3)_2PC_2F_5$	$(CH_3)_2As\ C_2F_5$	$(CH_3)_2Sb\ C_2F_5$	Assignment
2983 (m)	3019 (m)	3015 (m)	C-H antisym. stretch
2935 (m) 2895 (wsh)	2940 (m) 2824 (w)	2925 (m)	C-H sym. stretch
1438 (m)	1438 (msh) 1420 (m)	1414 (m)	C-H antisym. bend
1324 (s) 1279 (w) 1214 (ssh) 1209 (s)	1332 (s) 1313 (ssh) 1275 (m) 1209 (s)	1320 (s) 1290 (ssh) 1200 (s)	C-F stretches of CF_3 group
1114 (s) 1099 (s)	1106 (s) 1092 (ssh)	1086 (s)	C-F stretches of CF_2-M group
969 (s)	950 (s)	925 (s)	CH_3 rock
895 (m)	900 (m)		C-C stretch
861 (m)	850 (s)	822 (m)	CH_3 wag
744 (msh) 739 (m)	742 (ssh) 736 (s)	773 (s) 726 (s)	C-F deform.
944 (s) 734 (msh) 709 (m)			Not assigned

The absorption bands at 2880-3015 and 1820-2940 cm.$^{-1}$ are assigned to C-H antisymmetric and symmetric stretching vibrations respectively.[9,10] Although the C-H antisymmetric bending frequencies[9] normally appear in the region of 1460 cm.$^{-1}$, the effect of the highly electronegative perfluoroalkyl groups in the compounds under examination may well be responsible for the observed absorptions attributed to those modes occurring

in the range 1405-1440 cm.$^{-1}$ The very strong bands occurring at 1200-1335 cm.$^{-1}$ are attributed to the C-F stretches of the CF_3 fragment of the pentafluoroethyl group[11,12] and probably obscure the less prominent bands due to C-H symmetric bending vibrations. The bands in the range 1085-1100 cm.$^{-1}$ are assigned to C-F stretches of the CF_2 unit attached directly to the metal atom. In the region 890-900 cm.$^{-1}$ is a band in the spectrum of each of the compounds attributed to C-C stretching in the pentaethyl group. The frequencies in the region 925-970 cm.$^{-1}$ are attributed to methyl rocking vibrations, while those at 820-860 cm.$^{-1}$ are tentatively assigned to methyl wagging. The strong bands occurring at 725-780 cm.$^{-1}$ are assigned to C-F deformation vibrations.

(b) Diethyltrifluoromethyl Compounds

The vibrational frequencies in the infra-red spectra of diethyltrifluoromethyl-phosphine, -arsine and -stibine, where applicable, are comparable with those of the dimethylpentafluoroethyl series. In Table 4.4 are listed the observed vibrational frequencies and their tentative assignments. The explanations offered for the assignments may be obtained by reference to the commentary pertaining to Table 4.3.

TABLE 4.4

Vibrational Frequencies for Diethyltrifluoromethyl Compounds

$(C_2H_5)_2PCF_3$	$(C_2H_5)_2AsCF_3$	$(C_2H_5)_2SbCF_3$	Assignments
2979 (m)	2980 (s)	2970 (m)	C-H antisym. stretch
2954 (msh)	2950 (ssh)	2935 (msh)	C-H sym. stretch
2898 (m)	2885 (s)	2882 (m)	
1458 (m)	1468 (m)	1469 (m)	C-H antisym. bend
1419 (w)	1429 (w)	1430 (w)	
1240 (m)	1224 (s)	1194 (m)	C-F sym. and antisym. stretch
1154 (s)	1176 (m)	1123 (s)	
1108 (s)	1142 (s)	1092 (s)	
	1115 (s)		
747 (m)	791 (m)	792 (m)	C-F deform.
986 (m)	976 (m)	952 (w)	Not assigned
	719 (m)		

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CHAPTER V

EXPERIMENTAL

1. GENERAL TECHNIQUES

The general techniques described in this Chapter are also applicable to the experimental Chapters to follow. Only those techniques which were used exclusively in the investigations described in the following Sections will appear in the relevant experimental Chapters.

(a) Vacuum System

Volatile materials were manipulated in a conventional Pyrex glass vacuum system[1,2] and fractionated by trap-to-trap distillation with the aid of appropriate slush baths. In general, reactions between perfluoroiodoalkanes and organometallic compounds were carried out in heavy walled Pyrex tubes of approximately 50 ml. capacity. The volatile reactants were condensed from the vacuum system into the tubes which were then sealed while evacuated.

(b) Fractionation of Reaction Mixtures

After preliminary trap-to-trap distillation, the fractions containing the organometallic compounds

were subjected to vapour phase chromatography in order to isolate the individual constituents. A Perkin-Elmer model 154-C vapour fractometer was used for this purpose. Nitrogen was the carrier gas and di-isodecyl phthalate on brick dust the column packing material. Each pure fraction, as it emerged from the column was collected in a separate U-tube cooled in liquid air. The retention times of the new compounds prepared are given in Table 5.6.

(c) Vapour Pressure-Temperature Measurements

The vapour pressures of the new compounds were measured over a range of temperatures using the isoteniscope method.

(d) Analyses

(i) Phosphorus was determined by carefully oxidising the appropriate compound with nitric acid in a sealed tube. The solution was diluted with water, ammonium molybdate added, and the phosphomolybdate titrated with standard alkali.[3]

(ii) Arsenic was determined iodometrically[4] after nitric acid decomposition of the compound.

(iii) Antimony was determined by titration with potassium permanganate[5] after oxidative decomposition of

the compound with nitric and sulphuric acids, followed by reduction with hydrazine.

(iv) Carbon and Hydrogen analyses were performed by the C.S.I.R.O. Microanalytical Laboratories, Melbourne.

(v) Molecular weights of gases were determined by Regnault's method. For those compounds having very low vapour pressure at room temperature, the conventional apparatus was modified to allow determinations to be made at suitably high temperatures (see Figure 5.1).

(vi) Infra-red spectra were recorded in the range 700-4000 $cm.^{-1}$ using a Perkin-Elmer model 21 double-beam spectrophotometer fitted with sodium chloride optics. Spectra of gases were recorded using a 10 cm. gas cell equipped with sodium chloride windows.

2. PREPARATIONS OF REACTANTS

(a) Perfluoroiodoalkanes

The perfluoroiodoalkanes used in this study were prepared by heating together mixtures of iodine and the silver salts of the appropriate perfluoroalkyl carboxylic acids. The silver salts were formed by treating freshly prepared silver oxide with the acid required. Thus silver nitrate was treated with excess sodium carbonate solution and the precipitate formed

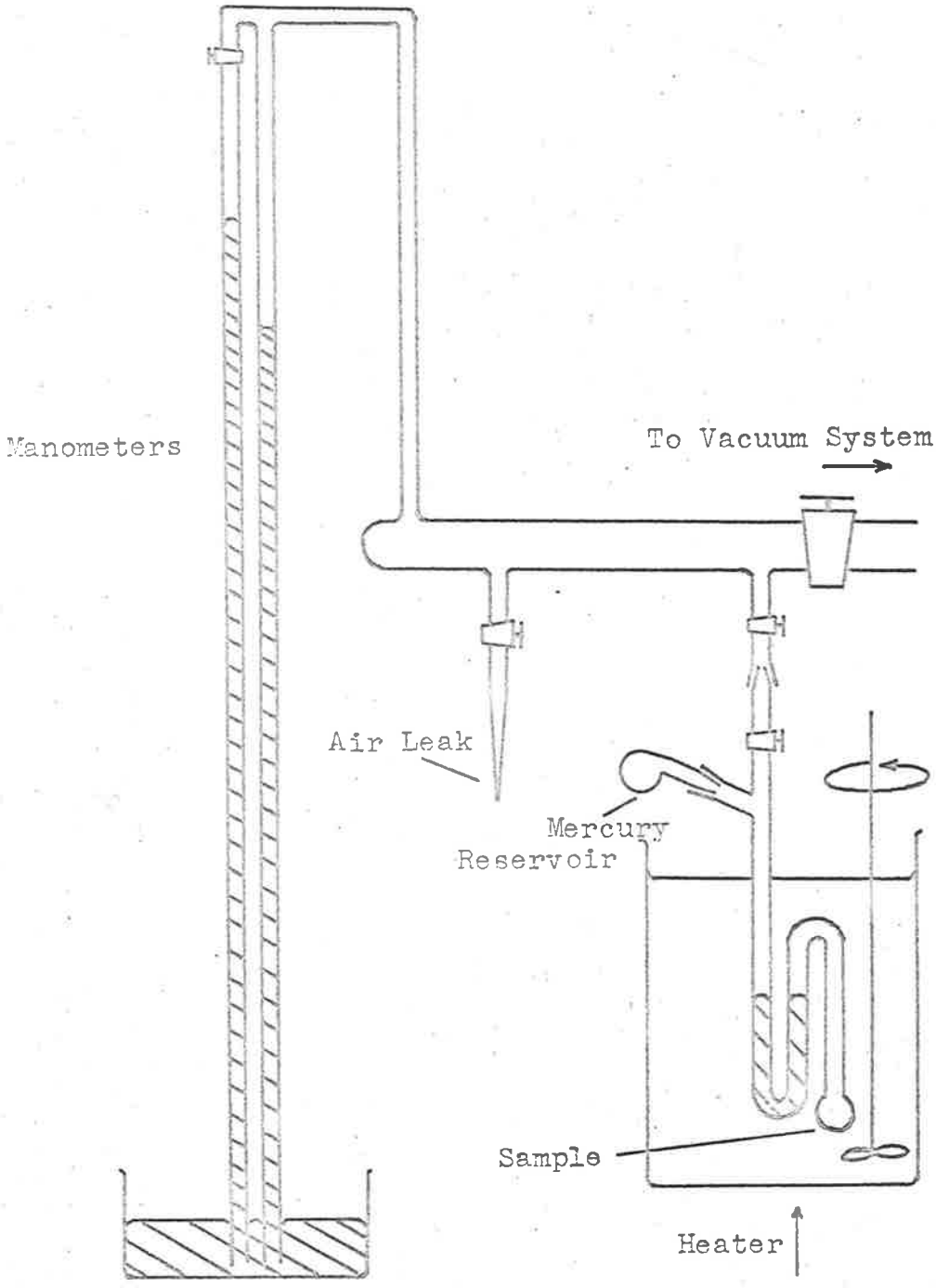
Manometers
To Vacuum System
Air Leak
Mercury
Reservoir
Sample
Heater

FIGURE 5.1

repeatedly washed until free of nitrate and carbonate. The purified silver oxide was then treated with a slight excess of the required acid and the resulting solution concentrated at reduced pressure until crystals appeared. The silver salt was then dried in a vacuum desiccator containing phosphorus pentoxide.

(i) Trifluoroiodomethane[6]

Silver trifluoroacetate (220 gm., 1.0 mole) was intimately mixed with dry, finely divided iodine (635 gm., 2.5 mole) and placed in the reaction vessel A (see Figure 5.2). The mixture was carefully heated so that a steady stream of gas bubbled through the scrubbing tower B. This tower contained a solution of sodium hydroxide (10%) to absorb carbon dioxide produced in the reaction, and sodium thiosulphate (5%) to absorb any iodine carried over by the gases. The trifluoroiodomethane then passed through a series of drying tubes D and E containing calcium chloride and phosphorus pentoxide respectively. The product was finally collected in a trap cooled to -196°C and purified in the vacuum system by trap-to-trap distillation (Found: mol.wt. 196. Calc. for CF_3I: mol.wt. 196). The yield was 95%.

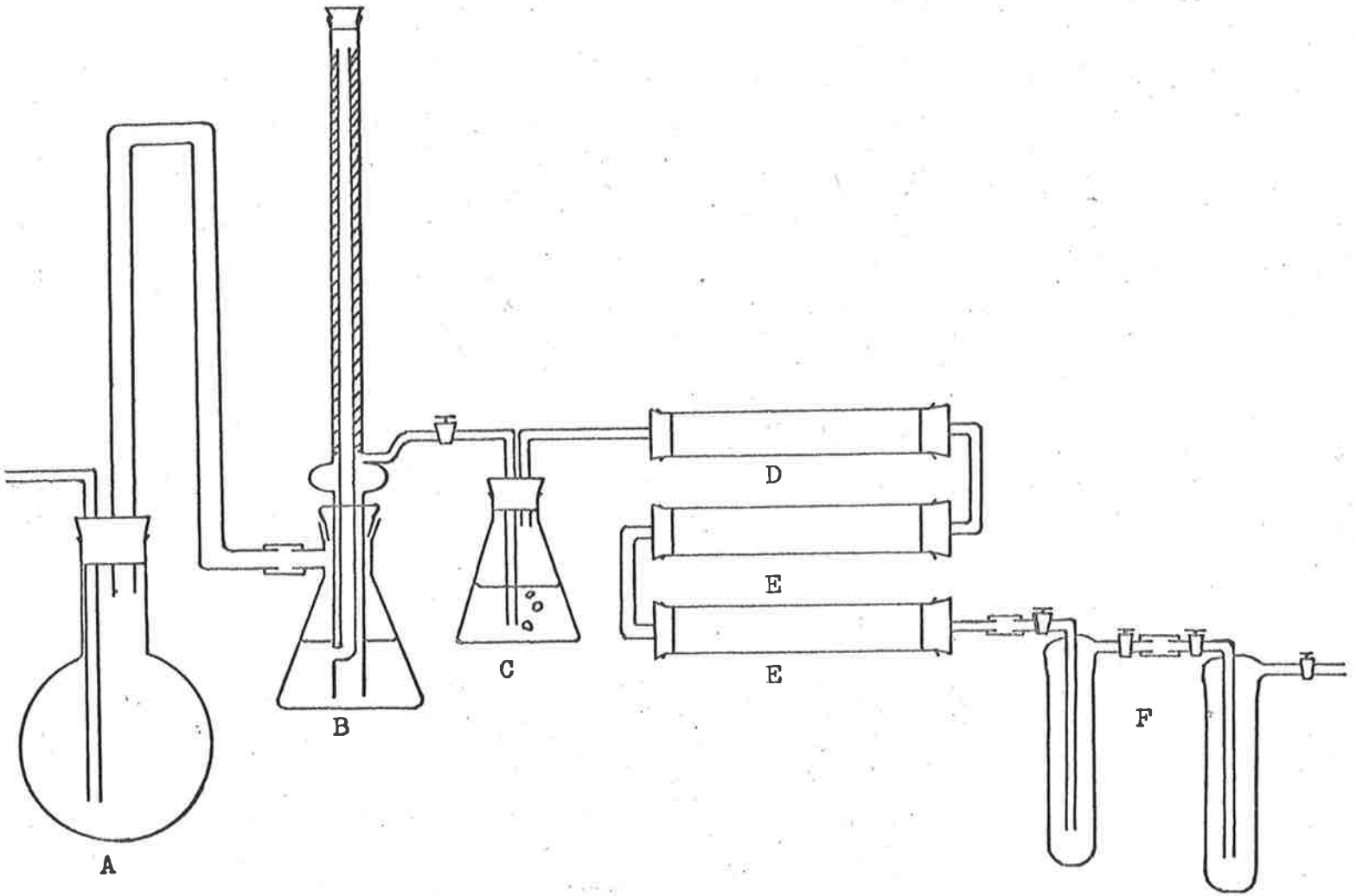

FIGURE 5.2

(ii) Pentafluoroiodoethane[7]

Silver pentafluoropropionate (163 gm., 0.6 mole), prepared from silver oxide and pentafluoropropionic acid was mixed with iodine (254 gm., 1.0 mole). The mixture was gently heated and the gas liberated collected directly in a trap at -196°C. A vacuum jacketed condenser fitted with a cold finger (see Figure 5.3) was then attached to the top of the trap and the temperature allowed to rise to 20°C. All the carbon dioxide was removed in this way, the pentafluoroiodoethane being retained by maintaining the temperature of the cold finger at -50°C. The yield of product (Found: mol.wt. 246; Calc. for C_2F_5I: mol.wt. 246) was 125 gm. (85%).

(b) Derivatives of Group V B Elements

(i) Trimethylphosphine was prepared using a method based on that of Mann and Wells.[8] "Grignard" magnesium (108 gms., 6 atoms/mole PCl_3) and methyl iodide (640 g., 4.5 mole) in dry diethyl ether (1100 ml.) were used to prepare an ethereal solution of methylmagnesium iodide. The solution was cooled in dry ice and vigorously stirred while phosphorus trichloride (103 gm., 0.75 mole) in ether (250 ml.) was added at

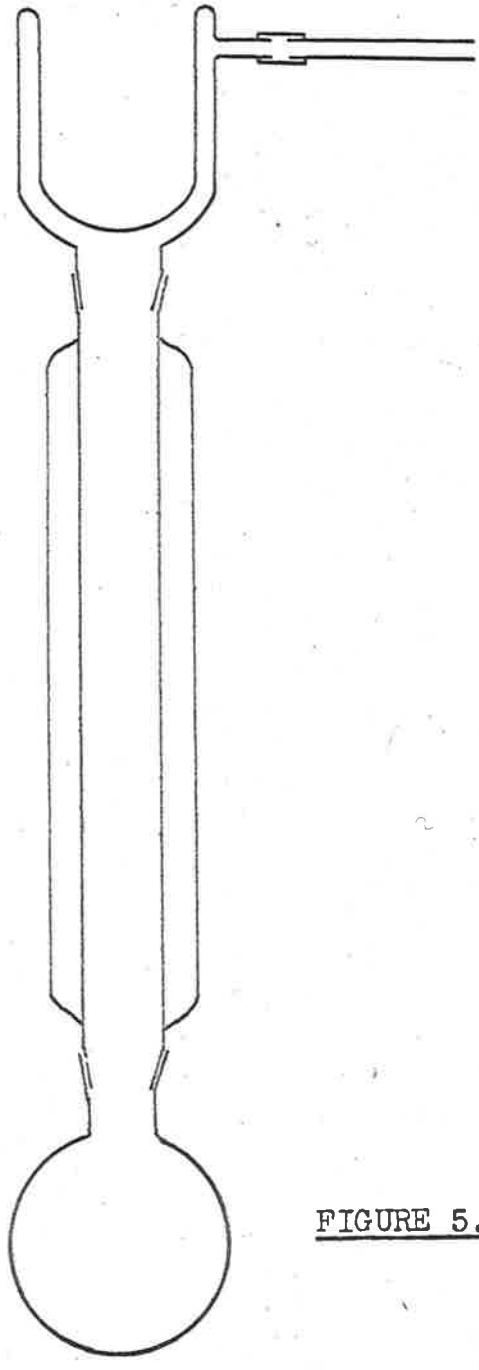

FIGURE 5.3

such a rate that the heat evolved during the reaction just prevented the mixture from solidifying. Nitrogen was passed through the reaction vessel throughout the preparation. The final mixture was allowed to remain at -50°C (approximately) for three hours and at room temperature for a further ten hours. All the volatile constituents were then distilled directly from the reaction vessel into a flask containing a solution of silver iodide in aqueous potassium iodide. (This solution was prepared by adding solid potassium iodide to silver nitrate (125 gm., 0.75 mole) in water (400 ml.) until the silver iodide, first precipitated, just disappeared.) At the completion of the distillation the aqueous and ethereal layers were contacted by vigorously shaking. The heavy white precipitate formed at the junction of the two layers was filtered off, washed with potassium iodide solution and dried by pumping. Free trimethylphosphine was generated by heating the complex[9] $[AgI.P(CH_3)_3]_4$ in an evacuated tube connected to a trap cooled to -196°C. Final purification was achieved using trap-to-trap distillation through traps cooled to -46, -95 and -196°C. The yield of trimethylphosphine (Found: mol.wt. 76; Calc. for C_3H_9P: mol.wt. 76) was 31 gm. (54% based on phosphorus trichloride).

(ii) Triethylphosphine[10] was prepared by an analogous procedure, using ethylmagnesium iodide (4.5 mole) and phosphorus trichloride (0.75 mole). The yield was 41 gm. (50%). The triethylphosphine was characterized by treating a sample with excess ethyl iodide in a sealed tube in the absence of air. The tetraethylphosphonium iodide resulting was treated with an acetone solution of mercuric iodide, such that the molecular ratio of the two reactants was 1:2. The tetraethylphosphonium pentaiododimercurate so formed had a m.p. 117°C (lit.[11] 117°C).

(iii) Trimethylarsine.[12] Methylmagnesium iodide was prepared from magnesium (72 gm., 3.0 mole) and methyl iodide (426 gm., 3.0 mole) in sodium-dried ether (750 ml.). To this solution, which was cooled in dry ice, was slowly added arsenic trichloride (90 gm., 0.5 mole) in ether (250 ml.). Vigorous stirring was necessary to quickly remove the yellow solid which tended to deposit on the walls of the reaction vessel during this addition. Nitrogen was bubbled through the reaction mixture continously. When the addition was complete, the mixture was allowed to stand at room temperature for a further six hours before being hydrolysed at -78°C by the careful addition of ammonium

sulphate solution (approximately 2N). The ether layer was then removed through a siphon tube by applying a pressure of nitrogen. The ether solution was dried over calcium chloride and distilled and the distillate shaken with successive amounts of "silver iodide solution" until no further crystals of $[(CH_3)_3As.AgI]_4$ were deposited. The silver iodide complex was removed by filtration, dried under vacuum and carefully heated to liberate trimethylarsine, which was passed through a trap at -46°C in the vacuum system before being collected as a pure product in a trap cooled to -196°C (Found: mol.wt. 120; Calc. for C_3H_9As: mol.wt. 120). The yield was 35 gm. (58% based on arsenic trichloride).

(iv) Triethylarsine[12] was prepared in a manner similar to that used for trimethylarsine. A yield of 64 gm. (58%) was obtained from ethylmagnesium iodide (2.6 mole) and arsenic trichloride (90 gm., 0.5 mole). The product was characterized by analysis of its mercuric chloride adduct (Found: C, 16.3; H, 3.4%; m.p. 164°C; Calc. for $C_6H_{15}AsHgCl_2$: C, 16.6; H, 3.3%; Lit.[13] m.p. 164°C).

(v) Trimethylstibine[10] was prepared by a method modified from that of Hibbert. Methylmagnesium

iodide in ether was produced from magnesium (15.3 gm., 0.62 mole) and methyl iodide (88.8 gm., 0.62 mole). The solution was cooled in an ice-salt bath and antimony trichloride (47.0 gm., 0.21 mole) in ether (230 ml.) slowly added with vigorous stirring. A yellow solid formed as the two solutions were mixed but rapidly disappeared as the reaction proceeded. When the reaction was complete, two layers formed in the mixture, the upper being liquid, and the lower oily and semi-solid. The entire mixture was then distilled until the distillation temperature reached 125°C. Throughout the preparation, nitrogen was passed through the reaction mixture. To isolate the trimethylstibine, the distillate was treated with a carbon tetrachloride solution of bromine until no further precipitation of trimethylantimony dibromide occurred.[14] The dibromide was filtered off and dried by pumping. Free trimethyl-stibine was generated by cautiously adding water to the dibromide, intimately mixed with the stoichiometric quantity of zinc dust. The vessel in which this step occurred was equipped with an outlet leading through an ice-cooled trap into a collecting trap cooled to -196°C. Nitrogen was passed through the system continuously. A vigorous reaction commenced immediately the water contacted the solid mixture but once the initial vigour

had subsided, gentle heating was applied to distil out a mixture of trimethylstibine and water. The product was dried over anhydrous sodium sulphate and finally purified by vacuum trap-to-trap distillation through traps at -46, -95 and -196°C. The yield was 19 gm. (44%). (Found: mol.wt. 228; Calc. for C_3H_9Sb: mol.wt. 228).

(vi) Triethylstibine. Ethylmagnesium iodide was prepared by reacting ethyl iodide (235 gm., 1.5 mole) with magnesium (12 gm., 0.5 mole) in ether (400 ml.). Freshly distilled antimony trichloride (115 gm., 0.5 mole) in ether (300 ml.) was added slowly to the Grignard Reagent which had been previously cooled to -10°C. The mixture was allowed to stand at room temperature for eight hours and the volatile materials then distilled off. An atmosphere of nitrogen had been maintained in the reaction vessel to this stage. In the latter part of the distillation, the nitrogen flow was discontinued and the pressure reduced to enable the less volatile components of the mixture to distil with minimum decomposition. The distillate was treated with iodine (127 gm., 0.5 mole) and the volume of solution reduced by heating on a water bath until crystals of triethylantimony di-iodide deposited.[14] When, after

repeated evaporation and cooling, it was impossible to obtain any further crystals, the combined solid was pumped to remove ether and then intimately mixed with the stoichiometric quantity of zinc dust. This mixture was carefully treated with water and the volatile material liberated collected in a trap cooled to -196°C. The liquid obtained was dried over anhydrous sodium sulphate, from which it was finally distilled, the yield being 70 gm. (66%).

3. REACTION OF TRIETHYL COMPOUNDS WITH TRIFLUOROIODOMETHANE

(a) Triethylphosphine

Triethylphosphine (4.44 gm., 37.6 mmole) and trifluoroiodomethane (10.8 gm., 55.0 mmole) were sealed in an evacuated tube and allowed to stand at room temperature for three days. The volatile constituents of the mixture were then distilled into the vacuum system, leaving a white crystalline residue. This was identified as tetraethylphosphonium iodide by isolation of the pentaiododimercurate, m.p. and mixed m.p. 117°C (Lit.[11] 117°C) (Found: C, 7.98; H, 1.64%; Calc. for $C_8H_{20}P\,Hg_2I$: C, 8.11; H, 1.69%). The volatile materials were fractionated through traps at -46 and

-196°C, the phosphorus-containing compounds, together with other minor constituents collecting in the former. Four components of the less volatile fraction were separated by vapour phase chromatography. By comparison with the retention times of authentic samples and by infra-red spectroscopic examination these components were identified as ethyl iodide, trifluoroiodomethane, triethylphosphine and diethyltrifluoromethylphosphine (Found: P, 19.4%; mol.wt. 157; Calc. for $C_5H_{10}F_3P$: P, 19.6%; mol.wt. 158). The former two components, when combined, constituted approximately 10% of this fraction, the triethylphosphine and diethyltrifluoromethylphosphine comprising 60% and 30% respectively. Four successive treatments of this fraction, obtained by the distillation described above, with additional trifluoroiodomethane under the original conditions, caused approximately 80% conversion of triethylphosphine to diethyltrifluoromethylphosphine.

