STUDIES ON HETEROATOM PHOSPHORUS-FLUORINE COMPOUNDS

by

Michael James Christopher Hewson, B.Sc., (Leicester)

A thesis submitted for the degree of
Doctor of Philosophy
of Loughborough University of Technology

November 1971

Supervised by

Prof. R. Schmutzler (internally Oct. 1968 - Dec. 1968)
and (externally Dec. 1968 - Oct. 1971)

Dr. A. H. Norbury (internally Dec. 1968 - Oct. 1971)

To my Mother and Father

ACKNOWLEDGMENTS

I would like to express my deep appreciation to Prof. R. Schmutzler for his inspiration, encouragement and guidance during my studies and to Dr. A. H. Norbury for his help in the course of submitting this thesis.

Dr. M. Fild, Dr. M. Murray and Dr. O. Stelzer of the Technische Universität, Braunschweig, Germany are thanked for their help and encouragement through many informative discussions. Dr. M. Murray is also thanked for help in the measurement and interpretation of n.m.r. spectra. Thanks are also due to the technical staff of the Institute for Microbiology of the Technische Universität, Braunschweig for the measurement of Mass Spectra.

I would also like to acknowledge gifts of chemicals from Prof. H. Hoffmann, Farbenfabriken Bayer, Wuppertal-Elberfeld Germany; Dr. G. Wunsch B.A.S.F., Ludwigshafen, Germany and Dr. W. E. White, Ozark Mahoning Co., Tulsa, Oklahoma, U.S.A.

I acknowledge a University of Loughborough Research Grant for the first three months of my studies and financial support through a position as Research Demonstrator at the Technische Universität, Braunschweig, Germany.

PUBLICATIONS

Part of the work reported in this thesis has been published as the following papers:

(i) Phosphorus-Fluorine Chemistry. Part XXIV. Preparation and N.m.r. Investigation of Fluoro-Phosphate Anions $[RPF_5]^-$ and $[R^1R^2PF_4]^-$ and of Dialkyl(or aryl) dialkylaminodifluorophosphoranes $R^1R^2PF_2NR^3_2$.
S. C. Peake, M. J. C. Hewson and R. Schmutzler, J. Chem. Soc., (A) 1970, 2364.

(ii) Fluorine-19 Nuclear Magnetic Resonance Studies of Methyl Substituted Piperidyl-Fluorophosphoranes.
M. J. C. Hewson, S. C. Peake and R. Schmutzler, Chem. Comm., 1971, in press.

(iii) Phosphorus-Fluorine Chemistry. Part XXIX. Aryloxy Substituted Fluorophosphoranes.
M. Fild, M. J. C. Hewson, S. C. Peake and R. Schmutzler. Inorg. Chem., 1971, 10, in press

(iv) Nuclear Magnetic Resonance Studies of Diazadiphosphetidines and Phosphadiazetidinones.
R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray and R. Schmutzler, Ber. Bunsenges. Physik. Chem., in press

(v) Fluorophosphoranes Containing Unsymmetrically Substituted Secondary Amino Groups.
Presented at the Sixth International Symposium on Fluorine Chemistry by M. J. C. Hewson, S. C. Peake and R. Schmutzler in Durham, England, July 1971

(vi) Pentafluorophenoxy Compounds of Phosphorus.
Presented at the Sixth International Symposium on Fluorine Chemistry by M. Fild, M. J. C. Hewson and R. Schmutzler in Durham, England, July 1971.

'STUDIES ON HETEROATOM-PHOSPHORUS-FLUORINE COMPOUNDS'

SUMMARY

This thesis is concerned with phosphorus-fluorine compounds in which phosphorus has a coordination number of either four, five or six and with special emphasis on compounds substituted by heteroatom-containing organic groups.

A new series of aryloxy-fluorophosphoranes of general formula $R_nPF_2(OC_6F_5)_{3-n}$ (where n = 0, 1, 2; R = Me, Ph, Me_2N, Et_2N) have been prepared from the reaction of the Lewis base silyl ether pentafluorophenyltrimethylsilyl ether with the Lewis acid fluorophosphoranes R_nPF_{5-n} (where n = 0, 1, 2; R = Me, Ph, Me_2N, Et_2N). In contrast to alkoxy-fluorophosphoranes, which are known to be thermally unstable, these new aryloxy-fluorophosphoranes are found to be stable. All the reactions discussed are characterised by multi-substitution contrasting to the substitution pattern for other heteroatom-fluorophosphoranes. An insight was obtained into the reaction of aryltrimethylsilyl ethers with fluorophosphoranes from the reaction of the fluorophosphoranes $PhPF_4$ and Me_2NPF_4 with the silyl-ethers $PhOSiMe_3$ and $C_6F_5OSiMe_3$, respectively, in which it was ascertained that the reactions proceeded via trifluorophosphorane intermediates to give difluorophosphoranes as the only phosphorus-fluorine product.

The analogous reactions of the Si-N bonded Lewis bases

$RR'NSiMe_3$ (where $RR'N$ = 2-Methylpiperidyl-, 3-Methylpiperidyl-, 2-Methylpyrryl-) and R_2NSiMe_3 (where R_2N = 4-Methylpiperidyl-, 2,5-Dimethylpyrryl-) with the Lewis acid fluorophosphoranes R''_nPF_{5-n} (where n = 0, 1, 2; R'' = Me, Ph) have been shown to produce the monosubstituted asymmetric aminofluorophosphoranes $RR'NPR''_nF_{4-n}$ and the symmetric aminofluorophosphoranes $R_2NPR''_nF_{4-n}$. In some cases these aminofluorophosphoranes are found to undergo thermal rearrangements to give ionic isomers of the type $[(RR'N)_2PF_2]^+ [PF_6]^-$ or $[(RR'N)_2PR''F]^+ [R''PF_5]^-$, these ionic compounds being formed from the rearrangement of the corresponding covalent tetra- and tri-fluorophosphoranes.

The structures of these new fluorophosphoranes have been studied by n.m.r. spectroscopy and trigonal bipyramidal structures assigned in which the heteroatom-organo group occupies an equatorial position leaving the axial positions occupied by fluorine atoms.

Room temperature ^{19}F n.m.r. studies of the tetrafluorophosphoranes are consistent with non-rigid pseudorotating structures. At low temperature, however, n.m.r. spectra of rigid non-pseudorotating structures are observed. Low temperature n.m.r. studies of all the asymmetric aminofluorophosphoranes have shown the existence of high energy barriers to rotation about the P-N bond. The effective cessation of rotation about the P-N bond is manifested in the observation of magnetically non-equivalent equatorial fluorine atoms for the tetrafluorophosphoranes (where $RR'N$ = 2-Methyl- and 3-Methyl-piperidyl-) and magnetically non-equivalent axial fluorine atoms for 2-Methyl-pyrryltetrafluorophosphorane and all the di- and tri-fluorophosphoranes. For the symmetric

amino-substituted fluorophosphoranes no such observations are made. Possible causes of such high barriers to rotation and possible structures resulting from this increased rigidity are discussed.

Reactions of alkyl- and aryl-silyl ethers $ROSiMe_3$ (where R = Me, Et, Ph, C_6F_5-) with the phosphonitrilic fluoride trimer $(PNF_2)_3$, have been investigated and a series of stable compounds of the type $P_3N_3F_5OR$ have been prepared. In all cases the product obtained in highest yield was the monosubstituted derivative. Characterisation was carried out by n.m.r., mass spectroscopic and elemental analysis.

The direct aminolysis of the Lewis acid trifluorophosphoranes R_2PF_3 (where R = Me, Ph) with the secondary amines R'_2NH (where R' = Me, Et) has been studied and in view of the known Lewis acid character of fluorophosphoranes, it was expected that the reactions might lead to the formation of diorgano-tetrafluorophosphates $[R_2PF_4]^-$. However, the reactions proceeded, as expected, giving dialkylamino-difluorophosphoranes of the type $R'R''PF_2NR_2$ (where R' = Me, R'' = Ph or $R' = R''$ = Me, Ph; R = Me, Et) but with no formation of any diorgano-tetrafluorophosphates.

An attempt was made at the preparation of bis(dialkylamino)aryl-fluorophosphoranes by the reaction of phenyltetrafluorophosphorane with the secondary amines Me_2NH and Et_2NH. Monosubstitution was found to take place but no further substitution was observed. There is either rearrangement of the monosubstituted product to give an ionic species or no further reaction takes place.

Studies have also been carried out into the relative differences in reactivities of the two aminofluorophosphoranes,

Me_2NPF_4 and Et_2NPF_4. It was found that under certain reaction conditions Me_2NPF_4 showed a tendency towards the formation of ionic products whereas Et_2NPF_4 tended towards formation of covalent products. The reactions discussed are the reactions of the two aminofluorophosphoranes with the silylamines $RN(SiMe_3)_2$ (where R = Me, Ph), where Et_2NPF_4 reacts to give covalent 1,3-diaza-2,4-fluorophosphetidines $(Et_2NPF_2NMe)_2$ and $(Et_2NPF_2-NPh)_2$ and Me_2NPF_4 reacts to give ionic compounds containing the hexafluorophosphate ion $[PF_6]^-$ and with the silyl-thioethers $RSSiMe_3$ (where R = Me, Et, Ph) in which both aminofluorophosphoranes react to give ionic compounds containing the hexafluorophosphate ion $[PF_6]^-$. The thermal stability of aminofluorophosphoranes has also been investigated and it was found that diethylaminofluorophosphoranes are thermally more stable than the corresponding dimethylaminofluorophosphoranes, the latter showing a tendency towards the formation of dimethylaminophosphonium hexafluorophosphates. The difference in chemical nature was also demonstrated by the reaction of phosphorus pentafluoride with the Lewis bases R_2NSiMe_3 and $(R_2N)_2SiMe_2$ (where R = Me, Et). The reaction of the Lewis acid PF_5 with the aminofluorophosphoranes $(Me_2N)_nPF_{5-n}$ (where n = 1, 2, 3) have been shown to produce ionic compounds of the type $[(Me_2N)_nPF_{4-n}]^+[PF_6]^-$. The formation of ionic phosphorus-fluorine compounds is discussed.

CONTENTS

INTRODUCTION

INTRODUCTION

The work presented in this thesis is concerned with the chemistry of compounds containing phosphorus in the coordination number of either four, five or six and the compounds discussed are classed as heteroatom-phosphorus-fluorine compounds, in which organo groups are bonded to phosphorus through an heteroatom such as nitrogen, oxygen or sulphur.

In recent years several reviews have appeared in the literature dealing with phosphorus-fluorine compounds. Phosphorus-fluorine compounds in which P has a coordination number of three, four, five or six have been reviewed by Schmutzler[1] and later a complete review appeared[2] on a relatively new class of phosphorus-fluorine compounds, derived from the "parent" compound PF_5, called fluorophosphoranes having one or more of the fluorine atoms about phosphorus substituted by varying organo groups. Hydrocarbon substituted fluorophosphoranes were the first type of fluorophosphoranes to be investigated but it was not until 1962 that the first report[3] appeared of an heteroatom substituted fluorophosphorane and the heteroatom groups which have so far been introduced into fluorophosphoranes include RO-, ArO-, RS-, ArS-, R_2N-, $RR'N$-, RHN-, and ArHN-.

Other classes of heteroatom phosphorus-fluorine compounds to be considered are those in which phosphorus is present as part of a ring system. Fluorophosphetidines in which phosphorus, in coordination number five, is part of a four-membered ring system $(P\text{-}N)_2$ have, in recent years, been extensively investigated.[2, 4] More recently five-coordinate heteroatom phosphorus-fluorine compounds have been investigated in which phosphorus is part of a $\overline{\text{C-N-P-N}}$ ring[5, 6] and $\overline{\text{C-O-P-O-C}}$ ring[7, 8] system. A large class of compounds in which phosphorus is part of a ring system are the phosphonitriles $(PNX_2)_n$ where phosphorus has a coordination number of four. Many extensive reviews have appeared in the literature but of recent ones a few might be noted.[4, 9-12]

The following is a general survey of substituted phosphorus-fluorine compounds within the scope of the definition of heteroatom phosphorus-fluorine compounds.

Heteroatom phosphorus-fluorine compounds in which phosphorus has coordination number five.

(i) Nitrogen containing compounds.

At present nitrogen-containing phosphorus-fluorine compounds in which phosphorus has a coordination number of five can be divided into four distinct groups: alkyl (aryl)aminofluorophosphoranes $(RR'N)_nPF_{5-n}$ (where $n = 1, 2$; $R = R' =$ alkyl, aryl; $R =$ alkyl, aryl and $R' = H$, alkyl, aryl); alkyl(or aryl)dialkylaminofluorophosphoranes $RR'NPR''_nF_{4-n}$ (where $n = 1, 2$; $R = R' =$ alkyl, aryl; $R =$ alkyl, $R' =$ aryl; $R'' =$ alkyl, aryl); 1,3-diaza-2,4-fluorophosphetidines $R_nF_{3-n}P\text{-}NR')_2$ (where $n = 0, 1$; $R = R' =$ alkyl, aryl) and fluoro-1,2,4-phosphadiazetidine-3-ones $O{=}C(NR')_2PF_{3-n}R_n$ (where $n = 0,1,2$; $R =$ alkyl, aryl, alkylamino; $R' =$ alkyl, aryl).

a. Alkyl(or aryl)aminofluorophosphoranes

The synthetic methods employed for the preparation of this class of compounds are: aminolysis of fluorophosphoranes using primary or secondary amines and cleavage reactions of silicon-nitrogen compounds with fluorophosphoranes.

The reactions of phosphorus trifluoride, PF_3, and phosphorus pentafluoride, PF_5, with primary or secondary amines afford amino-substituted fluorophosphoranes according to the equations,

$$2PF_5 + 2R_2NH \longrightarrow R_2NPF_4 + [R_2NH_2]^+[PF_6]^- \qquad (13\text{-}15)$$

$$Me_2NH + 2Me_2NPF_4 \longrightarrow (Me_2N)_2PF_3 + Me_2NH{\cdot}PF_5 \qquad (13\text{-}15)$$

$$2PF_5 + 2RNH_2 \longrightarrow RNHPF_4 + [RNH_3]^+[PF_6]^- \qquad (16)$$

$$PF_5 + 2RNH_2 \longrightarrow (RNH)_2PF_3 \qquad (16)$$

$$2PF_3 + 5RNH_2 \longrightarrow 2(RNH)_2PF_2H + [RNH_3]^+[HF_2]^- \qquad (17)$$

The cleavage reactions of Si-N bonded compounds provides a convenient route to alkyl(or aryl)aminofluorophosphoranes of the type $(R_2N)_nPF_{5-n}$.

$$PF_5 + R_2NSiMe_3 \longrightarrow R_2NPF_4 + Me_3SiF \qquad (18\text{-}21)$$

$$R_2NPF_4 + R_2NSiMe_3 \longrightarrow (R_2N)_2PF_3 + Me_3SiF \qquad (18)$$

The trisubstituted derivative, $(Me_2N)_3PF_2$,[22] is best prepared from the reaction of tris(dimethylamino)phosphine, $(Me_2N)_3P$, with sulphur tetrafluoride, SF_4, or perfluoroketones, as no reaction is found to take place between the disubstituted derivatives, $(R_2N)_2PF_3$, and silylamines. Although in general the preparation of disubstituted compounds requires high reaction temperatures it has been found[23] that the reaction of $BzMeNSiMe_3$ with $BzMeNPF_4$ proceeds exothermically to give disubstituted aminofluorophosphoranes. Attempts at preparing mixed aminofluorophosphoranes from the reaction of Et_2NPF_4 with Me_3SiNMe_2 was successful in producing three possible products, $(Et_2N)_2PF_3$, $(Et_2N)(Me_2N)PF_3$, and $(Me_2N)_2PF_3$.[24]

b. Alkyl(or aryl)dialkylaminofluorophosphoranes

The synthetic methods employed for the preparation of this type of compound include: aminolysis of hydrocarbon-fluorophosphoranes with primary or secondary amines; cleavage reactions involving Si-N bonded compounds and oxidative fluorination of amino-chlorophosphines.

Aminolysis reactions are applicable to the synthesis of di- and tri-fluorophosphoranes according to the equations,

$$2RPF_4 + 2R'_2NH \longrightarrow RPF_3NR'_2 + [R'_2NH_2]^+[RPF_5]^- \quad (25,26)$$

$$2R_2PF_3 + 3R'_2NH \longrightarrow R_2PF_2NR'_2 + [R'_2NH_2]^+[HF_2]^- \quad (27)$$

$$ArPF_3Cl + 2R'_2NH \longrightarrow ArPF_3NR'_2 + [R'_2NH_2]^+ Cl^-. \quad (3)$$

The same compounds can be prepared from the reaction of alkyl(or aryl)fluorophosphoranes with Si-N bonded compounds according to the equations,

$$RPF_4 + Me_3SiNR'_2 \longrightarrow RPF_3NR'_2 + Me_3SiF \quad (18,24)$$

$$Ph_2PF_3 + Me_3SiNR'_2 \longrightarrow Ph_2PF_2NR'_2 + Me_3SiF. \quad (18,24)$$

The reaction of trifluorophosphoranes with Si-N bonded compounds is limited to diphenyltrifluorophosphorane.

Oxidative fluorination reactions involving SbF_3 and AsF_3 are less applicable to the synthesis of aminofluorophosphoranes than they are to the preparation of hydrocarbon substituted fluorophosphoranes.[1, 2] However, the chlorophosphines R(or Ar)PClNR were found to react with group V trifluorides to give fluorophosphoranes although in some cases oxidation of trivalent phosphorus is incomplete. Reactions take place according to the equation,

$$3R(Ar)PClNR'_2 + 3MF_3 \longrightarrow 3R(Ar)PF_3NR'_2 + 2M + MCl_3 \qquad (28)$$

(where M = Sb or As).

Fluorination reactions involving the amino substituted chlorophosphines $(R_2N)_nPCl_{3-n}$ afford only the corresponding fluorophosphines.[1] Attempts at the fluorination of $(Me_2N)_3PCl_2$ using NaF in tetramethylene sulphone gave only the trifluorophosphorane, $(Me_2N)_2PF_3$.[15]

c. Five-coordinate phosphorus as part of a ring system

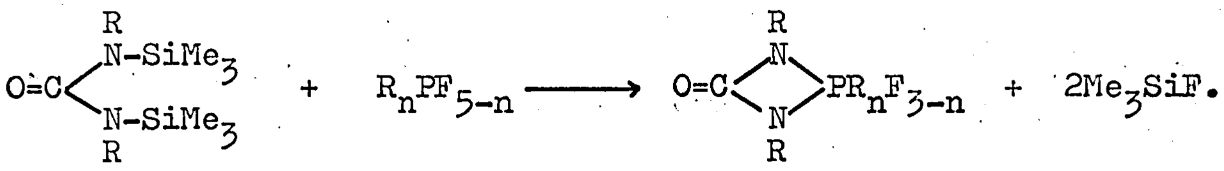
The reactions of fluorophosphoranes with N-substituted hexamethyldisilazanes have been found to be a useful route to the synthesis of 1,3-diaza-2,4-fluorophosphetidines[19,20,24,29] reactions proceeding according to the equations,

$$2PF_5 + 2(Me_3Si)_2NR \longrightarrow (F_3PNR)_2 + 4Me_3SiF$$

$$2R(orAr)PF_4 + 2(Me_3Si)_2NR' \longrightarrow R(Ar)PF_2NR' + 4Me_3SiF$$

The reaction of primary and secondary amines with PF_5 can also be utilised as a synthetic route to phosphetidines although the reactions are of a complex nature and yields dependent on amine used. A review[2] lists known fluorophosphetidines and their methods of preparation.

More recently the cleavage reactions of disilylureas, $O{=}C(RNSiMe_3)_2$, by fluorophosphoranes have been studied[5, 6] and it was found that the reactions gave a new series of compounds, fluoro-1,2,4-phosphadiazetidine-3-ones. The reactions take place according to the equations,



(ii) Sulphur-containing compounds.

First examples of fluorophosphoranes substituted by organo-sulphur groups were reported from the reaction of thiols or mercaptides with fluorophosphoranes according to the equations,

$$2NaSR + R'PF_4 \longrightarrow (RS)_2PR'F_2 + 2NaF \quad (30)$$

$$2RSH + R'PF_4 \longrightarrow (RS)_2PR'F_2 + 2HF. \quad (30)$$

Recently, however, a convenient route to thio-substituted fluorophosphoranes was found in the cleavage reactions of Si-S bonded compounds by fluorophosphoranes according to the equation,

$$R_nPF_{5-n} + R'SSiMe_3 \longrightarrow R_nP(SR')F_{4-n} + Me_3SiF. \quad (31,32)$$

(iii) Oxygen-containing compounds.

In general it can be said that alkoxy-substituted fluorophosphoranes are thermally unstable decomposing to give a phosphoryl compound and an alkyl fluoride. In contrast aryloxy-substituted fluorophosphoranes are thermally stable.

Two methods of preparation have been reported, these being one, the reaction of phosphites with fluorinating agents and two the cleavage reactions of Si-O bonded compounds with fluorophosphoranes.

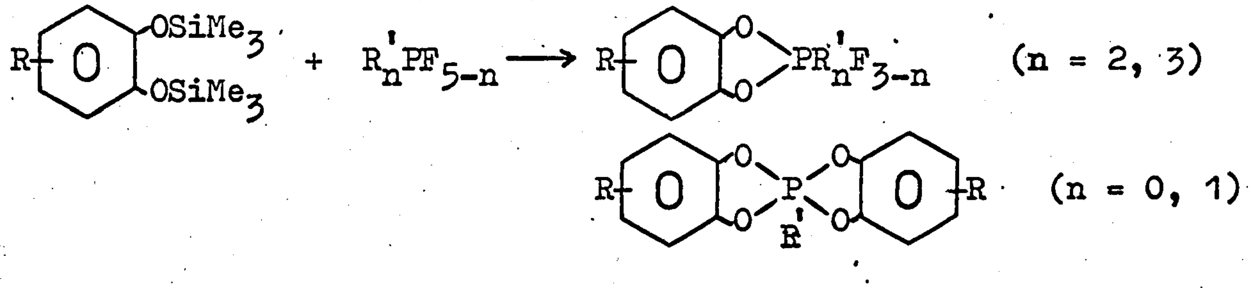
The reaction of triethylphosphite, $(EtO)_3P$, and trimethylphosphite, $(MeO)_3P$, with fluoro-olefins and phosphorus-pentafluoride, respectively, have been shown to produce the alkoxy fluorophosphoranes $R_fP(OEt)_3F$ [33] and $MeOPF_4$,[34] respectively. The compounds $(EtO)PRF_3$ [35] have been reported from the reaction of silyl ethers with fluorophosphoranes. All the above reactions were carried out at low temperature because of the thermal instability of the products.

Aryloxy fluorophosphoranes have been prepared from cleavage reactions of aryly-silyl ethers with fluorophosphoranes giving a thermally stable series of compounds of the type $(PhO)_{3-n}PF_2R_n$ [23, 36] and $(C_6F_5O)_{3-n}PF_2R_n$ [36] (Chapter 1.). The reactions take place according to the equation,

$$(3-n)ArOSiMe_3 \quad + \quad R_nPF_{5-n} \longrightarrow (ArO)_{3-n}PF_2R_n \quad + \quad (3-n)Me_3SiF$$

It was also reported [37] that the reaction of trimethyl- and triphenyl-phosphite with difluoroazirine is a route to the fluorophosphoranes $(PhO)_3PF_2$ and $(MeO)_3PF_2$, however, this seems unlikely in view of recent work.[23, 36] (Chapter 1).

Recent investigations [7, 8, 38] have led to the preparation of phosphoranes involving the 1,3,2-dioxa-4,5-benzophosphole ring system. These compounds are prepared from the cleavage reactions of o-phenylenedioxy-bis(trimethylsilane) derivatives by fluorophosphoranes and the resulting compounds have phosphorus atoms with a coordination number of five. The reactions take place according to the equation,



(iv) Mixed heteroatom phosphorus-fluorine compounds

Attempts at preparing 'mixed' heteroatom fluorophosphoranes have not all been successful and this might be accounted for in as much as the Lewis acid properties of these heteroatom substituted fluorophosphoranes are less than those of the hydrocarbon-fluorophosphoranes and the heteroatom groups show a greater tendency to lability than hydrocarbon groups. (Chapter 6).

The reaction of Me_2NPF_4 with $PhOSiMe_3$ produces an ionic product [23, 36, 39] according to the equation,

$$2PhOSiMe_3 \quad + \quad 2Me_2NPF_4 \longrightarrow [(Me_2N)_2P(OPh)_2]^+[PF_6]^- \quad + \quad 2Me_3SiF.$$

The analogous reactions with alkyl- or aryl- substituted silyl thioethers and aminofluorophosphoranes also produce an ionic compound containing the hexafluorophosphate ion $[PF_6]^-$. (Chapter 6). A simple transamination reaction was observed for the reaction of $MeSPPhF_3$ with $(Me_2N)_2SiMe_2$ giving Me_2NPPhF_3 as product. [42]

However, some reactions have been successful in the formation of 'mixed' heteroatom fluorophosphoranes. The reaction of the aminofluorophosphoranes R_2NPF_4 with perfluorophenyltrimethylsilyl ether (Chapter 1) have been shown to produce difluorophosphoranes containing two different heteroatom groups, <u>i.e.</u>,

$$R_2NPF_4 \quad + \quad 2C_6F_5OSiMe_3 \longrightarrow R_2NPF_2(OC_6F_5)_2 \quad + \quad 2Me_3SiF.$$

The reaction of 1-difluoro-1-N-benzylmethyl-1,2,4-phosphadiazetidine-3-one with sodium methoxide is successful in replacing one of the fluorine atoms and giving 1-fluoro-1-N-benzylmethyl-1-methoxy-1,2,4-phosphadiazetidine-3-one. [43]

Physical and Chemical Properties of Heteroatom-Substituted Fluorophosphoranes

(i) Hydrolytic Behaviour

The hydrolytic stability of heteroatom-substituted fluorophosphoranes is comparable to that of the analogous hydrocarbon substituted compounds although it has been noted [29] that fluorophosphetidines have a greater stability to hydrolysis. Phenoxy-substituted fluorophosphoranes [23, 36] on the other hand, in comparison to other difluorophosphoranes, appear to be more sensitive to moisture.

(ii) Thermal stability

The thermal stability of these compounds is dependent on the heteroatom as well as the number of fluorine atoms in the molecule. In general it has been noted that aminofluorophosphoranes of the type $RPF_3NR'_2$ have a tendency to rearrange to give ionic isomers of the type $[R(R'_2N)_2PF]^+[RPF_5]^-$ (Chapter 6). An interesting example is $PhPF_3NEt_2$ which does not rearrange even over a period of years. [24]

Rearrangements have also been observed for certain phenoxy fluorophosphoranes. [23, 36, 39]

$$2(PhO)PF_3(NMe_2) \longrightarrow [(PhO)_2P(NMe_2)_2]^+[PF_6]^-$$

$$2(PhO)_2PF_3 \longrightarrow [(PhO)_4P]^+[PF_6]^-$$

This, however, assumes the formation of a trifluorophosphorane intermediate. (Chapter 1) In general, however, phenoxyfluorophosphoranes are thermally stable contrasting to alkoxyfluorophosphoranes which, even at room temperature, thermally decompose according to the equation,

$$ROPR'F_3 \longrightarrow R'P(:O)F_2 + RF. \qquad (33\text{-}35, 40, 189)$$

The analogous alkylthio [23, 31, 32] substituted compounds are more stable and show no sign of thiophosphoryl formation apart from the reaction of dimethyltrifluorophosphorane, Me_2PF_3 with tBuSNa or $tBuSSiMe_3$ which proceeds, presumably via the formation of a difluorophosphorane intermediate, subsequently giving a thiophosphoryl compound and tertiary-butyl fluoride according to the equations,

$$Me_2PF_3 + tBuSNa \longrightarrow Me_2P(:S)F + tBuF + NaF \quad (41)$$

$$Me_2PF_3 + tBuSSiMe_3 \longrightarrow Me_2P(:S)F + tBuF + Me_3SiF \quad (41)$$

Studies of the thermal stability of alkyl- and arylthio fluorophosphoranes by Peake et.al.,[23, 31] have shown that on heating to elevated temperatures decomposition takes place resulting in the formation of more stable hydrocarbon substituted fluorophosphoranes plus three-coordinate phosphorus compounds or ionic phosphorus compounds, according to the equations,

$$PhSPF_4 \longrightarrow [(PhS)_4P]^+[PF_6]^- + PF_5$$

$$PhSPPhF_3 \longrightarrow (PhS)_2 + PhPF_4 + (PhS)_2PPh$$

$$PhSPPh_2F_2 \longrightarrow (PhS)_2 + Ph_2PF_3 + PhSPPh_2.$$

Heteroatom phosphorus-fluorine compounds in which phosphorus has a coordination number four.

The examples of phosphorus compounds in which phosphorus has a coordination number of four are many and many reviews have appeared in the literature concerned with such compounds. Reviews which might be noted are by Van Wazer, [44] Schmutzler [1] and Haiduc.[4] This introduction is limited to a class of phosphorus compounds in which phosphorus is part of a ring system i.e., cyclic phosphonitriles $(PNX_2)_n$ and in particular the fluorophosphonitriles $(PNF_2)_n$. The chlorophosphonitriles were the first compounds of this class to be prepared by Rose[45] from the reaction of phosphorus pentachloride, PCl_5, with ammonium chloride, NH_4Cl, but it was not until later that Stokes[46-51] established the cyclic nature of these compounds, (where n = 3-7). The chlorophosphonitriles have, for a long time, been considered the 'parent' compounds of this large class rather than the hypothetical hydrides $(PNH_2)_n$ and recent reviews concerning these compounds[1,4,9-12,62,63,76,77] are fairly comprehensive. The analogous fluorophosphonitriles cannot, however, be made by the analogous method, reaction of phosphorus pentachloride with ammonium fluoride,[61] as the reaction proceeds to give ammonium hexafluorophosphate, $[NH_4]^+[PF_6]^-$ However, fluorination of the chlorophosphonitriles is a method which can be utilised in the preparation of the fluoro compounds and a recent review[1] lists preparative methods available.

The derivative chemistry of the chloro-cyclophosphonitriles is extensive and a recent review[4] discusses thoroughly this derivative chemistry. Chlorine has been successfully replaced from chlorophosphonitriles by many organo groups including, F, Br, Alk, Ar, R_f, OR, OAr, R_2N-, RHN-, and Ar_2N-. In contrast the corresponding derivative chemistry of fluorophosphonitriles is not as extensive.

Partial substitution of fluorine atoms by hydrocarbon groups has been accomplished by the reaction of $(PNF_2)_3$ with organo lithium reagents [52-55] according to the equation,

$$nArLi \quad + \quad (PNF_2)_3 \longrightarrow P_3N_3F_{6-n}Ar_n \quad + \quad nLiF \quad (n = 6).$$

Partially substituted chloro-fluoro-phosphonitriles have been prepared [56] by the partial fluorination of the trimeric chloro-compound giving the compounds $P_3N_3F_nCl_{6-n}$ (where n = 1-6).

The reaction of phosphonitrilic fluorides with the Si-N bonded compound Me_2NSiMe_3 have been investigated [57] and it was found that this was a useful route to amino-substituted phosphonitrilic fluorides, reaction taking place according to the equation,

$$mMe_2NSiMe_3 \quad + \quad (PNF_2)_n \longrightarrow P_nN_nF_{2n-m}(NMe_2)_m \quad + \quad mMe_3SiF.$$

(where n = 3-6; m = 1-3).

The corresponding reaction of $(PNF_2)_3$ with Si-S bonded compounds does not produce the expected thio-substituted derivatives (Chapter 3), no reaction takes place. However, a report has appeared [58] in which it was stated that thioethyl derivatives of $(PNF_2)_3$ can be prepared from the reaction of sodium ethyl mercaptide with $(PNF_2)_3$ according to the equation,

$$(PNF_2)_3 \quad + \quad nNaSEt \longrightarrow P_3N_3F_{6-n}(SEt)_n \quad + \quad nNaF \quad (n = 1-5).$$

The analogous reaction of Si-O bonded compounds with $(PNF_2)_3$ leads to alkoxy- and aryloxy-substituted fluorophosphonitrilic trimer (Chapter 3). The reason for this might be explained from the greater nucleophilicity of Si-O bonded compounds over Si–S bonded compounds.

The ammonolysis of $(PNF_2)_3$ has also been reported [59] from which the compound $(NH_2)P_3N_3F_5$ was isolated. Recently an anionic derivative, $Cs^+[P_3N_3F_7]^-$, [60] of $(PNF_2)_3$ was isolated from the reaction of $(PNF_2)_3$ with CsF. However, it is still not certain whether this derivative retains a cyclic structure or is of a linear structure, although limited experimental data suggest a linear structure of $Cs^+[PF_3{=}NPF_2{=}NPF_2{=}N]^-$ meaning cleavage of the cyclic structure. This reaction compares with the reaction of fluorophosphoranes with CsF. [23, 27]

Properties of Halo-Phosphonitriles and Derivatives

(i) Hydrolytic Behaviour

Halogenophosphonitriles are hydrolysed by water [4, 11] although such decompositions are often much slower than those of analogous phosphorus halides. [1, 2] Hydrolysis of the side group precedes decomposition and in each case the initial product is a hydroxyphosphonitrile or the tautomeric isomer eg.,

$$(PNX_2)_3 \;+\; 6H_2O \longrightarrow 6HX \;+\; (PN(OH)_2)_3 \rightleftharpoons (HOP(:O)NH)_3$$

Further decomposition takes place with the formation of phosphoric acid and ammonia.

In general cyclic trimers are more resistant to hydrolysis than the higher homologues and the fluorophosphonitriles appear to hydrolyse more readily than the chloro derivatives the mechanism probably being similar. In general phosphonitriles substituted with organo groups are more stable to hydrolysis than the halogen derivatives although they too may be degraded by aqueous base or acid. [4, 11]

(ii) Thermal Stability

One of the main properties of cyclic phosphonitriles is their ability to form linear or cross-linked polymers. [4, 11] It may be noted that $(PNF_2)_3$ can be heated in a sealed tube at 300°C for several hours without change but at 350°C for 15 hours in an autoclave linear polymeric difluorophosphonitrile is formed. [64, 65]

Thermal rearrangement is also characteristic of certain organo cyclophosphonitriles; thus alkoxy phosphonitriles rearrange to give N-alkyl substituted compounds of the type $(ROP(:O)NR)_n$ [66,67]

Allcock in his review [11] discusses the chemical and physical properties of this class of compound thoroughly.

Heteroatom phosphorus-fluorine compounds in which phosphorus has a coordination number of six

The compounds to be discussed in this class are tetra- penta- and hexa-fluorophosphates, $[R_2PF_4]^-$,$[RPF_5]^-$,$[PF_6]^-$ and these anions are invariably accompanied by a fluorophosphonium cation of the type $[R_nPF_{4-n}]^+$ in which phosphorus is present in coordination number four. The compounds to be discussed in this thesis are formed from either the thermal rearrangement of heteroatom fluorophosphoranes rearranging to give stable ionic isomers, or because of a difference in acceptor (donor) properties of reactants in a reaction mixture. Thermal stability of heteroatom fluorophosphoranes is discussed in chapter 6 and the donor-acceptor properties are discussed in chapter 6. Schmutzler in a review [1] gives a comprehensive list of hexafluorophosphates and discusses the existence of penta- and tetrafluorophosphates.

Properties of ionic phosphorus-fluorine compounds

Hexafluorophosphates belong to the most stable halogenocomplexes known. The symmetrical ion is not attacked by aqueous alkali even on boiling and is only slowly attacked in acidic media. This hydrolytic stability decreases as organo groups are introduced.

Thermal stability is also greater than for the corresponding five-coordinate phosphorus-fluorine compounds. This might be expected in view of the formation of certain ionic compounds. Amino- tetra- and trifluorophosphoranes are known to rearrange to give stable phosphonium hexafluorophosphates. (Chapter 6) However, diazonium hexafluorophosphates on heating to high temperatures decompose to give fluoro-hydrocarbons, nitrogen and PF_5, [1, 68] according to the equations,

$$[C_6H_5N{=}N]^+[PF_6]^- \longrightarrow C_6H_5F + N_2 + PF_5$$

$$[o\text{-}CH_3C_6H_4N{=}N]^+[PF_6]^- \longrightarrow o\text{-}CH_3C_6H_4F + N_2 + PF_5$$

$$[Cl\text{-}C_6H_5N{=}N]^+[PF_6]^- \longrightarrow Cl\text{-}C_6H_5F + N_2 + PF_5$$

Thermal decomposition of alkali or alkaline earth hexafluorophosphates also gives phosphorus pentafluoride, [1]

$$NaPF_6 \longrightarrow NaF + PF_5 \quad \text{(at } 400^\circ C\text{)}$$

$$Ba(PF_6)_2 \longrightarrow BaF_2 + 2PF_5 \quad \text{(at less than } 400^\circ C\text{)}$$

Structure and Stereochemistry of Heteroatom-Substituted Phosphorus-Fluorine Compounds

The structure of heteroatom-substituted phosphorus-fluorine compounds is dependent on the class of compound and the coordination number of the phosphorus atom.

The structure of five-coordinate heteroatom phosphorus-fluorine compounds is characterised by the same trigonal bipyramidal framework that has been established for other fluorophosphoranes.[1, 2] The general rule employed is that the most electronegative group will choose an axial site, thus invariably fluorine atoms will occupy the axial sites leaving the equatorial sites for hydrocarbon or heteroatom-containing groups. However this rule is not obeyed for fluorophosphetidines,[2] phosphadiazetidine-3-ones [5,6] or benzophosphole ring systems,[7, 8] in which phosphorus is bonded to a nitrogen or an oxygen atom through an axial position leaving a fluorine atom in equatorial position. This arises from the steric requirements of such ring systems about phosphorus in which a P-N-P angle of 90° involving the use of an axial site is energetically more favourable than a P-N-P angle of 120° involving the use of an equatorial site.

The structures of hexa-[1], penta-[23, 27] and tetra-[23, 27] fluorophosphate ions are characterised by octahedral structures in which organo groups are found in the axial sites leaving equatorial sites occupied by fluorine atoms.

Phosphonitrilic fluoride trimer, $(PNF_2)_3$ has a planar P-N framework[1, 4, 11] and its planar nature was established by X-ray crystal-structure analysis.[69] The corresponding tetramer was also found to have a basic planar structure[70] but as n increases then the basic structure deviates from a planar one.[1, 4, 11]

The use of ^{19}F and ^{31}P n.m.r analysis was found to be useful in establishing structures of the heteroatom fluorophosphoranes and fluorophosphate anions but due to the complicated spin nature of fluorophosphonitriles n.m.r. analysis was not found to be a good analytical tool.

The ^{19}F n.m.r. data of heteroatom tetrafluorophosphoranes are characteristic of four apparently magnetically equivalent fluorine atoms. This phenomenon is explained by the existence of, at room temperature, a non-rigid pseudorotating structure. On lowering the temperature this rotation can be slowed down to within the time scale of the n.m.r. measurement so as to permit observation of two distinct fluorine atom environments. This would be expected if one postulates a trigonal bipyramidal structure.[1, 2, 23, 31, 71]

The ^{19}F n.m.r. data of organo-substituted trifluorophosphoranes are characteristic of two distinct fluorine atom environments, one equatorial and two axial fluorine atoms,[1, 2] of characteristic chemical shift and coupling constant. Apart from halo- and perfluoromethyl- substituted fluorophosphoranes[1, 2] there is no observation of a non-rigid pseudorotating structure at room temperature.

Organo-substituted difluorophosphoranes are all characterised by low fluorine chemical shifts and coupling constants[1, 2] which are consistent with axial fluorine atoms in an axial environment about phosphorus. No pseudorotation process is observed as this would involve the positioning of an organo group in an energetically unfavourable axial position in the intermediate form of a pseudorotation process.

Fluorophosphate anions are characterised by high ^{19}F

n.m.r. chemical shifts, relative to CCl_3F as reference standard, and coupling constants of about 700 Hz.[1] Hexafluorophosphate is characterised by six magnetically equivalent fluorine atoms, whereas penta-fluorophosphates have two distinct fluorine environments, one axial fluorine atom and four equatorial fluorine atoms and tetrafluorophosphates have only one fluorine environment, four magnetically equivalent equatorial fluorine atoms. The corresponding fluorophosphonium cations invariably have higher chemical shifts and larger coupling constants relative to the fluorophosphate anions. (Chapter 6)

The ^{31}P chemical shifts of phosphorus-fluorine compounds are related to the coordination number of the phosphorus atom and it can be said that as the coordination number increases then the phosphorus chemical shift becomes more positive.[72]

An interesting feature to be noted is that for di- and tri- fluorophosphetidines the ^{19}F n.m.r. data are consistent with magnetically equivalent fluorine atoms.[2] X-ray crystallographic studies of the fluorophosphetidine $(PhPF_2NMe)_2$ have established that the two N atoms are in axial and equatorial positions of the trigonal bipyramid and the phenyl is in the equatorial position.[73] This observed magnetic equivalence is believed to be caused by a positional exchange process involving the fluorines and hydrocarbon groups and may be of the type postulated for the trifluorophosphorane $(CH_2)_4PF_3$.[19, 74]

GENERAL EXPERIMENTAL TECHNIQUE

GENERAL EXPERIMENTAL TECHNIQUES

Since all starting materials and products of the reactions are highly moisture sensitive it was necessary to take special precautions for the exclusion of moisture during all preparative procedures.

Apparatus - All glass apparatus was baked under vacuum and flushed with dry nitrogen before use. "Kel-F" grease was used to grease all ground glass joints, to prevent attack of corrosive fluorophosphoranes on the grease. The contact of fluorophosphoranes with glass was minimised to prevent hydrolysis of phosphorus-fluorine compounds by the **hydrolytic** effect of glass and water. The fluorophosphoranes were stored in Monel cylinders or "Teflon" vials. The less corrosive di- and tri- fluorophosphoranes could also be stored in glass containers at reduced temperature. Any reactions involving gaseous reactants were carried out in heavy-walled glass reaction tubes with constrictions to facilitate sealing under vacuum. Other reactions were carried out in small three necked flasks fitted with an addition funnel, thermometer, magnetic stirring bar and reflux condenser attached by means of P.V.C. tubing to a trap held at -78°C by means of a "dry-ice" acetone mixture. All experiments carried out at normal temperature and pressure were protected at the open end by means of drying tubes containing calcium chloride, silica-gel or phosphorus pentoxide.

Materials - Solvents and internal n.m.r. standards were dried by distillation off sodium wire (ether, benzene, tetrahydrofuran, toluene), off phosphorus pentoxide (acetonitrile, carbon tetrachloride, tri- and di- chloromethane, trichlorofluoromethane and tetramethylsilane) or lithium aluminium hydride (benzene, toluene and tetrahydrofuran). Phosphorus pentafluoride was obtained as a technical product from Ozark Mahoning Co., Tulsa, Oklahoma, U.S.A. The fluorophosphoranes R_nPF_{5-n} were prepared by known literature methods: $MePF_4$ [78, 79], $PhPF_4$ [78-81], Me_2PF_3 [79, 81-83], Ph_2PF_3 [78, 79, 81], $PhMePF_3$ [82,83], Me_2NPF_4 [13-15, 18, 21], Et_2NPF_4 [13, 14, 18], $(Me_2N)_2PF_3$ [13-15, 18], $(Me_2N)_3PF_2$ [22]. They were all stored over sodium fluoride to absorb any hydrogen fluoride generated and distilled before use.

N.m.r. Spectra - All room temperature ^{19}F, ^{31}P and ^{1}H n.m.r. spectra and low temperature ^{19}F n.m.r. spectra were obtained on a Varian Associates HA-60 spectrometer fitted with a frequency generator for wide lock measurements. Unless otherwise stated tetramethylsilane was used as internal standard for ^{1}H measurements, trichlorofluoromethane was used as internal standard for ^{19}F measurements and 85% phosphoric acid was used as external standard, in sealed capillaries, for ^{31}P measurements.

Mass Spectra - Mass spectra were recorded on an A.E.I. MS 9 mass spectrometer or an Atlas CH 4 spectrometer. In all cases the presence of extraneous peaks was observed probably due to hydrolysis of samples on introduction into the spectrometer.

Infra-Red - Infra-red spectra were recorded on a Beckmann IR 20A spectrometer using KBr plates or liquid cells. Samples were made as solutions in carbon tetrachloride or as a Nujol Mull.

Analysis - Analyses were carried out by J. Beller Göttingen, Germany; the staff of Analytical Dept. of Farbenfabriken Bayer, Wuppertal Elberfeld, Germany or the technical staff of the Technische Universität, Braunschweig, Germany.

CHAPTER I

ARYLOXY SUBSTITUTED FLUOROPHOSPHORANES

CHAPTER I

ARYLOXY SUBSTITUTED FLUOROPHOSPHORANES

Recent attempts at preparing fluorophosphoranes substituted by oxygen-containing groups have given varying results. The first examples reported were monofluorophosphoranes of general formula $R_fP(OEt)_3F$ (where R_f = perfluoroalkenyl), [33] which were prepared by the addition of triethylphosphite to fluoro-olefins such as perfluoroisobutene or perfluoro-cyclobutene at -70°C. Attempts at the preparation of alkoxy fluorophosphoranes have shown that formation readily occurs but that the compounds are only stable at low temperatures. Methoxy tetrafluorophosphorane has been reported, [34] from the reaction of trimethylphosphite with phosphorus pentafluoride at low temperature, but it was found to be thermally unstable, decomposition occuring on warming to room temperature. Compounds of the type $ROPR'F_3$ (where R' = Me, Et.) were also found to be thermally unstable,[35] these observations being noted elsewhere in the literature. [24, 33, 40] Decomposition with the formation of alkyl fluoride and a phosphoryl compound takes place readily according to the equation,

$$ROPR'_nF_{4-n} \longrightarrow P(:O)R'_nF_{3-n} + RF.$$

A report of the reaction of difluorodiazirine with trimethyl- and triphenyl- phosphite indicated the formation of the difluorophosphoranes $(MeO)_3PF_2$ and $(PhO)_3PF_2$ as by-products. [37] Both of these compounds were characterised by ^{19}F n.m.r. analysis only but in view of work recently reported [23, 36] and the work presented here these results are cast into doubt. It is thought that the ^{19}F n.m.r. data reported correspond to the hexafluorophosphate ion $[PF_6]^-$ rather than the reported difluorophosphoranes.

In contrast to the alkoxy fluorophosphoranes the corresponding phenoxy fluorophosphoranes are found to be thermally stable. A stable series of such compounds, $(PhO)_{3-n}PR_nF_2$ (where n = 0, 1, 2; R = Me, Ph) [23, 36] have been prepared from the reaction of phenyltrimethylsilyl ether with the fluorophosphoranes R_nPF_{5-n} (where n = 0, 1, 2; R = Me, Ph). The formation of only difluorophosphoranes can be explained by the reactions proceeding via the formation of either tetra- or tri- fluorophosphorane intermediates which either react further with the silyl-ether or decompose giving stable difluorophosphoranes as the only phosphorus-fluorine product.

The formation of an ionic species was also observed during the reaction of phosphorus pentafluoride with phenyltrimethylsilyl ether and was identified as tetra-phenoxy phosphonium hexafluorophosphate, $[(PhO)_4P]^+[PF_6]^-$ The formation of this ionic species was found to be catalysed by the presence of small amounts of sodium fluoride and in the presence of sodium fluoride the ionic product was the only phosphorus-fluorine species formed. Its formation can be explained by the rearrangement of a possible trifluorophosphorane intermediate to its stable ionic isomer. The possible existence of $(PhO)_2PF_3$ as its ionic isomer has been reported by Kolditz et al. [84]

$$2(PhO)_2PF_3 \longrightarrow [(PhO)_4P]^+[PF_6]^-$$

Under the reaction conditions employed for the reaction of phosphorus pentafluoride with phenyltrimethylsilyl ether the rearrangement of the proposed trifluorophosphorane intermediate is not fast enough to prevent the formation of the covalent difluorophosphorane species.