Properties of Diethyltrifluoromethylphosphine

(i) The vapour pressure of diethyltrifluoromethylphosphine at the temperatures indicated, appears in Table 5.1.

From these values the expression

$$\log_{10} P(\text{mm}) = 6.813 - \frac{1457}{T}$$

was derived. The extrapolated boiling point was 97°C.

TABLE 5.1

Vapour Pressure-Temperature Relationships for Diethyltrifluoromethylphosphine

Temp. (°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	$Log_{10} P$
27.5	3.279	79.5	1.9004
36.9	3.226	120.0	2.0792
40.1	3.194	142.0	2.1523
43.1	3.164	163.0	2.2122
47.1	3.124	190.0	2.2788
52.3	3.074	226.5	2.3551
58.2	3.019	268.5	2.4289
66.5	2.946	340.5	2.5321
72.3	2.896	402.5	2.6047
77.7	2.851	465.5	2.6680
87.0	2.778	590.5	2.7713

(ii) Diethyltrifluoromethylphosphine (0.251 gm., 1.59 mmole) and 5N sodium hydroxide (5 ml.) were heated together at 100°C in a sealed tube for 12 hr. The volatile materials were then fractionated in the vacuum system. Fluoroform (0.057 gm., 0.81 mmole) was recovered but no fluoride was found in the solution remaining. Thus 51% hydrolysis of the phosphine had occurred.

(iii) A sample of the phosphine (0.18 gm.) was condensed into a tube containing a solution of silver

iodide in aqueous potassium iodide (20%) silver iodide (2.5 ml.). On shaking these two immiscible liquids at 10-15°C, a mass of white crystals deposited. Gentle warming caused obvious decomposition and at 48°C the diethyltrifluoromethylphosphine was recovered quantitatively.

(iv) A mixture of diethyltrifluoromethyl-phosphine (0.19 gm.) and excess ethyl iodide (0.65 gm.) was allowed to stand in a sealed tube for three days at room temperature and then at 75°C for a further three days. At the end of this time a white crystalline deposit had formed (0.073 gm.) which was stable even after the removal of the unchanged reactants if kept under vacuum. On contact with moist air it rapidly decomposed giving ahighly coloured oil. The solid formed initially was considered to be the quaternary compound $[(C_2H_5)P\,CF_3]I$, but its instability prevented an analysis being performed.

(v) The infra-red spectrum of the new phosphine is shown in Figure 5.4 (a).

(b) Triethylarsine

Triethylarsine (3.98 gm., 24.6 mmole) and trifluoroiodomethane (9.9 gm., 50.5 mmole) were allowed

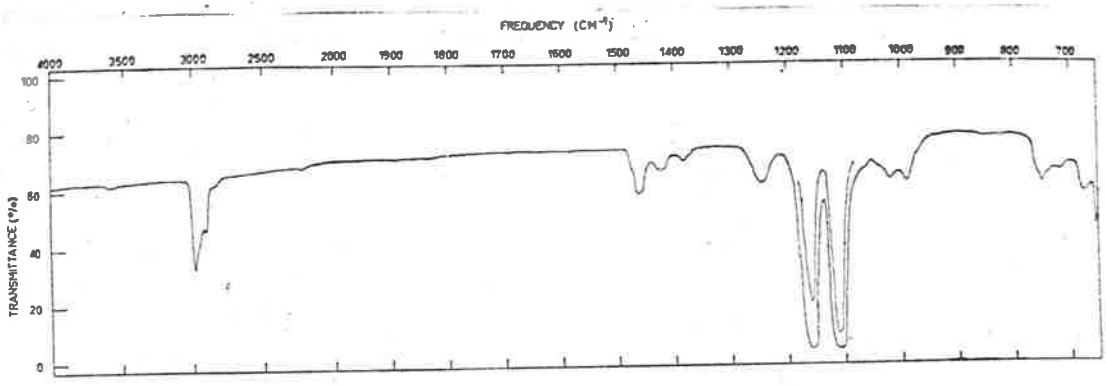

Figure 5.4 (a)

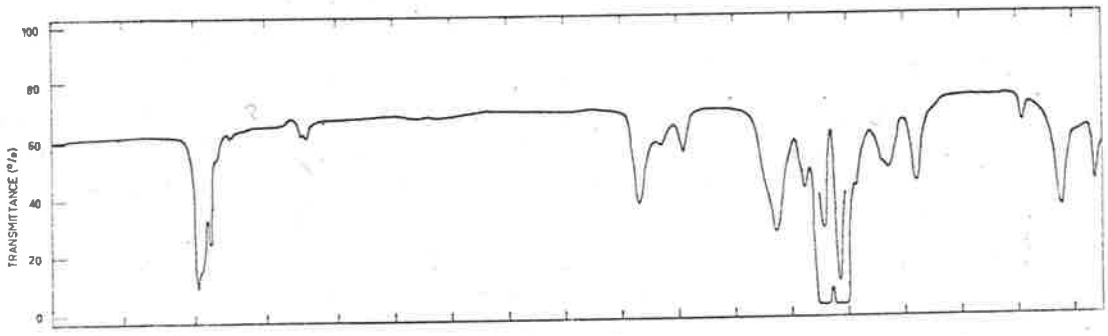

Figure 5.4 (b)

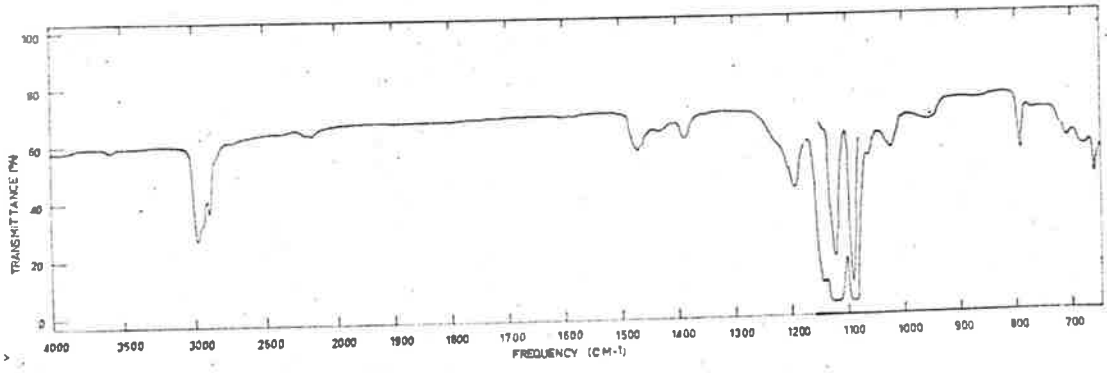

Figure 5.4 (c)

to stand at room temperature for 24 hr. and then at 100°C for 24 hrs. After removal of the volatile components of the reaction mixture, tetraethylarsonium iodide (0.32 gm.) remained (Found: C, 30.1; H, 6.29; I, 39.8%; Calc. for $C_8H_{20}AsI$: C, 30.2; H, 6.29; I, 39.9%). The volatile reaction products were subjected to trap-to-trap distillation and the following fractions obtained: fluoroform (-196°C) (Found: mol.wt. 70; Calc. for CHF_3: mol.wt. 70); trifluoroiodomethane (-135°C) (Found: mol.wt. 196; Calc. for CF_3I: mol.wt. 196); a mixture of trifluoroiodomethane and ethyl iodide (-95°C); a mixture of triethylarsine and diethyltrifluoromethylarsine (-46°C) (Found: As, 36.8%; mol.wt. 201; Calc. for $C_5H_{10}F_3As$: As, 37.0%; mol.wt. 202). The latter fraction also contained minor quantities of ethyl iodide and trifluoroiodomethane. The fraction consisting of the arsenic-containing material was heated with additional trifluoroiodomethane and an overall 60% conversion of triethylarsine to diethyltrifluoromethylarsine was achieved. Diethyltrifluoromethylarsine has a boiling point of 110°C (Lit.[15] 111°C).

Properties of Diethyltrifluoromethylarsine

(i) Diethyltrifluoromethylarsine (0.194 gm.,

0.96 mmole) and 5N sodium hydroxide (5 ml.) were heated together in a sealed tube at 100°C for 12 hrs. Fractionation of the volatile constituents in the vacuum system gave fluoroform (0.043 gm., 0.61 mmole) indicating 64% hydrolysis as no fluoride was found in the solution after the reaction.

(ii) No reaction occurred when the arsine (0.17 gm.) and silver iodide in aqueous potassium iodide were shaken together even at 0°C.

(iii) Treatment of diethyltrifluoromethylarsine (0.23 gm.) with ethyl iodide (1.1 gm.) for three days at room temperature and a further three days at 75°C, yielded white crystals (0.024 gm.) which, when exposed to air, rapidly decomposed giving an oil. The material was thought to be $(C_2H_5)_2AsCF_3I$.

(iv) The infra-red spectrum of the arsine is shown in Figure 5.4(b).

(c) Triethylstibine

Triethylstibine (8.00 gm., 38.3 mmole) and trifluoroiodomethane (11.4 gm., 58.2 mmole) were allowed to stand in a sealed tube at room temperature for 48 hrs. There was deposited a small quantity of white crystalline

solid (0.32 gm.) which did not increase when the mixture was heated at 100°C for 15 hrs. The solid was identified as tetraethylstibonium iodide (Found: C, 26.4; H, 5.40; I, 34.7%; Calc. for $C_8H_{20}SbI$: C, 26.3; H, 5.48, I, 34.8%). Trap-totrap distillation was used for a preliminary separation of the volatile products and gave a trace of fluoroform (-196°C), unreacted trifluoroiodomethane (-135°C), a mixture of trifluoroiodomethane and ethyl iodide (-95°C) and a mixture of triethylstibine and diethyltrifluoromethylstibine (-46°C). The identity of these materials was established with the aid of vapour phase chromatography, infra-red spectral analysis and molecular weight measurement. By treating the mixture of stibines with additional trifluoroiodomethane, more tetraethylstibonium iodide was formed and a total conversion of 70% of triethylstibine to diethyltrifluoromethylstibine (Found: Sb, 48.7%; mol.wt. 247; Calc. for $C_5H_{10}F_3Sb$: 49.0%; mol.wt. 249) was achieved.

Properties of Diethyltrifluoromethylstibine

(i) The vapour pressures of diethyltrifluoromethylstibine recorded at a number of temperatures are shown in Table 5.2.

TABLE 5.2

Vapour Pressure-Temperature Relationships for Diethyltrifluoromethylstibine

Temp (°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	Log_{10} P
30.2	3.298	43.5	1.6385
37.6	3.220	60.5	1.7818
43.7	3.158	77.0	1.8865
48.4	3.111	91.5	1.9614
52.6	3.071	100.5	2.0021
53.8	3.059	103.5	2.0149
69.7	2.918	158.5	2.2001
78.7	2.843	205.0	2.3118
84.4	2.798	239.5	2.3793
86.0	2.786	252.0	2.4014
95.6	2.712	323.5	2.5099
110.3	2.609	453.5	2.6566

The extrapolated boiling point was found to be 136°C and the above data may be represented by the equation

$$\log_{10} P(\text{mm}) = 6.285 - \frac{1396}{T}$$

(ii) Diethyltrifluoromethylstibine (0.255 gm., 1.02 mmole) and 5N sodium hydroxide (5 ml.) were heated together at 100°C in a sealed tube for 12 hrs. Trap-to-trap distillation within the vacuum system

enabled fluoroform (0.069 gm., 0.99 mmole) to be isolated. This represented 97% hydrolysis of the stibine since no fluoride was found in the solution remaining.

(iii) The infra-red spectrum of the stibine is shown in Figure 5.4(c).

4. REACTION OF TRIMETHYL COMPOUNDS WITH PENTAFLUORO-IODOETHANE

(a) Trimethylphosphine

Trimethylphosphine (4.7 gm., 61.8 mmole) and pentafluoroiodoethane (15.4 gm., 62.7 mmole) were allowed to stand at room temperature in a sealed tube for 14 hrs. The mixture set solid due to the formation of tetramethylphosphonium iodide (4.50 gm., 20.6 mmole) (Found: C, 21.9; H, 5.48; I, 58.0%; Calc. for $C_4H_{12}PI$: C, 22.0; H, 5.50; I, 58.2%). Following the removal of the solid, the volatile materials were again treated with excess pentafluoroiodoethane, the new solid being removed after 12 hrs., and the procedure repeated once more. The combined weight of tetramethylphosphonium iodide (5.1 gm., 23.4 mmole) represented 38% conversion of the trimethylphosphine. The volatile constituents of the reaction mixture were then subjected to

preliminary trap-to-trap distillation. The fraction condensing at -196°C contained only pentafluoroiodoethane (Found: mol.wt., 246; Calc. for C_2F_5I: mol.wt. 246), while the fraction condensed at -63°C was shown by vapour phase chromatography to consist of pentafluoroiodoethane, trimethylphosphine (1.25 gm., 16.5 mmole) (Found: mol.wt. 76; Calc. for C_3H_9P: mol.wt. 76) and dimethylpentafluoroethylphosphine (3.96 gm., 22.0 mmole — 36% conversion of trimethylphosphine) (Found: P, 17.2%; mol.wt., 180; Calc. for $C_4H_6F_5P$: P, 17.2%; mol.wt. 180).

Properties of Dimethylpentafluoroethylphosphine

(i) The vapour pressure-temperature data for dimethylpentafluoroethylphosphine is shown in Table 5.3.

TABLE 5.3

Vapour Pressure-Temperature Relationships for Dimethylpentafluoroethylphosphine

Temp.(°C)	$10^3 \times 1/T$ (°A)	Pressure (Mm)	Log_{10} P
15.8	3.462	229.5	2.3608
20.6	3.406	255.5	2.4074
26.7	3.336	300.0	2.4771
30.0	3.300	335.2	2.5255
33.5	3.263	376.5	2.5758
40.4	3.191	460.0	2.6628
46.5	3.130	528.0	2.7226
52.8	3.069	643.5	2.8085

The extrapolated boiling point was calculated to be 57°C and the equation derived from the above data to be

$$\log_{10} P(mm) = 6.551 - \frac{1218}{T}$$

(ii) Dimethylpentafluoroethylphosphine (0.220 gm., 1.22 mmole) and 5N sodium hydroxide (5 ml.) were heated together in a sealed tube at 100°C for 12 hrs. Fractionation in the vacuum system indicated that fluoroform (0.062 gm., 0.88 mmole) corresponding to 72% hydrolysis had been liberated.

(iii) When the phosphine (0.24 gm.) and silver iodide in aqueous potassium iodide (20% silver iodide, 3 ml.) were shaken together at room temperature, a white crystalline solid deposited. By heating this solid at 50°C complete recovery of the original phosphine was accomplished.

(iv) Reaction of dimethylpentafluoroethyl-phosphine (0.23 gm.) with excess methyl iodide (1.2 gm.) at room temperature for three days and at 75°C for a further three days, yielded a white crystalline material (0.22 gm.) which underwent quite rapid decomposition on exposure to air. It was considered to be $[(CH_3)_3P\,C_2F_5]I$.

(v) The infra-red spectrum of the new compound is shown in Figure 5.5(a).

(b) Trimethylarsine

Trimethylarsine (2.89 gm., 24.1 mmole) and pentafluoroiodoethane (6.75 gm., 24.7 mmole) were allowed to stand at room temperature in a sealed tube for 24 hrs. The volatile materials were then removed from the crystalline solid deposited and the former treated with additional excess pentafluoroiodoethane. The combined solid formed after these two treatments (4.5 gm.) represented 39% conversion of trimethylarsine to tetramethylarsonium iodide (Found: C, 19.4; H, 4.83; I, 51.4%; Calc. for $C_4H_{12}AsI$: C, 19.5; H, 4.88; I, 51.6%). Trap-to-trap distillation through traps cooled to -63 and -196°C was used to separate most of the excess pentafluoroiodoethane from the volatile reaction products. The material collecting in the trap at -63°C was separated by vapour phase chromatography into three components, viz., pentafluoroiodoethane, trimethylarsine (Found: mol.wt. 120; Calc.for C_3H_9As: mol.wt. 120) and dimethylpentafluoroethylarsine (2.15 gm., 9.6 mmole -- 40% conversion of trimethylarsine)(Found: As, 33.4%; mol.wt.225; Calc. for $C_4H_6F_5As$: As, 33.3%; mol.wt. 224).

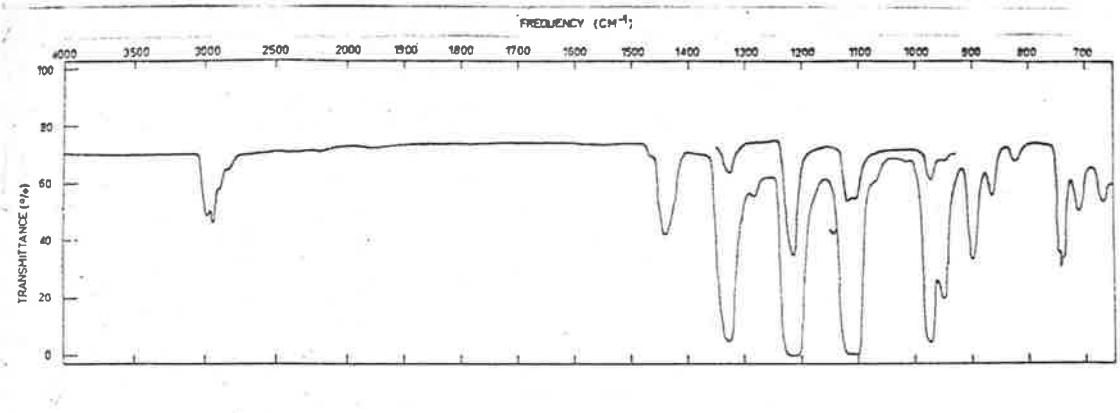

Figure 5.5 (a)

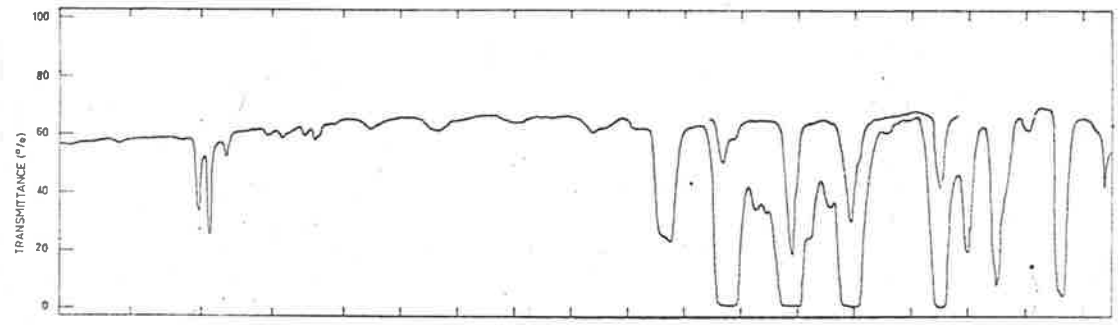

Figure 5.5 (b)

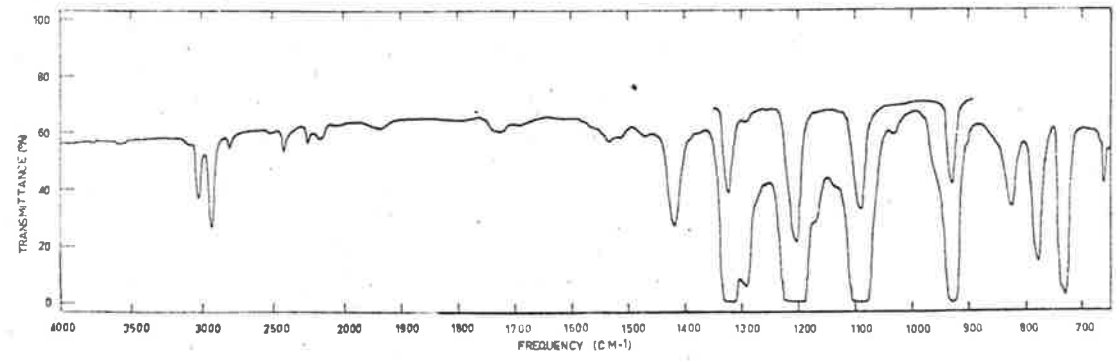

Figure 5.5 (c)

Properties of Dimethylpentafluoroethylarsine

(i) The vapour pressure-temperature data for dimethylpentafluoroethylarsine are given in Table 5.4.

TABLE 5.4

Vapour Pressure-Temperature Relationships for Dimethylpentafluoroethylarsine

Temp.(°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	Log_{10} P
15.2	3.470	89.8	1.9533
19.5	3.419	112.5	2.0511
27.8	3.324	164.5	2.2161
31.0	3.289	190.0	2.2788
41.0	3.185	286.0	2.4564
44.9	3.146	339.0	2.5302
51.5	3.083	430.0	2.6335

(ii) Dimethylpentafluoroethylarsine (0.216 gm., 0.96 mmole) and 5N sodium hydroxide (5 ml.) were heated together in a sealed tube for 12 hrs. at 100°C. Fractionation in the vacuum system gave an amount of fluoroform (0.061 gm., 0.87 mmole) corresponding to 91% hydrolysis. No fluoride was liberated.

(iii) The arsine (0.18 gm.), when treated with an aqueous solution (3 ml.) of silver iodide (20%) in potassium iodide, did not yield a solid product even at 0°C.

(iv) A white crystalline solid (0.21 gm.) was formed when dimethylpentafluoroethylarsine (0.22 gm.) and excess methyl iodide (0.93 gm.) were allowed to react in a sealed tube for three days at room temperature, and then for a further three days at 75°C. The compound, formulated as $[(CH_3)_3 As C_2F_5] I$, could not be analysed due to its rapid decomposition in air.

(v) The infra-red spectrum of the new arsine is shown in Figure 5.5(b).

(c) Trimethylstibine

Trimethylstibine (5.46 gm., 32.7 mmole) and pentafluoroiodoethane (8.49 gm., 34.1 mmole) were allowed to stand at room temperature in a sealed tube for 72 hrs. The volatile reaction products were then removed by pumping, leaving a white solid. By successively treating the volatile materials with excess pentafluoroiodoethane and removing the solid deposited, ultimately a stage was reached when no further solid appeared. The combined weight of solid product, identified as tetramethylstibonium iodide (Found: C, 15.5; H, 3.84; I, 41.2%. Calc. for $C_4H_{12}SbI$: C, 15.5; H, 3.88; I, 41.1%) was 4.3 gm. (13.9 mmole) and represented 43% conversion of the original trimethylstibine. A preliminary trap-

to-trap distillation through traps at -63 and -196°C enabled most of the unreacted pentafluoroiodoethane (-196°C) to be separated from the antimony compounds (-63°C). This latter fraction was shown by vapour phase chromatography to contain predominantly dimethylpentafluoroethylstibine (Found: Sb, 44.8%; mol.wt. 270; Calc. for $C_4H_6F_5Sb$: Sb, 45.0%, mol.wt. 271), together with small amounts of pentafluoroiodoethane and trimethylstibine.

Properties of Dimethylpentafluoroethylstibine

(1) The vapour pressure-temperature data for the stibine are shown in Table 5.5.

TABLE 5.5

Vapour Pressure-Temperature Relationships for Dimethylpentafluoroethylstibine

Temp.(°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	$\text{Log}_{10} P$
14.8	3.474	58.5	1.7672
19.7	3.417	73.0	1.8633
26.5	3.338	98.0	1.9912
30.7	3.293	118.0	2.0719
35.3	3.244	144.0	2.1584
40.1	3.194	174.0	2.2405
44.9	3.146	211.5	2.3253
49.7	3.099	260.0	2.4150
57.8	3.023	359.5	2.5557
61.4	2.990	413.5	2.6165
65.6	2.954	487.0	2.6875

The extrapolated boiling point was found to be 79°C and the equation describing the relation between vapour pressure and temperature to be

$$\log_{10} P = 7.929 - \frac{1778}{T}$$

(ii) Dimethylpentafluoroethylstibine (0.245 gm., 0.91 mmole) and 5N sodium hydroxide (5 ml.) were heated together at 100°C in a sealed tube for 12 hrs. Trap-to-trap distillation of the volatile materials enabled fluoroform (0.064 gm., 0.91 mmole) to be isolated, indicating that complete hydrolysis had occurred.

(iii) The infra-red spectrum of the stibine is shown in Figure 5.5(c).

TABLE 5.6

Compound	Column length (metres)	Pressure (lbs./ sq.in.)	Flow Rate (ccs/min)	Temp. (°C)	Retention Time (min)
$(CH_3)_2PC_2F_5$	2	4	30	50	7.4
$(CH_3)_2AsC_2F_5$	2	4	30	50	11.8
$(CH_3)_2SbC_2F_5$	2	7	62	50	21.4
$(C_2H_5)_2PCF_3$	1	10	176	62	2.9
$(C_2H_5)_2AsCF_3$	1	6.5	105	45	4.1
$(C_2H_5)_2SbCF_3$	1	10	176	65	10.1

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CHAPTER VI

PERFLUOROALKYLBISMUTH COMPOUNDS

1. INTRODUCTION

Alkylperfluoroalkyl derivatives of phosphorus, arsenic and antimony are well known and have been most successfully prepared by the action of perfluoroiodoalkanes on the appropriate trialkyl derivatives of these elements.[1,2,3] The corresponding tetra-alkyl 'onium iodide is formed simultaneously with the perfluoroalkyl derivative in each case and the reactions may be represented thus:

$$2M R_3 + R_fI \longrightarrow R_2M R_f + R_4M I.$$

However, prior to this investigation, no perfluoroalkyl derivatives of bismuth were known.[4] It has now been found that perfluoroiodoalkanes react with trialkylbismuth compounds, forming alkylperfluoroalkylbismuth derivatives.[5,6] Although the main features of the reactions producing perfluoroalkylbismuth compounds are essentially similar to those in which the corresponding derivatives of the Group V B elements are formed, some important differences do exist. These will be discussed together with the mechanism of the reactions, following a description of the new compounds prepared.