Another ionic compound was found to be formed from the reaction of dimethylamino-tetrafluorophosphorane with phenyltrimethylsilyl ether, [23, 36, 39] and was identified as bis(dimethylamino)-bis(phenoxy)-phosphonium hexafluorophosphate, $[(Me_2N)_2P(OPh)_2]^+[PF_6]^-$. This reaction was also found to be dependent on the presence of a catalytic amount of sodium fluoride. No covalent product was isolated and the reaction was envisaged as proceeding via a trifluorophosphorane intermediate which rearranged under the influence of sodium fluoride to give the hexafluorophosphate product. The reaction mechanism was elucidated to some extent by ^{19}F n.m.r. analysis of the reaction mixture. Although no evidence was obtained for the trifluorophosphorane, evidence was obtained for the presence of a pentafluorophosphate intermediate, therefore one can envisage the reaction as proceeding according to the following equations,

$$Me_2NPF_4 \quad + \quad PhOSiMe_3 \longrightarrow Me_2NPF_3OPh \quad + \quad Me_3SiF$$

$$2Me_2NPF_3OPh \longrightarrow [Me_2NPF(OPh)_2]^+[Me_2NPF_5]^-$$

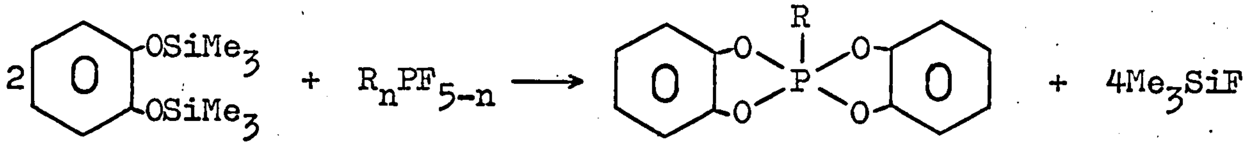
$$\text{or} \quad [(Me_2N)_2PFOPh]^+ \, [PhOPF_5]^-$$

$$\downarrow$$

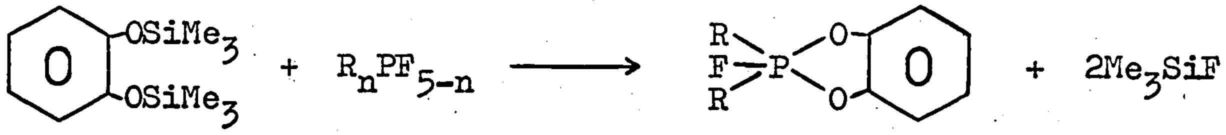
$$[(Me_2N)_2P(OPh)_2]^+[PF_6]^-$$

Attempts at preparing disubstituted oxyfluorophosphoranes have been carried out from the reaction of o-phenylenedioxybis(trimethylsilane) with the fluorophosphoranes R_nPF_{5-n}

(where n = 0, 1, 2; R = Me, Et, Ph) and the reactions produced spiro-phosphoranes containing the 1,3,2-dioxa-4,5-benzophosphole ring system, or monofluorophosphoranes depending on the value of n. The reactions proceeded according to the equations, [8, 9]

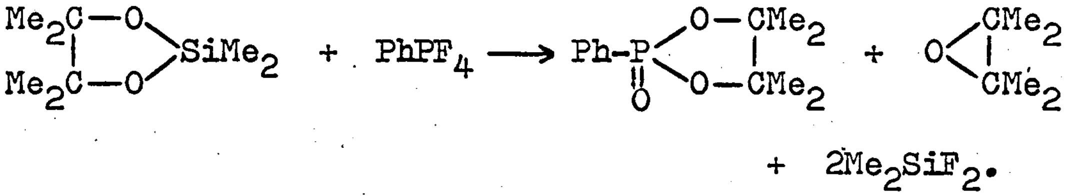


(where n = 0, 1; R = F when n = 0)



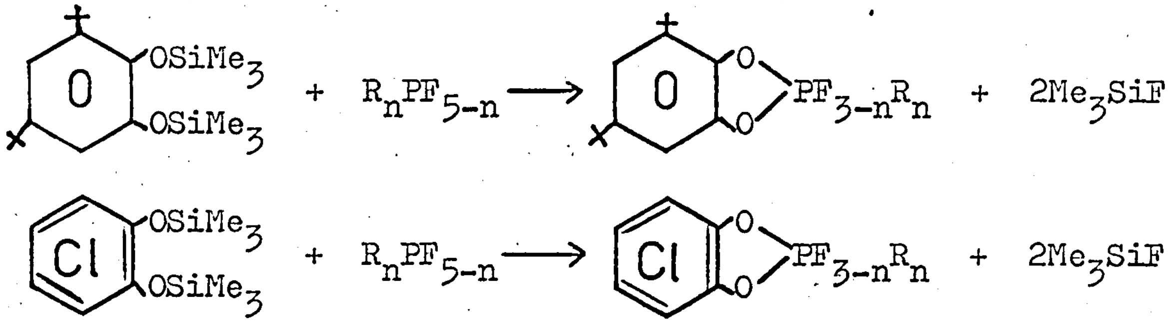
(where n = 2, 3; F = R when n = 3).

The reaction of 4,4,5,5-tetramethyl-1,3-dioxa-2-silacyclopentane with phenyltetrafluorophosphorane [8, 9] has been investigated but the expected five-coordinate phosphorus compound was not formed, instead the pinacol ester of phenylphosphonic acid was isolated. It is believed that the five-coordinate phosphorus compound is formed which then decomposes with the loss of 2,3-dimethyl-2,3-epoxybutane leaving the four-coordinate phosphoryl compound. The reaction takes place according to the equation,



The analogous reactions of 2,4-tertiarybutyl-o-phenylenedioxy-bis(trimethylsilane) and perchloro-ophenylenedioxy-bis(trimethylsilane) with fluorophosphoranes, however, have been found to be a route to dioxy-substituted fluorophosphoranes. [85]

The reactions take place according to the equations,



Although these fluorophosphoranes can be isolated they are found to be relatively unstable and will rearrange on standing to give spiro compounds.

Reactions have since been carried out between perfluorophenyl-trimethylsilyl ether and fluorophosphoranes and a stable series of difluorophosphoranes of general formula $(C_6F_5O)_{3-n}PR_nF_2$ (where n = 0, 1, 2; R = Me, Ph, Me_2N, Et_2N) have been prepared.

Synthesis

The preparation of perfluorophenoxy-substituted fluorophosphoranes is achieved by the cleavage of the Si-O bond of the Lewis base perfluorophenyl-trimethylsilyl ether with the Lewis acid fluorophosphoranes R_nPF_{5-n}, the reactions proceeding according to the equation,

$$(3-n)C_6F_5OSiMe_3 \; + \; R_nPF_{5-n} \longrightarrow (C_6F_5O)_{3-n}PR_nF_2 \; + \; (3-n)Me_3SiF.$$

(where n = 0, 1, 2; R = Me, Ph, Me_2N, Et_2N).

This type of reaction is analogous to those employed for the preparation of organothio- [23, 31] and diorganoamino- [2, 18] fluorophosphoranes. These reactions are carried out by the cleavage of the Si-S and Si-N bonds of organothio- and diorganoamino- trimethylsilanes, respectively.

All the reactions of perfluorophenyltrimethylsilyl-ether with fluorophosphoranes proceed smoothly producing an almost theoretical yield of the volatile by-product trimethylfluorosilane, Me_3SiF. Yields of pure perfluorophenoxydifluorophosphoranes are in the range 41-93% and they are, in most cases the exclusive phosphorus-fluorine compounds produced.

Substitution occurs to such an extent as to leave only two unreacted fluorine atoms in the final product, these being the axial fluorine atoms. These reactions contrast to the analogous cleavage reactions of Si-S and Si-N bonded compounds by fluorophosphoranes where the preference is for monosubstitution to take place. Multisubstitution has as yet only been observed for one case in the cleavage reactions of organothiosilanes and only a few examples of disubstitution have been observed in the cleavage reactions of diorganoaminosilanes. The general trend, as was noticed for the reaction of phenyltrimethylsilyl ether with fluorophosphoranes, is for multisubstitution to take place, monosubstitution taking place only when one equatorial fluorine atom is available for reaction viz.,

$$R_2PF_3 + C_6F_5OSiMe_3 \longrightarrow R_2PF_2OC_6F_5 + Me_3SiF.$$

The reaction of dimethylaminotetrafluorophosphorane Me_2NPF_4, with perfluorophenyltrimethylsilyl ether produces, besides the expected covalent difluorophosphorane, an ionic compound which was subsequently identified as $[(Me_2N)_2P(OC_6F_5)_2]^+[PF_6]^-$. A ^{19}F n.m.r. spectrum of the reaction mixture also showed evidence for the presence of a trifluorophosphorane and a phosphonium hexafluorophosphate intermediate. It is therefore assumed that the reaction proceeds via the formation of a trifluorophosphorane intermediate which subsequently rearranges via the formation of a pentafluorophosphate species to give, ultimately, the phosphonium hexafluorophosphate. This is the reaction mechanism postulated for the analogous reaction of phenyltrimethylsilyl ether with dimethylaminotetrafluorophosphorane. However, on addition of trace amounts of NaF there was no change in the overall yield of the ionic product, this being formed only in small amounts, the main product remaining the covalent difluorophosphorane.

The reaction between phenyltrimethylsilyl ether and phenyltetrafluorophosphorane was studied by ^{19}F n.m.r. analysis of successive samples of the reaction mixture as the reaction proceeded. Assuming the formation of a 1:1 adduct then it was found that this adduct broke down at +80°C and on measuring a sample at -50°C the ^{19}F n.m.r. spectrum showed, besides the expected difluorophosphorane product, the presence of a trifluorophosphorane species assumed to be $PhOPF_3Ph$. One can therefore assume that the reaction proceeds via this trifluorophosphorane species which reacts further with the silyl-ether giving the final difluorophosphorane.

Properties

The covalent perfluorophenoxy-difluorophosphoranes are all white crystalline solids with an odour of perfluorophenol. Handling is best achieved in a dry box because of moisture sensitivity. All the compounds were found to be thermally stable up to their melting points which contrasts to the observation on the analogous thiophenyldiphenyldifluorophosphorane, $PhSPF_2Ph_2$, [23, 31] which rapidly decomposes at 100°C. Several of these new oxyfluorophosphoranes were heated to their melting points and on cooling ^{19}F n.m.r. measurements made. The n.m.r. data were found to be consistent with those previously recorded. The hexafluorophosphate species is a colourless crystalline solid which was found to be less sensitive to moisture than the covalent difluorophosphoranes.

Nuclear Magnetic Resonance Data

^{19}F and ^{31}P n.m.r. spectral data for these new perfluorophenoxydifluorophosphoranes, $(C_6F_5O)_{3-n}PR_nF_2$ are listed in Table 1.1. The measurements suggest that the molecules are of a trigonal bipyramidal structure with the two fluorine atoms occupying the axial positions of this structure. The low fluorine chemical shifts (in the range +5.6 to +50.3p.p.m.) and P-F coupling constants (in the range 742 to 870 Hz) are characteristic of fluorine atoms in difluorophosphoranes. [2] The positive chemical shifts for phosphorus (in the range +3.9 to +84.0 p.p.m.) are characteristic of pentacoordinate phosphorus compounds. [72] The variation in δP can be explained by the electronegativity effects of the groups attached to the phosphorus, and the greater the electronegativity the higher the chemical shift.

^{19}F n.m.r. data for the trifluorophosphorane intermediates are listed in Table 1.2. The data are indicative of a trifluorophosphorane having a trigonal bipyramidal structure with two fluorine atoms occupying axial sites and the remaining fluorine atom occupying an equatorial site.

Table 1.1

N.m.r. Data for the Perfluorophenoxydifluorophosphoranes

Compound	F p.p.m.	P p.p.m.	J_{PF} (Hz)
$(C_6F_5O)_3PF_2$	+ 50.3	+ 84.0	809
$(C_6F_5O)_2PF_2Me$	+ 21.9	+ 54.9	870
$C_6F_5OPF_2Me_2$	+ 5.6	+ 3.9	742
$(C_6F_5O)_2PF_2Ph$	+ 38.2	+ 60.7 [a]	817
$C_6F_5OPF_2Ph_2$	+ 34.0	+ 45.5 [a]	813
$(C_6F_5O)_2PF_2NMe_2$	+ 50.4	+ 76.7	772
$(C_6F_5O)_2PF_2NEt_2$	+ 52.4	+ 75.3	778

a. Spectra recorded on solutions in tetrahydrofuran; otherwise acetonitrile was used as solvent.

^{19}F N.m.r. Data of the Aromatic Fluorine Atoms

Compound	ortho	para	meta
$(C_6F_5O)_3PF_2$	+ 155.9	+ 159.3	+ 163.0
$(C_6F_5O)_2PF_2Me$	+ 157.0	+ 161.3	+ 164.5
$C_6F_5OPF_2Me_2$	+ 156.6	+ 162.4	+ 164.2
$(C_6F_5O)_2PF_2Ph$	+ 156.2	+ 161.4	+ 164.0
$C_6F_5OPF_2Ph_2$	+ 157.2	+ 164.0	+ 166.2
$(C_6F_5O)_2PF_2NMe_2$	+ 157.0	+ 160.7	+ 163.0
$(C_6F_5O)_2PF_2NEt_2$	+ 156.4	+ 161.7	+ 164.0

All chemical shifts are in p.p.m.

Table 1. 2.

^{19}F n.m.r. data for the trifluorophosphorane intermediates

Compound	δ_{Fa}	δ_{Fe}	J_{PFa}	J_{PFe}	J_{FaFe}
$Me_2NPF_3OC_6F_5$	+53.0	+72.9	775	920	68
$PhOPF_3Ph$	+38.3	+65.4	864	986	72

Fa refers to axial fluorine and Fe to equatorial fluorine atoms.

Chemical shifts in p.p.m. and coupling constants in Hz.

A doublet of doublets is observed at low fields, attributed to the axial fluorine atoms and a doublet of triplets is observed at higher field, attributed to the single fluorine atom in an equatorial site[2]. The spectra arise from the two different fluorine environments in the trigonal bipyramidal structure of these trifluorophosphoranes.

The n.m.r. data for the hexafluorophosphate and the pentafluorophosphate are listed in Table 1.3. The ^{19}F and ^{31}P n.m.r. data for the hexafluorophosphate are in agreement with those known from the literature.[1, 72] The ^{19}F spectrum of the pentafluorophosphate shows a second order (AB_4X) pattern of the type which has been observed for the anions $[PhPF_5]^-$, $[Me_2NPF_5]^-$, and $[MePF_5]^-$.[23, 26, 27] One observes a doublet of quintets of a second order nature which is attributed to a single fluorine atom coupling with four other fluorine atoms and phosphorus and a doublet of doublets attributed to four magnetically equivalent fluorine atoms coupling with the remaining fluorine atom and with the phosphorus atom. From these

Nuclear Magnetic Resonance Data for the Ionic Species

Compound	δ F	δ P an.	J_{PF}	δ P cat.
$[(Me_2N)P(OC_6F_5)_2]^+[PF_6]^-$	+72.5	+145.0	725	a

	δ Fa	δ Fe	J_{PFa}	J_{PFe}	J_{FaFe}
$[(Me_2N)_2PFOC_6F_5]^+$ $[C_6F_5OPF_5]^-$	+59.0	+68.2	663	745	62
or					
$[Me_2NPF(OC_6F_5)_2]^+$ $[Me_2NPF_5]^-$	b.				

an. refers to anion: cat. refers to cation.
Fa and Fe refer to axial and equatorial fluorine atoms, resp.
a. δ P for the cation; b. δF for the cation; both were not observable from the spectra as concentrations of samples were too small

data one can assume that the pentafluorophosphate species is of an octahedral structure. The fluorine atom which is in a position trans to the dimethylamino- or perfluorophenoxy-group has an environment different to that of the remaining four fluorine atoms, thus accounting for the results.

Chemical shift data for the perfluorophenyl group are shown in Table 1.1. The ^{19}F n.m.r. spectra of the aromatic fluorine atoms, in all cases, are of a complicated nature as all five fluorine atoms are magnetically non-equivalent. The magnetic spin system is of an $AA'XX'Y$ type in which spin-spin coupling occurs between all the fluorine atoms of the aromatic perfluorophenyl ring. The highly positive chemical shifts are consistent with data reported for other compounds containing the perfluorophenyl group.[86, 87] There is no evidence for the coupling between phosphorus and the aromatic ring fluorine atoms as has been observed for the case of perfluorophenyl- fluorophosphines and fluorophosphoranes.[86]

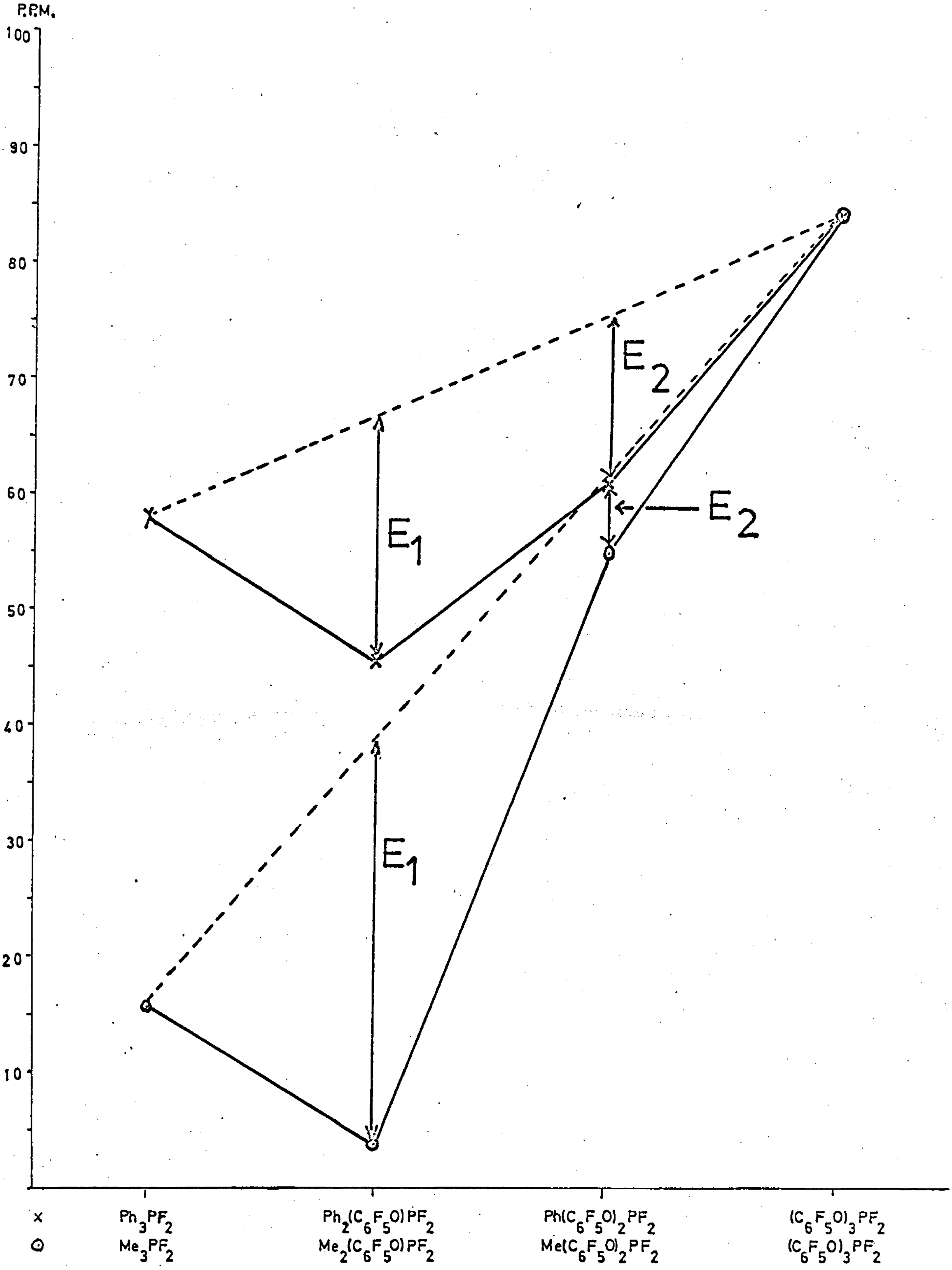
Substitution Series Comparison of ^{31}P chemical shifts

A plot can be made as shown in Figure 1.1 showing the variation of δP with the ratio of phenyl or methyl groups to perfluorophenoxy groups in these five-coordinate phosphorus compounds. The general shape is the same as that described by Letcher and Van Wazer[88] for similar plots of substitution series of three and four coordinate phosphorus compounds. The parameters E_1 and E_2 are termed deviations from additivity of chemical shift contribution and used to estimate the change in total π bonding of a mixed species relative to the amount of π bonding of each substituent in the respective symmetrical molecule. The method is empirical and based on data assembled for several similar substitution series of phosphines, phosphoryl and thiophosphoryl compounds. As yet, there are only few examples for the case of a five-coordination series, so no estimations can be made. Apart from the two series reported here only two other series are known.

	δP p.p.m.		δP p.p.m.
Ph_3PF_2 [22]	+58.1	Ph_3PF_2 [22]	+58.1
Ph_2MePF_2 [2, 24]	+43.2	Ph_2PhOPF_2 [23,36]	+34.4
$PhMe_2PF_2$ [2, 24]	+27.4	$Ph(PhO)_2PF_2$ [36]	+69.0
Me_3PF_2 [2, 89]	+15.8	$(PhO)_3PF_2$ [23, 36]	+88.4

Figure 1.1

^{31}P n.m.r chemical shifts for a substitution series of phosphorus compounds, showing the deviations from additivity, E_1 and E_2 in the shifts of the intermediate compounds.



The plots are consistent with the results reported by Letcher and Van Wazer in as much as π contributions vary within a definite series and the deviations from additivity are negative.

Mass Spectral Data

Mass spectra have been obtained for the following compounds, $(C_6F_5O)_3PF_2$, $PhPF_2(OC_6F_5)_2$, $Ph_2PF_2OC_6F_5$, $MePF_2(OC_6F_5)_2$ and $Me_2NPF_2(OC_6F_5)_2$. Figures 1.2, 1.3, 1.4, 1.5 and 1.6 show relative abundance diagrams for each of the compounds, respectively. Tables 1.4, 1.5, 1.6, 1.7, and 1.8 show the main fragments whose formation is evident from the spectra. In all cases extraneous peaks were present, probably due to hydrolysis of the compounds on introduction to the spectrometer. It was not possible to obtain an adequate spectrum of the compound $Me_2PF_2OC_6F_5$ due to its extreme moisture sensitivity.

In all cases the strongest peak observed is formed by the fission of one P-O bond causing the loss of a C_6F_5O- group and leaving the ion $[(C_6F_5O)_{2-n}PF_2R_n]^+$ (where n = 0, 1, 2; R = Me, Ph, Me_2N). The molecular ion is also observed in every case but is weak, approximately 1% relative to the strongest peak. From the data obtained it can be seen that a general fragmentation takes place involving successive P-O and P-F bond fissions and this is indicated in Figure 1.7. Cleavage of P-C, C-O and in the case of the amino compound P-N bonds is observed and the ions resulting are present in relatively high abundance. In general the fragmentation patterns observed are analogous to those observed in investigations carried out on other perfluorophenyl phosphorus compounds.[87, 90, 91] The cleavage of C-O bonds is evident in all cases with the formation of the $C_6F_5^+$ ion which is present in relatively high abundance and, when more than one C_6F_5- group is present in the molecule, the formation of perfluorobiphenyl is evident. However, the relative abundance of the perfluorobiphenyl ion is only of the order 1%. When there is only one C_6F_5- group present in the molecule then no evidence is seen of this ion. This suggests that the ion is formed by simultaneous cleavage of two C-O bonds from an ionic fragment with subsequent loss of a neutral fragment and formation of the perfluorobiphenyl ion and not the combination of two C_6F_5 groups which may have been formed via a different fragmentation route. The existence of the C_6F_5 group in a higher percentage than the perfluorobiphenyl ion might indicate the relative instability of the perfluorobiphenyl ion or that its formation only takes place to a small degree compared to other fragmentation patterns which take place.

A similar process was also observed for the compound $Ph_2PF_2OC_6F_5$ in which the biphenyl ion $C_6H_5-H_5C_6^+$ was formed in about 4% abundance. However, the phenyl ion C_6H_5 was found to be present in a greater percentage, ca. 50%. Therefore one might assume a similar fragmentation pattern to explain the observed results.

Fig. 1.2 Mass Spectral Relative Abundance Diagram.