2. PREPARATION OF METHYLTRIFLUOROMETHYLBISMUTH COMPOUNDS

Trimethylbismuth was converted quantitatively to a mixture of dimethyltrifluoromethylbismuth (82%) and methylbistrifluoromethylbismuth (18%) when treated with excess trifluoroiodomethane at 100°C. The two products were separated by vapour phase chromatography. Unlike the other Group V B elements, bismuth is not normally capable of forming stable quaternary compounds,[7] thus precluding the formation of tetramethylbismuthonium iodide. In the reaction of trimethylbismuth with trifluoroiodomethane, the methyl groups which were displaced by trifluoromethyl, appeared in the reaction products as methyl iodide. The inability of methyl iodide to react with trimethylbismuth under the conditions employed, allowed all of the bismuthine to react with the trifluoroiodomethane. In the analogous reactions, even assuming the absence of side reactions,[8] only 50% of the trimethyl-phosphine, -arsine and -stibine could conceivably be converted to the appropriate methyltrifluoromethyl derivatives due to the simultaneous formation of an equimolar amount of the corresponding tetramethyl 'onium iodide. With bismuth it was theoretically possible to achieve 100% conversion to methyltrifluoromethyl compounds and it was found that

in practice this did actually occur. In the reactions of triethyl-phosphine, -arsine and -stibine with trifluoroiodomethane, it was found that not all of the displaced ethyl groups reacted to form the tetraethyl 'onium iodide, thus leaving more of the triethyl compounds available for reaction with trifluoroiodomethane. In these cases also, the yields of trifluoromethyl derivatives were correspondingly high.[3]

The ratio of dimethyltrifluoromethylbismuth to methylbistrifluoromethylbismuth varied with the temperature and the proportion of trifluoroiodomethane to trimethylbismuth used, but was always much greater than unity. The length of time of heating seemed to have little effect on the ratio of the products, indicating that in a sealed tube, equilibrium conditions were reached fairly rapidly. The formation of any methylbistrifluoromethylbismuth was unexpected due to the complete absence of analogous products from the similar reactions of the trimethyl derivatives of the other Group V B elements. Methylbistrifluoromethyl-phosphine has been prepared only by treatment of tristrifluoromethylphosphine with methyl iodide, while methylbistrifluoromethylarsine has been prepared by an analogous reaction and also by the action of trifluoro-

iodomethane on dimethyltrifluoromethylarsine.[9] However the reaction of trifluoroiodomethane with triethylarsine was found to yield small amounts of ethylbistrifluoromethylarsine.[2] In fact ethylbistrifluoromethylarsine was also the major product in the reaction of diethyliodoarsine with trifluoroiodomethane in the presence of mercury, only a small amount of diethyltrifluoromethylarsine being formed.[10] No explanation has been given for this as yet.

Like the corresponding arsine, dimethyltrifluoromethylbismuth can be converted to the methylbistrifluoromethyl compound by the action of trifluoroiodomethane.[9] This suggested that in the reaction between trimethylbismuth and trifluoroiodomethane, a step-wise replacement of methyl by trifluoromethyl groups had occurred.

$$(CH_3)_3Bi + CF_3I \longrightarrow (CH_3)_2Bi\,CF_3 + CH_3I \quad \ldots\ldots (1)$$

$$(CH_3)_3Bi + CF_3I \longrightarrow CH_3Bi\,(CF_3)_2 + CH_3I \quad \ldots\ldots (2)$$

Tristrifluoromethylphosphine was found to be a sufficiently powerful trifluoromethylating species to form dimethyltrifluoromethylbismuth on reaction with

trimethylbismuth, and methylbistrifluoromethylbismuth when reacted with dimethyltrifluoromethylbismuth. These reactions may be represented thus:

$$(CF_3)_3P + (CH_3)_3Bi \longrightarrow (CH_3)_2Bi\,CF_3 + CH_3P\,(CF_3)_2$$

..... (3)

$$(CF_3)_3P + (CH_3)_2Bi\,CF_3 \longrightarrow CH_3Bi\,(CF_3)_2 + CH_3P\,(CF_3)_2$$

..... (4)

The exchange reactions depicted by equations (1) and (2) may be reversed since treatment of methylbistrifluoromethylbismuth with methyl iodide yielded dimethyltrifluoromethylbismuth, which in turn when treated with methyl iodide, gave trimethylbismuth. A temperature of 100°C was used in both experiments. The appropriate quantity of trifluoroiodomethane was liberated in each case. Thus:

$$(CF_3)_2Bi\,CH_3 + CH_3I \longrightarrow CF_3Bi\,(CH_3)_2 + CF_3I$$

..... (5)

$$CF_3Bi\,(CH_3)_2 + CH_3I \longrightarrow (CH_3)_3Bi + CF_3I$$

..... (6)

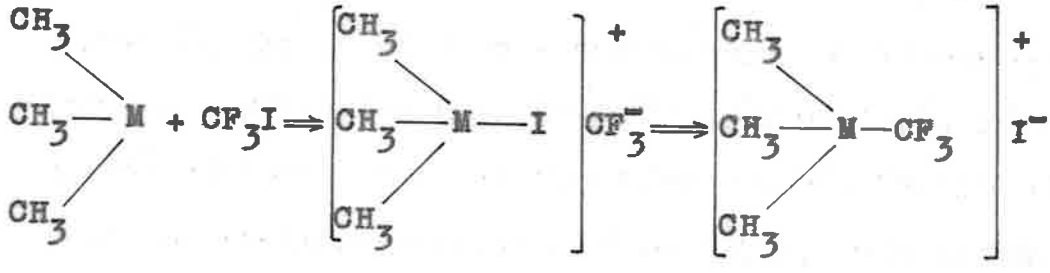
Despite the relative ease with which it was possible to replace the first two methyl groups by trifluoromethyl, replacement of the third was not accomplished under any of the variety of conditions tried. This inability of methylbistrifluoromethyl compounds to undergo conversion to tristrifluoromethyl compounds when treated with trifluoroiodomethane is typical for the Group VB elements.[9] The fully trifluoromethylated derivatives have been prepared, together with the appropriate iodotrifluoromethyl compounds, in the case of phosphorus, arsenic[11] and antimony[12] by the direct action of trifluoroiodomethane on the finely divided element. Such a reaction was not successful in the case of bismuth. This fact was attributed to the decreasing order ($P > As > Sb$) of thermal stability of the tristrifluoromethyl compounds which was reflected in the careful temperature control necessary for the preparation of the stibine.[12] When bismuth was treated with trifluoroiodomethane, no reaction occurred below 200°C. At 245°C some reaction was induced, but apart from bismuth triiodide and some pyrolysis products of trifluoroiodomethane, only very minor quantities of a difficultly separable mixture of iodotrifluoromethylbismuth compounds were obtained. The latter compounds, like their alkyl

analogues,[13] were very reactive towards air and moisture.

Some evidence for the existence of tristrifluoromethylbismuth has been obtained however.[14] The preparative method used involved passing trifluoromethyl radicals, generated either from hexafluoroacetone[15] or from hexafluoroethane, over a bismuth mirror. The quantities of the compound obtained by this method were very small, and accordingly the investigation of its chemistry was limited. The details of this and other fully trifluoromethylated metal derivatives are given in Chapter VIII.

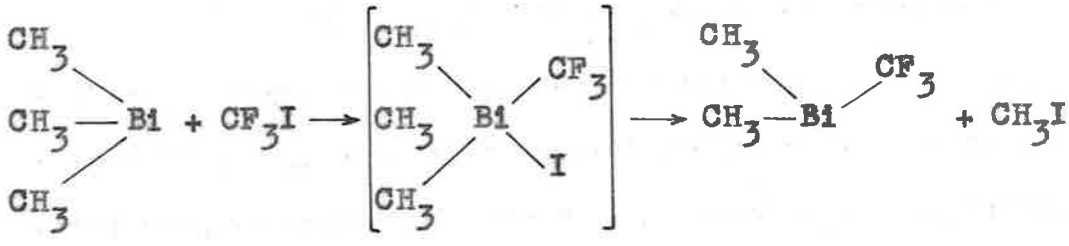
3. MECHANISM OF REACTION

The mechanism by which trifluoromethyl radicals replaced methyl groups in trimethylbismuth was almost certainly similar to that operating when trimethylphosphine, -arsine and -stibine reacted with trifluoroiodomethane.[1] In the latter cases a positive iodine complex was thought to form initially and that rearrangement occurred via a pentavalent state of the "metal" giving a trimethyltrifluoromethyl 'onium iodide.

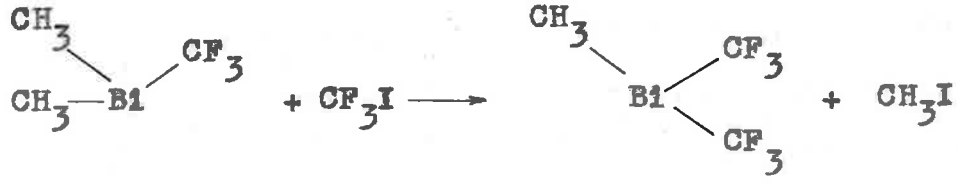


The loss of methyl iodide from the quaternary compound then left the dimethyltrifluoromethyl derivative which was observed as a major reaction product. More detailed descriptions of this mechanism have been presented in Chapters III and IV.

Pentavalent bismuth derivatives are known to exist,[13] but generally only the arylhalobismuth compounds are sufficiently stable to be isolated. However a reaction mechanism involving such a valency state for alkyl derivatives is certainly feasible. Thus the route by which dimethyltrifluoromethylbismuth and methyl iodide were formed from trimethylbismuth and trifluoroiodomethane, was envisaged as follows:



An analogous scheme representing the replacement of a second methyl group accounted for the methylbistrifluoromethylbismuth also found as a reaction product.



4. OTHER ALKYLPERFLUOROALKYLBISMUTH COMPOUNDS

All the alkylperfluoroalkylbismuth compounds prepared in this investigation are listed in Table 6.1. In each case a mixture of dialkylperfluoroalkyl- and alkylbisperfluoroalkyl-bismuth compounds was obtained from the reaction of a trialkylbismuth with a perfluoroiodoalkane. This inferred that the replacement of the second alkyl group from trialkylbismuth compounds occurred more readily than from trialkyl derivatives of any of the other Group VB elements. It was found that there was conversion of all the trialkylbismuth to alkylperfluoroalkylbismuth compounds in each case, but the proportion of the alkylbisperfluoroalkyl compound decreased with increasing size both of the alkyl and perfluoroalkyl groups present (see Table 6.1). By removing the liberated alkyl iodide from the equilibrium reaction mixtures and treating the mixture of alkylperfluoroalkylbismuth compounds with additional perfluoroiodoalkane, it was possible to obtain higher yields of the alkylbisperfluoroalkylbismuth compound in each case.

The mechanism proposed for these reactions is identical with that already discussed in relation to the formation of the methyltrifluoromethylbismuth compounds.

TABLE 6.1

Alkylperfluoroalkylbismuth Compounds

Compound	Yield (%)	Boiling Point (^{o}C)
$(CH_3)_3Bi$	--	110
$(CH_3)_2Bi\,CF_3$	82	121
$CH_3Bi\,(CF_3)_2$	18	132
$(CH_3)_2Bi\,C_2F_5$	84	130
$CH_3Bi\,(C_2F_5)_2$	16	147
$(CH_3)_2Bi\,C_3F_7$	92	137
$CH_3Bi\,(C_3F_7)_2$	8	162
$(C_2H_5)_3Bi$	--	150*
$(C_2H_5)_2Bi\,CF_3$	98	123*
$C_2H_5Bi\,(CF_3)_2$	2	130*

* denotes decomposition temperature

5. CHEMICAL PROPERTIES OF ALKYLPERFLUOROALKYLBISMUTH COMPOUNDS

(a) Oxidation

The alkylperfluoroalkylbismuth compounds were readily oxidised on exposure to oxygen in the same way

as trialkylbismuth compounds. Those of lower molecular weight tended to ignite spontaneously if injected as a fine stream into air, while those of higher molecular weight fumed strongly under these conditions. The vapours of all the compounds prepared were extremely lachrymatory.

(b) Hydrolysis

The compounds were rapidly hydrolysed by 5N sodium hydroxide, liberating the appropriate fluorocarbon R_fH, quantitatively. Fluoride was not produced in such reactions. The production of fluorocarbons by hydrolysis simplified the analysis of the bismuth compounds considerably, since the former were easily separated from the other components of the mixture by distillation within the vacuum system. The susceptibility of the perfluoroalkyl derivatives of the Group VB elements towards alkaline hydrolysis increases with increasing atomic number of the element.[9] This is illustrated by the dimethyltrifluoromethyl derivatives of these elements (see Table 6.2) and it was found that the bismuth compound fitted into this sequence perfectly.

(c) Reaction with Halogens

Halogens react with alkyl[15] and perfluoroalkyl

TABLE 6.2

Hydrolysis of Dimethyltrifluoromethyl Compounds

Compound	% Hydrolysis after 3 days at 20°C
$(CH_3)_2 P\,CF_3$	6.5
$(CH_3)_2 As\,CF_3$	9
$(CH_3)_2 Sb\,CF_3$	100
$(CH_3)_2 Bi\,CF_3$	100

derivatives of phosphorus,[16] arsenic[17] and antimony[18] forming initially dihalides, the particular element being in a pentavalent state. Although no pentavalent alkylbismuth halides have been reported, the reaction of halogens with trialkylbismuth compounds to form alkylhalobismuth derivatives and an alkyl halide, probably involves an intermediate pentavalent bismuth compound. It has been established that pentavalency is the preferred state for bismuth in its organic derivatives, but examples are apparently confined almost exclusively to the aryl series.[13]

In the present study it was shown that halogens reacted with alkylperfluoroalkylbismuth compounds, even under very carefully controlled conditions, cleaving

both alkyl and perfluoroalkyl groups at random. The groups removed, appeared in the reaction mixture as alkyl and perfluoroalkyl halides respectively. The bismuth remained bound in a mixture of involatile, highly air and water reactive compounds in which the ratio, halogen:alkyl:perfluoroalkyl, was not consistent with any reasonable formula. Due to the complexity of such mixtures and also to the great difficulty experiences in handling them, isolation of their pure components was not accomplished. This inability of halogens to preferentially cleave either one or other type of group was in contrast to observations made in the study of mixed alkylperfluoroalkyl derivatives of other elements. For example, electrophilic reagents have been shown to remove alkyl groups preferentially from alkylperfluoroalkyl derivatives of lead[19] and tin.[20] Thus the route to pure perfluoroalkylhalobismuth compounds must still be sought. Such derivatives would be important since, by analogy to corresponding compounds of the other Group VB elements, they could be expected to be intermediates in the preparation of aminobismuthines and dibismuthines. Apart from the incomplete evidence for the existence of tetramethyl-dibismuth,[21] no compounds containing bismuth-bismuth bonds are known.

(d) Coordination Compounds

The basicities of comparable derivatives of the Group VB elements are formally regarded to decrease with increasing atomic number of the element even though there are important exceptions to this sequence.[22] Attachment of perfluoroalkyl groups to these elements causes considerable reduction of the availability of the lone electron pair on the elements and a corresponding decrease in the basicities results.[8,23] For a particular element, the basicity decreases with increasing number of attached perfluoroalkyl groups, no basic properties being found in the case of the trisperfluoroalkyl derivatives.[8]

Trialkylbismuth compounds exhibit no electron donor properties and do not form complexes with the strong electron acceptor, boron trifluoride.[24] It was to be expected therefore, that the alkylperfluoroalkylbismuth compounds would also be devoid of electron donor properties. However acceptor properties were found with both dialkylperfluoroalkyl- and alkylbisperfluoroalkylbismuth compounds, since each formed weakly bound adducts at low temperatures with the strong base, dimethylamine. These adducts consisted of the reactants in equimolar proportions. This ability for a Group VB

element to act as an electron acceptor was not unprecedented for antimony and bismuth halides have been shown to form weak complexes with donor solvents, e.g. diethyl ether.[25] In addition a complex of tristrifluoromethylstibine with pyridine has been reported.[18]

The complexes of the perfluoroalkylbismuthines, formulated as $R_2BiR_f.(CH_3)_2NH$ and $RBi(R_f)_2.(CH_3)_2NH$, decomposed on standing at room temperature and rapidly evolved fluoroform when treated with water. The latter reaction was no doubt similar to the alkaline hydrolysis occurring when the pure bismuth compound was treated with aqueous sodium hydroxide, since hydroxyl ions were common to both systems and known to be capable of causing this type of decomposition.

6. PHYSICAL PROPERTIES OF ALKYLPERFLUOROALKYLBISMUTH COMPOUNDS

(a) Boiling Points

The boiling points (see Table 6.1) of the compounds prepared were determined by extrapolation of the vapour pressure-temperature data obtained with the aid of an isoteniscope.

In all cases, except that of trimethylbismuth, the compounds decomposed at or below their extrapolated boiling points, liberating metallic bismuth and a mixture of hydrocarbons and perfluorocarbons. The boiling point sequence did not follow that exhibited by the trifluoromethyl derivatives of phosphorus, arsenic and antimony, where the boiling point rises with the attachment of the first trifluoromethyl group and then falls with subsequent attachments.[1]

The thermal stability of bismuth alkyls decreases with increasing size of the alkyl group[26] and an analogous gradation was evident with the perfluoroalkyl derivatives whose stabilities decreased with both increasing alkyl and perfluoroalkyl chain length. In addition the stabilities decreased with increasing number of perfluoroalkyl groups.

(b) Infra-red spectra

The infra-red spectra of the organobismuth compounds were recorded and tentative vibrational assignments made and compared with those of related compounds.

In the frequency range studied, viz. 700-4000 cm.$^{-1}$, generally only those frequencies associated with

C-H and C-F vibrations appear, although overtone frequencies derived from symmetric and antisymmetric Bi-C stretching frequencies have also been tentatively assigned in this region.

(i) Methyltrifluoromethylbismuthines

The observed frequencies and suggested assignments are listed in Table 6.3.

Absorption bands at 2980-2990 and 2905-2920 cm.$^{-1}$ in the spectra of the three compounds listed are assigned to C-H antisymmetric and symmetric stretching vibrations respectively.[27] The limits of variation in the positions of these bands are then particularly narrow.

Deacon and Jones[28] have compared the C-H bending frequencies for a variety of methyl derivatives of different elements and cited the range 1390-1485 cm.$^{-1}$ for this mode. The bands in the range 1375-1475 cm.$^{-1}$ found in the spectra of the bismuth compounds may then well be attributed to the C-H antisymmetric bending frequency. Symmetric bending of the C-H bonds gives rise to absorption at lower frequencies and the bands in the region 1150-1170 cm.$^{-1}$ in trimethylbismuth and dimethyltrifluoromethylbismuth are attributed to this mode. The corresponding absorption bands of methylbis-trifluoromethylbismuth are hidden by the much stronger

TABLE 6.3

Vibrational Frequencies of Methyltrifluoromethylbismuthines

$(CH_3)_3Bi$	$(CH_3)_2Bi\,CF_3$	$CH_3Bi(CF_3)_2$	Assignment
2988 (m)	2980 (wsh*)	2984 (m)	C-H antisymm. stretch
2908 (m)	2918 (m)	2908 (m)	C-H symm. stretch
1615 (w)	1600 (w)	1608 (w)	2 x CH_3 rock (?)
1473 (w)	1445 (w)	1466 (w)	C-H antisymm. bend
1417 (w)	1407 (w)	1404 (wsh)	
1382 (w)	1380 (wsh)	1379 (w)	
1261 (w)	1262 (w)	1253 (w)	2x Bi-C antisymm. stretch (?)
1167 (msh)	1168 (w)		C-H symm. bend
1160 (m)	1152 (wsh)	Hidden by C-F	
1150 (msh)			
	1103 (ssh)	1168 (msh)	C-F symm. and antisymm. stretch.
	1092 (s)	1153 (s)	
	1032 (m)	1104 (ssh)	
	1020 (msh)	1093 (s)	
		1049 (wsh)	
		1025 (w)	
915 (w)	908 (w)	907 (w)	2 x Bi-C symm. stretch
772 (m)	794 (w)	817 (wsh)	CH_3 rock
	819 (wsh)		
	745 (w)	770 (w)	CF_3 symm. deform.
	700 (w)	695 (w)	
	950 (w)	947 (w)	Not assigned
	935 (wsh)	933 (wsh)	
	1757 (w)	1848 (w)	
	1730 (wsh)		

* Denotes shoulder

C-F stretching frequencies. The methyl rocking vibrations[27] cause absorption bands at 770-820 cm.$^{-1}$ As trifluoromethyl replace methyl groups it becomes more difficult to distinguish this band from the very strong one due to the CF_3 symmetric deformation. The weak band at 1600-1615 cm.$^{-1}$ is tentatively assigned to an overtone of the methyl rocking vibration.

A number of very strong absorption bands caused by symmetric and antisymmetric C-F stretching appears in the range 1020-1170 cm.$^{-1}$ while weaker ones, assigned to CF_3 deformation, occur between 695 and 770 cm.$^{-1}$ Beg and Clark[29] have made similar assignments for C-H and C-F absorption in methyltrifluoromethyl phosphines.

In a variety of methyl-containing compounds Deacon and Jones[12] have observed a shift in the M-C (where M is N or P; and C or Si) asymmetric stretching frequency to lower energies with increasing atomic number of M. Thus the adsorption band due to this vibration appearing at 650 cm.$^{-1}$ in trimethylphosphine[30] would be expected to appear near 600 cm.$^{-1}$ in trimethylbismuth. On this basis the weak band at 1261 cm.$^{-1}$ in trimethylbismuth has been tentatively

assigned to an overtone of the Bi-C antisymmetric stretching frequency. The fundamental vibration would then be calculated as occuring at 630 cm.$^{-1}$ Accordingly the band occurring at 1262 cm.$^{-1}$ in dimethyltrifluoromethylbismuth and at 1253 cm.$^{-1}$ in methylbistrifluoromethylbismuth is in each case assigned to an overtone of the Bi-C antisymmetric stretching frequency.

Raman measurements on trimethylbismuth[30] have enabled Rosenbaum et al. to assign the fundamental Bi-C symmetric stretching frequency to the band observed at 460 cm.$^{-1}$ The weak bands at 905-915 cm.$^{-1}$ in the spectra of the three bismuth compounds discussed are considered to be due to overtones of this vibration.

(ii) Other perfluoroalkylbismuthines

Although basically similar to those already discussed, the spectra of the more complex alkylperfluoroalkylbismuth compounds are necessarily more complicated with the result that some bands are partly or even wholly obscured, while others are split to give a number of submaxima. Consequently detailed assignment in the cases of these compounds is most difficult. However, where possible, with the aid of assignments made by Pitcher and Stone[31] for some perfluoroalkyl metal carbonyls, tentative assignments for the individual

modes associated with the complex perfluoroalkyl groups have been made.

Table 6.4 contains the important maxima observed in the infra-red spectra of these compounds. The bands attributed to C-H absorptions have already been discussed and attention will be confined to features in these spectra which are different from those of the methyltrifluoromethylbismuth compounds. The strong absorption bands between 1025 and 1340 cm.$^{-1}$ are attributed to a variety of C-F vibrations. The three frequencies in the range 1190-1310 cm.$^{-1}$ for the pentafluoroethyl compounds and 1210-1340 cm.$^{-1}$ for the heptafluoropropyl compounds are considered to be due to C-F stretching in the CF_3 fragment of the perfluoroalkyl group. In the range 1105-1185 cm.$^{-1}$ are bands in the spectra of the C_3F_7 compounds which are attributed to C-F stretching vibrations in the $C-CF_2-C$ segment. The bands due to C-F stretching in the CF_2 segments attached directly to the metal appear in both types of compounds in the range 1025-1075 cm.$^{-1}$ Bands due to CF_3 deformation modes occur between 715 and 765 cm.$^{-1}$ in this group of compounds. In addition those which appear exclusively in the C_3F_7 compounds in the range 870-880 cm.$^{-1}$ are also attributed to this type of vibration.

TABLE 6.4

Vibrational Frequencies of Complex Perfluoroalkylbismuth Compounds

$(CH_3)_2BiC_2F_5$	$CH_3Bi(C_2F_5)_2$	$(CH_3)_2BiC_3F_7$	$CH_3Bi(C_3F_7)_2$	Assignments
2998 (w)	2998 (w)	2999 (w)	2990 (wsh)	C-H antisymm. stretch
2910 (m)	2916 (w)	2925 (w)	2924 (w)	C-H symm. stretch
1392 (m)	1406 (w) 1374 (w)	1402 (w)	1410 (w)	C-H antisymm. bend
1313 (s) 1200 (ssh) 1193 (s)	1313 (s) 1205 (ssh) 1193 (s)	1339 (s) 1239 (s) 1210 (s)	1339 (s) 1246 (s) 1217 (s)	C-F stretches of CF_3 group
		1171 (s) 1107 (s)	1185 (m) 1120 (m)	C-F stretches of $C-CF_2-C$ group
1075 (s)	1075 (m)	1074 (m) 1028 (m)	1073 (w) 1035 (w)	C-F stretches of CF_2-M group
903 (s)	898 (s)	810 (m)	809 (m)	C-C stretch
746 (w)	781 (w)	767 (w)	765 (w)	CH_3 rock
738 (msh) 718 (s)	761 (w) 728 (s)	877 (?) 745 (m) 721 (s)	873 (?) 733 (m) 723 (s)	CF_3 deform.