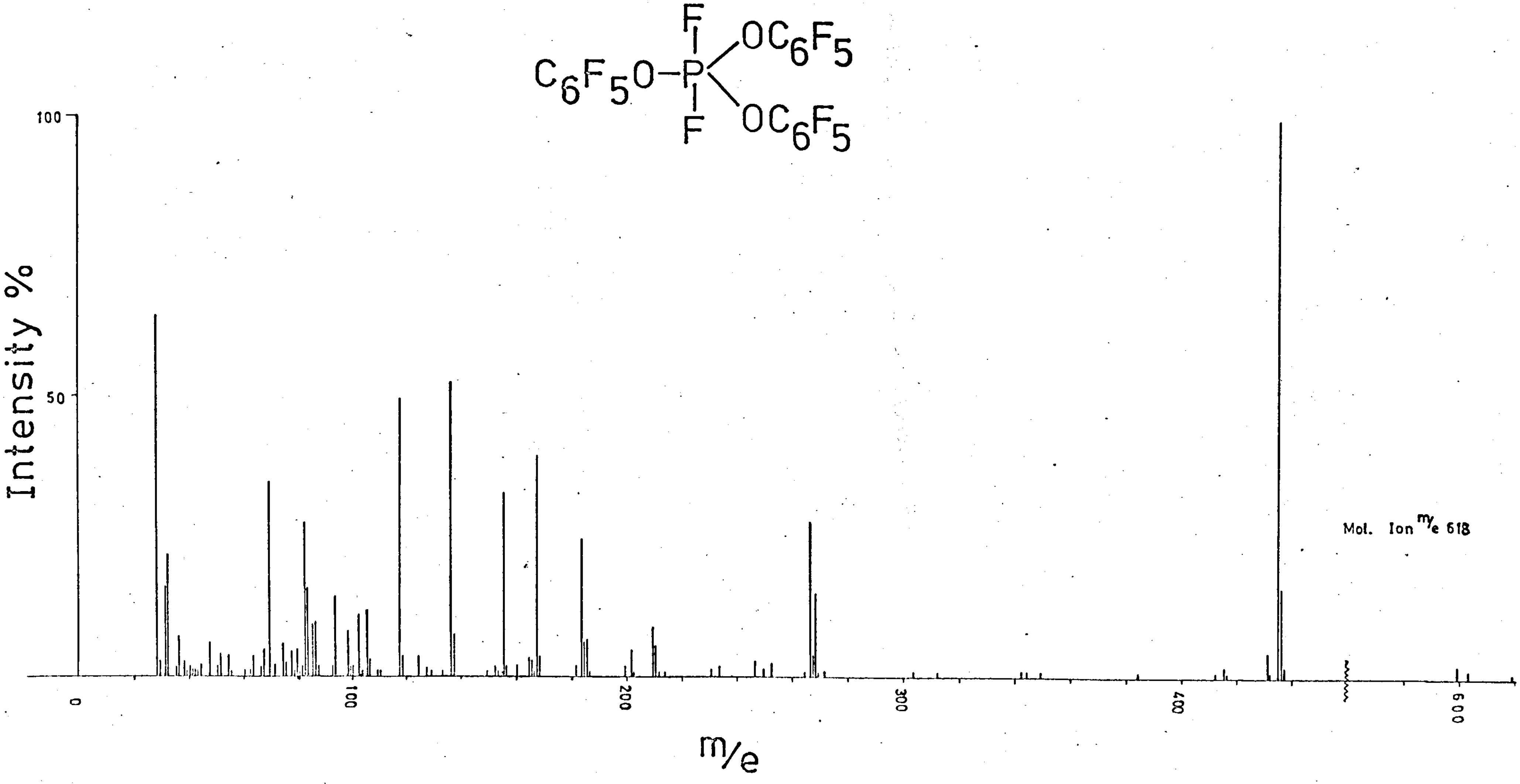


Table 1.4

Mass Spectral Data for $(C_6F_5O)_3PF_2$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
618	1.0	$(C_6F_5O)_3PF_2$ (mol. ion.)
599	2.3	$(C_6F_5O)_3PF$
580	< 1.0	$(C_6F_5O)_3P$
435	100.0	$(C_6F_5O)_2PF_2$ (Basis peak)
416	1.0	$(C_6F_5O)_2PF$
397	< 1.0	$(C_6F_5O)_2P$
252	2.8	$(C_6F_5O)PF_2$
233	2.0	$(C_6F_5O)PF$
214	1.0	$(C_6F_5O)P$
69	34.8	PF_2
50	1.5	PF
31	16.0	P
268	15.0	$(C_6F_5O)PF_2O$
249	1.8	$(C_6F_5O)PFO$
230	1.5	$(C_6F_5O)PO$
85	9.5	OPF_2
66	1.3	OPF
47	6.0	OP
183	24.8	C_6F_5O
167	39.6	C_6F_5
19	2.0	F (P-F bond cleavage)

Fig.1.3 Mass Spectral Relative Abundance Diagram.

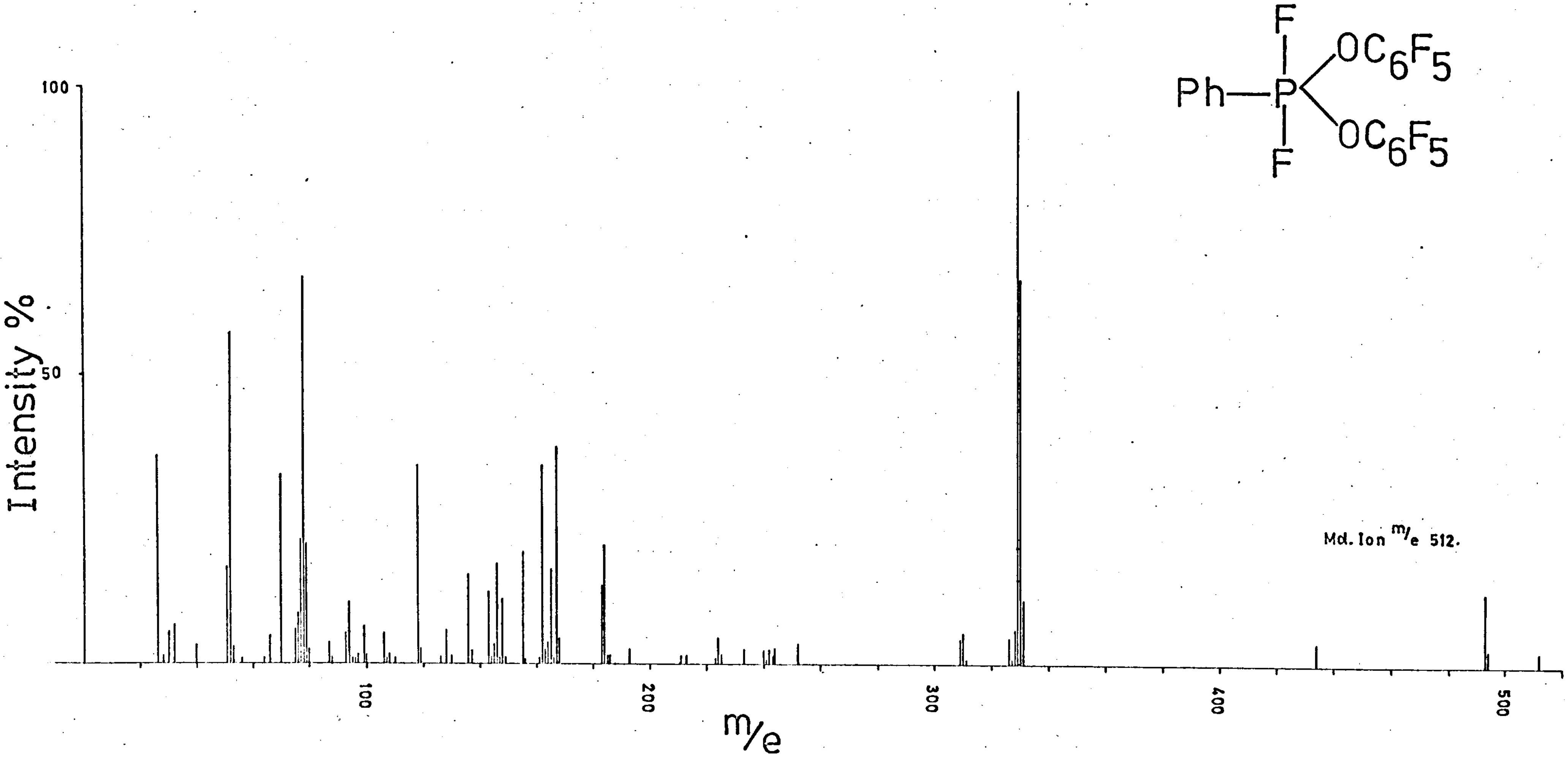


Table 1.5

Mass Spectral Data for $(C_6F_5O)_2PF_2Ph$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
512	2.5	$(C_6F_5O)_2PF_2Ph$ (Mol. ion.)
493	12.6	$(C_6F_5O)_2PFPh$
474	$<$ 1.0	$(C_6F_5O)_2PPh$
329	100.0	$(C_6F_5O)PF_2Ph$ (Basis peak.)
310	5.5	$(C_6F_5O)PFPh$
291	$<$ 1.0	$(C_6F_5O)PPh$
146	17.5	PF_2Ph
127	$<$ 1.0	PFPh
108	1.6	PPh
435	4.1	$(C_6F_5O)_2PF_2$
416	$<$ 1.0	$(C_6F_5O)_2PF$
397	1.0	$(C_6F_5O)_2P$
252	3.5	$(C_6F_5O)PF_2$
233	2.6	$(C_6F_5O)PF$
214	$<$ 1.0	$(C_6F_5O)P$
69	32.8	PF_2
50	$<$ 1.0	PF
31	5.6	P
183	13.7	C_6F_5O
167	37.7	C_6F_5

Table 1.5 cont.

m/e	relative abundance %	possible positive ion fragment
326	4.4	$(C_6F_5O)POFPh$
244	2.7	$(C_6F_5-C_6H_5)$
77	21.8	Ph
32	6.5	O
334	1.0	$(C_6F_5-C_6F_5)$

Fig. 1.4 Mass Spectral Relative Abundance Diagram.

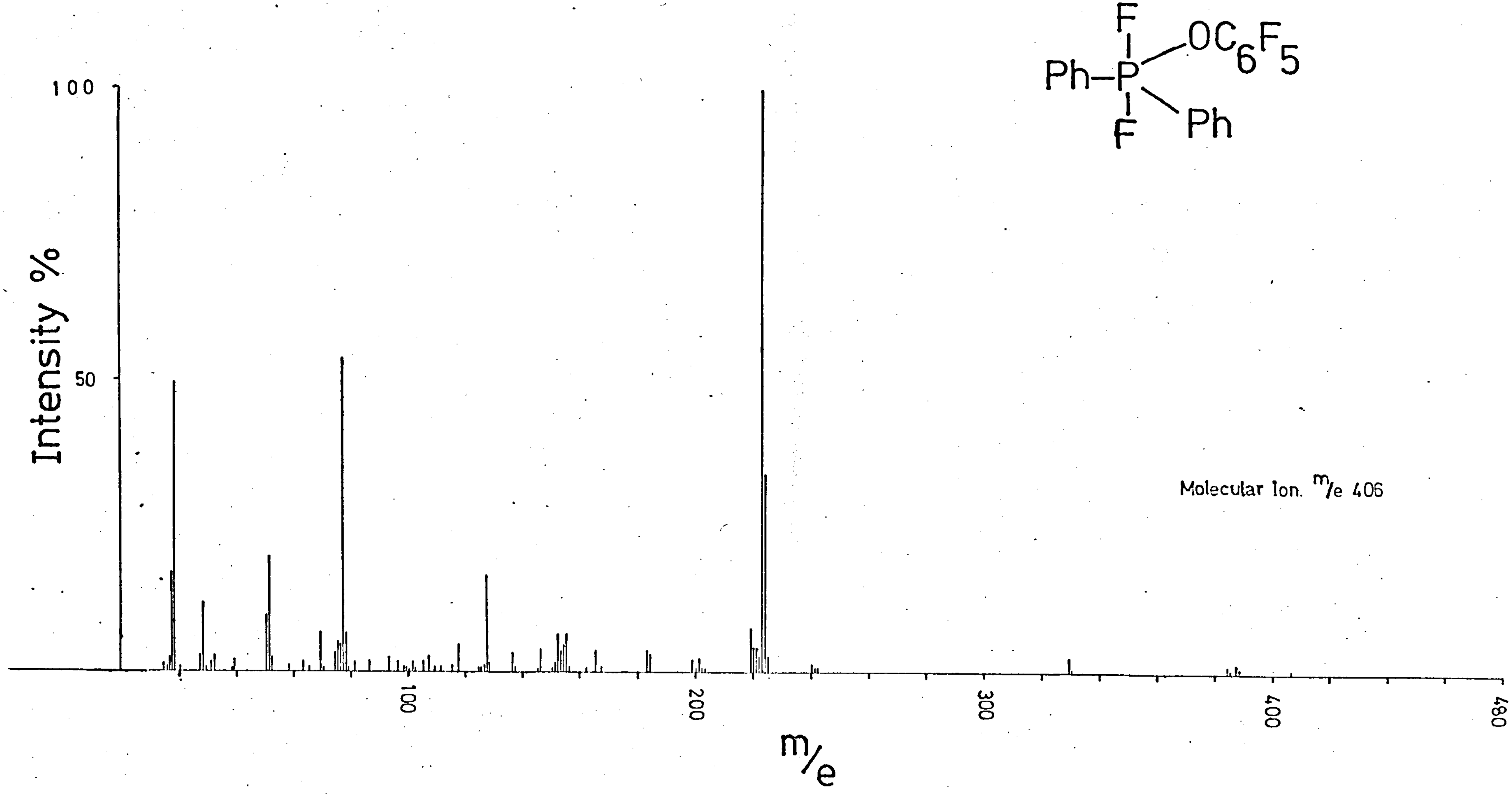


Table 1.6

Mass Spectral Data for $(C_6F_5O)PF_2Ph_2$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
406	1.0	$C_6F_5OPF_2Ph_2$ (Mol. Ion.)
387	1.2	$C_6F_5OPFPh_2$
368	1.0	$C_6F_5OPPh_2$
223	100.0	PF_2Ph_2 (Basis peak.)
204	< 1.0	$PFPh_2$
185	< 1.0	PPh_2
329	2.5	$C_6F_5OPF_2Ph$
310	< 1.0	C_6F_5OPFPh
291	< 1.0	C_6F_5OPPh
146	3.7	PF_2Ph
127	16.9	PFPh
108	1.0	PPh
69	6.6	PF_2
50	9.0	PF
31	1.6	P
19	1.0	F
239	1.0	Ph_2PF_2O
220	4.0	Ph_2PFO
201	2.1	Ph_2PO

Table 1.6 cont.

m/e	relative abundance %	possible positive ion fragment
183	3.3	C_6F_5O
167	1.0	C_6F_5
77	53.5	Ph
154	4.0	C_6H_5-C_6H_5

Fig. 1.5 Mass Spectral Relative Abundance Diagram.

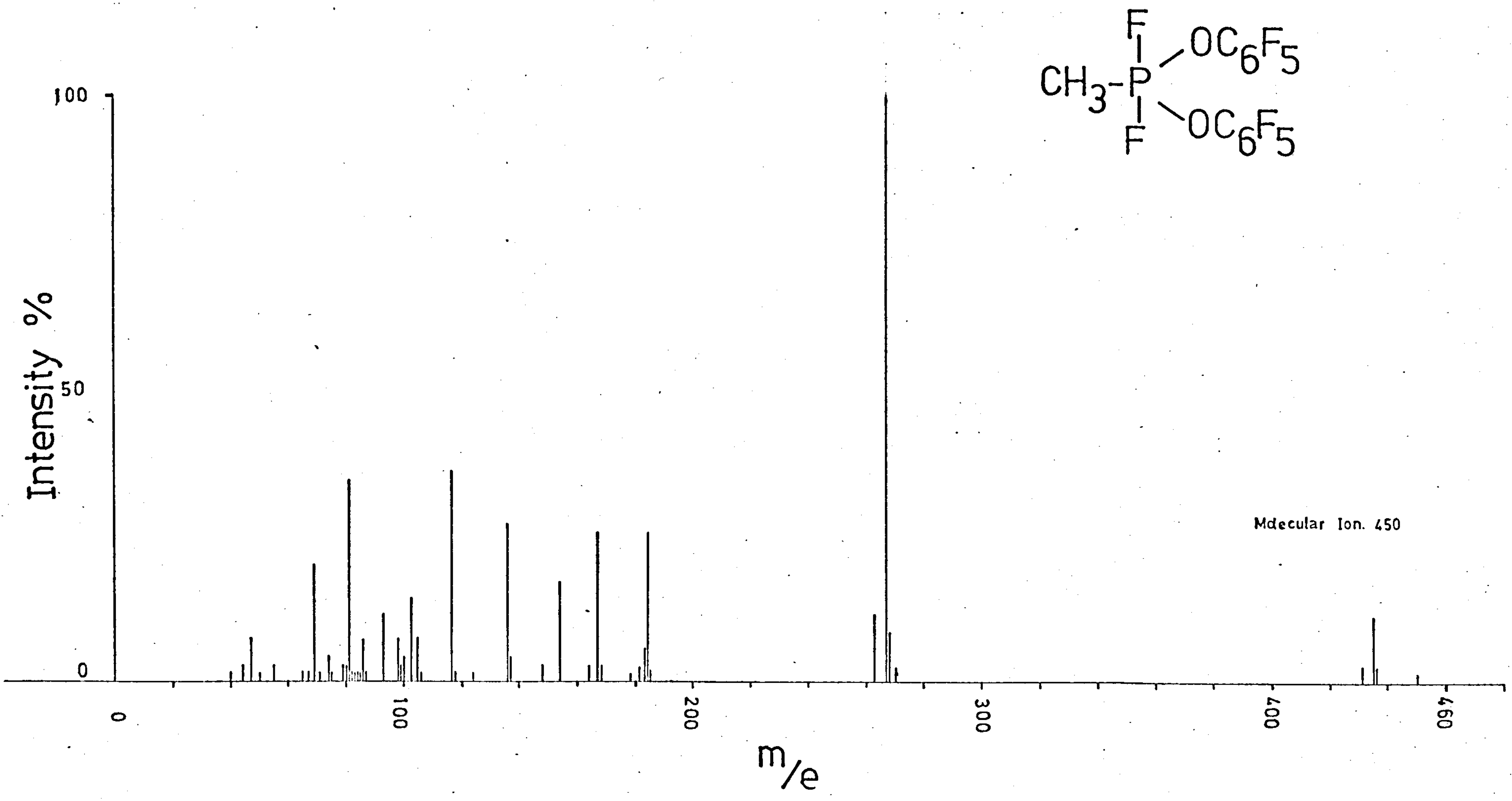


Table 1.7

Mass Spectral Data for $MePF_2(OC_6F_5)_2$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
450	1.4	$(C_6F_5O)_2PF_2Me$ (Mol. Ion.)
431	3.0	$(C_6F_5O)_2PFMe$
412	< 1.0	$(C_6F_5O)_2PMe$
267	100.0	$(C_6F_5O)PF_2Me$ (Basis peak.)
248	< 1.0	$(C_6F_5O)PFMe$
229	< 1.0	$(C_6F_5O)PMe$
84	1.4	PF_2Me
65	1.4	PFMe
46	< 1.0	PMe
435	11.4	$(C_6F_5O)_2PF_2$
69	20.0	PF_2
50	1.4	PF
31	1.0	P
100	4.3	OPF_2Me
85	1.4	OPF_2
81	34.5	OPFMe
334	1.0	$C_6F_5-C_6F_5$
184	25.7	C_6F_5OH
183	5.7	C_6F_5O
167	25.7	C_6F_5

Fig. 1.6 Mass Spectral Relative Abundance Diagram.

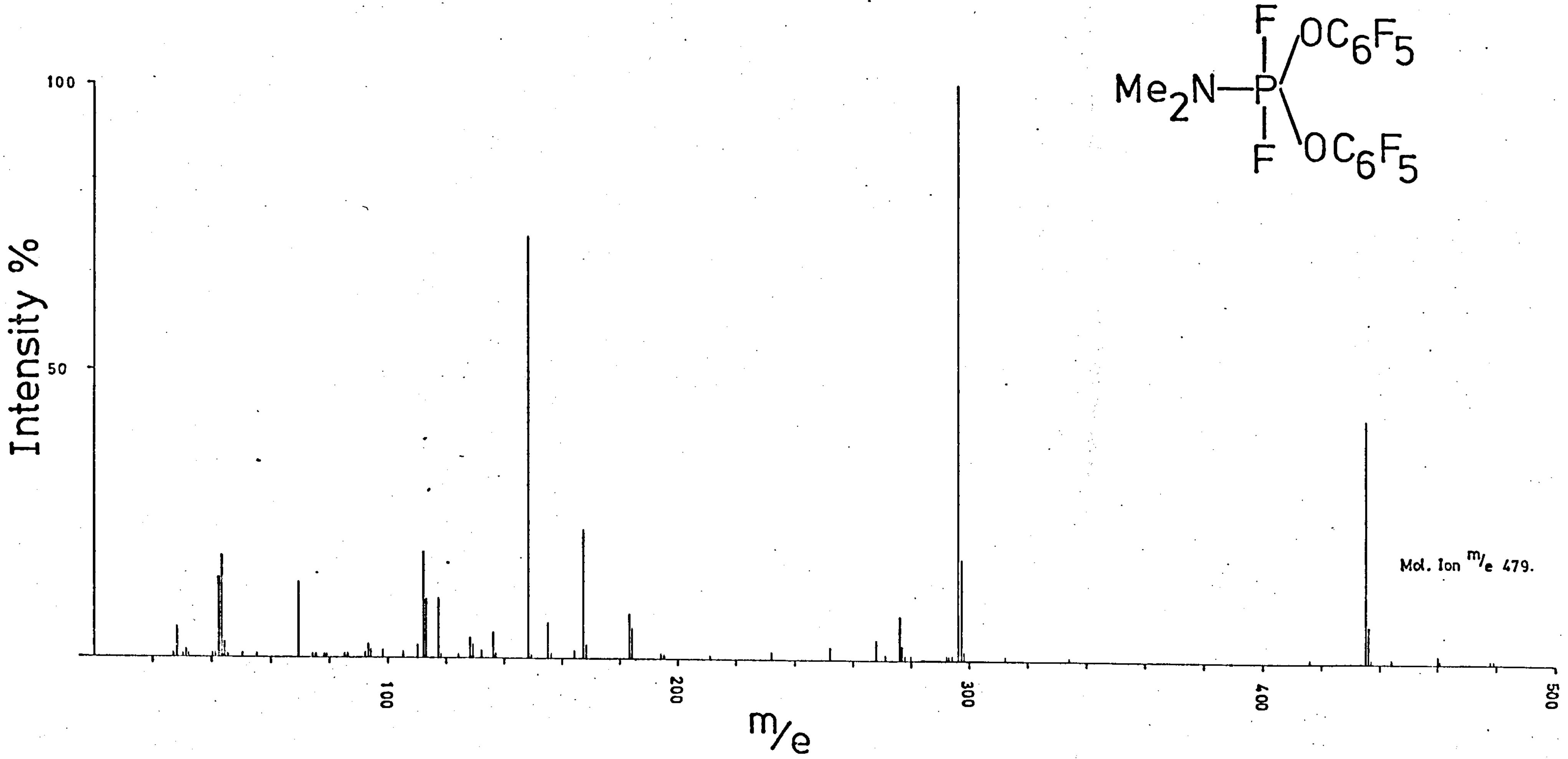


Table 1.8

Mass Spectral Data for $Me_2NPF_2(OC_6F_5)_2$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
479	< 1.0	$(C_6F_5O)_2PF_2NMe_2$ (Mol. Ion.)
460	1.8	$(C_6F_5O)_2PFNMe_2$
441	< 1.0	$(C_6F_5O)_2PNMe_2$
296	100.0	$(C_6F_5O)PF_2NMe_2$ (Basis peak.)
277	2.4	$(C_6F_5O)PFNMe_2$
258	< 1.0	$(C_6F_5O)PNMe_2$
113	10.2	PF_2NMe_2
94	1.6	$PFNMe_2$
75	< 1.0	$PNMe_2$
435	42.1	$(C_6F_5O)_2PF_2$
416	< 1.0	$(C_6F_5O)_2PF$
397	< 1.0	$(C_6F_5O)_2P$
252	2.2	$(C_6F_5O)PF_2$
233	1.4	$(C_6F_5O)PF$
69	13.6	PF_2
50	< 1.0	PF
31	1.5	P
44	3.0	Me_2N
334	1.0	$C_6F_5-C_6F_5$
167	22.6	C_6F_5
211	1.5	$C_6F_5-NMe_2$

Table 1.8 cont.

m/e	relative abundance %	possible positive ion fragment
184	5.1	C_6F_5OH
183	8.0	C_6F_5O
148	73.6	C_6F_4
129	2.3	C_6F_3 or OPF_2NMe_2
110	2.3	C_6F_2 or $OPFNMe_2$
43	17.6	CH_2-N-CH_3
42	14.1	CH_2-N-CH_2
41	1.0	CH-N-CH_2

For all mass spectral measurements the ionising potential was 70 e.v.

The temperatures of the samples at the inlet were:
$(C_6F_5O)_3PF_2$ 90°C; $(C_6F_5O)_2PF_2Ph$ 150°C; $(C_6F_5O)PF_2Ph_2$ 60°C; $(C_6F_5O)_2PF_2Me$ Room Temp; and $(C_6F_5O)_2PF_2NMe_2$ 120°C.