The strong absorptions occurring at 895-905 cm.$^{-1}$ in the spectra of the C_2F_5 compounds and at 805-810 cm.$^{-1}$ in the spectra of the C_3F_7 compounds are attributed to C-C stretching vibrations.

In Table 6.5 are listed the infra-red spectral bands of diethyltrifluoromethylbismuth and ethylbistrifluoromethylbismuth.

TABLE 6.5

Vibrational Frequencies of Ethyltrifluoromethylbismuthines

$(C_2H_5)_2BiCF_3$	$C_2H_5Bi(CF_3)_2$	Assignment
2950 (wsh)	2960 (w)	C-H antisymm. stretch
2930 (w)	2910 (w)	C-H symm. stretch
1396 (w) 1326 (w)	1365-1400 (w)	C-H antisymm. bend
1171 (m) 1116 (s) 1061 (s) 1009 (m)	1170 (m) 1147 (s) 1068 (s) 1013 (m)	C-F symm. and antisymm. stretch
743 (m) 691 (m)	750 (w) 698 (m)	CF_3 symm. deform.

The presence of the bands in the spectra of these compounds is understood by reference to Table 6.5 and the explanations offered for the methyltrifluoromethyl compounds can be applied in this case also.

7. ATTEMPTS TO PREPARE ARYLPERFLUOROALKYLBISMUTH COMPOUNDS

(a) Triphenylbismuth did not react with trifluoroiodomethane under conditions regarded as suitable for the formation of phenyltrifluoromethylbismuth compounds. Although phenyltrifluoromethyl derivatives of other Group VB elements have been prepared using conditions comparable with those employed in this case, the yields have been low and a number of by-products were formed, thus rendering the method of limited value.[32]

(b) The reaction of triphenylbismuth with tristrifluoromethylphosphine resulted in partial phenylation of the phosphine and the accompanying formation of metallic bismuth. This ability of triphenylbismuth to act as a strong phenylating agent is well known.[13] The trifluoromethyl groups displaced from tristrifluoromethylphosphine appeared in the reaction products as hexafluoroethane.

(c) A mixture of diphenyliodobismuth, trifluoroiodomethane and excess mercury did not yield diphenyltrifluoromethylbismuth. The phenylating ability of phenylbismuth compounds was again evident, for in this case phenylmercuric iodide and metallic bismuth were obtained.

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CHAPTER VII

EXPERIMENTAL

1. GENERAL TECHNIQUES

(a) In the main, the techniques used in the study of the alkylperfluoroalkyl bismuth compounds were the same as those described in Chapter V.

(b) Isolation of the new bismuth derivatives was accomplished with the aid of vapour phase chromatography. The retention times of these compounds on a one metre column of di-isodecyl phthalate are given in Table 7.5.

(c) Analyses

(i) The perfluoroalkyl content of each compound was determined by hydrolysis of a weighed amount of the derivative with hot 5N-sodium hydroxide. The perfluorocarbon liberated (e.g. CF_3H from $(CH_3)_2BiCF_3$) was collected and weighed, after purification by trap-to-trap distillation in the vacuum system.

(ii) Bismuth remaining in the solution after alkaline hydrolysis, was determined as the oxyiodide.[1] After acidification with nitric acid, the solution was successively concentrated and treated with further nitric acid to convert all the bismuth to bismuth nitrate before precipitation as the oxyiodide.

2. PREPARATION OF REACTANTS

(a) Trimethylbismuth[2]

Methylmagnesium iodide (1.4 mole) in diethyl ether (500 ml.) was treated at room temperature with a slurry of bismuth trichloride (148 g., 0.47 mole) in ether (200 ml.). Stirring was continued for a further two hours after the addition of bismuth trichloride and the mixture allowed to stand at room temperature for a further ten hours before all the volatile constituents were removed by vacuum distillation. Most of the ether was then separated from the trimethylbismuth by careful fractional distillation at one atmosphere pressure of nitrogen. The final purification was performed with the aid of a vacuum system by using repeated trap-to-trap distillations through traps at -46°C and -196°C, the trimethylbismuth being retained in the trap at -46°C. This procedure was continued until the trimethylbismuth fraction had the correct vapour pressure over a range of temperatures.[3] A yield of 45 gm. (40%) of pure product was obtained.

(b) Triethylbismuth

Triethylbismuth was prepared by R.S. Dickson using the reaction of lithium tetraethylaluminate with bismuth trichloride.[4]

(c) Heptafluoroiodopropane[5]

Silver heptafluorobutyrate (160 gm., 0.5 mole) was prepared from silver oxide and heptafluorobutyric acid and mixed with iodine (254 gm., 1.0 mole). The mixture was gently heated and the gas liberated collected directly in a trap at -196°C. A vacuum jacketed condenser fitted with a cold finger (see Figure 5.3) was then attached to the top of the trap and the temperature allowed to rise slowly to 20°C. All the carbon dioxide was removed in this way, the heptafluoroiodopropane being retained by maintaining the temperature of the cold finger at -25°C. The yield of product (Found: mol.wt. 296. Calc. for C_3F_7I: mol.wt. 296) was 127 gm. (86%).

(d) The preparations of the other perfluoroiodoalkanes used in this investigation have been described in Chapter V.

(e) Tristrifluoromethylphosphine[6]

Red phosphorus (50 gm., 1.6 gm. atoms) which had been dried over phosphorus pentoxide, and trifluoroiodomethane (51 gm., 0.26 mole) were treated at 220°C in a brass autoclave for 48 hrs. The volatile reaction products were then fractionated within the vacuum system through traps at -63°C (to remove iodobistrifluoromethyl-

phosphine and di-iodotrifluoromethylphosphine), -95°C (to remove tristrifluoromethylphosphine), -135°C (to remove trifluoroiodomethane) and -196°C (to remove phosphorus pentafluoride). The two iodotrifluoromethylphosphines and the unreacted trifluoroiodomethane together with additional CF_3I (20 g., 0.10 mole) were returned to the autoclave into which no air or moisture had been allowed to enter. The heating and subsequent fractionation procedures were then repeated. The final yield of pure tristrifluoromethylphosphine obtained after repeated trap-to-trap distillation was 19.7 g. (23% based on trifluoroiodomethane used) (Found: mol.wt. 238. Calc. for C_3F_9P: mol.wt. 238). The iodotrifluoromethylphosphines were again returned to the autoclave in readiness for subsequent preparations of tristrifluoromethylphosphine.

(f) Diphenyliodobismuth[7]

Triphenylbismuth (9.8 gm., 22.3 mmole) was dissolved in diethyl ether (150 ml.) and iodine (5.6 gm., 22.0 mmole) in 50 ml. of ether added slowly with stirring. The diphenyliodobismuth precipitated almost immediately as a yellow solid. This was filtered from the mixture, washed with ether until a clear filtrate was obtained and dried by pumping. The yield was

10.7 gm., 99%) (Found: 29.4; H, 2.08; I, 25.7%. Calc. for $C_{12}H_{10}BiI$: C, 29.3; H, 2.04; I, 25.9%).

3. PREPARATION OF ALKYLPERFLUOROALKYLBISMUTH COMPOUNDS

(a) Methyltrifluoromethylbismuthines

Trimethylbismuth (22.08 gm., 86.5 mmole) was heated at 100°C in a sealed tube for 12 hrs. with trifluoroiodomethane (21.56 gm., 110 mmole). Fractional distillation through traps cooled to -46, -95, -135 and -196°C gave a preliminary separation of the reaction products. The trap cooled to -196°C contained a trace of fluoroform, that at -135°C contained most of the unreacted trifluoroiodomethane, while that at -95°C contained most of the methyl iodide formed in the reaction. The highest boiling fraction of the reaction products consisted of all the bismuth-containing material, together with traces of methyl iodide and trifluoroiodomethane. The individual components of this fraction were isolated by vapour phase chromatography, the major constituents being dimethyltrifluoromethylbismuth (21.8 gm., 82% conversion of trimethylbismuth) (Found: CF_3, 22.6; Bi, 67.2%; mol.wt. 310. Calc. for $C_3H_6F_3Bi$: CF_3, 22.4; Bi, 67.9; mol.wt. 308) and methylbistrifluoromethylbismuth (5.64 gm., 18% conversion

of trimethylbismuth) (Found: CF_3, 38.1; Bi, 57.7%; mol.wt. 365. Calc. for $C_3H_3F_6Bi$: CF_3, 38.1; Bi, 57.3%; mol.wt. 362).

The vapour pressures of the two bismuth compounds were measured over a range of temperatures and the values obtained are shown in Table 7.1 and Table 7.2. For dimethyltrifluoromethylbismuth the vapour pressures are given by $\log_{10} P_{(mm)} = 7.158 - {}^{1683}/_{T}$ from which the latent heat of vaporisation, 7754 cal/mol and Trouton's constant 19.7, were obtained. The corresponding equation for methylbistrifluoromethylbismuth is $\log_{10} P_{(mm)} = 7.674 - {}^{1941}/_{T}$, giving latent heat of vaporisation, 9210 cal/mol and Trouton's constant 22.7. The infra-red spectra of the new bismuthines are shown in Figure 7.1(a) and Figure 7.1(b) respectively.

(b) <u>Methylpentafluoroethylbismuthines</u>

Trimethylbismuth (4.90 gm., 19.3 mmole) and pentafluoroiodoethane (10.83 gm., 44 mmole) were heated in a sealed tube at 100°C for 12 hrs. Fractionation of the products gave dimethylpentafluoroethylbismuth (5.55 gm., 84% conversion of trimethylbismuth) (Found: C_2F_5, 32.8; Bi, 58.9%; mol.wt. 357. Calc. for $C_4H_6F_5Bi$: C_2F_5, 33.2; Bi, 58.9%, mol.wt. 358) and

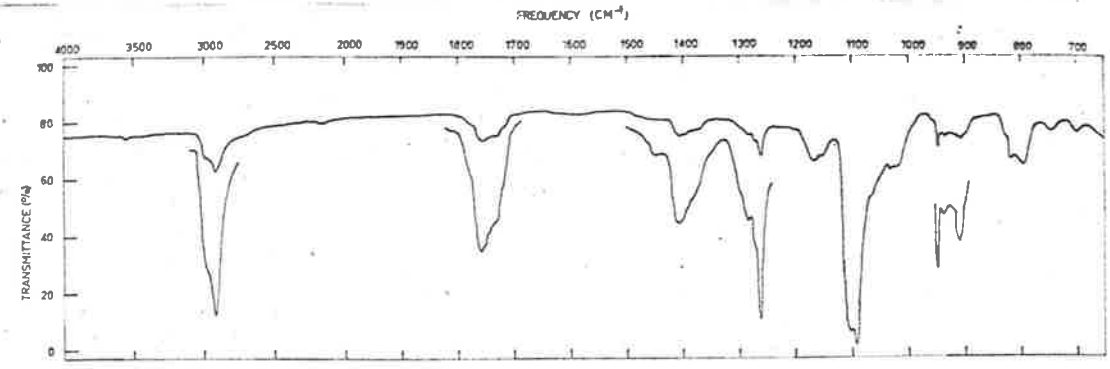

Figure 7.1(a)

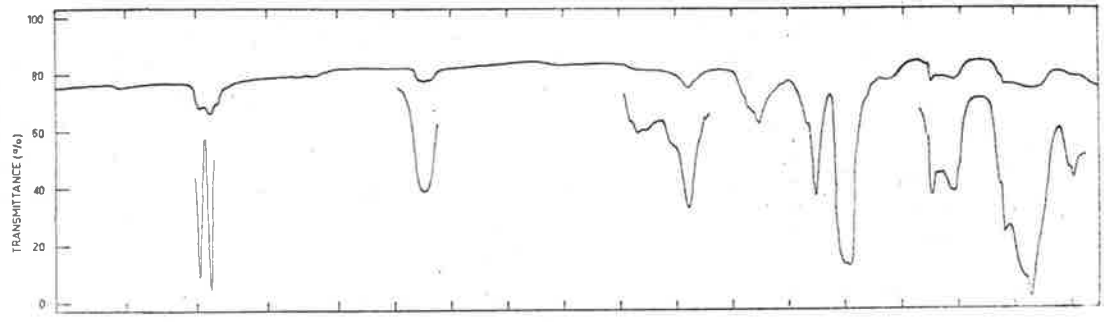

Figure 7.1(b)

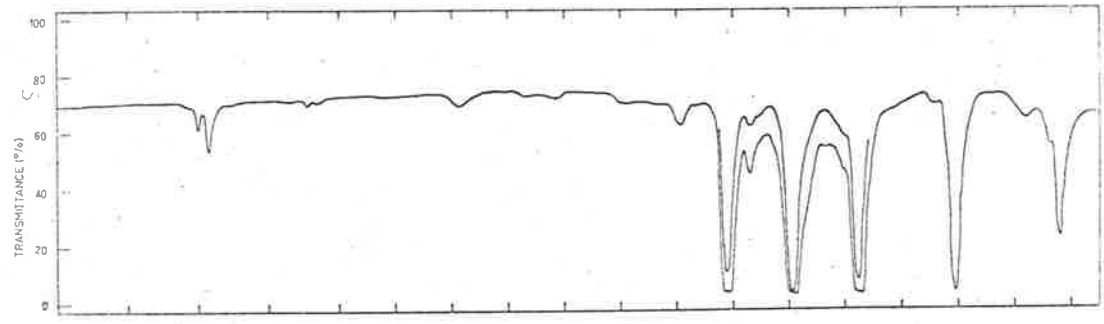

Figure 7.1(c)

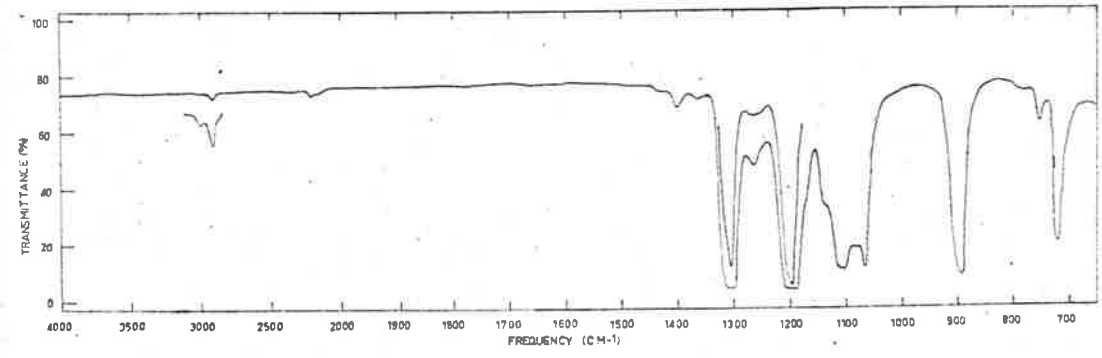

Figure 7.1(d)

TABLE 7.1

Vapour Pressure-Temperature Relationships for Dimethyltrifluoromethylbismuth

Temp. (°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	$\text{Log}_{10} P$
28.5	3.317	49.0	1.6902
38.0	3.215	65.0	1.8129
50.5	3.091	93.5	1.9708
59.3	3.009	125.0	2.0969
68.0	2.933	165.0	2.2175
78.0	2.849	229.0	2.3598
85.0	2.793	288.0	2.4594
92.0	2.740	338.5	2.5295
98.0	2.695	402.5	2.6047
104.5	2.657	520.0	2.7160
113.0	2.591	694.0	2.8414
120.0	2.545	757.0	2.8791

TABLE 7.2

Vapour Pressure-Temperature Relationships for Methylbistrifluoromethylbismuth

Temp. (^{o}C)	$10^{3} \times {}^{1}/_{T}$ (^{o}A)	Pressure (mm.)	Log_{10} P
27.5	3.328	16.5	1.2175
39.0	3.205	23.5	1.3711
44.5	3.150	34.0	1.5315
52.0	3.077	45.0	1.6532
57.5	3.026	62.5	1.7959
64.0	2.967	79.0	1.8976
70.0	2.915	104.5	2.0191
80.5	2.829	132.0	2.1206
93.0	2.732	245.0	2.3892
98.0	2.695	295.0	2.4548
102.0	2.667	334.0	2.5237
110	2.611	398.0	2.5999
116	2.571	477.0	2.6785
119	2.551	530.0	2.7243
123	2.525	588.0	2.7694
126	2.506	634.0	2.8021
129	2.488	690.0	2.8388
131	2.475	735.0	2.8663

methylbispentafluoroethylbismuth (1.43 gm., 16% conversion of trimethylbismuth (Found: C_2F_5, 50.9; Bi, 44.2%; mol.wt. 460. Calc. for $C_5H_3F_{10}Bi$: C_2F_5, 51.5; Bi, 42.5%; mol.wt. 462). The infra-red spectra of these compounds are shown in Figure 7.1(c) and Figure 7.1(d) respectively.

(c) Methylheptafluoropropylbismuthines

Trimethylbismuth (6.85 gm., 27 mmole) and heptafluoroiodopropane (18.4 gm., 61 mmole) were heated at 100°C in a sealed tube for 8 hrs., yielding dimethylheptafluoropropylbismuth (10.1 gm., 92% conversion of trimethylbismuth) (Found: C_3F_7, 41.0; Bi, 51.5%; mol.wt. 408. Calc. for $C_5H_6F_7Bi$: C_3F_7, 41.4; Bi, 51.2%; mol.wt. 408) and methylbisheptafluoropropylbismuth (1.21 gm., 8% conversion of trimethylbismuth) (Found: C_3F_7, 60.3; Bi, 36.4%; mol.wt. 558. Calc. for $C_7H_3F_{14}Bi$: C_3F_7, 60.1; Bi, 37.2%; mol.wt. 562). The yield of methylbisheptafluoropropylbismuth, which was low in this reaction, was increased by the direct reaction of dimethylheptafluoropropylbismuth (7.39 gm., 17.9 mmole) with heptafluoroiodopropane (10.0 gm., 33.8 mmole) at 100°C for 8 hrs. The unchanged dimethylheptafluoropropylbismuth (3.17 gm., 7.8 mmole) and the methylbisheptafluoropropylbismuth (5.68 gm.,

10.1 mmole) were separated using vapour phase chromatography. The conversion of mono- to bis-perfluoroalkylbismuth compound by this process was 56%. Where necessary, to obtain higher yields of the other bisperfluoroalkylbismuth compounds, a similar procedure was used.

The vapour pressure-temperature data for dimethylheptafluoropropylbismuth are given in Table 7.3. The results are expressed by the equation

$$\log_{10} P(mm) = 6.811 - \frac{1612}{T}$$

The corresponding data for methylbisheptafluoropropylbismuth are given in Table 7.4, the equation being

$$\log_{10} P(mm) = 6.703 - \frac{1662}{T}$$

The infra-red spectra of the two compounds are shown in Figure 7.2(a) and Figure 7.2(b) respectively.

(d) Ethyltrifluoromethylbismuthines

Triethylbismuth (7.34 gm., 24.8 mmole) and trifluoroiodomethane (12.0 gm., 61.2 mmole) were heated in a sealed tube at 100°C for 6 hrs. Diethyltrifluoromethylbismuth was formed almost exclusively. Fractionation

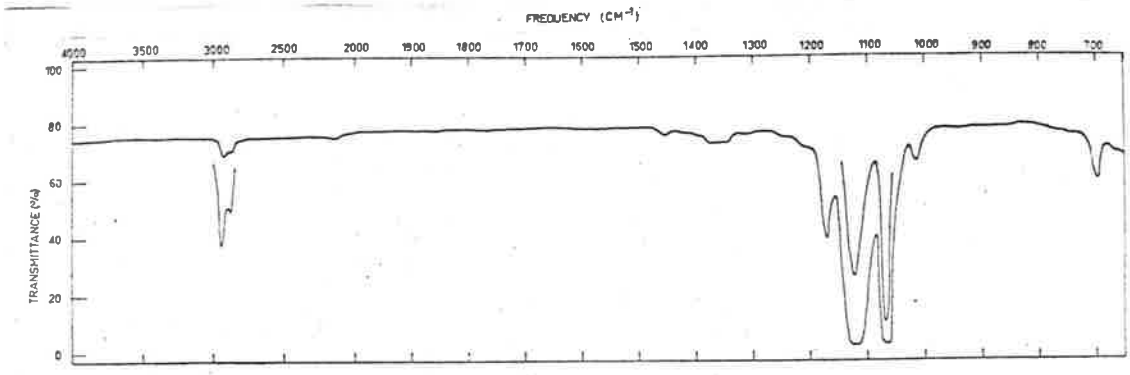

Figure 7.2(a)

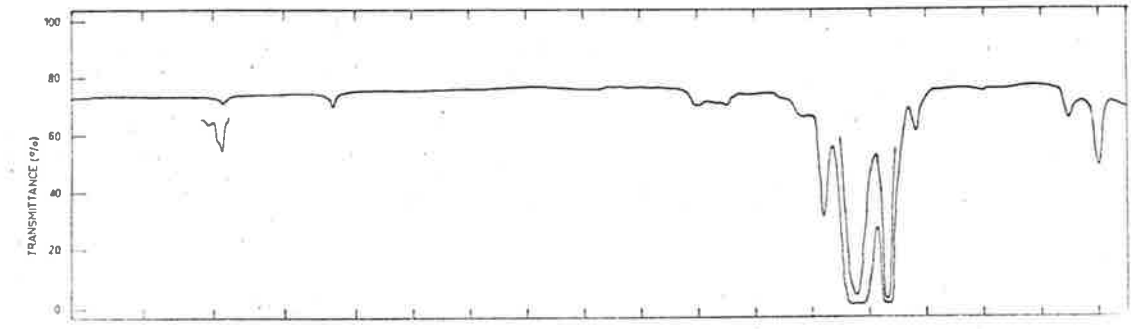

Figure 7.2(b)

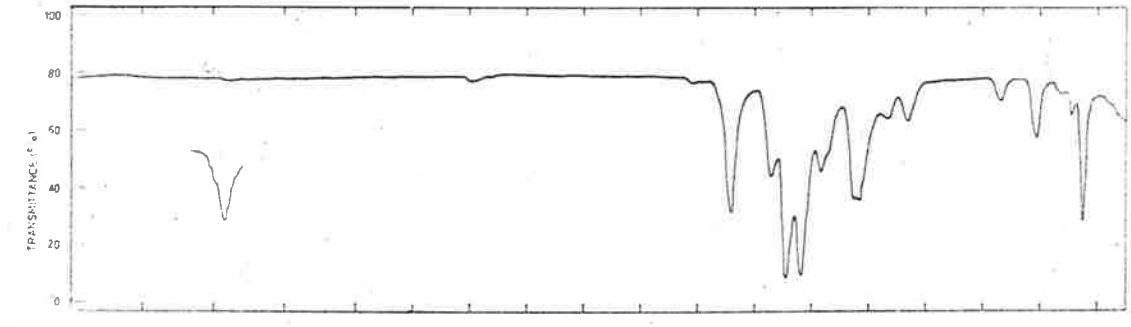

Figure 7.2(c)

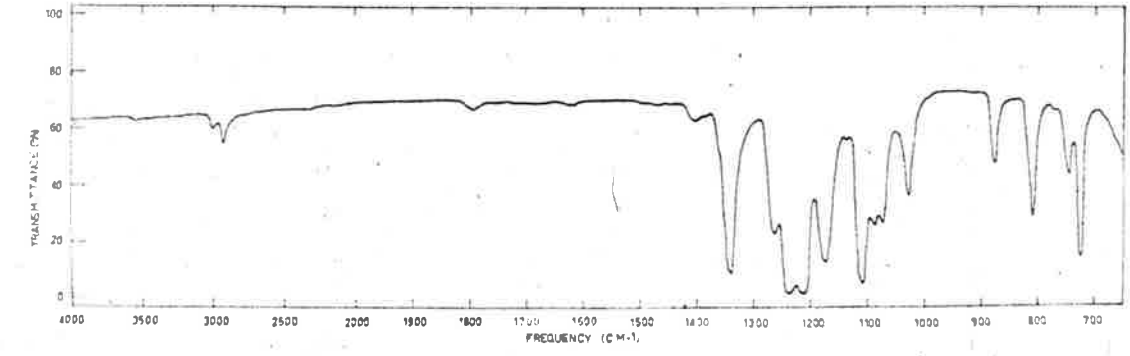

Figure 7.2(d)

TABLE 7.3

Vapour Pressure-Temperature Relationships for Dimethylheptafluoropropylbismuth

Temp. (°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	Log_{10} P
28.7	3.315	35.0	1.5441
46.5	3.130	59.5	1.7745
54.7	3.051	87.5	1.9420
64.3	2.964	113.0	2.0531
69.3	2.921	131.5	2.1189
75.7	2.868	160.0	2.2041
86.8	2.780	217.0	2.3365
96.5	2.706	282.5	2.4494
106.0	2.639	535.0	2.7284
135.0	2.451	756.0	2.8785

TABLE 7.4

Vapour Pressure-Temperature Relationships for Methylbisheptafluoropropylbismuth

Temp. (°C)	$10^3 \times 1/T$ (°A)	Pressure (mm)	Log_{10} P
45.0	3.195	62.0	1.7924
83.0	2.809	127.5	2.1055
98.0	2.695	176.0	2.2455
106.0	2.639	210.0	2.3222
111.5	2.601	240.0	2.3802
118.0	2.558	274.0	2.4378
125.0	2.513	330.0	2.5185
131.5	2.472	385.0	2.5855
141.0	2.415	483.5	2.6843
148.0	2.375	567.5	2.7540
154.5	2.339	655.0	2.8162
161.0	2.304	748.0	2.8739

TABLE 7.5

Compound	Column Length (metres)	Pressure (lbs/sq. in)	Flow Rate (ccs/min)	Temp. (°C)	Retention Time (min)
$(CH_3)_2BiCF_3$	1	11	198	70	9.0
$CH_3Bi(CF_3)_2$	1	11	198	70	22.6
$(CH_3)_2BiC_2F_5$	1	10	176	67	8.2
$CH_3Bi(C_2F_5)_2$	1	10	176	67	13.1
$(CH_3)_2BiC_3F_7$	1	10	176	65	8.0
$CH_3Bi(C_3F_7)_2$	1	10	176	65	18.3
$(C_2H_5)_2BiCF_3$	1	10	176	68	13.9
$C_2H_5Bi(CF_3)_2$	1	10	176	68	22.4

of the mixture followed by further heating of the diethyltrifluoromethylbismuth with additional trifluoroiodomethane resulted in the formation of ethylbistrifluoromethylbismuth. However, the conditions used in this subsequent reaction, viz. 100°C for 4 hrs., caused considerable decomposition of the bismuth compounds. The products were diethyltrifluoromethylbismuth (5.90 gm., 76% conversion of triethylbismuth) (Found: CF_3, 20.3; Bi, 61.3%; mol.wt. 337. Calc. for $C_5H_{10}F_3Bi$: CF_3, 20.5; Bi, 61.4%; mol.wt. 336) and ethylbistrifluoromethylbismuth (1.30 gm., 14% conversion of triethylbismuth) (Found: CF_3, 36.5; Bi, 55.9%; mol.wt., 376. Calc. for $C_4H_5F_6Bi$: CF_3, 36.7; Bi, 55.6%; mol.wt. 376).