Figure 1.7

Fragmentation Pattern of P-O and P-F Bond Fission in Pentafluorophenylphenoxy-Substituted-Fluorophosphoranes

$$\begin{tikzcd}
R_nPF_2(OC_6F_5)_{3-n} \arrow[r] \arrow[d] & R_nPF_2(OC_6F_5)_{2-n} \arrow[r] \arrow[d] & R_nPF_2(OC_6F_5)_{1-n} \arrow[r] \arrow[d] & R_nPF_2 \arrow[d] \\
R_nPF(OC_6F_5)_{3-n} \arrow[r] \arrow[d] & R_nPF(OC_6F_5)_{2-n} \arrow[r] \arrow[d] & R_nPF(OC_6F_5)_{1-n} \arrow[r] \arrow[d] & R_nPF \arrow[d] \\
R_nP(OC_6F_5)_{3-n} \arrow[r] & R_nP(OC_6F_5)_{2-n} \arrow[r] & R_nP(OC_6F_5)_{1-n} \arrow[r] & R_nP
\end{tikzcd}$$

(where n = 0, 1, 2; R = Me, Ph)

The P-O bond fission can be seen from left to right and P-F bond fission from top to bottom.

Discussion

The main characteristic of this series of reactions is the multisubstitution of fluorine atoms in the 'parent' fluorophosphoranes, PF_5 and RPF_4. This is analogous to the reaction of phenyltrimethylsilyl ether with the fluorophosphoranes, R_nPF_{5-n}. [23, 36] In the analogous cleavage reactions of Si-S bonded compounds [23, 31] and Si-N bonded compounds [2, 18] with fluorophosphoranes monosubstitution was found to be preferred. As yet there is only one example of disubstitution for Si-S bond cleavage and this was observed during the reaction of $i\text{-}C_3H_7SSiMe_3$ with $PhPF_4$ at high temperature, the reaction producing the disubstituted product according to the equation,

$$PhPF_4 \quad + \quad 2i\text{-}C_3H_7SSiMe_3 \longrightarrow (i\text{-}C_3H_7S)_2PF_2Ph \quad + \quad Me_3SiF. \qquad (41$$

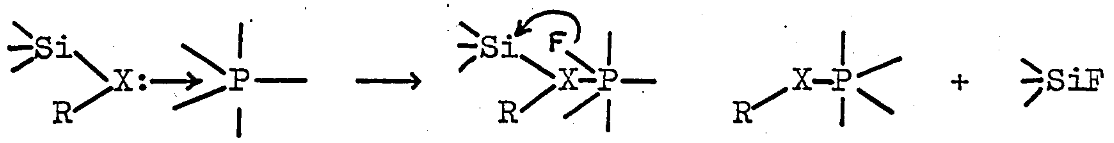
There have not been many examples of disubstitution reported for Si-N bond cleavage. The compounds $(R_2N)_2PF_3$ (where R = Me, Et) have been obtained from the reactions of the aminotetrafluorophosphoranes, R_2NPF_4, with the corresponding aminosilanes, but high temperatures were required to effect a reaction. The reactions proceed according to the equation,

$$R_2NPF_4 \quad + \quad R_2NSiMe_3 \longrightarrow (R_2N)_2PF_3 \quad + \quad Me_3SiF. \qquad (18)$$

However, it was observed that the reaction of $BzMeNPF_4$ with $BzMeNSiMe_3$ was exothermic producing the disubstituted aminofluorophosphorane.[23]

Monosubstitution occurs in the reaction of alkylsilyl ethers with fluorophosphoranes; however, these compounds are thermally unstable, decomposing at room temperature to give the corresponding phosphoryl compound and an alkyl fluoride. Although it has been found that the difluorophosphorane Me_2PF_3 reacts with arylsilylethers [23, 36] no reaction was observed when dimethyltrifluorophosphorane was allowed to react with compounds of the type R_2NSiMe_3 Alk-$OSiMe_3$ and $R_3Si-O-SiR_3$ [2]. It has also been observed that the reaction of Si-S bonded compounds with Me_2PF_3 is not a route to monosubstituted-thio-difluorophosphoranes. No products were identified from the reaction of Me_2PF_3 with alkyl- and aryl-thiosilylethers,[23, 31] and the reaction of Me_2PF_3 with $tBuSSiMe_3$ was found to produce the thiophosphoryl compound $Me_2P(:S)F$ rather than the expected difluorophosphorane Me_2PF_2StBu.[41] These contrasting results are presumably explained by the decreased Lewis acid character of Me_2PF_3 compared with other fluorophosphoranes and the different Lewis base character of the silyl compounds employed.

In all the reactions involving the Lewis acid fluorophosphoranes and the Lewis base Si-O, Si-N and Si-S bonded compounds the reactions presumably proceed by nucleophilic attack on the penta-coordinate phosphorus atom by the silyl oxygen, nitrogen and sulphur with the formation of a hexacoordinate adduct. Then follows a nucleophilic attack of a fluorine atom on the silicon atom with subsequent cleavage of the Si-O, Si-N or Si-S bond and formation of the products. The formation of strong Si-F bond is probably the driving force of the reaction, the P-F bond being relatively weaker. The reaction may proceed as follows:



If a large alkyl group is present such as tBu- then one might have to consider steric hindrance as a possible reason for the observed results from the reaction of $tBuSSiMe_3$ with Me_2PF_3. The formation of a thiophosphoryl bond may be energetically more favourable.

In the reactions of arylsilyl ethers with fluorophosphoranes where multisubstitution takes place it is reasonable to assume the intermediacy of tetra- and tri-fluorophosphoranes. The existence of trifluorophosphorane intermediates has been shown in the following reactions,

$$PhOSiMe_3 \quad + \quad PhPF_4 \longrightarrow PhOPF_3Ph \quad + \quad Me_3SiF, \text{ and}$$

$$Me_2NPF_4 \quad + \quad C_6F_5OSiMe_3 \longrightarrow Me_2NPF_3OC_6F_5 \quad + \quad Me_3SiF.$$

The evidence for the existence of these trifluorophosphoranes was obtained from ^{19}F n.m.r. analysis of the respective reaction mixtures. Phenoxyphenyltrifluorophosphorane was observed at -50°C, the room temperature spectrum showing a very broad doublet, and perfluorophenoxy-dimethylamino trifluorophosphorane was observed at room temperature. Both spectra were consistent with those recorded for other trifluorophosphoranes [2] and the structure of these compounds is of a trigonal bipyramidal type in which the axial sites are occupied by fluorine atoms. In no other case has an intermediate species been observed.

The formation of the final difluorophosphorane can occur in one of two ways, either by the reaction of the intermediate species, as they are formed, with more of the arylsilyl ether to give the difluorophosphoranes according to the equations

$$RPF_4 \quad + \quad R'OSiMe_3 \longrightarrow RPF_3OR' \quad + \quad Me_3SiF$$

$$RPF_3OR' \quad + \quad R'OSiMe_3 \longrightarrow RPF_2(OR')_2 \quad + \quad Me_3SiF,$$

or, by the reaction of the starting materials producing tetra- and tri- fluorophosphorane intermediates which subsequently disproportionate giving the appropriate difluorophosphorane and the fluorophosphorane starting material according to the equations,

$$3R'OPF_4 \longrightarrow (R'O)_3PF_2 + PF_5 \quad (R = \text{Aryl})$$

$$2RPF_3OR' \longrightarrow RPF_2(OR')_2 + RPF_4. \quad (R = \text{Aryl})$$

For both of these proposed reaction routes the results are identical. In order to prove whether either one of these reaction schemes takes place in preference to the other would necessitate the isolation of an intermediate and a study made of its thermal and chemical properties under the reaction conditions employed for the preparation of the difluorophosphoranes. Attempted isolation of such an intermediate has so far proved impossible due to its apparent high chemical reactivity within the reaction mixtures investigated.

The formation of the ionic compounds $[(Me_2N)_2P(OPh)_2]^+[PF_6]^-$ (see ref. 23, 36) $[(Me_2N)_2P(OC_6F_5)_2]^+[PF_6]^-$ (this work) and $[(PhO)_4P]^+[PF_6]^-$ [23,36] can be explained by the rearrangement of the trifluorophosphorane intermediates to form their stable ionic isomers. There is the possibility of two competing reactions taking place in which, either the covalent difluorophosphoranes are formed, or the ionic isomers are formed according to the equations,

$$(PhO)_2PF_3 + PhOSiMe_3 \longrightarrow (PhO)_3PF_2 + Me_3SiF \quad \text{and}$$

$$2(PhO)_2PF_3 \longrightarrow [(PhO)_4P]^+[PF_6]^-,$$

$$Me_2NPF_3OR' + R'OSiMe_3 \longrightarrow Me_2NPF_2(OR')_2 + Me_3SiF$$

(where $R' = C_6F_5-$) and

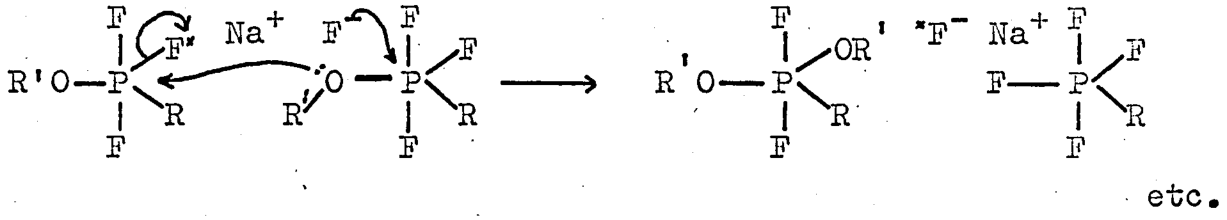
$$2Me_2NPF_3OR' \longrightarrow [(Me_2N)_2P(OR')_2]^+[PF_6]^-$$

(where $R' = Ph, C_6F_5-$).

All three of the ionic compounds were found in the reaction mixtures at the same time as the difluorophosphoranes were formed but only in small concentrations.

It was found that the presence of trace amounts of sodium fluoride had no influence on the products formed when the fluorophosphoranes PF_5 and Me_2NPF_4 were allowed to react with perfluorophenyltrimethylsilyl ether. In the former case there was no evidence for the formation of an ionic compound and in the latter case only a very small amount of an ionic compound was formed. This, however, contrasts to the analogous reactions of the two mentioned fluorophosphoranes with phenyltrimethylsilyl ether in which PF_5 reacts, under the influence of NaF, with $PhOSiMe_3$ to give an ionic product as the only phosphorus-fluorine product and Me_2NPF_4 reacts, under the influence of NaF with $PhOSiMe_3$ to give also an ionic product as the only phosphorus-fluorine product. For the latter reaction when conducted without the presence of NaF a small amount of the ionic compound is formed but no covalent phosphorus-fluorine compound is formed.

It might be assumed that NaF exists in the reaction mixture as Na^+ and F^- and the catalytic influence might be explained by the following reaction mechanism,



(where R' = Ph, or C_6F_5;;R = Me_2N: or R' = Ph and R = F).

This reaction mechanism assumes the formation of a trifluorophosphorane intermediate. The mechanism is also dependent on the lability of the groups present in the molecule and only occurs when PhO, C_6F_5 or Me_2N are present. The assumption made here is that the oxygen or nitrogen atom of the organo group takes part in a nucleophilic attack on a phosphorus atom in a neighbouring molecule resulting in the cleavage of a P-O bond and subsequent formation of a new P-O bond. At the same time one might envisage a nucleophilic attack on the molecule losing an $R'O$ group by the fluoride ion with formation of a new P-F bond and cleavage of a P-F bond in the other molecule taking part.

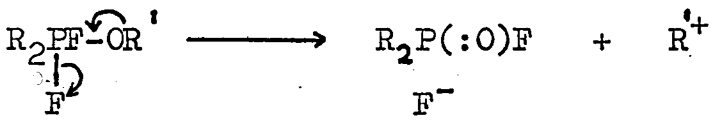
The effectiveness of a nucleophile is dependent on the groups attached to, for example, the nitrogen or oxygen atom. For the C-N bond there is an electron-inductive effect by the nitrogen on the methyl groups which would be of an enhancing effect on the nucleophilicity of the nitrogen. For Ph and C_6F_5 it has been well established [92] that C_6F_5 inductively withdraws electrons more strongly than the phenyl group, therefore one would expect the nucleophilicity of the O atom of a phenoxy group to be greater than that of an O atom of a perfluorophenoxy group. This, therefore, might be an explanation of the fact that phenoxytrifluorophosphoranes show a greater tendency for the formation of ionic compounds.

For the two previously mentioned competing reactions the preference for formation of ionic compounds is greater when reactions are carried out involving phenyltrimethylsilyl ether. When hydrocarbon fluorophosphoranes are employed in reactions then the formation of ionic compounds is not observed as this would require the cleavage of a strong P-C bond which under the reaction conditions is not energetically favourable.

The thermal stability of these perfluorophenoxy- and phenoxy- fluorophosphoranes which contrasts to that of the corresponding alkoxy fluorophosphoranes can probably be explained as follows. Alkoxyfluorophosphoranes decompose according to the equation,

$$R'OPRF_3 \longrightarrow R'F + RP(:O)F_2.$$

The driving force behind this reaction is the formation of a strong P-O phosphoryl bond which is stronger than the corresponding P-O single bond, P=O bond energy in the range 120 to 150 k.cals./mol. [93] and P-O bond energy approx. 86 k.cals./mol. This is analogous to the well known Arbusov reaction [94, 95] in which it was observed that the reactions of trialkyl phosphites and dialkyl phosphinites with alkyl halides give phosphonate and phosphinate esters, the driving force of the reaction once again being the formation of a strong P=O bond. Such decompositions are not observed for aryloxy substituted fluorophosphoranes. The nature of the organo group attached to the oxygen atom is probably an important factor in determining whether such a decomposition takes place or not. The inductive electron releasing effect/of alkyl groups enables easy donation of the oxygen pπ electrons to form the P-O double bond whereas the strongly inductive electron withdrawing effect of the phenyl and perfluorophenyl groups reduces the ability of the oxygen atom to donate its pπ electrons for formation of a P=O bond. Another factor to be considered is the stability of the carbonium ion which is undoubtedly formed during the decomposition as an intermediate. The differences in thermal stability can also be explained by the ability of alkyl groups to form carbonium ions which are more stable than aryl carbonium ions,



$$\underset{F}{R_2PF}-OR' \longrightarrow \underset{F^-}{R_2P(:O)F} + R'^+$$

All the data obtained for the new perfluorophenoxydifluorophosphoranes suggest that their structures are of a trigonal bipyramidal nature, in which the two fluorine atoms, as the most electronegative ligands, occupy the axial sites.

Experimental

Since all of the starting materials and products containing a P-F bond are sensitive to moisture it was necessary to take all the precautions as described in the Section on Experimental Technique. The fluorophosphoranes were prepared as described elsewhere in the literature (see Experimental Technique). Perfluorophenyltrimethylsilyl ether was prepared using the method reported for the preparation of the analogous silyl ether, phenyltrimethylsilyl ether.[96]

Preparation of Compounds

Perfluorophenyltrimethylsilyl ether: The reaction was carried out in a 1l three-necked flask fitted with a reflux condenser, mechanical stirrer and addition funnel. A drying tube was placed on the top of the reflux condenser to protect the apparatus from atmospheric moisture. Trimethylchlorosilane (38.2 g., 0.035 mole) was added dropwise to a stirred mixture of perfluorophenol (65.0 g., 0.035 mole), triethylamine (35.8 g., 0.035 mole) and dry ether (500 ml.). An exothermic reaction took place and a white solid was precipitated in the reaction mixture. After the addition had been completed, about 0.5 h., the reaction mixture was refluxed for 12 h. in order to complete the reaction. On cooling to room temperature the reaction mixture was filtered under an atmosphere of dry nitrogen. The precipitate was washed several times with dry ether and the washings added to the filtrate which was subsequently distilled first removing the ether and then distilled under vacuum through a 12 ins. Vigreux column to yield a colourles liquid of b.p. 63°C/20 mm. (81.5 g., 96.5%) This colourless liquid was identified by ^1H n.m.r. and elemental analysis as $C_6F_5OSiMe_3$.

Found:	C, 42.0; H, 3.5%
Calc. for $C_9H_9F_5OSi$	C, 42.2; H, 3.5%.

Tris(perfluorophenoxy)difluorophosphorane: Phosphorus Pentafluoride (5.2 g., 0.04 mole) was condensed onto perfluorophenyltrimethylsilyl ether (10.7 g., 0.04 mole) in a glass reaction tube cooled to -196°C which was attached to a vacuum line. After condensation had been completed the tube was sealed and allowed to warm up to room temperature and left at room temperature for 36 h. On opening the tube and connecting to a weighed trap cooled to -78°C a volatile product was seen to boil off and collected in the trap. This volatile product was identified by ^1H analysis as trimethylfluorosilane, Me_3SiF, and the weight collected (3.1 g.) represented 84% reaction having taken place. The solid product remaining in the reaction tube was recrystallised twice from dry acetonitrile affording a white crystalline solid of m.p. 143-146°C. and was subsequently identified as tris(perfluorophenoxy)difluorophosphorane. The weight collected (12.6 g.) represents 84% yield of $(C_6F_5O)_3PF_2$.

Found:	C, 35.2;	F, 52.5;	P, 5.0%
Calc. for $C_{18}F_{17}O_3P$	C, 35.0;	F, 52.3;	P, 5.0%

Bis(perfluorophenoxy)methyldifluorophosphorane:

The reaction was carried out in a manner similar to that described in the previous experiment. Methyltetrafluorophosphorane (6.2 g., 0.05 mole) was condensed onto perfluorophenyltrimethylsilyl ether (12.8 g., 0.05 mole) in a glass reaction tube. On sealing the tube and allowing to warm up to room temperature it was heated at 100°C for 36 h. On cooling to room temperature a white crystalline solid was seen to separate out of the reaction mixture. On opening the tube and connecting to a weighed trap cooled to -78°C a volatile liquid was found to have collected in the trap which was subsequently identified as trimethylfluorosilane and the weight collected (9.1 g.) represented 98% reaction having taken place. The white solid remaining in the reaction tube was recrystallised twice from dry acetonitrile affording a white crystalline solid of m.p. 125-127°C and was subsequently identified as bis(perfluorophenoxy)methyldifluorophosphorane. The weight collected (10.5 g) represents 93% yield of $(C_6F_5O)_2PF_2Me$.

Found:	C, 34.7;	H, 0.6;	F, 50.4;	P, 6.8%
Calc. for $C_{13}H_3F_{12}O_2P$	C, 34.7;	H, 0.6;	F, 50.6;	P, 6.9%

Bis(perfluorophenoxy)phenyldifluorophosphorane: The reaction was carried out in a 25ml. three necked flask fitted with a thermometer, reflux condenser and dropping funnel. The reflux condenser was attached by means of P.V.C. tubing to a trap cooled to -78°C and a drying tube was attached to the open end of the trap to protect the apparatus from atmospheric moisture. Phenyltetrafluorophosphorane (6.1 g., 0.03 mole) was placed in the flask and heated to 60°C. Perfluorophenyltrimethylsilyl ether (8.5 g.,0.03 mole) was placed in the addition funnel and slowly added to the stirred $PhPF_4$ in the flask over a half hour period. A slightly exothermic reaction was observed and a volatile product collected in the trap. The reaction mixture was heated at 120°C for 3 h. to complete the reaction and on cooling to room temperature a white solid was seen to separate out of the reaction mixture. The liquid which collected in the trap was shown by ^1H n.m.r. to be trimethylfluorosilane, Me_3SiF, and the weight collected (1.9 g) represented 63% reaction having taken place. The white solid remaining in the flask was washed with benzene to remove excess phenyltetrafluorophosphorane and subsequently **recrystallised** twice from acetonitrile affording a white crysyalline solid of m.p. 127-130°C, and was identified as bis(perfluorophenyl)phenyldifluorophosphorane. The weight collected (13.6 g) represents 88% yield of $(C_6F_5O)_2PF_2Ph$.

Found: C, 42.1; H, 1.0; F, 44.4; P, 6.2%

Calc. for $C_{18}H_5F_{12}O_2P$ C, 42.2; H, 1.0; F, 44.5; P, 6.1%

Perfluorophenoxydimethyldifluorophosphorane:

Dimethyltrifluorophosphorane (5.8 g., 0.05 mole) and perfluorophenyltrimethylsilyl ether (12.6 g., 0.05 mole) were charged into a 30 ml. 'Monel' cylinder and heated at 100°C for nine hours. On cooling to room temperature and connecting to a trap cooled to -78°C a colourless liquid collected in the trap and was identified by ^1H n.m.r. to be trimethylfluorosilane, Me_3SiF, and the weight collected (4.1 g.) represented 89% reaction having taken place. A brown crystalline solid remained in the cylinder which was washed with cold benzene in order to remove any excess fluorophosphorane. Purification was carried out by vacuum sublimation (40°C/0.05 mm) using a water-cooled finger on which white needle-like crystals were seen to form. These crystals were subsequently identified as perfluorophenoxydimethyldifluorophosphorane. Due to the extreme sensitivity of this compound to moisture an adequate melting point could not be determined. The weight collected (13.2 g.) represents 93% yield of $(Me)_2PF_2OC_6F_5$.

Found: C, 34.3; H, 2.1; F, 46.3; P, 10.8%

Calc. for $C_8H_6F_7OP$ C, 34.1; H, 2.1; F, 46.6; P, 11.0%

Perfluorophenoxydiphenyldifluorophosphorane:

Diphenyltrifluorophosphorane (9.1 g., 0.04 mole) and perfluorophenyltrimethylsilyl ether (9.6 g., 0.04 mole) were allowed to react together in a manner similar to that described for the preparation of bis(perfluorophenoxy)-

phenyldifluorophosphorane. The reaction mixture was heated at 150°C for 3 h. and trimethylfluorosilane was found to be formed and collected in the trap. The weight collected (3.1 g.) represented 86% reaction having taken place. On cooling the reaction mixture to room temperature a white solid was seen to separate out of the mixture which was filtered, washed with dry benzene to remove any excess fluorophosphorane and subsequently recrystallised from acetonitrile affording a white crystalline solid of m.p. 100-102°C. This compound was identified as perfluorophenoxydiphenyldifluorophosphorane. The weight collected (13.8 g.) represents 92% yield of $Ph_2PF_2OC_6F_5$.

Found:	C, 53.3;	H, 2.6;	F, 32.3;	P, 7.8%
Calc. for $C_{18}H_{10}F_7OP$	C, 53.3;	H, 2.5;	F, 32.7;	P, 7.6%

<u>Bis(perfluorophenoxy)dimethylaminodifluorophosphorane</u>: Dimethylaminotetrafluorophosphorane (7.0 g., 0.05 mole) and perfluorophenyltrimethylsilyl ether (11.9 g., 0.05 mole) were allowed to react together in a manner similar to that described for the preparation of bis(perfluorophenoxy)phenyldifluorophosphorane. No exothermic reaction was observed and the reaction mixture was heated at 80°C for 12 h. Trimethylfluorosilane was formed and collected in the trap and the weight collected (3.5 g.) represented 83% reaction having taken place. The remaining liquid residue was distilled at normal pressure affording a colourless liquid of b.p. 62°C which was subsequently identified as dimethylaminotetrafluorophosphorane. The solid residue remaining in the distillation flask was washed with benzene to remove excess fluorophosphorane and recrystallised twice from

acetonitrile affording a white crystalline solid of m.p. 135-137°C which was identified as bis(perfluorophenoxy)-dimethylaminodifluorophosphorane. The weight collected (10.1 g.) represents 71% yield of $Me_2NPF_2(OC_6F_5)_2$.

Found: C, 35.1; H, 2.6; N, 2.6; P, 6.8%

Calc. for $C_{14}H_6F_{12}NO_2P$: C, 35.1; H, 1.3; N, 2.9; P, 6.5%

Bis(perfluorophenoxy)diethylaminodifluorophosphorane: Diethylaminotetrafluorophosphorane (8.9 g., 0.05 mole) and perfluorophenyltrimethylsilyl ether (12.5 g., 0.06 mole) were allowed to react together in a manner similar to that described for the preparation of bis(perfluorophenoxy)-phenyldifluorophosphorane. Trimethylfluorosilane was found to be formed and was collected in the trap. The weight collected (3.9 g.) represented 75% reaction having taken place. The liquid residue remaining in the flask was distilled at normal pressure affording a colourless liquid of b.p. 98°C which was identified as diethylaminotetrafluorophosphorane. The solid residue remaining in the distillation flask was washed with dry benzene to remove any excess fluorophosphorane and recrystallised from acetonitrile affording a white crystalline solid of m.p. 98-100°C, and subsequently identified as bis(perfluorophenoxy)diethylaminotetrafluorophosphorane. The weight collected (10.2 g.) represents 81% yield of $Et_2NPF_2(OC_6F_5)_2$.

Found: C, 38.4; H, 3.1; N, 2.5; P, 6.2%

Calc. for $C_{16}H_{10}F_{12}NO_2P$, C, 38.0; H, 1.8; N, 2.7; P, 6.1%

CHAPTER II

FLUOROPHOSPHORANES SUBSTITUTED BY ASYMMETRIC AMINO GROUPS

CHAPTER II

FLUOROPHOSPHORANES SUBSTITUTED BY ASYMMETRIC AMINO GROUPS

There have been many reports of fluorophosphoranes substituted by secondary amino groups R_2N [2] and even the gas phase reaction of phosphorus pentafluoride with ammonia has been reported [97] producing cis-diamidotrifluorophosphorane, $(NH_2)_2PF_3$. As yet there are few examples known containing asymmetric primary or secondary amino groups, RHN- or $RR'N$ (where $R \neq R'$). The first examples reported were $PhEtNPF_3Ph$ [3] and $MeHNPF_3Ph$.[25] Preparations of primary aminofluorophosphoranes have been carried out in which it was shown that the compounds have interesting stereochemical properties resulting from the restriction of the P-N bond rotation. [25, 98] In further reports of fluorophosphoranes substituted with asymmetric amino groups P-N bond restriction was observed and energy barriers to rotation were calculated. [98-100] Compounds of the type $RR'PF_3$ (where $R = Me_2N$, Et_2N; $R' = C_4H_9NH$, CH_3NH, $i\text{-}C_3H_7NH$) have been prepared, [101] the n.m.r. spectra revealing magnetic non-equivalence of the axial fluorine atoms. The amino-methyldifluorophosphoranes $RR'MePF_2$ (where $R = EtNH$, $MeNH$, $i\text{-}C_3H_7NH$; and $R' = Et_2N$, $i\text{-}C_3H_7NH$, $C_6H_{11}NH$) have been prepared [102] from the reaction of methyltetrafluorophosphorane with the respective amines. The complete reaction is undertaken in two stages, the monosubstituted compound being isolated first and then being allowed to react with the second amine. The reaction of phosphorus pentafluoride with primary amines is known to produce, amongst other products, asymmetric amino-tetra- and tri- fluorophosphoranes of the type $RNHPF_4$ (where R = Et, tBu, 2,6-$Et_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$ and i-C_3H_7) and $(RNH)_2PF_3$ (where R = Me, Et, and tBu).[16, 103] The analogous asymmetric aminofluorophosphorane $MeNHPF_4$,[104] however, is conveniently prepared from the reaction of phosphorus pentafluoride with methylaminotrimethylsilane, $MeNHSiMe_3$. The reaction of phosphorus trifluoride with the primary amines RNH_2 (where R = Me, Et, nBu) afford asymmetric aminodifluorophosphoranes of the type $(RNH)_2PF_2H$.[17] Recently compounds of the type $BzMeNR_nPF_{5-n}$ (where n = 0, 1, 2; R = Ph) have been prepared,[23] where once again ^{19}F n.m.r. revealed magnetic non-equivalence of the axial fluorine atoms.

The following is concerned with asymmetric aminofluorophosphoranes of the type $RR'NPR''_nF_{4-n}$ (where n = 0, 1, 2; RR' = 2-methylpiperidyl-, 3-methylpiperidyl-; R'' = Me, Ph) and also (where n = 0, 1; RR' = 2-methylpyrryl-; R'' = Ph). The symmetric aminofluorophosphoranes $R_2NPR''_nF_{4-n}$ (where n = 0, 1, 2; R_2 = 4-methylpiperidyl-; R'' = Me, Ph) and also (where n = 0, 1; R_2 = 2,5-dimethylpyrryl-; R'' = Ph) have also been prepared.

Synthesis

The preparation of the amino-substituted fluorophosphoranes $RR'NPR''_nF_{4-n}$ and $R_2NPR''_nF_{4-n}$ is carried out by the reaction of the Lewis acid fluorophosphoranes R''_nPF_{5-n} (where R'' = Me, Ph; n = 0, 1, 2.) with the Lewis base methyl-substituted piperidyl silylamines and the methyl-substituted pyrrylsilylamines $RR'NSiMe_3$ and R_2NSiMe_3 according to the equations,

$$RR'NSiMe_3 \quad + \quad R''_nPF_{5-n} \longrightarrow RR'NPR''_nF_{4-n} \quad + \quad Me_3SiF$$

and

$$R_2NSiMe_3 \quad + \quad R''_nPF_{5-n} \longrightarrow R_2NPR''_nF_{4-n} \quad + \quad Me_3SiF.$$

These reactions are analogous to those used for the preparation of other heteroatom-substituted fluorophosphoranes (Introduction). The reactions of methyl-substituted piperidyl trimethylsilanes with fluorophosphoranes were found to be exothermic producing the volatile by-product trimethylfluorosilane which was identified by its ^{1}H n.m.r. spectrum. The aminofluorophosphoranes are purified by vacuum distillation or, in the case of the difluorophosphoranes, by recrystallisation from a suitable solvent. The yields of these aminofluorophosphoranes are in the range 40-96%; they are not in every case the exclusive phosphorus-fluorine compound produced.

The corresponding reactions of methyl-substituted pyrrylsilylamines with fluorophosphoranes, in contrast to the above mentioned reactions, are not exothermic, the reaction mixtures having to be heated for long periods in order to induce reaction. Again the volatile by-product, trimethylfluorosilane is formed and identified by its ^{1}H n.m.r. spectrum. Purification is also carried out by vacuum distillation and yields are in the range 10-83%. Once again these compounds are not the exclusive phosphorus-fluorine compounds formed.

It was, however, noticed that no reaction took place when methyltetrafluorophosphorane, $MePF_4$, was allowed to react with methyl-substituted pyrrylsilylamines even when the reaction mixtures were heated in a vacuum for long periods at high temperatures.

Properties

The piperidyl- tetra- and tri- fluorophosphoranes are all colourless liquids which on long standing turn brown in colour. The piperidyl- difluorophosphoranes and the pyrryl- tetra- fluorophosphoranes are white crystalline solids. They all show a stability to hydrolysis comparable to other fluorophosphoranes.[2] This stability is in the order $PF_2 > PF_3 > PF_4$.

The trifluorophosphoranes show a tendency to undergo rearrangement to their ionic isomers in the same fashion as has been observed for other aminofluorophosphoranes [2, 26, 105, 106] the rearrangement proceeding according to the equation,

$$2RR'NPR''F_3 \longrightarrow [(RR'N)_2PR''F]^+[R''PF_5]^-.$$

(where RR'N = 2-Me-, 3-Me-, or 4-Me-piperidyl; 2-Me-, or 2,5-dimethyl-pyrryl; R'' = Me, Ph). The rearranged products were only characterised using ^{19}F n.m.r. spectroscopy. This rearrangement was observed to take place completely over a two month period if the compounds were stored at room temperature but the compounds could be kept for an indefinite period if stored at low temperatures.

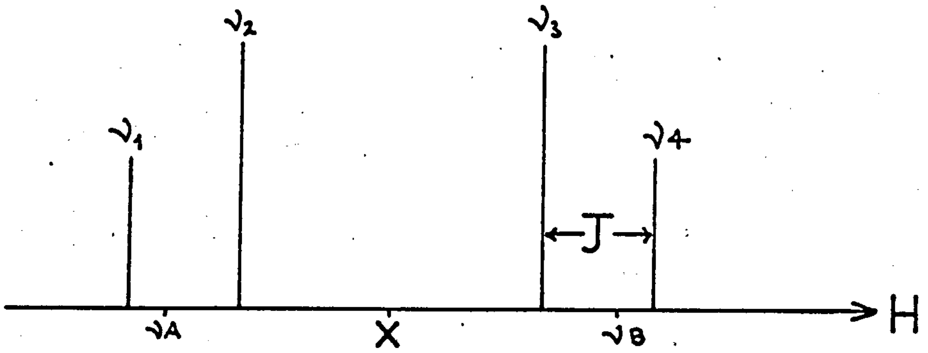
During the isolation and purification of the tetrafluorophosphoranes it was noticed that large amounts of undistillable oils were produced which subsequently solidified on cooling. These solid residues were shown by ^{19}F and ^{31}P n.m.r. analysis to contain the hexafluorophosphate anion $[PF_6]^-$. If the reaction conditions were too vigorous, the reaction mixture of phosphorus pentafluoride and the corresponding silylamines being allowed to warm up too fast or reaction mixtures being heated above 100°C during distillation, then the only phosphorus-fluorine compound formed is the hexafluorophosphate species at the expense of the covalent tetrafluorophosphoranes. The formation of this ionic compound is presumably due to the rearrangement of the tetrafluorophosphoranes to their ionic isomers according to the equation,

$$2RR'NPF_4 \xrightarrow{\qquad} [(RR'N)_2PF_2]^+[PF_6]^-.$$

(where RR'N = 2-Me-, 3-Me-, or 4-Me-piperidyl-; or 2-Me-, or 2,5-dimethyl-pyrryl). These ionic compounds were isolated by dissolving in acetonitrile and subsequently recrystallised from the same solvent affording white crystalline solids. Only the pyrryl-ionic compounds were successfully isolated, the corresponding piperidyl compounds remaining as thick oils. The ionic compounds were characterised by ^{19}F and ^{31}P n.m.r. spectroscopy. After isolation of the covalent tetrafluorophosphoranes had been completed no further rearrangement was observed.

Nuclear Magnetic Resonance Data

The notation used in the classification of the spin systems discussed is that of Bernstein, Pople and Schneider.[107] The main interesting feature in the reported ^{19}F n.m.r. data of these compounds is the magnetic non-equivalence of either the two axial or two equatorial fluorine atoms giving rise to AB type spectra.[108-110] When one AB spectrum is an integral part of a complete spectrum then it is termed an ab sub-spectrum. The spin coupling of two magnetic nucleii leading to an AB spectrum is characterised by one chemical shift difference $\Delta\nu$ and one coupling constant called J, the spectrum being a function of $J/\Delta\nu$ (where $J \approx \Delta\nu$). The spectrum consists of four lines two for the A part and two for the B part and is symmetrical about the middle x.



The coupling constant J between the two magnetic nucleii A and B can be obtained directly from the spectrum and if all the lines are resolved then the chemical shift difference is given by $\Delta\nu = \sqrt{(\nu_3 - \nu_2)(\nu_4 - \nu_1)}$ Thus chemical shifts of A and B can be found being symmetrical about x.

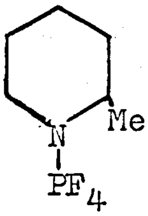
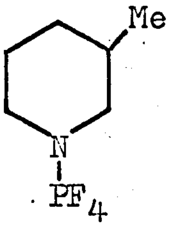
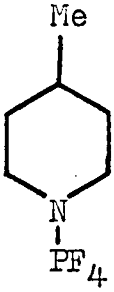
Room temperature and low temperature ^{19}F n.m.r. data for these new aminofluorophosphoranes are listed in Tables 2.1, 2.2, 2.3, 2.4, and 2.5. The room temperature ^{31}P n.m.r. data are listed in Table 2.6. In all cases the notation F^1 and F^2 refers to the axial fluorine atoms and F^3 and F^4 refers to the equatorial fluorine atoms.

The spectral data for these compounds suggest that the molecules are basically of a trigonal bipyramidal structure, the spectra having the same basic pattern as has been observed for other fluorophosphoranes.[2, 72] This suggests that the amino and hydrocarbon groups occupy the equatorial positions of the trigonal bipyramid leaving the axial positions occupied by the fluorine atoms.

Tables 2.1, 2.4 and 2.5 show the ^{19}F n.m.r. data of the piperidyl- , 2-Me-pyrryl-, and 2,5-dimethylpyrryl-

Table 2.1

^{19}F N.m.r. Data for Methylpiperidyl-tetrafluorophosphoranes

Compound	Temp. °C	J (Hz)		δ_F p.p.m.	
	+ 30	$J_{PF(av)}$	846	$\delta_{F(av)}$	+66.9
	-100 (in toluene)	J_{PF^3}	921	δ_{F^3}	+ 72.2
		J_{PF^4}	905	δ_{F^4}	+ 74.2
		J_{PF^1}	781	δ_{F^1}	+ 60.3
		J_{PF^2}	781	δ_{F^2}	+ 60.3
		$J_{F^3F^4}$	51		
		$J_{F^3F^1}$	74		
		$J_{F^4F^1}$	67		
	+ 30	$J_{PF(av)}$	849	$\delta_{F(av)}$	+ 67.8
	-100 (in toluene)	J_{PF^3}	940	δ_{F^3}	+ 72.1
		J_{PF^4}	940	δ_{F^4}	+ 74.0
		J_{PF^1}	763	δ_{F^1}	+ 60.2
		J_{PF^2}	763	δ_{F^2}	+ 60.2
		$J_{F^3F^4}$	50		
		$J_{F^3F^1}$	77		
		$J_{F^4F^1}$	63		
	+ 30	$J_{PF(av)}$	856	$F(av)$	+ 67.6
	Due to viscosity problems no adequate low temperature spectrum could be obtained				

$J_{PF(av)}$ and $\delta_{F(av)}$ refer to the average values of coupling constants and chemical shifts, of the axial and equatorial fluorine atoms, respectively.

Table 2.2

^{19}F N.m.r. Data for Methylpiperidyl-trifluorophosphoranes

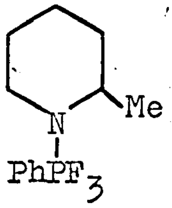
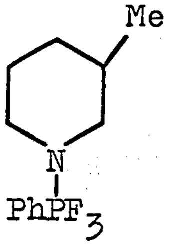
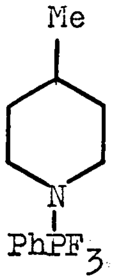
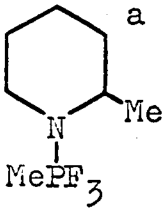
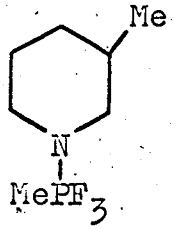
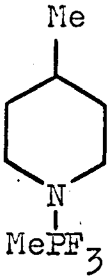
Compound	Temp. °C	J (Hz)		δ F p.p.m.	
	+ 30	J_{PF^1}	828	δF^1	+42.6
		J_{PF^2}	814	δF^2	+44.3
		J_{PF^3}	965	δF^3	+67.8
		$J_{F^1F^2}$	14		
		$J_{F^1F^3}$	55		
		$J_{F^2F^3}$	55		
	+ 30	J_{PF^1}	823	δF^1	+43.4
		J_{PF^2}	820	δF^2	+43.7
		J_{PF^3}	1066	δF^3	+69.1
		$J_{F^1F^2}$	14		
		$J_{F^1F^3}$	55		
		$J_{F^2F^3}$	55		
	+ 30	J_{PF^1}	820	δF^1	+43.5
		J_{PF^2}	820	δF^2	+43.5
		J_{PF^3}	965	δF^3	+68.1
		$J_{F^1F^2}$	0		
		$J_{F^1F^3}$	56		
		$J_{F^2F^3}$	56		
	- 100	No significant change in spectral form.			

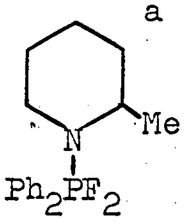
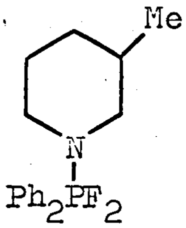
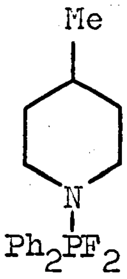
Table 2.2 cont.

Compound	Temp. °C	J (Hz)		δ_F p.p.m.	
 [a]	+ 30	J_{PF^3}	1313	δ_{F^3}	+ 64.1
		$J_{F^1F^3}$	53		
		$J_{F^2F^3}$	53		
	+ 30	J_{PF^1}	811	δ_{F^1}	+ 30.4
		J_{PF^2}	811	δ_{F^2}	+ 30.9
		J_{PF^3}	968	δ_{F^3}	+ 68.3
		$J_{F^1F^2}$	12		
		$J_{F^1F^3}$	55		
		$J_{F^2F^3}$	55		
	+ 30	J_{PF^1}	811	δ_{F^1}	+ 30.6
		J_{PF^2}	811	δ_{F^2}	+ 30.6
		J_{PF^3}	964	δ_{F^3}	+ 68.4
		$J_{F^1F^2}$	0		
		$J_{F^1F^3}$	54		
		$J_{F^2F^3}$	54		
		J_{F^1H}	12		
	- 100 (in toluene)	No significant change in spectral form.			

[a] Due to spin-spin coupling of phosphorus methyl protons with fluorine atoms no adequate calibration could be undertaken.

Table 2.3

^{19}F N.m.r. Data for Methylpiperidyl-difluorophosphoranes

Compound	Temp °C	J (Hz)	δF p.p.m.
 a	+ 30	J_{PF} 712	δF + 37.9
	− 70 (in toluene)	J_{PF^1} 689 J_{PF^2} 689 $J_{F^1F^2}$ 14	δF^1 + 34.6 δF^2 + 36.8
	+ 30	J_{PF} 708	δF + 37.6
	− 70 (in ether)	b	
	+ 30	J_{PF} 715	δF + 38.1
	− 80 (in ether)	No significant change in spectral form.	

a In original preparation [23] the ^{19}F n.m.r. data reported were not complete.

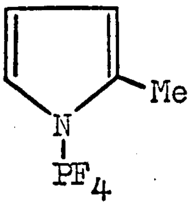
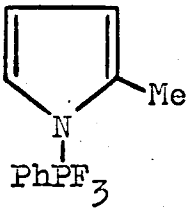
b No adequate low temperature spectra could be obtained.

All room temperature spectra were made on super-cooled liquids.

All compounds are of a trigonal bipyramidal structure in which the two fluorine atoms occupy the axial sites.

Table 2.4

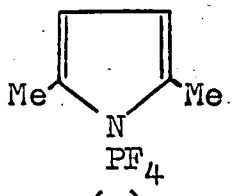
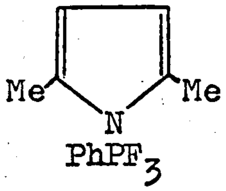
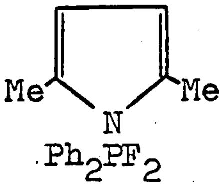
^{19}F N.m.r. Data for 2-Methylpyrrylfluorophosphoranes

Compound	Temp °C	J (Hz)		δF p.p.m.	
	+ 30 (in benzene)	$J_{PF(av)}$	892	$\delta F(av)$	+ 60.7
	− 100 (in toluene)	J_{PF^1}	838	δF^1	+ 46.6
		J_{PF^2}	856	δF^2	+ 50.4
		J_{PF^3}	967	δF^3	+ 73.2
		J_{PF^4}	967	δF^4	+ 73.2
		$J_{F^1F^2}$	17		
		$J_{F^1F^3}$	66		
		$J_{F^2F^3}$	76		
	+ 30	J_{PF^1}	866	δF^1	+ 28.5
		J_{PF^2}	866	δF^2	+ 28.5
		J_{PF^3}	975	δF^3	+ 65.9
		$J_{F^1F^2}$	0		
		$J_{F^1F^3}$	58		
		$J_{F^2F^3}$	58		
	− 80 (in toluene)	No significant change in spectral form.			

$J_{PF(av)}$ and $\delta F(av)$ refer to the average values of coupling constants and chemical shifts, of the axial and equatorial fluorine atoms, respectively.

Table 2.5

^{19}F N.m.r. Data for 2,5-Dimethylpyrrylfluorophosphoranes

Compound	Temp. °C	J (Hz)	δF p.p.m.
 (a)	+ 30	$J_{PF(av)}$ 922	$\delta F_{(av)}$ + 52.4
	+ 30	J_{PF^1} 858 J_{PF^2} 858 J_{PF^3} 975 $J_{F^1F^2}$ 0 $J_{F^1F^3}$ 62 $J_{F^2F^3}$ 62	δF^1 + 22.9 δF^2 + 22.9 δF^3 + 66.9
	- 100(in toluene)	No significant change in spectral form.	
 (a)	+ 30	J_{PF} 751	δF + 24.5

(a) Data recorded on reaction mixture as compound was only present in a small percentage.

$J_{PF(av)}$ and $\delta F_{(av)}$ refer to the average values of coupling constants and chemical shifts, of the axial and equatorial fluorine atoms, respectively.

Table 2.6

^{31}P N.m.r. Data for Methyl-substituted piperidyl- and pyrryl-fluorophosphoranes

Compound	δ_P p.p.m.	J_{PF} Hz.
2-Me-pip-PF_4	+ 70.6	846
2-Me-pip-PF_3Ph	+ 53.5	815 ax
		960 eq
2-Me-pip-PF_3Me	+ 39.0	815 ax
		965 eq
2-Me-pip-PF_2Ph_2	+ 51.8	712
3-Me-pip-PF_4	+ 72.2	849
3-Me-pip-PF_3Ph	+ 55.0	825 ax
		955 eq
3-Me-pip-PF_3Me	+ 40.7	822 ax
		965 eq
3-Me-pip-PF_2Ph_2	+ 51.7	708
4-Me-pip-PF_4	+ 72.4	856
4-Me-pip-PF_3Ph	+ 55.6	820 ax
		965 eq
4-Me-pip-PF_3Me	+ 40.8	811 ax
		964 eq
4-Me-pip-PF_2Ph_2	+ 55.1	715
2-Me-pyr-PF_4	+ 61.7	907
2-Me-pyr-PF_3Ph	+ 51.8	868 ax
		964 eq
2,5-Me_2-pyr-PF_3Ph	+ 46.2	860 ax
		975 eq

Table 2.6 cont.

All the spectra were recorded at room temperature.
ax and eq refer to spin-spin coupling between phosphorus and the axial and equatorial fluorine atoms, respectively.
pip. refers to the piperidyl group $C_5H_{10}N$.
pyr. refers to the pyrryl group C_4H_4N.

tetrafluorophosphoranes. At room temperature the ^{19}F n.m.r. spectra of the tetrafluorophosphoranes show a simple doublet which can be explained by the positional exchange of the fluorine atoms in the axial and equatorial positions of the trigonal bipyramid about phosphorus thus simplifying the ^{19}F n.m.r. pattern, as has been observed in the case of the 'parent' compound PF_5.[111] As has been observed for diorganoamino tetrafluorophosphoranes, R_2NPF_4[2, 112, 113] (where R = Me, Et, Ph), on cooling down to below - 60°C the rate of positional exchange is slowed down sufficiently, relative to the n.m.r. time scale, to permit observation of distinct axial and equatorial fluorine environments. The room temperature spectra, therefore, show a statistically weighted average for the coupling constants and chemical shifts of the corresponding low temperature spectra.

The low temperature spectra of 2-methyl- and 3-methylpiperidyltetrafluorophosphorane show, apart from the expected magnetic non-equivalence of the axial and equatorial fluorine atoms, magnetic non-equivalence of the two equatorial fluorine atoms F^3 and F^4. However, in contrast the low temperature spectrum of 2-methylpyrryltetrafluorophosphorane shows apart from the expected magnetic non-equivalence of the axial and equatorial fluorine atoms, magnetic non-equivalence of the two axial fluorine atoms F^1 and F^2.