The infra-red spectra of these compounds are shown in Figure 7.2 (c) and Figure 7.2 (d) respectively.

(e) Attempted preparations of trisperfluoroalkylbismuth compounds

(i) Methylbistrifluoromethylbismuth (0.527 gm., 1.46 mmole) and trifluoroiodomethane (7.33 gm., 37.4 mmole) were heated together for 75 hrs. in a sealed tube at 125°C. Fractionation through traps at -46, -95, -135 and -196°C enabled unreacted trifluoroiodomethane

to be separated from the reaction mixture. No material collected in the -95°C trap which would normally contain the methyl iodide if it had formed. Vapour phase chromatography showed that only one other volatile material was present in the reaction mixture and this was shown by infra-red spectroscopy to be unchanged methylbistrifluoromethylbismuth. A small quantity of an apparently heterogeneous solid remaining in the reaction vessel was shown to contain Bi, I, CF_3 and was probably formed by attack on the bismuth compound by iodine which had been formed by thermal decomposition of trifluoroiodomethane.

Similar results were obtained by irradiating a similar reaction mixture with ultraviolet light in a silica vessel, regardless of whether mercury was included as a halogen acceptor or not.

(ii) Reaction of bismuth alkyls with tristrifluoromethylphosphine.

(1) Trimethylbismuth (1.073 gm., 4.22 mmole) and tristrifluoromethylphosphine (1.027 gm., 4.31 mmole) were heated at 125°C for 12 hrs. The bismuth-containing products were separated from the other reaction products by fractional condensation into a trap at -46°C.

Vapour phase chromatography of this fraction revealed the presence of only unreacted trimethylbismuth (81%) and dimethyltrifluoromethylbismuth (19%). No more highly trifluoromethylated bismuth derivatives were present.

(2) Dimethyltrifluoromethylbismuth (1.281 gm., 4.16 mmole) and tristrifluoromethylphosphine (1.013 gm., 4.26 mmole) were heated at 120°C for one hr., after which time a grey deposit (possibly metallic bismuth) began to form. By a technique similar to that described above, it was possible to separate and identify dimethyltrifluoromethylbismuth (96%) and methylbistrifluoromethylbismuth (4%).

(3) Methylbistrifluoromethylbismuth did not react with tristrifluoromethylphosphine under the conditions tried.

(iii) Metallic bismuth (20.0 gm., 0.096 gm. atoms) and trifluoroiodomethane (20.3 gm., 0.104 mole) were heated at various temperatures in the range 100-200°C. In each case the entire quantity of trifluoroiodomethane was recovered unchanged, but after heating the mixture at 245°C for 65 hrs., the tube contained a mixture of bright orange and dark brown solids in addition to the unreacted bismuth metal. The volatile constituents of

the mixture were removed and found to contain, as well as unreacted trifluoroiodomethane, a white solid (Found: C, 19.5; F, 60.1; I, 18.2%). It was not affected by air or water. It did not contain bismuth and its analysis suggested it to be a polymeric perfluoroalkyl iodide.

The involatile solid was divided into portions, air and moisture being carefully excluded, and treated as follows:

(1) A sample was extracted successively with the organic solvents benzene, chloroform, diethyl ether, ethanol and acetone. The latter was the most effective in dissolving part of it, but on evaporation of the resulting orange coloured solution only an oily substance containing a considerable quantity of free iodine was deposited.

(2) The solid was shaken with mercury, firstly at room temperature and then at 100°C for 24 hrs., but no volatile material and only traces of mercuric iodide were formed.

(3) The solid was heated at a number of temperatures from 100-350°C but no volatile material formed.

(4) Vacuum sublimation of the mixture enabled a small quantity of bismuth tri-iodide (Found: Bi, 42.6; I, 57.4. Calc. for BiI_3: Bi, 42.2; I, 57.8%) to be isolated.

(5) Treatment of a sample with 5N-sodium hydroxide yielded a small quantity of fluoroform.

From this evidence it was concluded that the reaction had produced bismuth tri-iodide and small quantities of di-iodotrifluoromethylbismuth and iodobistrifluoromethylbismuth, but the thermal conditions necessary to cause reaction were probably unfavourable for the existence of tristrifluoromethylbismuth.

(iv) Silver trifluoroacetate and bismuth tri-iodide. Silver trifluoroacetate (13.5 gm., 61.1 mmole) and bismuth tri-iodide (11.8 gm., 20.0 mmole) were heated in a sealed tube at 120°C for 2 hrs. The reaction mixture was transformed from a fine powder to a very viscous semi-liquid mass which solidified on cooling to room temperature. At a temperature of 200°C, under vacuum, the white crystalline solid, bismuth trifluoroacetate, (Found: Bi, 37.7; C, 13.1; F, 30.6%. Calc. for $C_6F_9O_6Bi$: Bi, 38.1; C, 13.1; F, 31.2%) sublimed leaving a residue of silver iodide. The stoichiometry of the reaction assumed to occur is

given by

$$3\ CF_3COO\,Ag + BiI_3 \longrightarrow (CF_3COO)_3Bi + 3AgI$$

By heating bismuth trifluoroacetate it was hoped that, as in the formation of dimethyltrifluoromethylarsine from dimethyltrifluoroacetoxyarsine,[8] decarboxylation would occur. The bismuth trifluoroacetate was placed in a heavy walled glass vessel which was then evacuated and so attached to the vacuum system that any volatile materials liberated, condensed in a trap cooled to -196°C. The compound was then carefully heated but no volatile bismuth derivative was formed. Instead there was extensive degradation, metallic bismuth being deposited and a mixture of gases containing carbon dioxide and hexafluoroethane being liberated.

(v) This method involved the reaction of heptafluoropropylmagnesium halide, prepared from phenylmagnesium bromide and heptafluoroiodopropane,[9] with bismuth trichloride.

Heptafluoroiodopropane (50 gm., 0.17 mole) and diethyl ether (200 ml.) were placed in a multi-neck flask and cooled to 0°C. Phenylmagnesium bromide (0.17 mole) in ether (100 ml.) was slowly added to this solution through a dropping funnel and when 20% of this

reagent had been added, bismuth trichloride (13.5 gm., 0.042 mole) in ether (50 ml.) was introduced simultaneously. This operation was carried out, with stirring, over a four hour period and the stirring continued for a further seven hrs. The mixture was then refluxed for four hrs. before the ether was removed by distillation. The residue appeared to melt during the latter stages of the distillation. The less volatile liquids were then transferred to the vacuum system where they were fractionated using trap-to-trap distillation. Vapour phase chromatography and infra-red spectroscopy indicated that ether, heptafluoroiodopropane, iodo- and bromo-benzene were the major components. However this mixture of compounds, on standing in contact with air, deposited small but detectable quantities of bismuth oxide. This indicated that a volatile bismuth compound, possibly trisheptafluoropropylbismuth, had formed but the yield was far less than 1%. The solid remaining after the removal of the volatile components from the reaction mixture, was not examined exhaustively since the desired product would be volatile. A small quantity of triphenylbismuth was detected, together with larger amounts of material thought to be phenylhalobismuth compounds.

(f) Reactions of perfluoroalkylbismuth compounds

(i) Halogens

Dimethyltrifluoromethylbismuth and iodine were mixed in the molar ratios 1:1, 1:2 and 1:3 at -46°C and the temperature raised to -26°C, whereupon a smooth, although vigorous reaction occurred, giving initially a red-orange solid whose colour, in part, slowly changed to dark grey. At the completion of the reaction the volatiles were removed and fractionated in the vacuum system. The mixtures were found in each case to consist of variable proportions of methyl iodide (Found: mol.wt. 142. Calc. for CH_3I: mol.wt. 142) and trifluoroiodomethane (Found: mol.wt. 195. Calc. for CF_3I: mol. wt. 196). The solid, obviously heterogeneous in nature, contained variable proportions of Bi, I and CF_3 and could only be formulated as a mixture of bismuth tri-iodide, di-iodotrifluoromethylbismuth and iodobis-trifluoromethylbismuth. The inclusion of sodium-dried ether as solvent to give an initially homogeneous reaction mixture did not alter the course of the reaction.

Methylbistrifluoromethylbismuth and iodine or bromine reacted under similar conditions in an analogous manner, the volatile products being methyl iodide and trifluoroiodomethane or methyl bromide and trifluoro-

bromomethane respectively. No preferential cleavage of either methyl or trifluoromethyl groups could be induced.

(ii) Methyl iodide.

(1) Dimethyltrifluoromethylbismuth (1.10 gm., 3.6 mmole) and methyl iodide (0.863 gm., 5.9 mmole) were heated at 100°C for three hrs. After a preliminary fractionation, the high boiling fraction which contained the bismuth compounds was subjected to vapour phase chromatography. This showed that there had been ca. 0.5% conversion of the starting material to trimethylbismuth. A corresponding quantity of trifluoroiodomethane was also formed.

(2) Methylbistrifluoromethylbismuth (0.780 gm., 2.2 mmole) and methyl iodide (0.856 gm., 6.1 mmole) were heated at 100°C for three hrs. By vapour phase chromatography it was shown that there had been 1% conversion of the original bismuth compound to dimethyltrifluoromethylbismuth. A corresponding amount of trifluoroiodomethane was also formed but no trimethylbismuth could be detected.

(iii) Amines

(1) Dimethyltrifluoromethylbismuth (0.464 gm.,

1.5 mmole) and dimethylamine (0.147 gm., 3.3 mmole) were mixed at 15°C in a sealed tube and found to react giving a pale cream coloured crystalline solid which gradually underwent a number of colour changes, ultimately appearing to form a heterogeneous mixture. In another experiment, by carefully controlling the reaction temperature at 15°C and cooling the mixture to -78°C immediately the initial reaction had ceased, it was possible to pump off the excess dimethylamine (0.079 gm., 1.8 mmole) (Found: mol.wt. 45. Calc. for C_2H_7N: mol.wt. 45) leaving a solid product (0.532 gm.) whose composition corresponded to an equimolar combination of the amine and the bismuth compound. Decomposition occurred if the solid was allowed to stand at room temperature. The addition of water caused hydrolysis with the liberation of fluoroform and dimethylamine. Fluoroform was no doubt produced by alkaline hydrolysis of the trifluoromethyl-bismuth compound, since dimethylamine gives hydroxyl ions in contact with water.

(2) Methylbistrifluoromethylbismuth (0.364 gm., 1.0 mmole) and dimethylamine (0.116 gm., 2.5 mmole) reacted under the conditions described above. A solid adduct (0.431 gm.), consisting of the reactants in equimolar proportions, remained after the excess unreacted dimethylamine (0.071 gm., 1.5 mmole)was distilled from

the reaction mixture.

(3) Trimethylbismuth and dimethylamine did not react under these conditions.

(4) Dimethylheptafluoropropylbismuth (0.105 gm., 0.26 mmole) and dimethylamine (0.044 gm., 0.96 mmole) reacted in a sealed tube at -26°C to form a white crystalline solid product whose composition, after removal of the excess dimethylamine (0.032 gm., 0.71 mmole), was consistent with that of a 1:1 adduct (0.117 g.) of the two reactants. The adduct was even less stable than those of the trifluoromethylbismuth compounds and discoloured quickly if allowed to warm to 20°C. Addition of water to the adduct liberated a mixture of volatile materials which, with the aid of vapour phase chromatography and infrared spectroscopy, were shown to be dimethylamine and heptafluoropropane.

(5) Methylbisheptafluoropropylbismuth (0.254 gm., 0.45 mmole) and dimethylamine (0.058 gm., 1.3 mmole) reacted at -26°C forming a solid product (0.275 gm.) whose composition corresponded to an equimolar admixture of the reactants. A low thermal stability and a susceptibility to hydrolysis similar to that observed with the other adducts was evident in this case also.

4. ATTEMPTS TO PREPARE ARYLPERFLUOROALKYLBISMUTHINES

(a) Triphenylbismuth (7.3 gm., 16.6 mmole) and trifluoroiodomethane (14.0 gm., 71.4 mmole) were contacted in a sealed tube. At room temperature, apart from the partial solution of the bismuthine in trifluoroiodomethane, there was no obvious change in the appearance of the reactants. The mixture was then heated for 65 hrs. at 100°C. Under these conditions all the triphenylbismuth dissolved but could be recovered unchanged as a crystalline solid on cooling. The temperature was raised to 170°C for a further 24 hrs. and then the volatiles removed from the mixture and subjected to trap-to-trap distillation in the vacuum system. Only one fraction was obtained and proved to be unchanged trifluoroiodomethane (Found: mol.wt. 196. Calc. for CF_3I: mol.wt. 196). The solid residue was shown to be unchanged triphenylbismuth (Found: C, 49.0; H, 3.39%; m.pt. 77°C. Calc. for $C_{18}H_{15}Bi$: C, 49.1; H, 3.41%; Lit.[10] m.pt. 77.6°C).

(b) Triphenylbismuth (7.76 gm., 17.6 mmole) and tristrifluoromethylphosphine (4.2 gm., 17.6 mmole) were carefully heated in a sealed tube. When the triphenylbismuth had just melted, a single phase formed (ca.80°C) but then, as the temperature approached 100°C, two liquid phases became distinguishable. (The system reverted to a

single liquid phase when cooled to 80°C). Since no other apparent change had occurred in the reaction mixture when heated at 100°C for five hrs., the temperature was raised to 150°C for a further five hrs. Again no obvious change had occurred and the temperature was raised to 200°C for 12 hrs. Under these conditions, silvergrey crystals were deposited. The volatile constituents of the reaction mixture were subjected to trap-to-trap distillation through traps at -95, -135 and -196°C. Three fractions were collected. The one condensing at -95°C was shown by vapour phase chromatography to consist of two components which, when separated, were identified with the aid of infra-red spectroscopy[11] and molecular weight measurement as phenylbistrifluoromethylphosphine (1.6 gm., 6.5 mmole) (Found: mol.wt. 245. Calc. for $C_8H_5F_6P$: mol.wt. 246) and unreacted tristrifluoromethylphosphine (2.6 gm., 10.9 mmole) (Found: mol.wt. 238. Calc. for C_3F_9P: mol.wt. 238). No bismuth compound was found in this fraction. The fraction collecting in trap at -196°C had an infra-red spectrum identical with that of hexafluoroethane (0.41 gm., 3.0 mmole) (Found: mol.wt. 138. Calc. for C_2F_6: mol.wt. 138).

The major part of the solid reaction product was soluble in ethanol, from which it was crystallised and

shown to be unreacted triphenylbismuth (2.23 gm., 10.7 mmole) (Found: C, 48.8; H, 3.39%. Calc. for $C_{18}H_{15}Bi$: C, 49.1; H, 3.41%). The insoluble material which was metallic in appearance, was shown to be bismuth (1.4 gm., 6.7 gm. atom).

(c) Diphenyliodobismuth (5.8 g., 11.8 mmole), trifluoroiodomethane (15.2 g., 77.6 mmole) and mercury (83 gm., 0.415 gm. atoms) were sealed in a heavy walled tube and shaken at room temperature for five days. After two days white needles began to form, the quantity increasing as the shaking continued. Finally the volatile materials were taken into the vacuum system and, by trap-to-trap distillation through traps at -95, -135 and -196°C, it was established that only trifluoroiodomethane was present (Found: mol.wt. 196. Calc. for CF_3I: mol.wt. 196). The infra-red spectrum of this material was identical with that of authentic trifluoroiodomethane.

The solid reaction products were separated from the mercury by filtration, and then extracted for five hrs. with diethyl ether using a Soxhlet extractor. The ether extract was evaporated until crystals appeared. These were filtered off and recrystallised from ethanol and found to be triphenylbismuth (Found: C, 48.8;

H, 3.6%; m.pt. 77°C. Calc. for $C_{18}H_{15}Bi$: C, 49.1; H, 3.4%; Lit.[9] m.pt. 77.6°C).

The remaining solid reaction product was then extracted as before, this time with acetone for six hours. This, on cooling, yielded white plates almost insoluble in ethanol but which were recrystallised from a mixture of ethanol and acetone. This material was shown to be phenylmercuric iodide (Found: C, 17.6; H, 1.25; I, 31.6%; m.pt. 266°C, mixed m.pt. with authentic phenylmercuric iodide, 266°C. Calc. for C_6H_5HgI: C, 17.8; H, 1.24; I, 31.4%. Lit.[12] m.pt. 266°C).

A grey solid, metallic in appearance, remained after these two extraction procedures and was identified as elemental bismuth.

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CHAPTER VIII

1. INTRODUCTION

This part of the work was undertaken primarily in an attempt to prepare tristrifluoromethylbismuth. The method employed was used only when all the conventional techniques were found to be unsuccessful and was adapted from the classical one devised by Paneth[1] for the preparation of metal alkyl compounds by the action of alkyl radicals on metal mirrors. In the present study it was found that trifluoromethyl radicals reacted similarly with some metals.[2]

Free trifluoromethyl radicals were generated from either hexafluoroacetone[3] or hexafluoroethane.[4] Although previous workers have used other methods to generate trifluoromethyl radicals from these compounds, it was more convenient to use pyrolysis for the present study. The formation of the radicals from these compounds is indicated in the following equations:

$$CF_3CO\,CF_3 \longrightarrow 2\,CF_3\cdot + CO$$

$$F_3C\,CF_3 \longrightarrow 2\,CF_3\cdot$$

In order to determine the optimum experimental conditions using this procedure, preliminary investigations were

made using a tellurium metal mirror. Previous workers have established that tellurium was the metal which, in mirror form, reacted most satisfactorily with methyl radicals to form a single product whose physical and chemical properties enabled it to be readily isolated and identified.[5]

2. REACTION OF TRIFLUOROMETHYL RADICALS WITH TELLURIUM

Trifluoromethyl radicals reacted with a tellurium mirror forming a deep red liquid, similar in appearance to dimethylditelluride.[5] Its analysis was consistent with its formulation as bistrifluoromethyl-ditelluride. This previously unknown compound was the first perfluoroalkyl derivative of tellurium to be reported.[2] Bistrifluoromethylditelluride was found to be less stable at room temperature than was dimethyl-ditelluride and was slowly converted to a red solid polymeric material. Sunlight appeared to catalyse this process. However, in the dark, it could be kept for longer periods of time and at -78°C it could be stored indefinitely. It was soluble in chloroform, acetone and ethanol but insoluble in and unchanged by water. There was no obvious reaction when the compound was exposed to air. Hydrolysis with hot sodium hydroxide

solution caused the quantitative liberation of the trifluoromethyl groups as fluoroform, metallic tellurium being deposited in the solution. In this regard bistrifluoromethylditelluride showed a marked dissimilarity to its selenium analogue which, when treated with alkali, is decomposed to fluoride, carbonate, polyselenide ion and selenium.[6]

Bistrifluoromethylditelluride reacted instantly with mercury at room temperature to form bis(trifluoromethyltelluro)mercury. The analogous compounds, bis(trifluoromethylseleno)mercury[6] and bis(trifluoromethylthio)mercury,[7] have been prepared by similar reactions. The ease with which mercury reacts with these trifluoromethyl derivatives increases with increasing atomic number of the Group VI element. Thus, whereas the sulphur compound required ultra-violet irradiation to cause fission of the "metal-metal" bond, in the case of the selenium compound, the reaction with mercury was induced merely by shaking the mixture of reactants at room temperature. Bis(trifluoromethyltelluro)mercury was a crystalline solid, soluble in ethanol and acetone, from which it could be recrystallized as yellow plates.

3. REACTION OF TRIFLUOROMETHYL RADICALS WITH BISMUTH

The conditions used for the reaction of free

trifluoromethyl radicals with bismuth were identical with those found to be successful for the reaction with tellurium. In this case, however, the rate of formation of the product was extremely slow (less than one mgm. per hr.). The new material prepared in this manner was a colourless, rather involatile liquid whose infra-red spectrum possessed absorption bands indicating the presence of trifluoromethyl groups. Treatment of the compound with hot aqueous alkali caused the liberation of fluoroform. Positive tests for bismuth were made on a sample of the compound which had been previously decomposed by pyrolysis at 600°C.

Unfortunately the amounts of the material prepared using this technique were insufficient to enable quantitative analyses to be performed. Apart from the long time required to prepare even small samples, the compound, when formed, seemed to be unstable and, on standing at room temperature, deposited small amounts of solid on the walls of the containing vessel. Nevertheless it was apparent that a trifluoromethyl derivative of bismuth had been prepared. It was formulated as tristrifluoromethylbismuth. The only obvious alternative would be tetrakistrifluoromethyldibismuth but there were several objections to this choice. Firstly, by comparison with the incomplete evidence for the existence of the

methyl analogue, tetramethyldibismuth, reported by Paneth,[1] it was anticipated that tetrakistrifluoromethyldibismuth would probably be a solid of lower stability than tristrifluoromethylbismuth. Secondly, the dibismuth compound, again like tetramethyldibismuth as well as the ditellurides, would probably be highly coloured.

4. REACTION OF TRIFLUOROMETHYL RADICALS WITH LEAD

As there have been no reports of the existence of fully perfluoroalkylated lead derivatives, it was considered that the technique of passing trifluoromethyl radicals over a lead mirror might well be a route to such a compound. The mirror was most satisfactorily prepared by pyrolysing tetraethyl-lead vapour in the manner described by Paneth.[1] The rate of reaction of the trifluoromethyl radicals with the lead mirror was only slightly faster than that with the bismuth, and in this case also, the quantities of product were too small to permit complete analyses being performed. However, it was found that the compound which had been prepared contained both trifluoromethyl groups and lead. The compound was tentatively formulated as tetrakistrifluoromethyl-lead rather than hexakistrifluoromethyldilead, since formation of the latter under the conditions used was considered to be most unlikely, knowing that the alkyldilead compounds are particularly susceptible to disproportionation reactions.

5. REACTION OF TRIFLUOROMETHYL RADICALS WITH THALLIUM

The perfluoroalkyl chemistry of thallium has not been successfully studied to this stage and it was hoped that by using this rather unusual technique, trifluoromethylthallium compounds might be prepared. However no product was obtained when trifluoromethyl radicals were passed over a thallium mirror.

6. DISCUSSION

Clearly the reaction of trifluoromethyl radicals with metal mirrors, although capable of producing compounds not readily obtained by conventional techniques, had limited value as a synthetic method. Doubtless the technique could be improved by closely examining the effects of pumping speed, temperature of pyrolysis of the radical source, temperature of the metal mirror, rate of production of radicals, etc. However it was considered that such a detailed study was beyond the scope of the present investigation and once approximately optimum conditions for the system were determined, i.e. the conditions under which radicals reacted with tellurium to give an organometallic compound at what was considered to be a reasonable rate, they were not altered in subsequent experiments.

Qualitatively, there appeared to be no

significant difference in the rate at which methyl and trifluoromethyl radicals reacted with a particular metal. However there were great differences in the rates at which the free radicals reacted with the different metals selected for this study. Although the investigation was of a limited nature, it served to support Rice's[5] contention that tellurium was the element which, in mirror form, most readily reacted with free radicals to form a product which could be readily identified. So great was the difference in the rate of reaction of free radicals with tellurium compared with the other elements used in this series that it seemed to be necessary to consider some of the more important factors which may have been responsible for this difference.

(a) The Strength of the Metal-Metal Bonds

The strength of the metal-metal bonds in the crystal structure of the metal doubtless influenced the ease with which free radicals abstracted the metal atoms from the mirror surface. In Table 8.1 are listed the latent heat of sublimation of these metals. These were evaluated approximately using the following expression:

$$\Delta H_{sub(25^{o})} = C_p^{s}(T_{m.p.}-25) + \Delta H_{fus} + C_p^{l}(T_{b.p.} - T_{m.p.}) + \Delta H_{vap} - C_p^{v}(T_{b.p.} - 25)$$

where $\triangle H$ = latent heat of sublimation, fusion, and vaporization respectively,

and C_p = heat capacity for solid, liquid, and vapour respectively.

The thermodynamic values necessary for these calculations were obtained from the "Handbook of Chemistry."[9]

TABLE 8.1

Metal	M.Pt. (°C)	B.Pt. (°C)	Latent Heat of Sublimation (kcal./gm. atom)	Crystal Structure	Reaction Rate
Te	450	987	17.3	Hexagonal	Fast
Bi	271	1560	49.6	Rhombohedral	Slow
Pb	327	1750	48.6	F.C. Cubic	Slow
Tl	304	1467	43.5	C.P.Hex 230°B.C. Cubic	Nil

The latent heat of sublimation is an approximate measure of the ease with which atoms of the elements are released from the crystal structure. The marked difference between the value for tellurium and those for the other elements used was considered to be very significant. Thus the relatively low energy required to release tellurium from the metal mirror was probably one of the more important reasons for the faster rate at which the radicals reacted with this metal.

(b) Crystal Packing

In Table 8.1 are listed the crystal structures of the metals used in this study.[10] Although the structures are different in each case, there appeared to be no particularly significant difference in the way in which the tellurium atoms are packed at the metal surface as compared with the atoms of the other elements. It was therefore considered that the nature of the crystal packing was only of minor importance in these cases.

(c) Strength of the Metal-Carbon Bonds

Obviously the existence of an organometallic compound is dependent on the strength of the bond between carbon and the metal to which it is attached. Table 8.2 contains values of the energies of bonds between carbon and a number of elements,[11] including some of those under discussion. In general such values are not available for perfluoroalkyl organometallic compounds and only tentative conclusions could be drawn, assuming that the trends in the strengths of carbon-metal bonds applied in the cases where the hydrogen atoms attached to the carbon atoms were replaced by fluorine.

TABLE 8.2

Thermochemical Bond Energy Values for Elements Attached to Carbon

Group (B) III	E(kcal)	IV	E(kcal)	V	E(kcal)	VI	E(kcal)	VII	E(kca
B	89	C	83	N	73	O	86	F	116
Al	61	Si	72	P	63	S	65	Cl	81
Ga	-	Ge	-	As	48	Se	58	Br	68
In	-	Sn	54	Sb	47	Te	-	I	51
Tl		Pb	31	Bi	31				

Even though the values for the bond energies for the carbon-tellurium and carbon-thallium have not been measured, the trends within the Groups give an indication of the order of magnitude for such values in these cases. In a particular Group, the bond energy values decrease with increasing atomic number of the element attached to carbon. Inspection therefore suggested that the energy associated with the carbon-tellurium bond would probably be greater than those with the carbon-thallium, carbon-lead and carbon-bismuth bonds since tellurium is in the fourth row of the Periodic Table, while the other elements being discussed are in the fifth row.

It seemed reasonable to conclude therefore that the strength of the carbon-tellurium bond would be greater

than those of the other carbon-metal bonds and that a similar difference would also apply to the appropriate perfluoroalkyl derivatives.

(d) The Valence of the Metal

It was considered that the probability of forming an organometallic compound would decrease with increasing number of radicals which must be attached to the metal to satisfy its valence. In the case of tellurium, only one radical had to be attached to each metal atom, whereas bismuth and thallium each required three, while lead required four radicals.

(e) Steric Effects

The necessity for the attachment of more than one radical to the elements, other than tellurium, was considered to be the cause of yet another factor responsible for the slow rates of reaction found in these cases. Attachment of the first radical to the atoms on the metal surfaces no doubt limited the opportunity for other radicals to attach to the same atoms since the chance that the latter radicals might merely impinge on those already in position seemed to be high. The possibility that the attached radicals might even be removed by such a collision could not be ignored. This fact also could help account for the slower rate of reaction between the free radicals and these elements.

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CHAPTER IX

EXPERIMENTAL

This section of the work involved some specialised techniques in addition to the ones already described. The method of using the apparatus employed is understood by reference to the particular cases for which it was designed.

1. PREPARATION OF HEXAFLUOROACETONE

The method of preparation was based on that used by Morse et al.[1]

(a) Depolymerization and Dimerization

"Teflon" turnings (100 gm.) were packed into the sealed end of a heavy walled silica tube of internal diameter 4 cm. and length 80 cm. The turnings occupied approximately 20 cm. of this length. A tube furnace 15 cm. long was positioned such that the tetrafluoroethylene evolved when the "Teflon" was heated with a Meker burner, immediately passed through a zone in the silica vessel at 700-725°C. A pressure of approximately 70 cm. was maintained by controlling the rate of depolymerization and also by means of a tap located between the pyrolysis tube and the first collection trap. In this trap, cooled to -78°C, was collected the desired perfluoroisobutene, together with smaller amounts of the other

perfluorobutenes and some tetrafluoroethylene. The remainder of the unchanged tetrafluoroethylene was condensed in a subsequent trap at -196°C. A preliminary trap-to-trap vacuum fractionation through traps at -95, -135 and -196°C was performed, the separate fractions examined by infra-red spectroscopy and their molecular weights determined by Regnault's method. The material collecting in the trap at -95°C had an infra-red spectrum almost identical with that of perfluoroisobutene.[2] Those bands appearing in the spectrum of the sample which do not appear in that of authentic samples of perfluoroisobutene could be accounted for in terms of the presence of small amounts of perfluorocyclobutane. The molecular weights of these two substances are identical, so that their relative amounts in the mixture could not be determined by such a measurement (Found: mol.wt. 200. Calc. for C_4F_8: mol.wt. 200). Nor could separation be effected by vapour phase chromatography using as column packing materials, di-isodecyl phthalate, silver nitrate or dimethylsulphalone, irrespective of the variety of temperatures and carrier gas flow rates tried.

The material collecting in the trap at -135°C was distilled using an apparatus fitted with a Podbielniak[3] type fractionating column, and three main fractions of

approximately equal size were obtained, their boiling points being -75, -32 and -11° respectively. These fractions were examined as follows:-

(i) Fraction of Boiling Point -75°C

This fraction had an infra-red spectrum identical with that of tetrafluoroethylene (Found: mol.wt. 99. Calc. for C_2F_4: mol.wt. 100).

(ii) Fraction of Boiling Point -32°C

This fraction was shown to be pure perfluoropropene. Its infra-red spectrum was identical with that of the authentic compound as also was its molecular weight (Found: mol.wt. 149. Calc. for C_3F_6: mol.wt. 150).

(iii) Fraction of Boiling Point -11°C

The infra-red spectrum of this fraction closely resembled that of perfluoroisobutene, the small differences being interpreted as due to the presence of traces of the other C_4F_8 isomers. The molecular weight was also in agreement with the material being formulated as perfluoroisobutene (Found: mol.wt. 200. Calc. for C_4F_8: mol.wt. 200).

(b) Oxidation of Perfluoroisobutene

The apparatus used in the oxidation of perfluoroisobutene to hexafluoroacetone hydrate is represented in Figure 9.1. Potassium permanganate (150 gm.) and 600 ml. 5N sulphuric acid were placed in the reaction vessel B. The fractions containing perfluoroisobutene (75 gm.) were combined and condensed into the trap A which was then connected to a glass tube so that when the fluoro-olefin was allowed to warm to 0-10°C, it passed well below the surface of the permanganate solution. The solution was vigorously agitated by means of a magnetic stirrer and the gas passed into it at such a rate that the cold finger condenser at -78°C attached to the outlet of the reaction vessel would return the unreacted material to the oxidising solution. The carbon dioxide produced in the reaction passed through the condenser into the atmosphere. The temperature of the reaction mixture was raised to 40°C and the oxidation completed in four hours. The excess permanganate was then removed by bubbling sulphur dioxide into the solution. The precipitated manganese dioxide was removed by filtration. The filtered solid was washed with water (200 ml.) and the combined filtrates extracted for 24 hrs. with ether in a continuous extraction apparatus (see Figure 9.2). The ether solution was then

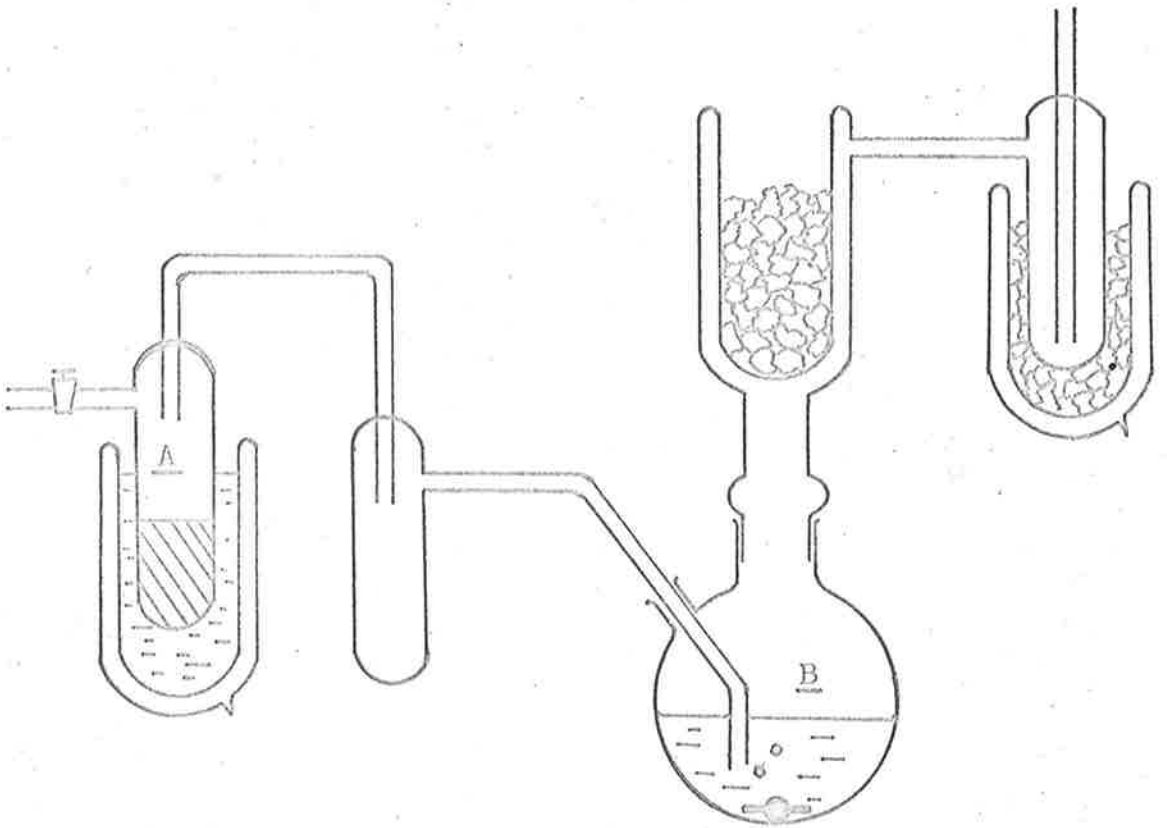

FIGURE 9.1

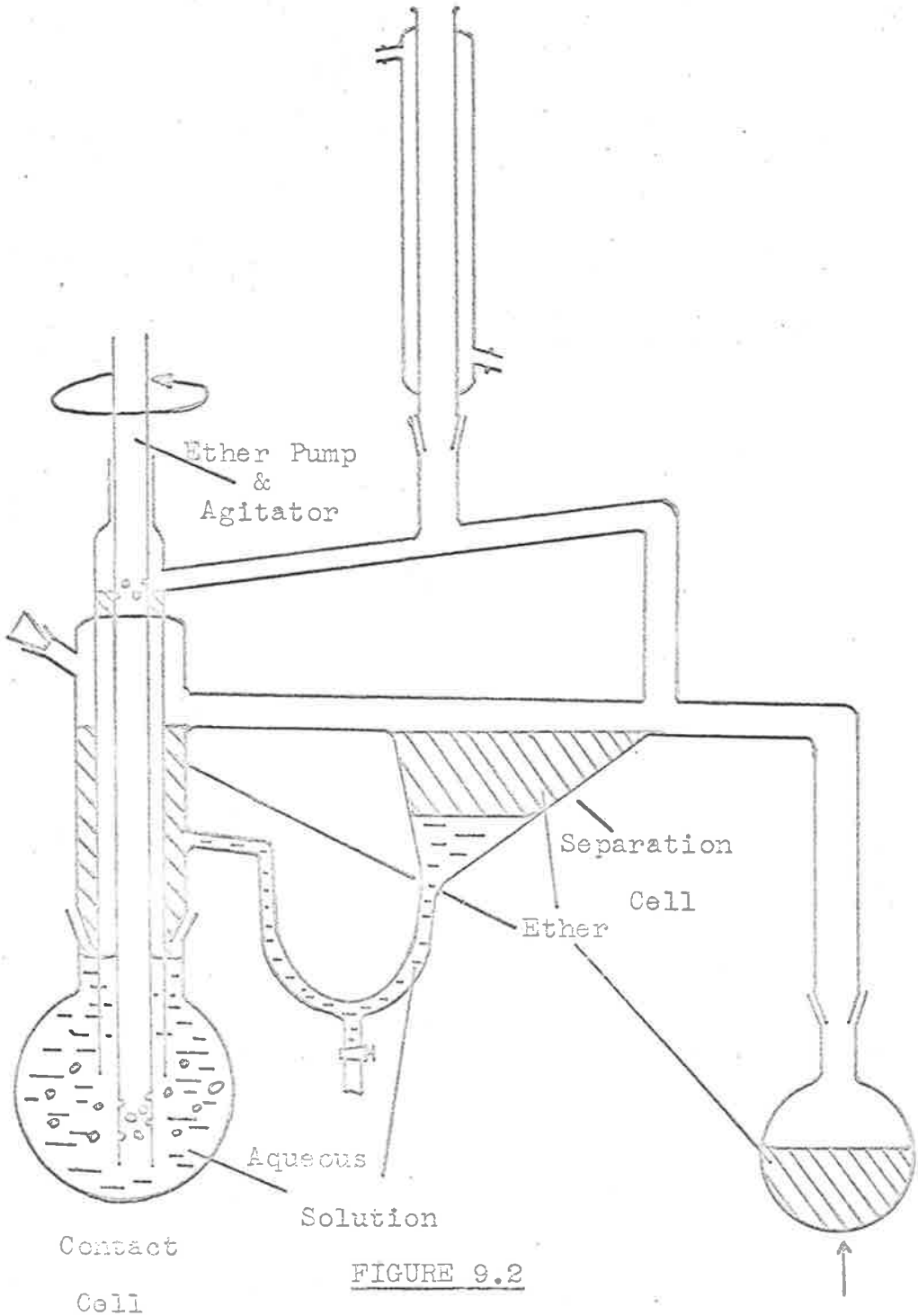
Ether Pump
&
Agitator
Separation
Cell
Ether
Aqueous
Solution
Contact
Cell

FIGURE 9.2

separated from the aqueous layer, dried over sodium sulphate and most of the solvent removed by distillation at atmospheric pressure. A subsequent distillation at reduced pressure yielded hexafluoroacetone hydrate (b.pt. 55°C at 80 mm.)(37 gm., 59% yield based on perfluoroisobutene).

(c) Dehydration of Hexafluoroacetone Hydrate

Dehydration was accomplished by dropping hexafluoroacetone hydrate onto phosphorus pentoxide. The free hexafluoroacetone evolved (Found: mol.wt. 158. Calc. for C_3F_6O: mol.wt. 158) was collected in a trap at -196°C. The yield was 34 gm. indicating that complete conversion of the hydrate to the desired product had occurred.

2. REACTION OF RADICALS WITH METAL MIRRORS

In order to establish the optimum conditions for the reaction of free radicals with metal mirrors, acetone was used as a source of radicals, both because of its availability and because of its similarity to hexafluoroacetone. According to Rice and Glasebrook,[4] tellurium was the metal which, in mirror form, most readily reacted with free radicals to form a product whose physical and chemical characteristics were conducive to

its ready isolation and identification. Consequently tellurium was the metal used in these preliminary experiments.

(a) Reaction of Methyl Radicals with Tellurium

The apparatus used is shown in Figure 9.3. "Analytical" grade acetone was placed in the supply bulb A. Section C, the pyrolysis and reaction zone, was made of heavy wall silica tube, the rest of the apparatus being constructed of glass. A single piece of tellurium metal (0.1-0.2 gm.) was placed in the reaction tube such that the mirror would be formed just on the pump side of the zone heated by the movable tube furnace D. The mirror was formed merely by gently heating the solid tellurium after the whole apparatus had been evacuated. By carefully applying the heat, it was possible to obtain a mirror of approximately uniform thickness and 2-3 cm. long. The furnace temperature was controlled at 860°C and the acetone admitted through the stop-cock B so that a pressure of 2-2.5 mm. was maintained at full pumping speed. The high temperature used was necessary to pyrolyse the acetone which was passing through the heated zone very rapidly. In the traps E and F which were cooled to -46°C, was condensed the red liquid, dimethylditelluride, described by Rice and Glasebrook. The unpyrolysed acetone

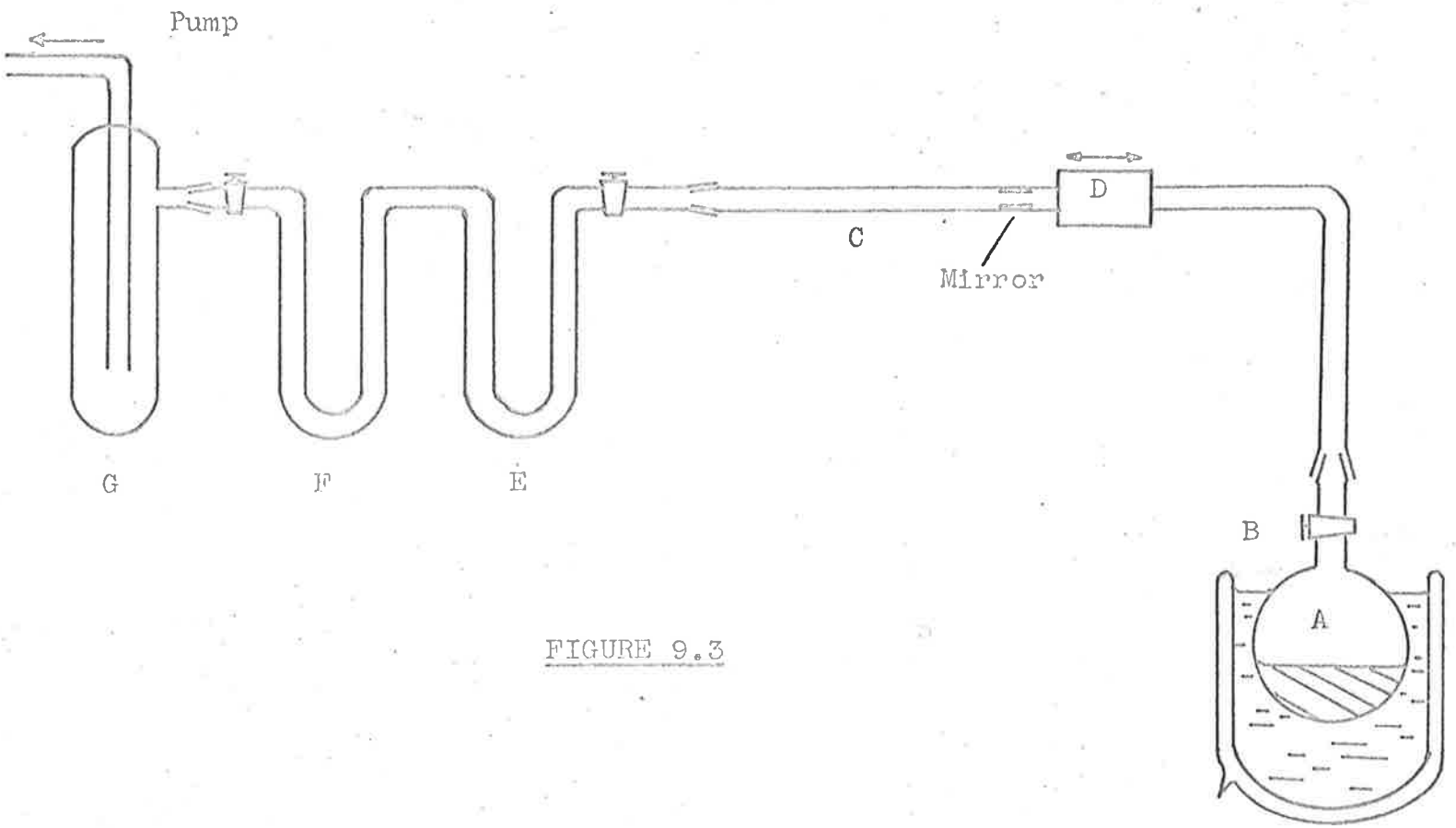

FIGURE 9.3

collected in the trap at -196°C (G). Other pyrolysis products, e.g. carbon monoxide, ethane, etc., either collected in this trap also or passed through the pump, depending on their vapour pressures at -196°C. As the edge of the mirror nearest the furnace slowly moved away from its original position, due partly to the attack on it by methyl radicals and also due to volatilization, the position of the furnace was adjusted so that the distance between it and the mirror was 1 cm. An approximate assessment of the progress of the reaction and its rate was made periodically, by strongly heating with a Meker burner a portion of the silica tube between the original mirror and the collecting traps. This caused pyrolysis of any organometallic compound which may have been formed and the resultant deposition of a new metal mirror on the walls of the tube. After two hrs., 10-15 mgm. of dimethylditelluride (Found: Te, 88.9%. Calc. for $C_2H_6Te_2$: Te, 89.5%) had collected. These conditions were optimum for the system and apparatus employed and were reproduced as accurately as possible in subsequent experiments.

(b) Reaction of Methyl Radicals with Bismuth

The apparatus and experimental conditions used were the same in this case as for the reaction of methyl

radicals with tellurium. Greater difficulty was experienced in forming the metal mirror in this case since bismuth, apart from being more difficult to volatilize, tended to aggregate into droplets rather than form the thin film required for the successful application of this technique. During the passage of the pyrolysis products of acetone over the bismuth mirror, evidence for the formation of a volatile bismuth compound was indicated by the deposition of a new bismuth mirror when strong heat was applied to a small section of the silica tube C, at a point between the reaction zone and the first collection trap. Normally trimethylbismuth could be condensed at -46°C in an evacuated apparatus, but in this system it was necessary to use a trap cooled to -78°C in order to condense any organobismuth compound formed, since, at the high pumping speeds used, the larger quantities of more volatile materials tended to delay the condensation of the bismuthine. At -78°C there was partial condensation of unpyrolysed acetone, with the result that great difficulty was experiences in fractionating the extremely small quantity of trimethylbismuth (ca. 3 mgm.) from the relatively large amounts of acetone (ca. 2 gm.). Repeated trap-to-trap distillation finally yielded a sample whose infra-red spectrum was identical with that of authentic trimethylbismuth.

(c) Reaction of Trifluoromethyl Radicals with Tellurium

Trifluoromethyl radicals were generated by passing hexafluoroacetone[5] at 2 mm. pressure through a zone heated to 900°C in the reaction tube. As the radicals passed over the preformed tellurium mirror, a deep red liquid slowly collected in a trap cooled to -46°C. The liquid compared in appearance with the dimethyldi-telluride obtained by passing methyl radicals over tellurium. The new material was fractionated in the vacuum system by trap-to-trap distillation to remove traces of other reaction products and unpyrolysed ketone, until reproducible infra-red spectra, showing no absorption band corresponding to carbonyl C-O stretching, were obtained. The crude product, prior to the purification procedure described above, contained some silicon tetra-fluoride, formed by the action of small amounts of atomic fluorine, resulting from the pyrolysis of hexafluoroacetone, on the walls of the silica reaction vessel. The strong band at 1025 cm.$^{-1}$ in the infra-red spectrum, characteristic of silicon tetrafluoride,[2] disappeared completely when the reaction products were fractionally distilled twice. The bistrifluoromethylditelluride remained in the trap at -46°C and all the by-products passed into that at -196°C. Bistrifluoromethylditelluride (Found: CF_3, 34.1; Te, 66.2%.

Calc. for $C_2F_6Te_2$: CF_3, 35.0; Te, 65.0%) melted at approximately -73°C, but due to its thermal instability and tendency to polymerize, its boiling point could not be determined. Ir the light it was less stable at room temperature than dimethylditelluride, although it could be kept in the dark for considerable periods of time and indefinitely at -78°C. It was soluble in most organic solvents, stable in air, insoluble in and unchanged by water.

(i) Analysis

The compound was analysed for CF_3 by hydrolysis with alkali and measurement of the quantity of liberated fluoroform.

Tellurium was estimated as the metal in the solution after hydrolysis.

(ii) Hydrolysis

Bistrifluoromethylditelluride (0.032 gm., 0.082 mmole), when treated with 5N sodium hydroxide (5 ml.) at 95°C for two hrs, gave a virtually quantitative yield of fluoroform (0.011 gm., 0.16 mmole) which was purified by distillation in the vacuum system. Metallic tellurium was deposited in the solution as the reaction proceeded.

(iii) Infra-red Spectrum

The infra-red spectrum of bistrifluoromethyl-ditelluride in the vapour phase possessed the following main absorption bands: 1367 (w), 1321(m), 1219(s), 1150(s), 1088(s), 1043(s), 917(m), 722(s).

(iv) Reaction with Mercury

Bistrifluoromethylditelluride (0.024 gm., 0.061 mmole) was condensed onto mercury (0.011 gm., 0.055 mmole) in an evacuated tube. At room temperature reaction occurred, indicated by the appearance of a yellow solid in the place of the mercury and the red liquid tellurium compound. The volatile material was removed by pumping and shown by infra-red spectral analysis to be bistrifluoromethylditelluride. The weight of the product remaining (0.033 gm.) corresponded to the combination of the reactants in equimolar proportions. By analogy to the comparable reaction of bistrifluoro-methyldiselenide with mercury, this new compound was considered to be bis(trifluoromethyltelluro)mercury. It was soluble in ethanol from which it could be crystallized as a yellow solid stable in air and possessing a most objectionable odour.