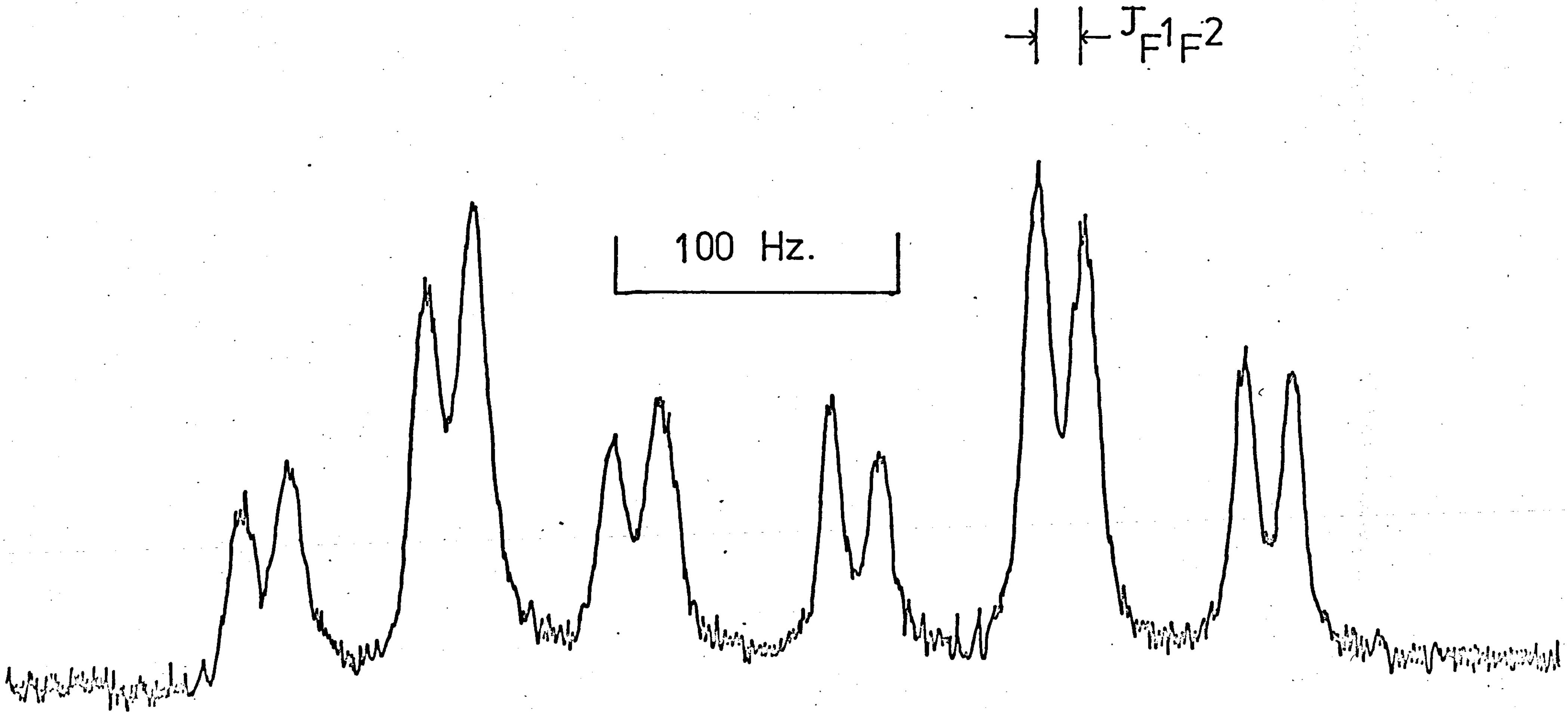
Figure 2.1 shows one half of the axial fluorine atom resonances of 2-methylpyrryltetrafluorophosphorane, the axial region being characterised by six ab sub-spectra. The corresponding equatorial region is characterised by a doublet of triplets indicating magnetic equivalence of the two equatorial fluorine atoms. A similar pattern is observed for the low temperature spectra of 2-methyl- and 3-methyl-piperidyltetrafluorophosphorane in which the equatorial region is characterised by six ab sub-spectra and the axial region by a doublet of triplets. However, in the case of the piperidyl compounds severe overlap of the resonance lines is observed between the axial equatorial fluorine atom resonances and the resonance lines are broad.

No adequate low temperature spectra could be obtained for the compounds 4-methyl-piperidyl- and 2,5-dimethyl-pyrryltetrafluorophosphorane but there is no evidence for magnetically non-equivalent axial or equatorial fluorine atoms.

The observed results can be explained by a slowing down of the positional exchange process of the fluorine atoms in the axial and equatorial positions to within the time scale of the n.m.r. measurement and cessation of the P-N bond rotation thus making a distinction between axial and equatorial fluorine atoms and also making a distinction between the two axial or two equatorial fluorine atoms.

Fig. 2.1

Axial Region.



^{19}F N.m.r. Spectrum of 2-Me-$C_4H_3NPF_4$ at -50°C

It is therefore concluded that for the case of the piperidyl tetrafluorophosphoranes the observed results can only arise when the piperidyl ring, although puckered, lies in the equatorial plane of the trigonal bipyramid about phosphorus thus placing the methyl groups, in the 2 and 3 positions, of the piperidyl ring in an environment closer to one equatorial fluorine atom than the other. However, because the ring is puckered one would expect with the proposed structure to have differing environments for the two axial fluorine atoms and thus observe magnetic non-equivalence of the two axial fluorine atoms as well. This might be the case but the effect might only be small and not observable from the n.m.r. measurement.

In the case of the pyrryltetrafluorophosphoranes the observed results can only arise when the pyrryl ring, which is planar, lies in the axial plane of the trigonal bipyramid about phosphorus thus placing the methyl group, in the 2 position, of the pyrryl ring closer to one axial fluorine atom than the other. In this case the equatorial fluorine atoms remain, clearly, magnetically equivalent.

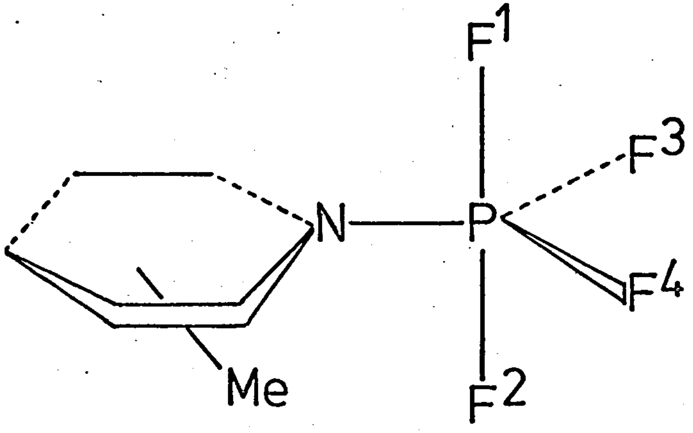
For 4-methylpiperidyltetrafluorophosphorane the methyl group in the 4-position of the piperidyl ring has no effect on the magnetic properties of the equatorial fluorine atoms, assuming the piperidyl ring lies in the equatorial plane as was observed for the other piperidyltetrafluorophosphoranes. In the case of 2,5-dimethylpyrryltetrafluorophosphorane it can clearly be seen that the pyrryl ring can lie in either the axial or equatorial plane of the trigonal bipyramid about phosphorus and not have any influence on the environments of either the axial or equatorial fluorine atoms. Figure 2.2 shows the proposed structures for the tetrafluorophosphoranes.

The use of Prentice Hall Framework Molecular Models was found to be useful in establishing the structures and explaining the n.m.r. data.

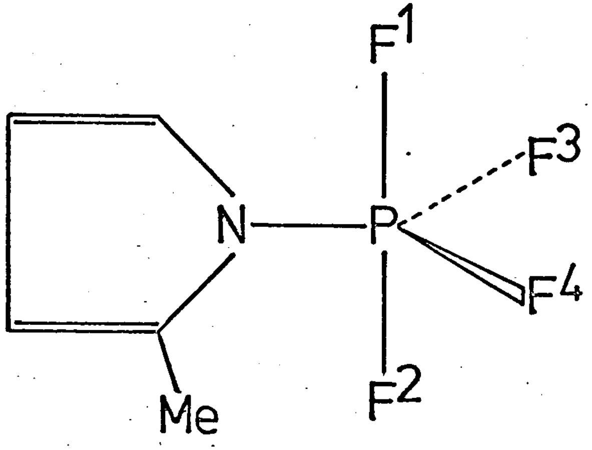
The room temperature spectra of the trifluorophosphoranes are all consistent with those expected for trifluorophosphoranes. The basic pattern is of a doublet of doublets attributed to the axial fluorine atoms and doublet of triplets attributed to the equatorial fluorine atoms. The interesting feature of these spectra is the observation of magnetically non-equivalent axial fluorine atoms for 2-methyl- and 3-methyl-piperidyltrifluorophosphorane. In contrast the ^{19}F n.m.r. spectrum of 4-methylpiperidyltrifluorophosphorane shows no evidence for the presence of magnetically non-equivalent axial fluorine atoms and even on cooling down to - 100°C the form shows no significant change to that of its room temperature spectrum. The ^{19}F n.m.r. data are shown in Table 2.2.

Figures 2.3 and 2.4 show the spectral form of 2-methyl-piperidyltrifluorophosphorane, Figures 2.5 and 2.6 show the spectral form of 3-methylpiperidylphenyltrifluorophosphorane and Figures 2.7 shows the spectral form of 4-methylpiperidyl-phenyltrifluorophosphorane. The characteristic feature of these spectra is the presence of four ab sub-spectra for the axial fluorine atom resonances of 2-methyl- and 3-methyl-piperidylphenyltrifluorophosphorane. The figures show only one half of the expected axial fluorine atom resonances. The spectral form of 4-methylpiperidylphenyltrifluoro-phosphorane is the form that has been observed for symmetric

Figure 2.2

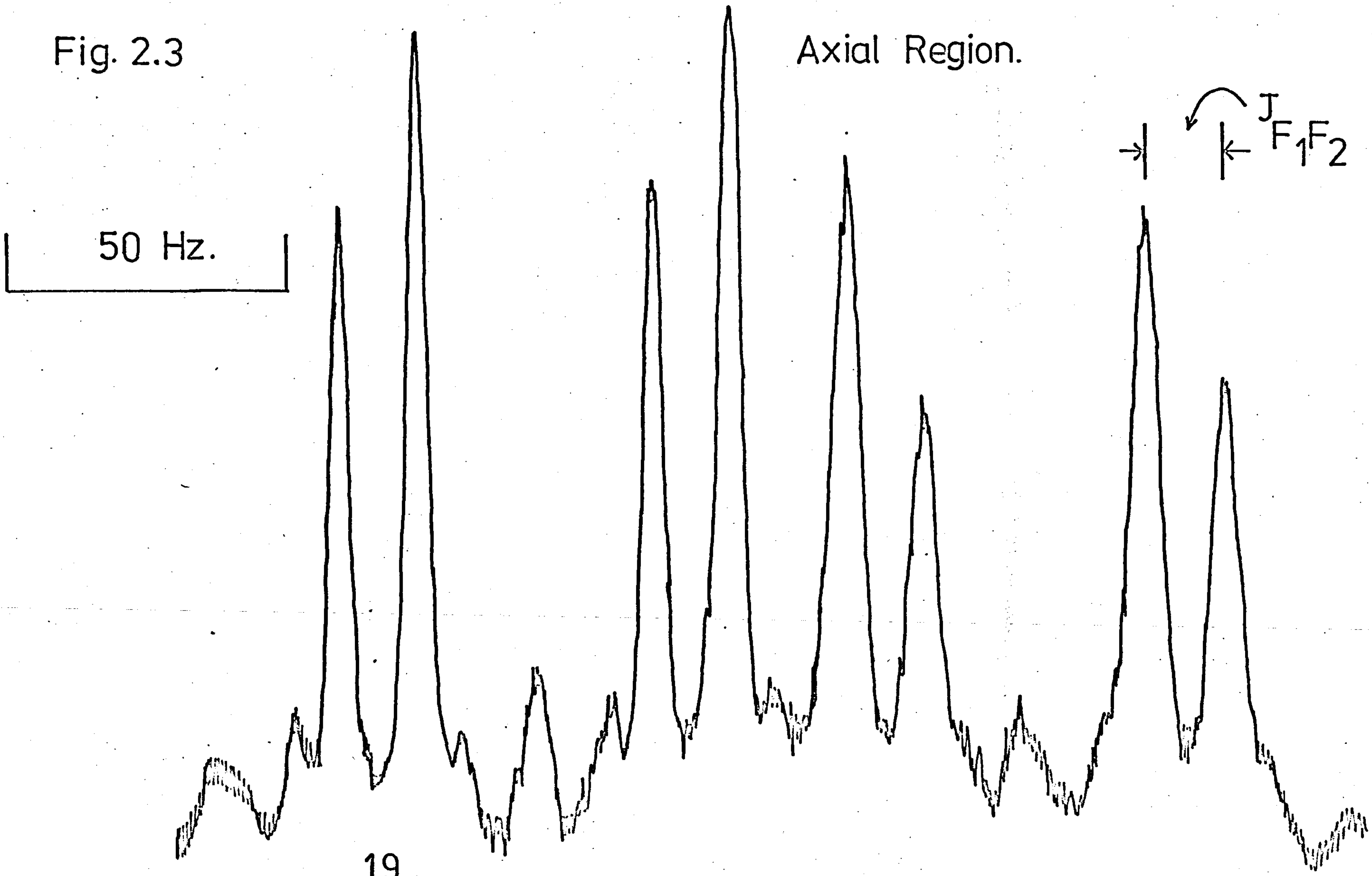


The piperidyl ring is puckered and therefore lies above and below the equatorial plane.



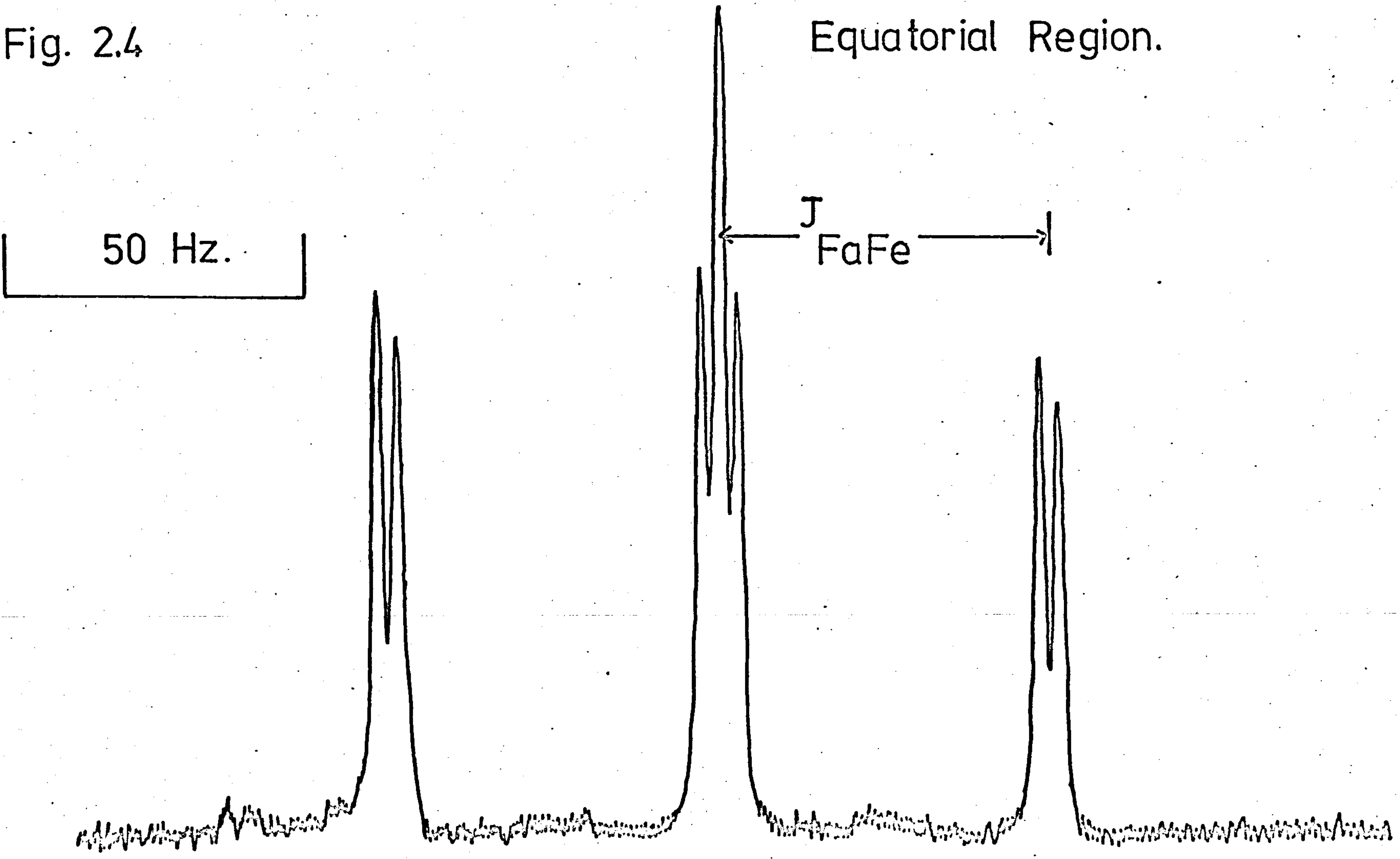
The pyrryl ring is planar and lies in the plane of the paper.

Fig. 2.3



^{19}F N.m.r. Spectrum of 2-Me-C_5H_9N-PF_3Ph.

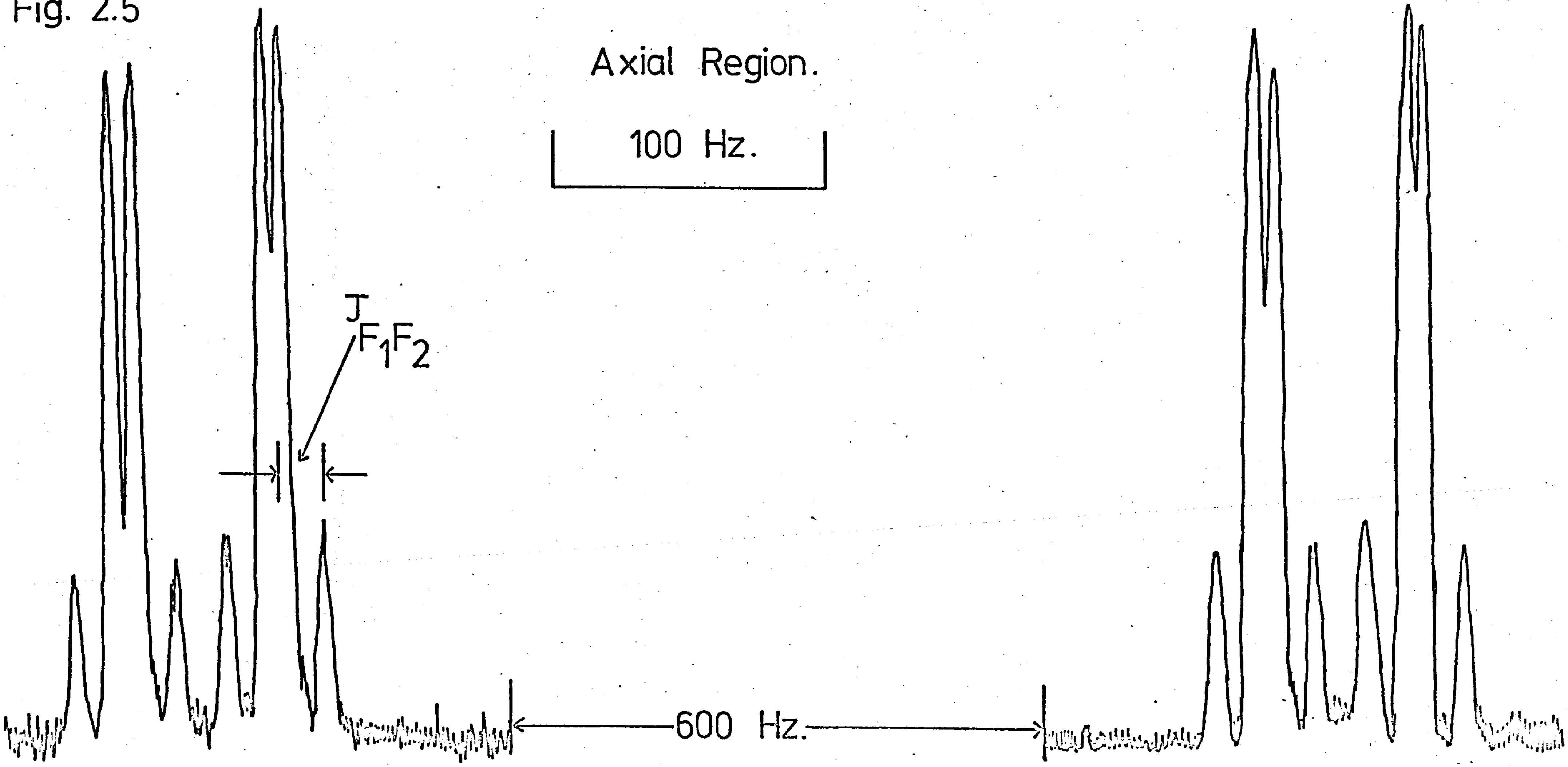
Fig. 2.4



Equatorial Region.

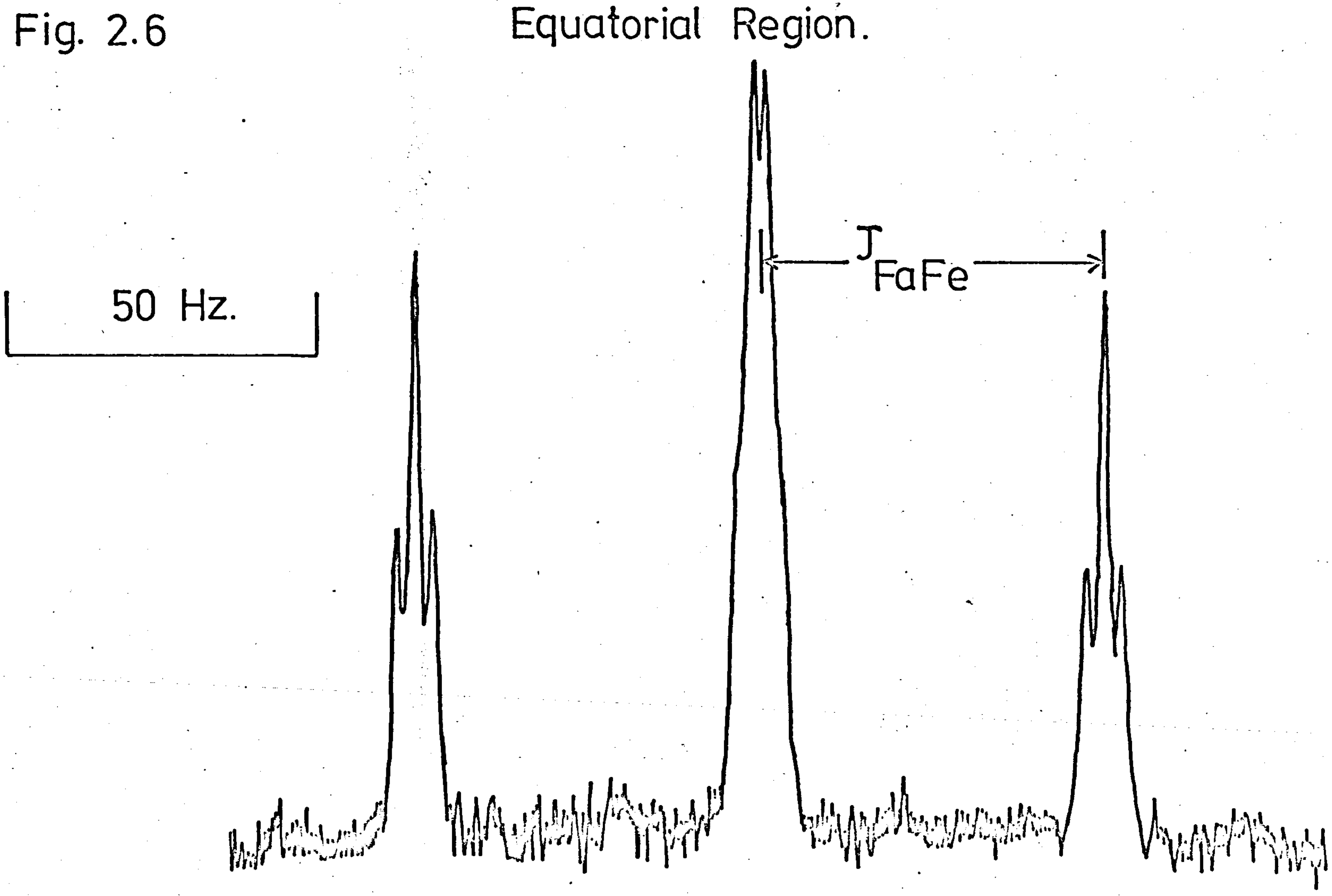
^{19}F N.m.r. Spectrum of 2-Me-C_5H_9N-PF_3Ph.