(d) Reaction of Trifluoromethyl Radicals with Bismuth

A bismuth mirror was formed in the manner

described previously and a stream of trifluoromethyl radicals passed over it for six hrs. During this operation, to deposit a detectable quantity of a second mirror by the pyrolysis of the new organometallic compound formed, it was necessary to heat for as long as ten mins. a section of the tube through which the products were passing. At the completion of the reaction, a small quantity (ca. 5 mgm.) of a rather involatile, colourless liquid had been retained in the collection trap cooled to -46°C. Infra-red analysis revealed the presence of CF_3 groups in this liquid but during the measurement it was noticed that the windows of the gas cell were becoming opaque due to decomposition of the sample. This was possibly caused by traces of water and oxygen on the walls and windows of the cell which could not be completely decontaminated using the customary technique of flaming. Hydrolysis of the sample caused the liberation of fluoroform. However, quantitative determinations of both bismuth and CF_3 (as fluoroform) were unsuccessful due to the very small amounts of material available and to the consequent significant losses in handling. Nevertheless it was apparent that a trifluoromethylbismuth compound had been formed and that this material was at least thermally and possibly chemically unstable. It has been tentatively formulated as tristrifluoromethylbismuth.

(e) Reaction of Trifluoromethyl Radicals with Lead

A lead mirror was prepared by pyrolysing tetraethyl-lead vapour as it passed through the reaction tube. Thus a stream of the vapour was pumped through the system and heat applied with a Meker burner to a section of the silica tube such that a lead mirror was deposited in the prospective reaction zone. The apparatus was then flamed to remove all traces of unchanged tetraethyl-lead and its volatile pyrolysis products before the reaction between the trifluoromethyl radicals and the metal was commenced. After treatment of the lead mirror with the free radicals for six hrs., a small quantity of liquid had collected in the trap at -78°C, the unchanged hexafluoroacetone and most of its decomposition products condensing at -196°C. Several trap-to-trap distillations were necessary to remove traces of hexafluoroacetone from a rather involatile, colourless liquid whose infra-red spectrum possessed no band corresponding to the carbonyl C-O stretching frequency but did have bands suggesting the presence of trifluoromethyl groups. The material was hydrolysed by hot 5N sodium hydroxide and fluoroform was produced. In addition, application of strong heat to a sample of the liquid caused deposition of metallic lead. Thus it was concluded that a trifluoromethyl-lead compound had been formed even though quantitative analyses could

not be performed due to the extremely small amounts of material prepared by this method. The substance was formulated as tetrakistrifluoromethyl-lead.

(f) Reaction of Trifluoromethyl Radicals with Thallium

A thallium mirror was prepared in the same manner as that used for tellurium and bismuth, although more difficulty was experienced in the case of thallium. After the passage of trifluoromethyl radicals over this metal for six hrs., no trace of a trifluoromethylthallium compound had collected in the traps provided.

3. Trifluoromethyl Radicals derived from Hexafluoroethane

Although trifluoromethyl radicals could be generated from hexafluoroacetone quite readily,[5] this source suffered from several disadvantages. Firstly, the preparation of hexafluoroacetone was difficult and took several days to complete. Secondly, the pyrolysis of the ketone produced, in addition to trifluoromethyl radicals, an appropriate amount of carbon monoxide and a number of other products which tended to complicate the system. Thirdly, the pyrolysis led to the formation of products which did not revert to the parent compound if not used in combination with the metal. Thus those radicals which did not undergo effective reaction with the

metal were wasted. Attention was therefore turned to hexafluoroethane as a source of trifluoromethyl radicals since it could be obtained commercially (E. I. Du Pont De Nemours and Co. Inc.).

The apparatus is shown in Figure 9.4. Hexafluoroethane gas was condensed into the appendix B of the bulb A and a cooling bath at a temperature calculated to give the desired vapour pressure of hexafluoroethane placed around the appendix. The quantity of gas used was sufficient to fill the bulb (3 l.) at atmospheric pressure. The gas, at the appropriate pressure, was then led into the glass reaction tube C at an acute angle in order to minimize turbulence and so ensure an even flow through the reaction zone. A platinum filament D wound on a silica tube (8 mm. diameter) was used to pyrolyse the hexafluoroethane. The silica former was joined through a "graded seal" to the reaction tube. In order to produce the mirror of a particular metal, a few small pieces of the metal previously placed in the appendix E were heated by means of a Meker burner and the vapour condensed onto the movable former F. This former consisted of a Pyrex glass tube, sealed at the base and containing silicone oil into which dipped a thermometer to indicate the reaction temperature. It was found most

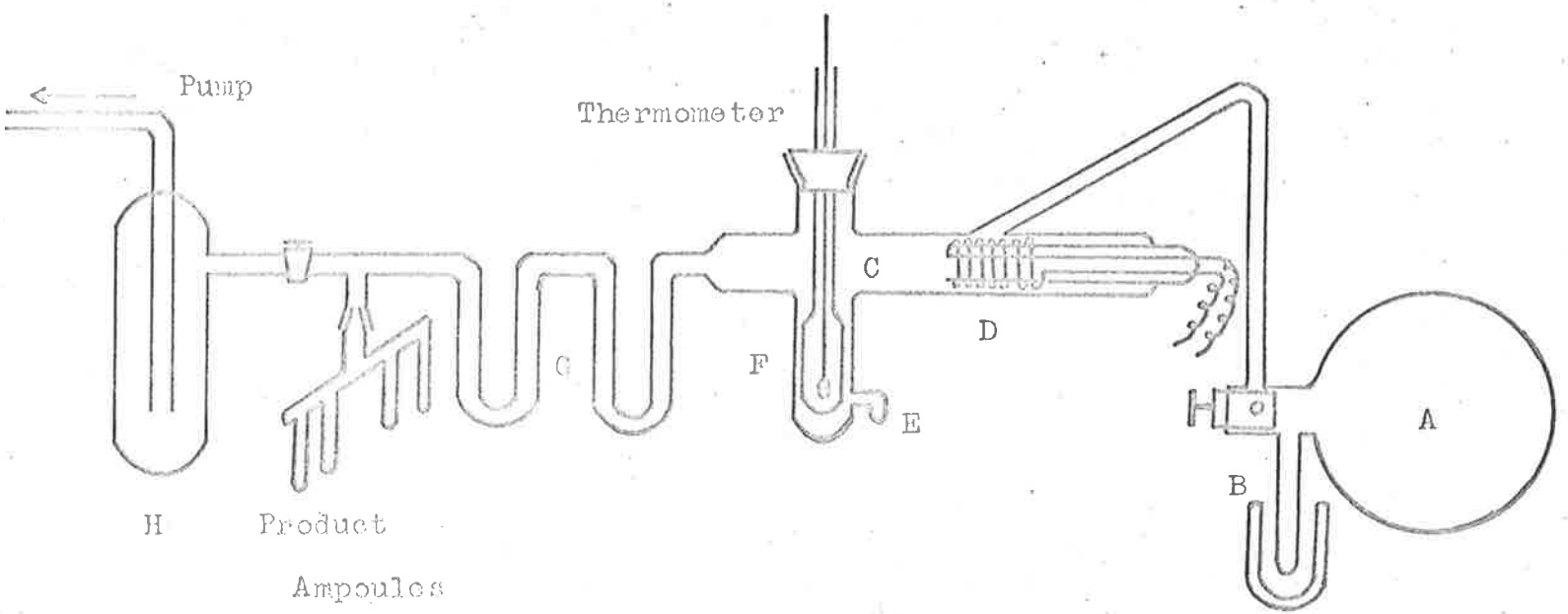

FIGURE 9.4

convenient to attach the former to the rest of the apparatus through a tightly fitting rubber stopper which, when lightly lubricated with a high temperature vacuum grease, was capable of holding a vacuum. By rotating the former when necessary, an evenly plated mirror was obtained. The mirror was then retracted to a position directly in line with the filament and 0.5-1.0 cm. from it. The filament was then heated till bright red-white by application of a suitable e.m.f. to the conducting leads, and hexafluoroethane passed through the system, whereupon free trifluoromethyl radicals were generated. The product formed by reaction of the radicals with the particular metal was condensed into a trap G at -78°C, the excess hexafluoroethane collecting in a trap H at -196°C located immediately before the vacuum pump.

The results obtained using this method with tellurium and bismuth were the same as those obtained when hexafluoroacetone was used as the source of free radicals. Both methods suffered from the obvious disadvantage in that only very small amounts of products could be obtained after many hours of operation.

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CHAPTER X

ATTEMPTED PREPARATIONS OF PERFLUOROALKYLTHALLIUM COMPOUNDS

1. INTRODUCTION

This section of the work is concerned with a preliminary study of a number of methods used in attempts to prepare perfluoroalkylthallium compounds. No such derivatives have been reported in the literature as yet. The variety of experimental conditions employed is described in Chapter XI.

Both mono- and tri-valent states of thallium are known to be stable in some circumstances, but whereas there is evidence for the existence of methylthallium and phenylthallium, the only stable organometallic dervatives of this element are those in which its valency is three.[1,2] In this study attempts were first made to synthetize perfluoroalkylthallium compounds by group exchange reactions using a variety of methylthallium compounds and perfluoroiodoalkanes. In all cases the desired products were not obtained and a number of other preparative methods were also tried, again without success.

2. REACTION OF TRIMETHYLTHALLIUM WITH PERFLUOROIODOALKANES

Trimethylthallium reacted violently and exothermically with trifluoroiodomethane and with heptafluoroiodopropane, at room temperature. A mixture of

coloured products, apparently heterogeneous in nature, was obtained and considered to have resulted from at least partial decomposition both of the starting materials and the products formed initially. By lowering the reaction temperature to -78°C however, it was possible to control the reaction and in each case a white solid was obtained. When the obvious signs of reaction had ceased, the mixture was allowed to warm to room temperature but no further reaction appeared to occur and the white solid did not become discoloured. The properties and the analysis of this product suggested it to be dimethylthallium fluoride. This was certainly not anticipated, since the rupture of a carbon-fluorine bond in a perfluoroiodoalkane during a reaction with an organometallic compound is most uncommon. It was thought that the initial reaction involved the formation of the appropriate dimethylperfluoroalkylthallium compound in each case and that this was extremely unstable, even at -78°C, and decomposed giving dimethylthallium fluoride. A similar reaction has been observed when tetramethyltin was treated with perfluoroiodoalkanes at higher temperatures, one product being in each case, trimethyltin fluoride.[8] Here also it was considered by the workers that the reaction involved the initial formation of the appropriate alkylperfluoroalkyl derivative, which then underwent thermal

decomposition. This mechanism was supported by the fact that pyrolysis of samples of trimethyltrifluoromethyltin yielded trimethyltin fluoride together with tetrafluoroethylene and perfluorocyclopropane.[4] In the present preliminary study, the volatile products of the reactions between trimethylthallium and perfluoroiodoalkanes were identified as methyl iodide and a fluorocarbon fraction. However the latter was not examined further.

The production of dimethylthallium fluoride in the reactions studied in this investigation indicated just how great the tendency is to form dialkylthallium halides which are known to be amongst the most stable and least reactive organometallic compounds.[1]

3. REACTION OF DIMETHYLTHALLIUM IODIDE WITH TRIFLUOROIODOMETHANE

By shaking at room temperature a mixture of dimethylthallium iodide, trifluoroiodomethane and excess mercury, it was hoped that halogen elimination would be induced in a manner similar to that observed when iodoarsines are treated with perfluoroiodoalkanes under these conditions to give perfluoroalkylarsines.[5]

The fact that an attempted reaction of dimethylthallium iodide with trifluoroiodomethane was not

successful supported the fact that this class of thallium compounds, i.e. dialkylthallium halides, are as stable as was previously indicated. There appeared to be no tendency for perfluoroiodoalkanes to attack more than one alkyl group in a trialkylthallium compound nor any group once the first such group had been replaced by a halogen.

4. REACTION OF THALLIUM ACETYLACETONATES WITH TRIFLUOROIODO-METHANE

A reaction between thallous acetylacetonate and trifluoroiodomethane to give iodotrifluoromethylthallium acetylacetonate was considered to be possible and accordingly the reaction was attempted. However no reaction occurred until a temperature of 150°C was reached but no trifluoromethylthallium compound was formed. Instead there was partial degradation of some of the acetylacetone groups and hydrogen abstraction from them by the trifluoromethyl group of trifluoroiodomethane, giving fluoroform. Most of the thallium remained in the form of the starting material but some had been converted to thallous iodide by the action of iodine which had been liberated from the trifluoroiodomethane. No volatile thallium compound was formed and infra-red spectral analysis indicated that no trifluoromethyl groups were present in the solid reaction product.

Similar products were obtained when dimethylthallium acetylacetonate was treated with trifluoroiodomethane at 150°C. Again partial decomposition of some of the acetylacetone groups occurred and fluoroform was produced. However no perfluoroalkylthallium compound was prepared using this method.

5. REACTION BETWEEN METHYL-LITHIUM, THALLOUS IODIDE AND HEPTAFLUOROIODOPROPANE

The preparation of trimethylthallium from thallous iodide, methyl-lithium and methyl iodide[6] may be represented by the following equation:

$$2CH_3Li + CH_3I + TlI \longrightarrow (CH_3)_3Tl + 2LiI$$

It seemed feasible that, by substituting a perfluoroiodoalkane for methyl iodide in such a reaction mixture, a perfluoroalkylthallium compound might form. Heptafluoroiodopropane was chosen for such an experiment due to the ease with which it could be handled in an open apparatus. This particular reaction was examined before it was discovered that the reaction between trimethylthallium and perfluoroiodoalkanes yielded dimethylthallium fluoride and so suggesting that perfluoroalkylthallium compounds were extremely unstable.

The reaction did not yield a perfluoroalkyl-thallium compound but gave instead dimethylthallium iodide. The formation of a dimethylthallium halide from such a reaction was not altogether surprising in view of the results of the other experiments described in this Chapter. On examining the mechanism proposed by Gilman for the reactions thought to occur during the preparation of trimethylthallium, it was anticipated that products in addition to those actually found, would have been formed in the present case. The mechanism in question involved the initial reaction of methyl-lithium with thallous iodide to give trimethylthallium and metallic thallium in a finely divided and highly reactive state. The transient existence of the latter product was actually observed during these preparations.

$$3CH_3Li + 2Tl\,I \longrightarrow (CH_3)_3Tl + 2\,Tl + 3\,LiI$$

The second stage proposed involved reaction of methyl iodide with the thallium metal to form dimethylthallium iodide.

$$2\,CH_3I + 2\,Tl \longrightarrow (CH_3)_2Tl\,I + Tl\,I$$

In the reaction employing heptafluoroiodopropane instead of methyl iodide, some reaction might be expected at this

stage to give a perfluoroalkylthallium compound or its decomposition products. No such compounds were found however. The final step in the mechanism was considered to be the reaction of methyl-lithium with dimethylthallium iodide.

$$CH_3Li + (CH_3)_2TlI \longrightarrow (CH_3)_3Tl + LiI$$

The results of the reaction involving heptafluoroiodopropane suggested that either the mechanism described above was not correct or more likely that the mode of reaction was different when the alkyl iodide was replaced by a perfluoroiodoalkane in such a reaction.

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CHAPTER XI

EXPERIMENTAL

1. PREPARATION OF REACTANTS

(a) Trimethylthallium[1]

Lithium metal (3.5 gm., 0.50 mole) was washed free of paraffin oil with sodium-dried ether, beaten into flat plates and cut into small pieces under an atomsphere of dry nitrogen. The lithium was then placed in a flask together with ether (60 ml.) and a solution of methyl iodide (28 gm., 0.20 mole) in ether (60 ml.) added dropwise at such a rate as to maintain reflux. When all the methyl iodide had been added, refluxing was continued for one hr. and the unreacted lithium (0.7 gm., 0.10 mole) removed by filtering through glass wool under an inert atmosphere. An excess of lithium was used to ensure the complete removal of methyl iodide in order that subsequently an accurately known quantity of this compound could be added to the mixture. The methyl-lithium, now in a dropping funnel, was added dropwise to a vigorously stirred suspension of thallous iodide (28.9 gm., 0.067 mole) in a solution of methyl iodide (11.4 gm., 0.08 mole) in ether (25 ml.). The final reaction mixture was then allowed to stand for 18 hrs. before the ether was removed by distillation using a water-bath at 70-80°C.

The residue was not heated above 90°C and all the volatile constituents were transferred under vacuum from the reaction vessel into the vacuum system. Trap-to-trap distillation was then used to separate trimethylthallium (9.33 gm., 0.037 mole) from the other volatile constituents of the mixture. The yield was 55% based on thallous iodide.

(b) Dimethylthallium Iodide[2]

Methyl-lithium (0.16 mole, 70% yield) was prepared from lithium (3.2 gm., 0.44 mole) in diethyl ether (50 ml.) and methyl iodide (31.2 gm., 0.22 mole) in ether (150 ml.). The methyl-lithium was added over a period of 30 min. to a stirred suspension of thallous chloride (19.2 gm., 0.08 mole) in ether (100 ml.). A jet black precipitate of thallium metal formed. The mixture was stirred for a further 15 min. before excess methyl iodide (15.6 gm., 0.11 mole) in ether (100 ml.) was added and stirring continued until the black precipitate had completely disappeared (one hr.). The insoluble material was allowed to settle; the clear supernatant solution was siphoned off under nitrogen and hydrolysed with water. The dried ether layer, when evaporated, yielded dimethylthallium iodide (21 gm., 0.058 mole - 72% yield based on thallous chloride).

(c) Thallous Acetylacetonate[3]

Thallous sulphate (15.2 gm., 0.03 mole) and barium hydroxide octahydrate (11.3 gm., 0.03 mole) were each separately dissolved in a minimum of water and the solutions mixed thoroughly. The barium sulphate was removed by filtration, washed several times with water and the filtrate evaporated to give yellow crystals of thallous hydroxide (11.5 gm., 0.052 mole). This, together with acetylacetone (5.2 gm., 0.052 mole) was dissolved in ethanol and the solution concentrated at room temperature under vacuum. Thallous acetylacetonate was obtained quantitatively as colourless crystals (Found: C, 19.8; H, 2.32%. Calc. for $C_5H_7O_2Tl$: C, 19.8; H, 2.31%).

(d) Dimethylthallium Acetylacetonate[4]

Dimethylthallium iodide (3.6 gm., 0.010 mole) and thallous acetylacetonate (3.0 gm., 0.010 mole) were reacted in boiling ethanol. Reaction had ceased when a filtered amples of the mixture yielded with potassium iodide, a white precipitate of dimethylthallium iodide (from dimethylthallium acetylacetonate) not contaminated with yellow thallous iodide (from unreacted thallous acetylacetonate). On cooling the filtered reaction mixture crystals of dimethylthallium acetylacetonate were deposited

and after vacuum sublimation had m.pt. 214°C (Lit.[4] m.pt. 214°C).

2. REACTIONS OF THALLIUM COMPOUNDS WITH PERFLUOROIODO-ALKANES

(a) Trimethylthallium and Trifluoroiodomethane

Trimethylthallium (2.39 gm., 0.0096 mole) and trifluoroiodomethane (4.93 gm., 0.025 mole) were condensed into an evacuated tube and the temperature allowed to rise from -196 to -78°C. A white solid began to deposit rapidly from the clear solution. (It was found in preliminary experiments that if the temperature was allowed to rise to approximately -10°C, a violent exothermic reaction occurred and could not be controlled even by plunging the reaction tube into liquid nitrogen. The solid deposited under such conditions was almost black and was heterogeneous in appearance. It was thought to consist of decomposition products of both the reactants and initial products.) When all obvious signs of reaction had ceased (one hr.), the reaction mixture was allowed to stand at room temperature for 24 hrs., after which time the solid still remained white and no further change had occurred. The volatile materials were then transferred to the vacuum system where they were fractionated

through traps at -95, -135 and -196°C. Two fractions so obtained were identified as trifluoroiodomethane (Found: mol.wt. 196. Calc. for CF_3I: mol. wt. 196), methyl iodide (Found: mot.wt. 143. Calc. for CH_3I: mol.wt. 142). The infra-red spectra of these compounds were recorded and compared with those of authentic samples. In addition, vapour phase chromatography and infra-red spectroscopy suggested that a fluorocarbon was also present in the volatile mixture. However in this preliminary investigation, attempts were not made to identify it or even to ascertain whether or not there was a mixture of fluorocarbons present which had not been separated on the particular chromatographic column used.

The solid reaction product remaining after removal of the volatile constituents of the mixture was stable at room temperature and did not melt even at 300°C. It was stable in air and soluble in water yielding a strongly basic solution. It was soluble in ethanol but insoluble in benzene and chloroform. These properties,[5] together with its analysis (Found: C, 9.48; H, 2.43; F, 6.8; Tl, 79.8%. Calc. for C_2H_6TlF: C, 9.49; H, 2.37; F, 7.5; Tl, 80.6%) suggested that the solid was dimethylthallium fluoride. Addition of sodium tetraphenylborate to an aqueous solution of the thallium

compound caused the precipitation of a white solid which, when recrystallized from acetone containing 5% water, was shown to be dimethylthallium tetraphenylborate (Found: C, 56.1; H, 4.81%. Calc. for $C_{26}H_{26}TlB$: C, 56.4: H, 4.70%). The conversion of trimethylthallium to dimethylthallium fluoride (2.32 gm.) was 96%.

(b) Trimethylthallium and Heptafluoroiodopropane

Trimethylthallium (2.45 gm., 0.010 mole) and heptafluoroiodopropane (8.09 gm., 0.027 mole) were allowed to stand in a sealed tube for two hrs. at -78°C. A white solid deposited at this temperature and appeared to be unchanged after the mixtures was allowed to stand at 20°C for a further 15 hrs. At the end of this time, the volatile materials were transferred to the vacuum system where they were fractionated by trap-to-trap distillation through traps at -78, -95 and -196°C. The various components were identified with the aid of vapour phase chromatography, infra-red spectroscopy and molecular weight measurement, and were found to be methyl iodide (Found: mol.wt. 142. Calc. for CH_3I: mol.wt. 142) and unreacted heptafluoroiodopropane (Found: mol.wt. 295. Calc. for C_3F_7I: mol.wt. 296). A third volatile component of the reaction products, containing C-F bonds, was not positively identified. The solid reaction

product possessed properties identical with those of the solid produced from the reaction between trifluoroiodomethane and trimethylthallium and was also proved to be dimethylthallium fluoride (Found: C, 9.41; H, 2.41; F, 6.8; Tl, 81.1%. Calc. for C_2H_6TlF: C, 9.49; H, 2.37; F, 7.5; Tl, 80.6%). The conversion of trimethylthallium to dimethylthallium fluoride (2.52 gm.) was 100%.

(c) Dimethylthallium Iodide and Trifluoroiodomethane

Dimethylthallium iodide (10.0 gm., 0.028 mole), trifluoroiodomethane (14.7 gm., 0.075 mole) and excess mercury (100 gm.) were shaken at room temperature for 65 hrs No reaction had occurred under these conditions and the reactants were recovered quantitatively. It was not considered that this approach warranted further investigation in view of the results of the previous two experiments described.

(d) Thallous Acetylacetonate and Trifluoroiodomethane

Thallous acetylacetonate (3.03 gm., 0.010 mole) and trifluoroiodomethane (6.67 gm., 0.034 mole) were heated in a sealed tube for 60 hrs. at 150°C. The volatile reaction products were transferred to the vacuum system where they were fractionated through traps at -95, -135 and -196°C. The material in the trap at -196°C was

mainly fluoroform, but both the infra-red spectrum of the sample and its low molecular weight (Found: mol.wt. 58. Calc. for CHF_3: mol.wt. 70) suggested that degradation products of acetylacetone were also present. The material retained in the trap at -135°C was mainly trifluoroiodomethane, but infra-red analysis again indicated the presence of products formed by the decomposition of the acetylacetone fragment. Similar products were found in the trap at -95°C, but chemical analysis indicated that no thallium compounds were present in any of the volatile fractions.

The solid reaction product was yellow and not colourless as was the starting material. Its infra-red spectrum indicated the absence of trifluoromethyl groups and suggested that it consisted mainly of thallous acetylacetonate together with smaller amounts of material formed by the partial pyrolysis of that compound. Small amounts of iodide were also detected in the solid residue. This was no doubt derived from trifluoroiodomethane and was probably present as thallous iodide.

(e) Dimethylthallium Acetylacetonate and Trifluoroiodomethane

Dimethylthallium acetylacetonate (2.7 gm., 0.008 mole) and trifluoroiodomethane (5.3 gm., 0.027 mole)

were heated together in a sealed tube for 48 hrs. at 150°C. The volatile products were found to be similar to those obtained from the reaction between thallous acetylacetonate and trifluoroiodomethane, while the solid contained all the thallium present in the form of the starting material, dimethylthallium acetylacetonate and its partial decomposition products. The infra-red spectrum of the solid indicated that trifluoromethyl groups were not present.

3. THALLOUS IODIDE, METHYL-LITHIUM AND HEPTAFLUOROIODOPROPANE

This procedure was based on that used for the preparation of trimethylthallium, the difference being that, instead of the inclusion of methyl iodide in the reaction mixture, heptafluoroiodopropane was used. Methyllithium (0.12 mole) in diethyl ether (100 ml.) was added over a period of 30 min. to a stirred suspension of thallous iodide (20.0 gm., 0.06 mole) in a solution of heptafluoroiodopropane (17.8 gm., 0.06 mole) in ether (50 ml.). The temperature was maintained at -55°C and nitrogen was passed through the system continuously. As in the preparation of trimethylthallium, there was deposition of finely divided metallic thallium which was removed by reaction as the temperature was slowly raised

to 20°C. The mixtures was allowed to stand for 15 hrs. before the volatile constituents were transferred to the vacuum system. Ether and heptafluoroiodopropane were the major components and no volatile thallium product was detected. Infra-red analysis to the solid reaction products indicated the complete absence of perfluoroalkyl groups. Some of the thallium was present as dimethylthallium iodide (6.9 gm., 0.02 mole) (Found: C, 6.60; H, 1.61%. Calc. for C_2H_6TlI: C, 6.67; H, 1.67%), and the remainder as unchanged thallous iodide. These two compounds were separated by extracting the solid mixture with ethanol. The dimethylthallium iodide dissolved, leaving a residue of thallous iodide.

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APPENDIX

Papers published or accepted for publication

Published:

1. Bell, Pullman and West, "Perfluoroalkyl-bismuth and -thallium Compounds", Proc.Chem.Soc., 1962, 224. Reprint appended.
2. Bell, Pullman and West, "Perfluoroalkylbismuth Compounds", Aust.J.Chem., 1963, 16, 636. Reprint appended.
3. Bell, Pullman and West, "The Reactions of Perfluoroalkyl Radicals with Metals", Aust.J.Chem., 1963, 16, 722. Reprint appended.

Accepted for publication:

Pullman and West, "Mixed Alkyl-perfluoroalkyl Derivatives of Group VB Elements", Aust.J.Chem., in the press. Photostat of proofs appended.

Bell, T. N., Pullman, B. J. & West, B. 0. (1962). Perfluoroalkyl-bismuth and -thallium compounds. *Proceedings of the Chemical Society*, Jun., 224.

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MIXED ALKYL-PERFLUOROALKYL DERIVATIVES OF GROUP VB ELEMENTS

By B. J. PULLMAN and B. O. WEST

MIXED ALKYL-PERFLUOROALKYL DERIVATIVES OF GROUP VB ELEMENTS

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Summary

Trifluoroiodomethane reacts with triethyl-phosphine, -arsine, and -stibine forming derivatives of the type $(C_2H_5)_3MCF_3$ together with $(C_2H_5)_4MI$, while pentafluoroiodoethane reacts with trimethyl-phosphine, -arsine, and -stibine giving derivatives of the form $(CH_3)_2MC_2F_5$ together with $(CH_3)_4MI$. The infrared spectra of the compounds are presented and the mechanism of the reaction discussed.

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† After this programme had been started Cullen[2] published results of similar exchange studies including that between trifluoroiodomethane and triethylarsine. Our results are in accord with his in this instance.

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The reaction between trifluoroiodomethane and trimethyl-phosphine, -arsine, and -stibine is known to give the appropriate dimethyltrifluoromethyl derivative and the corresponding tetramethyl 'onium iodide,[1] and formally involves the exchange of a methyl for a trifluoromethyl group. The reaction has been further investigated by the use of triethyl-phosphine, -arsine, and -stibine, and pentafluoroiodoethane in order to examine the effect of increasing size of the substituent groups.†

SYNTHESIS OF COMPOUNDS AND MECHANISM OF REACTION

It has now been established that the exchange reaction occurs readily between trifluoroiodomethane and the triethyl derivatives of phosphorus, arsenic, and antimony, and between pentafluoroiodoethane and the trimethyl derivatives of these elements to give as products dialkylperfluoroalkyl-phosphines, -arsines, and -stibines together with the appropriate tetra-alkyl 'onium iodide. Similar observations were made by Haszeldine and West for the reactions of trifluoroiodomethane with trimethyl-phosphine, -arsine, and -stibine. The reaction may be represented as

$$2R_3M + R_fI \rightarrow R_2MR_f + R_4MI$$

where

$$R_f = CF_3, C_2F_5, \quad R = CH_3, C_2H_5, \quad \text{and} \quad M = P, As, Sb.$$

In all cases excess of the perfluoroalkyl iodide was present in the initial reaction mixture. In general, reactions were carried out at room temperature (*c.* 20°) but it was found most convenient to heat reaction mixtures containing arsines and perfluoroalkyl iodides since these reactions were relatively slow at room temperature. Qualitatively, the rate of reaction with trifluoroiodomethane is slower in the case of the triethyl derivatives of phosphorus, arsenic, and antimony than for the trimethyl, as shown by the longer time required for the first deposition of tetraethyl 'onium compounds. The trimethyl compounds react very rapidly with trifluoroiodomethane at room temperature and react as readily with pentafluoroiodoethane judging by the rapid appearance of solid quaternary in the reaction tubes.

It was observed that the final reaction mixtures obtained when reacting triethyl-phosphine, -arsine, and -stibine with trifluoroiodomethane contained considerable quantities of ethyl iodide and unchanged triethyl compound while the reaction mixtures involving the trimethyl derivatives with pentafluoroiodoethane did not contain methyl iodide but did contain unreacted trimethyl compound even after periods of reaction up to six months.

The percentage conversion was improved by transferring all the volatile reaction products to a new reaction tube, additional perfluoroalkyl iodide being added if necessary. By repeating this process virtually complete conversion of a sample of a trialkyl compound to a mixture of the dialkylperfluoroalkyl and tetra-alkyl 'onium compounds could be achieved.

Evidence that these reactions were equilibrium controlled was obtained from the observation that the volatile products from reaction mixtures kept at room temperature for up to six months rapidly deposited fresh quaternary compound when transferred to another reaction vessel. This occurred even though the appropriate perfluoroalkyl iodide was in excess of that necessary to react with the trialkyl compound being used. There was no evidence for the formation of compounds of the type $RM(R_f)_2$ in any of the reactions studied. Compounds of this type were prepared by Haszeldine and West by heating together tristrifluoromethyl-phosphine or -arsine and methyl iodide.

Ethyl iodide was detected amongst the products of reaction between triethyl compounds and trifluoroiodomethane. This observation supports one of the two mechanisms proposed by Haszeldine and West.[1] Each mechanism postulates the formation of an intermediate quaternary compound $[R_3MR_f]^+I^-$. One assumes nucleophilic attack of a further molecule of the original trialkyl compound on an alkyl group in the quaternary, thus:

TAKE IN DIAGRAM MM HERE—

This implies direct formation of the quaternary compound from the intermediate and does not permit even the transient existence of free alkyl iodide. The other mechanism involves dissociation of the intermediate mixed alkyl–perfluoroalkyl quaternary compound thus:

TAKE IN DIAGRAM NN HERE—

Reaction of the liberated alkyl iodide with a molecule of the original compound then accounts for the appearance of the tetra-alkyl 'onium compound observed as a major reaction product. The fact that free alkyl iodide remains after reaction between trifluoroiodomethane and the triethyl compounds is no doubt related to the slower rate of the reaction found for ethyl iodide with triethyl derivatives of phosphorus, arsenic, and antimony compared with that of methyl iodide and trimethyl derivatives. Thus in the systems under consideration, the dilution by the newly formed alkyl-perfluoroalkyl compound plus the excess perfluoroalkyl iodide is probably sufficient to retard the formation of tetraethyl quaternary compounds under the mild thermal

conditions used. Thus, if the rate of dissociation of the intermediate quaternary compound is greater than the rate of formation of the appropriate tetraethyl quaternary compound, then a stage may be reached when all the original free trialkyl compound has been consumed by the formation both of an ethylperfluoroalkyl derivative and some tetraethyl quaternary compound but still leaving some free ethyl iodide. It appears that the relative proportions of ethyl iodide to tetraethyl 'onium iodide are quite variable and probably depend on factors such as the quantity of perfluoroalkyl iodide used (and therefore the extent of dilution) and the size of the reaction vessel.

The reaction of perfluoroalkyl iodide and trialkyl bismuthines[4] is in many ways analogous to those above. An intermediate unstable pentavalent bismuth compound is considered to form since bismuth quaternary compounds containing alkyl groups are not known. The existence of free alkyl iodide as a reaction product supports this hypothesis.

In Table 1 are listed the compounds prepared in this series, together with their extrapolated boiling points.

TAKE IN TABLE 1 HERE—

All the new alkyl-perfluoroalkyl compounds prepared in this series exhibit properties comparable with those of their dimethyltrifluoromethyl analogues. They are quite reactive in air, the dimethylpentafluoroethyl compounds tending to ignite and the diethyltrifluoromethyl ones fuming strongly. The electron donating power of the Group VB elements in these compounds is reduced in the manner expected due to the presence of the strongly electronegative perfluoroalkyl groups. This feature is exemplified in the reaction with silver iodide (in aqueous potassium iodide) with which only dimethylpentafluoroethylphosphine and diethyltrifluoromethylphosphine form complexes, which dissociate readily at room temperature. A similar unstable product was reported on reacting dimethyltrifluoromethylphosphine with silver iodide.[3] Reaction of the alkyl–perfluoroalkyl-phosphines and -arsines with the appropriate alkyl iodide produces crystalline compounds which rapidly decompose in air. They have been tentatively formulated as alkyl–perfluoroalkyl 'onium iodides of the form $[R_3MR_f]I$.

Hydrolysis of the alkyl–perfluoroalkyl compounds with hot aqueous alkali causes the liberation of the appropriate fluorocarbon compound, but not quantitatively.

—Folio 5 follows—

INFRARED SPECTRA

The infrared spectra of the organometallic compounds prepared were recorded and tentative vibrational assignments made and compared with those of related compounds. In general only those frequencies associated with C–H and C–F vibrations in the frequency range 700–4000 cm^{-1} have been studied.

(1) *Dimethylpentafluoroethyl Compounds.*—The observed frequencies and tentative assignments are listed in Table 2.

The absorption bands at 2980–3020 and 2820–2940 cm^{-1} are assigned to C–H antisymmetric and symmetric stretching vibrations respectively.[5,6] Although the C–H antisymmetric bending frequencies[5] normally appear in the region of 1460 cm^{-1}, the effect of the highly electronegative perfluoroalkyl groups in the compounds under examination may well be responsible for the observed absorptions attributed to those

TAKE IN TABLE 2 HERE—

modes occurring in the range 1410–1440 cm^{-1}. The very strong bands occurring at 1200–1335 cm^{-1} are attributed to the C–F stretches of the CF_3 fragment of the pentafluoroethyl group[4,7] and probably obscure the less prominent bands due to C–H symmetric bending vibrations. The bands in the range 1085–1100 cm^{-1} are assigned to C–F stretches of the CF_2 unit attached directly to the "metal" atom. In the region 890–900 cm^{-1} is a band in the spectrum of each of the compounds attributed to C–C stretching in the pentafluoroethyl group. The frequencies in the region 925–970 cm^{-1} are attributed to methyl rocking vibrations while those at 820–860 cm^{-1} are tentatively assigned to methyl wagging. The strong bands occurring at 725–780 cm^{-1} are assigned to C–F deformation vibrations.

(2) *Diethyltrifluoromethyl Compounds.*—The vibrational frequencies in the infrared spectra of diethyltrifluoromethyl -phosphine, -arsine, and -stibine, where applicable, are comparable with those of the dimethylpentafluoroethyl series. In Table 3 are listed the observed vibrational frequencies and their tentative assignments. The explanations offered for the assignments may be obtained by reference to the commentary on Table 1.

TAKE IN TABLE THREE HERE

EXPERIMENTAL

(*a*) *Techniques used.*—(i) Volatile materials were manipulated in a conventional glass vacuum system and fractionated by trap-to-trap distillation with the aid of appropriate slush baths. Reactions were carried out in heavy walled Pyrex tubes of approximately 50 ml capacity. The volatile reactants were condensed from the vacuum system into the tubes which were then sealed while evacuated.

(ii) Molecular weights of gases were determined by Regnault's method.

(iii) Fractionation of reaction products: after preliminary trap-to-trap distillation, the fractions containing the organometallic compounds were subjected to vapour phase chromatography in order to isolate the individual constituents. A Perkin–Elmer model 154 vapour fractometer was used. Nitrogen was the carrier gas and di-isodecyl phthalate the column packing material. Each pure fraction, as it emerged from the column was collected in a separate U-tube cooled in liquid air.

(iv) Infrared spectra were recorded in the range 700–4000 cm^{-1} using a Perkin–Elmer model 21 double-beam spectrophotometer fitted with sodium chloride optics. Spectra of gases were recorded in a 10 cm gas cell equipped with sodium chloride windows.

(*b*) *Analyses.*—(i) Phosphorus was determined by carefully oxidizing the appropriate compound with nitric acid in a sealed tube. The solution was diluted with water, ammonium molydate added, and titrated with standard alkali.[8]

(ii) Arsenic was determined iodometrically[8] after nitric acid decomposition of the compound.

(iii) Antimony was determined by titration with potassium permanganate after oxidative decomposition of the compound with nitric and sulphuric acids followed by reduction with hydrazine.

(*c*) *Preparation of Compounds.*—(i) *Diethyltrifluoromethylphosphine.* Triethylphosphine (4·44 g; 37·6 mM) and trifluoroiodomethane (10·8 g; 55·0 mM) were sealed in an evacuated tube and allowed to stand at room temperature for 3 days. The volatile constituents of the mixture were then distilled into the vacuum system leaving a white crystalline residue. This was identified as tetraethylphosphonium iodide by isolation of the pentaiododimercurate derivative, m.p. and mixed m.p. 117° (lit.[9] 117°) (Found: C, 8·0; H, 1·6%. Calc. for $C_8H_{20}PHg_2I_5$: C, 8·1; H, 1·7%). The volatile materials were fractionated through traps at −46 and −196°, the phosphorus-containing compounds together with other minor constituents collecting in the former. Four components of the less volatile fraction were separated by vapour phase chromatography and by comparison with the retention times of authentic samples and by infrared spectroscopic examination found to be trifluoroiodomethane, ethyliodide, triethylphosphine, and *diethyltrifluoromethylphosphine* (Found: P, 19·4%; mol. wt., 157. Calc. for $C_5H_{10}F_3P$: P, 19·6%; mol. wt., 158). The former two components, when combined, constituted approximately 10% of this fraction, the triethylphosphine and diethyltrifluoromethylphosphine comprising 60% and 30% respectively. Four successive treatments of this fraction obtained by the distillation described above with additional trifluoroiodomethane under the original conditions, caused approximately 80% conversion of triethylphosphine to diethyltrifluoromethylphosphine. The vapour pressure–temperature equation for the latter is $\log_{10}P_{(mm)} = 6{\cdot}813 - 1457/T$.

A sample of the phosphine (0·18 g) was condensed into a tube containing a solution of silver iodide in aqueous potassium iodide (20% silver iodide, 2·5 ml). On shaking these two immiscible liquids at 10–15°, a mass of white crystals deposited. Gentle warming caused obvious decomposition and at 48° the diethyltrifluoromethylphosphine was recovered quantitatively.

A mixture of diethyltrifluoromethylphosphine (0·19 g) and excess ethyl iodide (0·65 g) was allowed to stand in a sealed tube for 3 days at room temperature and then at 75° for a further 3 days. At the end of this time a white crystalline deposit had formed (0·073 g) which was stable even after the removal of the unchanged reactions if kept under vacuum. On contact with moist air it rapidly decomposed giving a highly coloured oil. The solid formed initially was considered to be the quaternary compound $[(C_2H_5)_3PCF_3]I$ but its instability prevented an analysis from being performed.

(ii) *Diethyltrifluoromethylarsine.* Triethylarsine (3·98 g; 24·6 mM) and trifluoroiodomethane (9·9 g; 50·5 mM) were allowed to stand in a sealed tube at room temperature for 24 hr and then at 100° for 24 hr. After removal of the volatile components of the reaction mixture, tetraethylarsonium iodide (0·32 g) remained (Found: C, 30·1; H, 6·3; I, 39·8%. Calc. for $C_8H_{20}AsI$: C, 30·2; H, 6·29; I, 39·9%). The volatile reaction products were subjected to trap-to-trap distillation and the following fractions obtained: fluoroform (−196°) (Found: mol. wt., 70. Calc. for CHF_3: mol. wt., 70), trifluoroiodomethane (−135°) (Found: mol. wt., 196. Calc. for CF_3I: mol. wt., 196), a mixture of trifluoroiodomethane and ethyl iodide (−95°), and a mixture (−46°) of triethylarsine and *diethyltrifluoromethylarsine* (Found: As, 36·8%; mol. wt., 201. Calc. for $C_5H_{10}F_3As$: As, 37·0%; mol. wt., 202). The latter fraction also contained minor quantities of trifluoroiodomethane and ethyl iodide. The fraction consisting of the arsenic-containing material was heated with additional trifluoroiodomethane and an overall 60% conversion of triethylarsine to diethyltrifluoromethylarsine was achieved. Diethyltrifluoromethylarsine has a boiling point of 110° (lit.[2] 111°).

No reaction occurred when the arsine (0·17 g) and silver iodide in aqueous potassium iodide were shaken together even at 0°.

Treatment of diethyltrifluoromethylarsine (0·23 g) with ethyl iodide (1·1 g) for 3 days at room temperature and a further 3 days at 75° yielded white crystals (0·024 g) which when exposed to air, rapidly decomposed into an oil. The material was thought to be $[(C_2H_5)_3AsCF_3]I$.

(iii) *Diethyltrifluoromethylstibine.* Triethylstibine (8·00 g; 38·3mM) and trifluoroiodomethane (11·4 g; 58·2mM) were allowed to stand in a sealed tube at room temperature for 48 hr. There was deposited a small quantity of white crystalline solid (0·32 g) which did not increase when the mixture was heated at 100° for 15 hr. The solid was identified as tetraethylstibonium iodide (Found: C, 26·4; H, 5·4; I, 34·7%. Calc. for $C_8H_{20}SbI$: C, 26·3; H, 5·5; I, 34·8%). Trap-to-trap distillation was used for a preliminary separation of the volatile reaction products giving a trace of fluoroform (−196°), unreacted trifluoroiodomethane (−135°), a mixture of trifluoroiodomethane and ethyl iodide (−95°), and a mixture of triethylstibine and diethyltrifluoromethylstibine (−46°). The identity of those materials was established with the aid of vapour phase chromatography, infrared spectral analysis and molecular weight measurement. By treating the mixture of stibines with additional trifluoroiodomethane, more tetraethylstibonium iodide was formed and a total conversion of 70% of triethylstibine to diethyltrifluoromethylstibine was achieved. For diethyltrifluoromethylstibine (Found: Sb, 48·7%; mol. wt., 247. Calc. for $C_5H_{10}F_3Sb$: Sb, 49·0%; mol. wt., 249) the vapour pressures are described by $\log_{10}P_{(mm)} = 6·285 - 1396/T$, the extrapolated boiling point being 136°.

(iv) *Dimethylpentafluoroethylphosphine.* Trimethylphosphine (4·7 g; 61·8mM) and pentafluoroiodomethane (15·4 g; 62·7 mM) were allowed to stand at room temperature in a sealed tube for 14 hr. The mixture set solid due to the formation of tetramethylphosphonium iodide (4·50 g; 20·6 mM) (Found: C, 21·9; H, 5·5; I, 58·0%. Calc. for $C_4H_{12}PI$: C, 22·0; H, 5·5; I, 58·2%). Following the removal of the solid, the volatile materials were again treated with excess pentafluoroiodoethane, the new solid product removed after 12 hr, and the procedure repeated once more. The combined weight of tetramethylphosphonium iodide (5·1 g; 23·4 mM) represented 38% conversion of the trimethylphosphine. The volatile constituents of the reaction mixture were then subjected to preliminary trap-to-trap distillation. The fraction condensing at −196° contained only pentafluoroiodoethane (Found: mol. wt., 246. Calc. for C_2F_5I: mol. wt., 246), while the fraction at −63° was shown by vapour-phase chromatography to consist of pentafluoroiodoethane, trimethylphosphine (1·25 g; 16·5 mM) (Found: mol. wt., 76. Calc. for C_3H_9P: mol. wt., 76) and *dimethylpentafluoroethylphosphine* (3·96 g; 22·0 mM—36% conversion of trimethylphosphine) (Found: P, 17·2%; mol. wt., 180. Calc. for $C_4H_6F_5P$: P, 17·2%; mol. wt., 180). The vapour pressure temperature relationship for the latter compound is described by the equation $\log_{10}P_{(mm)} = 6·551 - 1218/T$ from which the boiling point is calculated to be 57°.

When the phosphine (0·24 g) and silver iodide in aqueous potassium iodide solution (3 ml) were shaken together at room temperature a white crystalline solid deposited. By heating this solid to 50° complete recovery of the original phosphine was achieved.

Reaction of dimethylpentafluoroethylphosphine (0·23 g) with excess methyl iodide (1·2 g) at room temperature for 3 days and at 75° for a further 3 days, yielded a white crystalline material (0·22 g) which underwent quite rapid decomposition on exposure to air. It was considered to be $[(CH_3)_3PC_2F_5]I$.

—Folio 11 follows—

(v) *Dimethylpentafluoroethylarsine.* Trimethylarsine (2·89 g; 24·1 mm) and pentafluoroiodoethane (6·75 g; 27·4 mm) were allowed to stand in a sealed tube for 24 hr at room temperature. The volatile materials were then removed from the crystalline solid deposited and the former treated with additional excess pentafluoroiodoethane. The combined solid formed after these two treatments (4·5 g) represented 39% conversion of trimethylarsine to tetramethylarsonium iodide (Found: C, 19·4; H, 4·8; I, 51·4%. Calc. for $C_4H_{12}AsI$: C, 19·5; H, 4·9; I, 51·6%). Trap-to-trap distillation through traps cooled to −63° and −196° was used to separate most of the excess pentafluoroiodoethane from the volatile reaction products. The material collecting in the trap cooled to −63° was separated by vapour-phase chromatography into three components, viz., pentafluoroiodoethane, trimethylarsine (Found: mol. wt., 120. Calc. for C_3H_9As: mol. wt., 120), and *dimethylpentafluoroethylarsine* (2·15 g; 9·6 mm—40% conversion of trimethylarsine) (Found: As, 33·4%; mol. wt., 225. Calc. for $C_4H_6F_5As$: As, 33·3%; mol. wt., 224).

The arsine (0·18 g), when treated with a solution of silver iodide in aqueous potassium iodide solution (3 ml) did not yield a solid product even at 0°.

A white crystalline solid (0·21 g) was formed when dimethylpentafluoroethylarsine (0·22 g) and excess methyl iodide (0·93 g) were allowed to react in a sealed tube for 3 days at room temperature and for a further three days at 75°. The compound formulated as $[(CH_3)_3AsC_2F_5]I$, could not be analysed owing to its rapid decomposition in air.

(vi) *Dimethylpentafluoroethylstibine.* Trimethylstibine (5·46 g; 32·7 mm) and pentafluoroiodoethane (8·49 g; 34·1 mm) were allowed to stand at room temperature in a sealed tube for 72 hr. The volatile reaction products were then removed from the white solid formed, by pumping. By successively treating the volatile materials with excess pentafluoroiodoethane and removing the solid deposited, ultimately a stage was reached when no further solid appeared. The combined weight of solid product, identified as tetramethylstibonium iodide (Found: C, 15·5; H, 3·8; I, 41·2%. Calc. for $C_4H_{12}SbI$: C, 15·5; H, 3·9; I, 41·1%) was 4·3 g (13·9 mm) and represented 43% conversion of the original trimethylstibine. A preliminary trap-to-trap distillation through traps at −63° and −196° enabled most of the unreacted pentafluoroiodoethane (−196°) to be separated from the antimony compounds (−63°). This latter fraction was shown by vapour phase chromatography to contain predominantly *dimethylpentafluoroethylstibine* (Found: Sb, 44·8%; mol. wt., 270. Calc. for $C_4H_6F_5Sb$: Sb, 45·0%; mol. wt., 271) together with small amounts of pentafluoroiodoethane and trimethylstibine. For dimethylpentafluoroethylstibine the vapour pressure-temperature relationships is described by the equation $\log_{10}P_{(mm)} = 7·929 - 1778/T$ from which the boiling point is calculated to be 79°.

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TABLE 1

EXTRAPOLATED BOILING POINTS OF ALKYL–PERFLUOROALKYL COMPOUNDS

Compound	Extrapolated Boiling Point	Compound	Extrapolated Boiling Point
$(C_2H_5)_2PCF_3$	97°	$(CH_3)_2PC_2F_5$	57°
$(C_2H_5)_2AsCF_3$	110°*	$(CH_3)_2AsC_2F_5$	67°
$(C_2H_5)_2SbCF_3$	136°	$(CH_3)_2SbC_2F_5$	79°

* Lit.[2] 111°.

TABLE 2

VIBRATIONAL FREQUENCIES FOR DIMETHYLPENTAFLUOROETHYL COMPOUNDS

$(CH_3)_2PC_2F_5$	$(CH_3)_2AsC_2F_5$	$(CH_3)_2SbC_2F_5$	Assignment
2983m	3019m	3015m	C–H antisym. stretch
2935m	2940m	2925m	C–H sym. stretch
2895wsh	2824w		
1438m	1438m sh	1414m	C–H antisym. bend
	1420m		
1324s	1332s	1320s	C–F stretches of CF_3 group
1279w	1313s sh	1290s sh	
1214s sh	1275m	1200s	
1209s	1209s		
1114s	1106s	1086s	C–F stretches of CF_2–M group
1099s	1092s sh		
969s	950s	925s	CH_3 rock
895m	900m		C–C stretch
861m	850s	822m	CH_3 wag
744m sh	742s sh	773s	C–F deformation
739m	736s	726s	
944s		900w	
734m sh			Not assigned
709m			

TABLE 3

VIBRATIONAL FREQUENCIES FOR DIETHYLTRIFLUOROMETHYL COMPOUNDS

$(C_2H_5)_2PCF_3$	$(C_2H_5)_2AsCF_3$	$(C_2H_5)_2SbCF_3$	Assignments
2979m	2980s	2970m	C–H antisym. stretch
2954m sh	2950s sh	2935m sh	C–H sym. stretch
2898m	2885s	2882m	
1458m	1468m	1469m	C–H antisym. bend
1419w	1429w	1430w	
1240m	1224s	1194m	C–F sym. and antisym. stretch
1154s	1176m	1123s	
1108s	1142s	1092s	
	1115s		
747m	791m	792m	C–F deformation
986m	976m	952w	Not assigned
	719m		