Fig. 2.5



^{19}F N.m.r. Spectrum of 3-Me-C_5H_9N-PF_3Ph

Fig. 2.6



^{19}F N.m.r. Spectrum of 3-Me-C_5H_9N-PF_3Ph

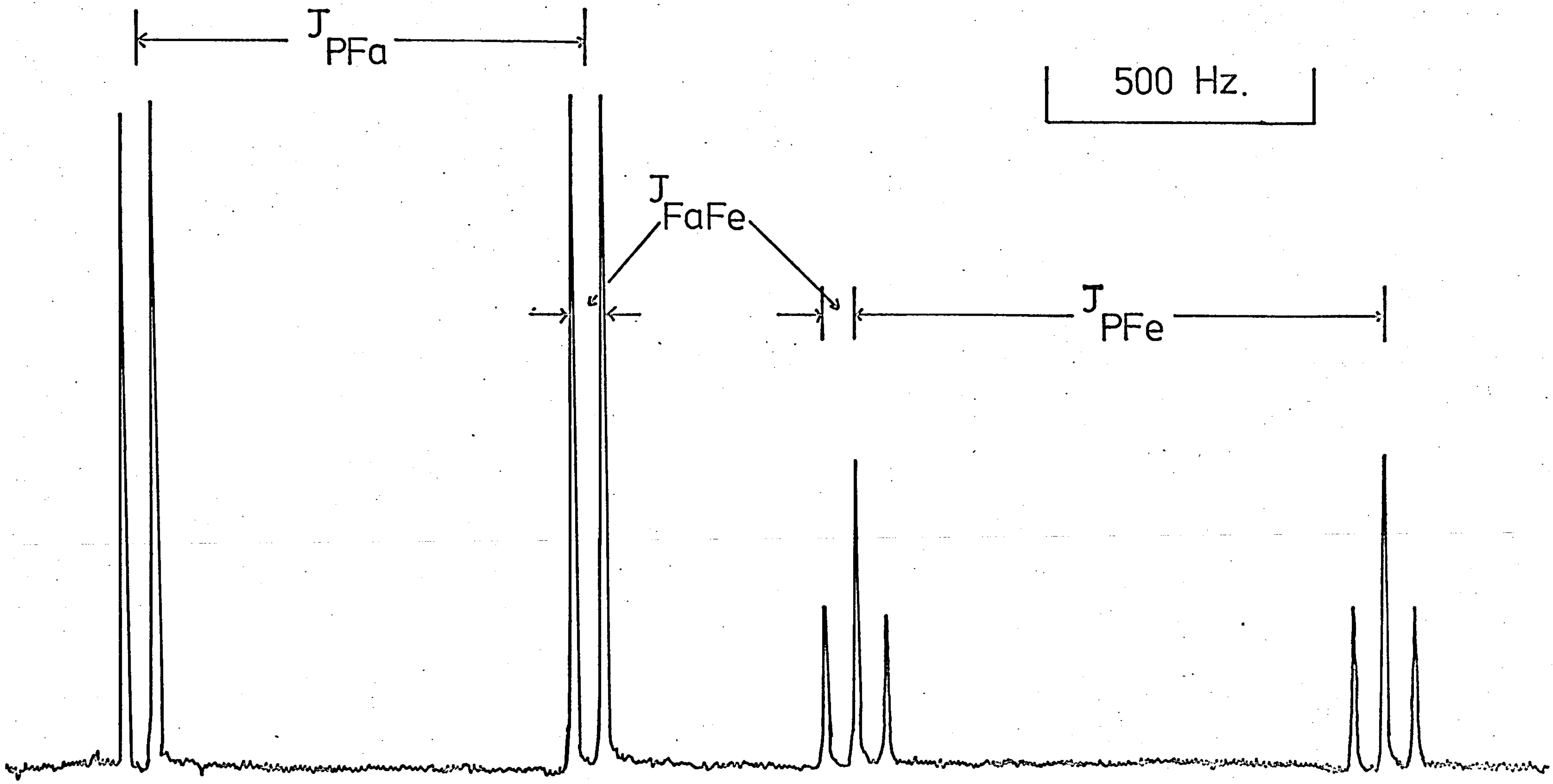


Fig. 2.7 ^{19}F N.m.r. Spectrum of 4-Me-C_5H_9N-PF_3Ph

aminofluorophosphoranes.[2]

The room temperature ^{19}F n.m.r. spectrum of 2-methyl pyrrylphenyltrifluorophosphorane is consistent with two magnetically equivalent axial fluorine atoms contrasting to the results obtained for the piperidyl trifluorophosphoranes and even on cooling to -100°C there is no significant change in the spectral form the observation still being consistent with magnetically equivalent axial fluorine atoms. The ^{19}F n.m.r. spectra of 2,5-dimethylpyrrylphenyltrifluorophosphorane at room temperature and at -100°C remains consistent, as one might expect, with magnetically equivalent axial fluorine atoms.

The observation of magnetically non-equivalent axial fluorine atoms for the piperidyl trifluorophosphoranes can only arise when the piperidyl ring lies in the axial plane of the trigonal bipyramid about phosphorus thus placing the methyl group in the 2 or 3 position of the ring in an environment closer to one axial fluorine atom than the other. This arises from cessation of the P-N bond rotation to within the time scale of the n.m.r. measurement. For 4-methylpiperidylphenyltrifluorophosphorane the environments of the two axial fluorine atoms are the same and even when the P-N bond rotation is effectively stopped one should not observe any difference in magnetic properties of the two axial fluorine as the stereochemical environments are still the same.

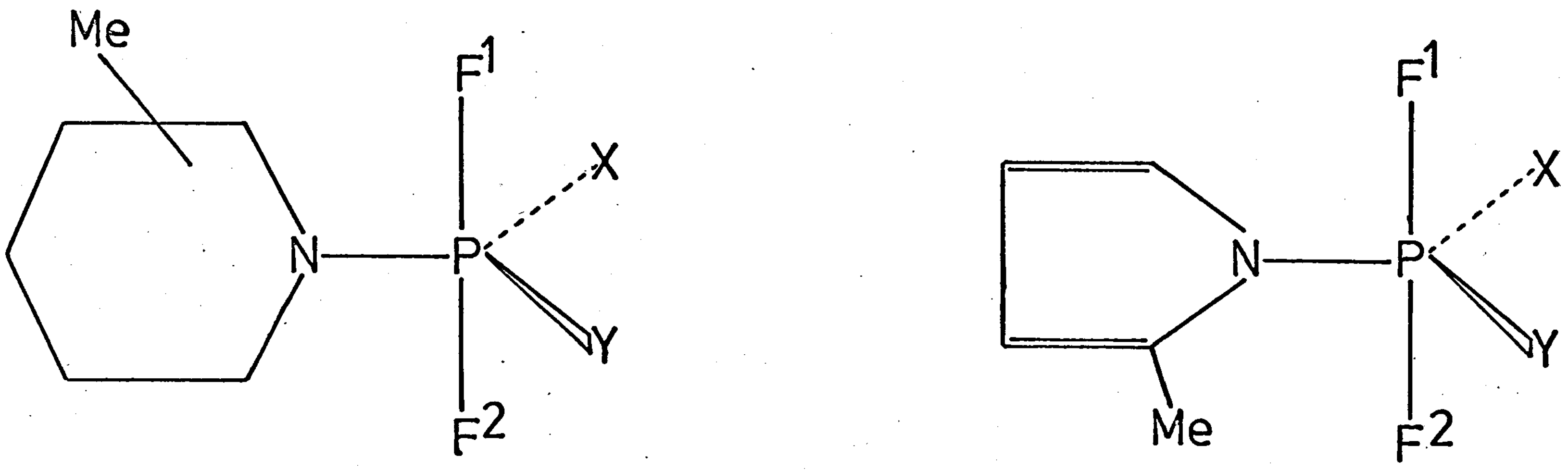
The observed magnetic equivalence of the axial fluorine atoms of 2-methylpyrrylphenyltrifluorophosphorane, even at low temperatures, is somewhat surprising as one might expect a difference in the environments of the two axial fluorine atoms and thus the observation of magnetically non-equivalent axial fluorine atoms. This result might be explained by the possibility of a very low energy barrier to rotation about the P-N bond and thus an inability to freeze this rotation sufficiently to permit observation of a difference in the magnetic properties of the axial fluorine atoms. Another point to be considered is that the pyrryl ring might prefer to lie in the equatorial plane of the trigonal bipyramid and thus the stereochemistry of the ring would have no influence on the magnetic properties of the axial fluorine atoms as the axial fluorine atom environments would be identical. Figure 2.8 shows the proposed structures for the trifluorophosphoranes.

An interesting feature of the ^{19}F n.m.r. spectra, in the equatorial region, of 2-methyl- and 3-methylpiperidylphenyltrifluorophosphorane (See Figures 2.4 and 2.6) is the multiplet nature of each of the individual lines of each of the doublet of triplets. This observed spin spin coupling is of the order 3.5 Hz and is believed to arise from long range spin spin coupling between the equatorial fluorine atom and the equatorial protons at the 2 and 6 positions of the piperidyl ring. For 2-methylpiperidylphenyltrifluorophosphorane this manifests itself in the doublet nature of each of the resonance lines whereas for 3-methylpiperidylphenyltrifluorophosphorane triplet nature of each of the resonance lines is observed. As can be seen there are for the 2-methyl- and 3-methyl- compound one and two protons, respectively, in the 2 and 6 positions of the ring, for long range spin spin coupling to the equatorial fluorine atom on phosphorus.

The room temperature spectra of the difluorophosphoranes show a simple doublet characteristic of fluorine atoms in the axial positions of a trigonal bipyramid. However, for 2-methylpiperidyldiphenyldifluorophosphorane the low temperature ^{19}F n.m.r. spectrum loses this form. On lowering the temperature the doublet collapses indicating loss of magnetic equivalence of the two axial fluorine atoms. At -100°C the spectral form is that of two ab sub-spectra being indicative of two distinct fluorine atom environments. The spectrum is shown in Figure 2.9. No adequate low temperature spectrum could be obtained for 3-methylpiperidyldiphenyldifluorophosphorane as a low enough temperature could not be reached without precipitation of the compound from the solvent. Line collapse was observed which indicates magnetic non-equivalence of the axial fluorine atoms. The spectral form of 4-methylpiperidyldiphenyldifluorophosphorane remains the same when measured between room temperature and -100°C thus indicating magnetic equivalence of the two axial fluorine atoms.

The observed results can be explained by an effective cessation of the P-N bond rotation at low temperatures thus placing the piperidyl ring in the axial plane of the trigonal bipyramid about phosphorus and so giving the axial fluorine atoms distinct environments. In the case of 4-methylpiperidyldiphenyldifluorophosphorane the environments of the two axial fluorine atoms remain the same at all temperatures as the compound is a symmetric amino fluorophosphorane. Figure 2.8 shows the proposed structure of the difluorophosphoranes.

Figure 2.8



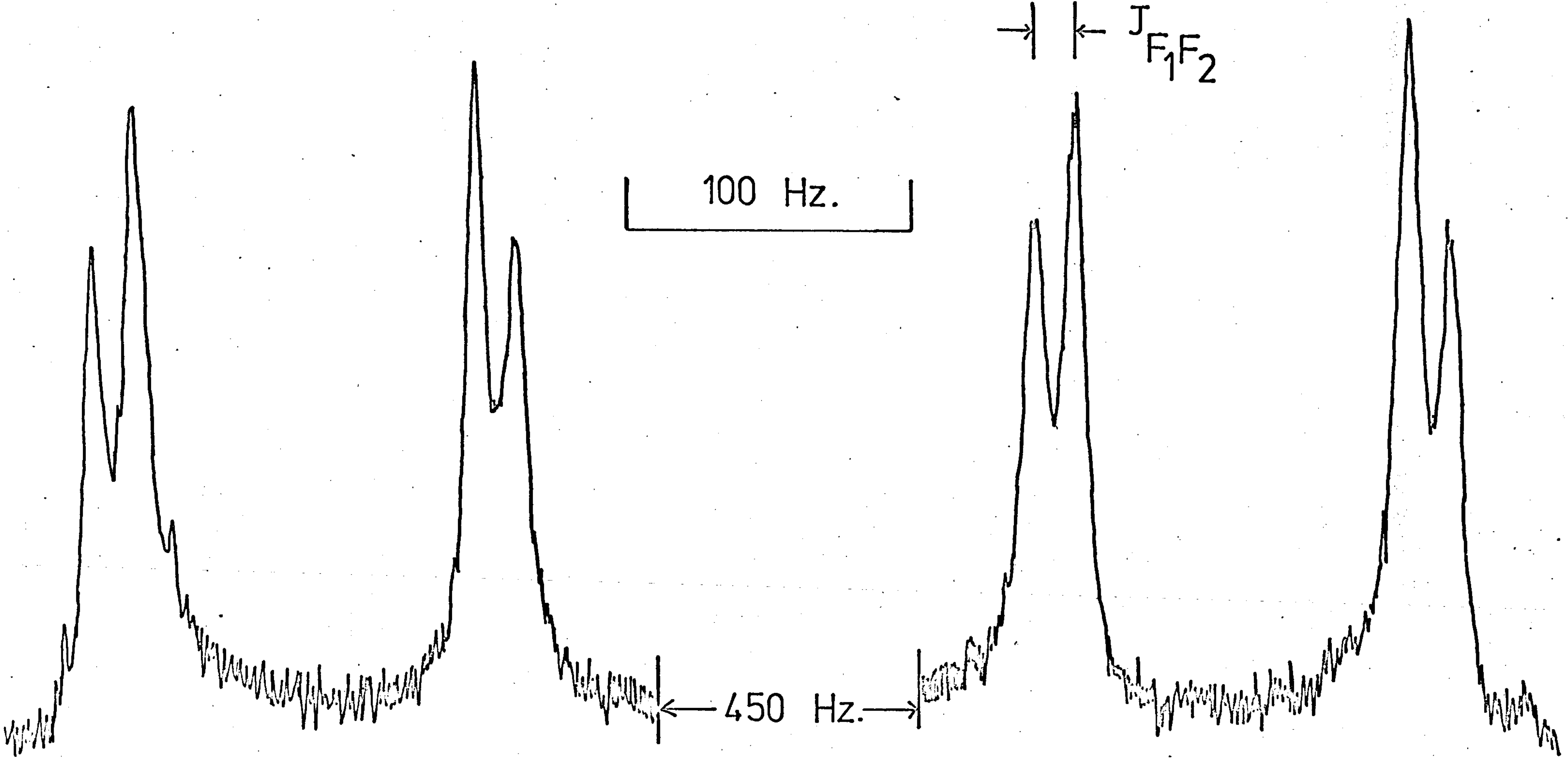
(where X=F, Y=Ph, Me;
X=Y=Ph)

The piperidyl ring is puckered and does not necessarily lie in the plane of the paper.

(where X=F, Y=Ph; or
X=Y=Ph)

The pyrrole ring is planar and lies in the plane of the paper.

Fig. 2.9



^{19}F N.m.r. Spectrum of 2-Me-C_5H_9N-PF_2Ph_2 at -70°C

The ^{31}P n.m.r. data for these new aminofluorophosphoranes are shown in Table 2.6 and are consistent with five-coordinate phosphorus-fluorine compounds. Although the observed ^{19}F room temperature spectra of 2-methyl- and 3-methylpiperidyl-phenyl(methyl)trifluorophosphorane show magnetically non-equivalent axial fluorine atoms the ^{31}P n.m.r. spectra show no extra peaks due to non-equivalence of the fluorine atoms. This observation might be explained from the fact that the chemical shift difference between the two axial fluorine atoms is small in comparison to the large chemical shift differences between phosphorus and fluorine and that the ^{31}P n.m.r. resonance lines are probably too broad, due to nitrogen quadropole relaxation, for any extra spin spin coupling to be observable.

Structure and Stereochemistry of Fluorophosphoranes Substituted by Asymmetric Amino Substituents

The observed findings can be rationalised in terms of two intramolecular stereochemical rate processes, each probably having energy barriers of the order 5 to 25 kcal /mol. The processes are intramolecular exchange of groups and called "pseudorotation", and restricted rotation about the phosphorus-nitrogen bond.

The former process was first recognised by Berry in 1960 [111] resulting in the concept of a non-rigid molecule and invoked to explain the n.m.r. data for many tetra- and trifluorophosphoranes. The latter process has only recently been recognised and several reports have appeared concerning phosphorus-heteroatom bond rotation in fluorophosphoranes.

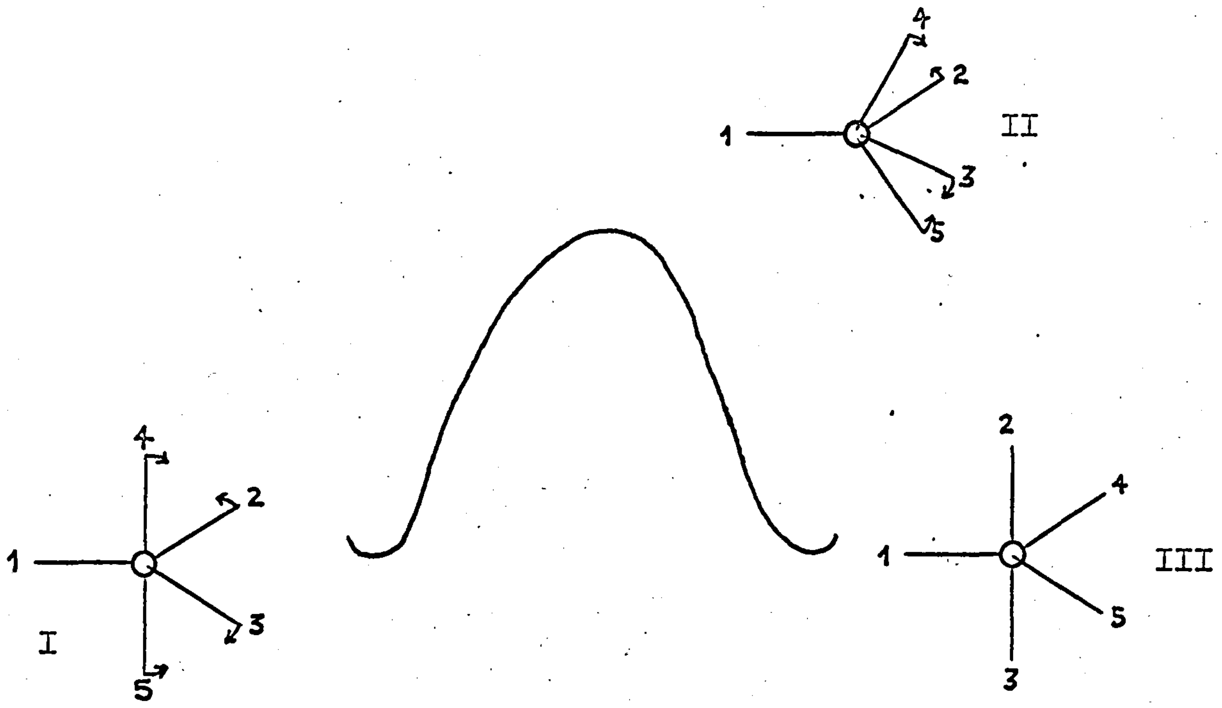
If for certain magnetic isotopes the rate processes have rate constants of a similar order of magnitude as the total spread (in Hz) of the n.m.r. spectrum then they may cause profound changes in the shape of the n.m.r. signals.[114] If the average lifetime of a number of magnetic isotopes undergoing an intramolecular rate process exceeds an upper limit then the n.m.r. spectra will show them as individual entities. Conversely if the lifetimes are short compared with the n.m.r. time scale then the n.m.r. spectrum will show a single resonance in which the chemical shifts and coupling constants are a statistically weighted average of the corresponding values in species undergoing the slow rate process. By varying the temperature in n.m.r. techniques the rate can be changed and information can be obtained about rate, energy barriers and ultimately the structure of the species being studied

Intramolecular Exchange

The concept of intramolecular exchange or pseudorotation was put forward by Berry [111] to explain the unusually simple ^{19}F n.m.r. spectrum of phosphorus pentafluoride indicating magnetically equivalent fluorine atoms. [74, 115-117] This equivalence was explained by a rapid positional exchange of the fluorine atoms in the axial and equatorial positions of the trigonal bipyramid about phosphorus. The figure below shows a positional exchange process.

If sufficient energy is available then a simple axial vibrating mode could convert the trigonal bipyramidal molecule I into its tetragonal pyramidal isomer II. A continuation of this process could thus convert molecule II

Intramolecular Positional Exchange of Ligands



into a trigonal bipyramid III thus achieving interchange of axial and equatorial fluorine atoms. Molecule III is the rotated version of molecule I. The rate of positional exchange is thought to depend on the amplitude of the axial bending vibration.[118] The energy barrier top coincides with the tetragonal pyramid II and can be overcome by classical molecular collisions, which are temperature dependent, or there may be a quantum mechanical tunnelling through the barrier which is not temperature dependent.[118] This process is thought to occur in a variety of trigonal bipyramidal molecules.[74, 112, 119, 120]

Trigonal bipyramidal geometry has been unambiguously established in vibrational spectral and electron diffraction studies of a series of tetrafluorophosphoranes including the parent compound PF_5 this being possible due to different time scales on which these techniques are operating. Electron diffraction is of the order 10^{-20},(Ref 120) I.R. and

Raman of the order 10^{-13} compared to the n.m.r. time scale of 10^{-1} to 10^{-9}. The fluorophosphoranes PF_5,[121] CH_3PF_4,[122, 123] CF_3PF_4,[124, 125] CCl_3PF_4,[126] $tBuPF_4$[127] and $PhSPF_4$[128] have all been studied and trigonal bipyramidal structures assigned. Positional exchange of fluorine atoms in phosphorus pentafluoride and its monosubstituted derivatives, RPF_4, is independent of temperature over a wide range although for monosubstituted dialkyl(aryl)aminotetrafluorophosphoranes R_2NPF_4[2, 112, 113, 128] and alkyl(aryl)thiotetrafluorophosphoranes $RSPF_4$[23, 31, 71] non-equivalence of the axial and equatorial fluorine atoms has been observed on cooling down to below -85°C, distinct axial and equatorial fluorine atom environments being observed. Thus a trigonal bipyramidal structure in which the amino or thio group is in an equatorial position is the only possible structure which can be assigned on the strength of the n.m.r. data.

Hindered Phosphorus-Heteroatom Bond Rotation in Fluorophosphoranes

The observation of non-equivalence of either axial or equatorial fluorine atoms in heteroatom fluorophosphoranes, shown by the n.m.r. data, can be explained by a slowing down of rotation about the phosphorus-heteroatom bond relative to the n.m.r. time scale. This is manifested in the positioning of one of the groups attached to the heteroatom in a position closer to one of the axial or equatorial fluorine atoms than the other thus creating distinct atom environments. This effect has been observed by other workers[98-100, 103, 104] in fluorophosphoranes of the type $RHNPR_nF_{4-n}$ and recently in phosphorus-heteroatom compounds of the type

$R_n(RS)PF_{4-n}$ [31, 71] and $BzMeNPR_nF_{4-n}$.[23, 129] Studies have also been made into measuring energy barriers to rotation for such compounds and calculated energy barriers are in the range 5 to 12 kcal/mol.

Low temperature n.m.r. studies of these new aminofluorophosphoranes indicated the effective cessation of firstly pseudorotation for the tetrafluorophosphoranes and secondly rotation about the P-N bond giving a rigid structure compared to the n.m.r. time scale. The broad doublets for the tetrafluorophosphoranes, at room temperature, collapse on cooling to give a complex 30 line spectrum compared to a 12 line spectrum observed for symmetric aminofluorophosphoranes. The trifluorophosphoranes are not involved in any positional exchange process as this would necessitate the positioning of an amino or hydrocarbon group, in the intermediate, in an energetically unfavourable axial position. However, the room temperature spectra of the trifluorophosphoranes are characterised by complex 22 line spectra compared to the normal 10 line spectra observed for symmetric aminotrifluorophosphoranes.[2] The only intramolecular rate process to be considered for the difluorophosphoranes is the cessation of the P-N bond rotation at low temperatures. At low temperatures a complex 8 line spectrum is observed compared to the normal doublet observed for difluorophosphoranes.[2]

Reasons for this high energy barrier to P-N bond rotation in fluorophosphoranes have been quoted[99, 104] as (a) $p\pi$-$d\pi$ bonding between the lone pair of electrons on the nitrogen and an empty d orbital on the phosphorus, and (b) hydrogen bonding between the axial fluorine atoms and the protons of the alkyl group attached to the nitrogen of the asymmetric group.

The proposed structure for the tetrafluorophosphoranes 2-methyl- and 3-methyl-piperidyltetrafluorophosphorane, in which the piperidyl ring prefers the equatorial plane of the trigonal bipyramid about phosphorus, can be explained by the preference of the ring to take up the position of least stereochemical hindrance which is the equatorial plane. If $p\pi$-$d\pi$ interaction is to be invoked between nitrogen and phosphorus then it would explain the spectroscopic results observed especially if sp^2 hybridisation of the nitrogen atomic orbitals is assumed with one of the nitrogen p orbitals being exclusively involved in $p\pi$-$d\pi$ bonding. If sp^3 hybridisation at nitrogen was assumed thus ruling out the possibility of any $p\pi$-$d\pi$ interaction then one would still observe magnetic non-equivalence of fluorine atoms in asymmetric aminofluorophosphoranes but one would expect to observe magnetic non-equivalence of either axial or equatorial fluorine atoms for symmetric aminofluorophosphoranes as the hydrocarbon groups attached to the nitrogen would be in positions closer to one fluorine atom than the other. This is not observed to be so. By the use of molecular models it can be seen that the possibility of any hydrogen bonding between equatorial fluorine atoms and protons of the alkyl group attached to nitrogen when the ring lies in the equatorial plane, is very small. By analogy 4-methylpiperidyltetrafluorophosphorane can be assumed to have the same structure.

In contrast to the piperidyl tetrafluorophosphoranes

2-methylpyrryltetrafluorophosphorane, from consideration of the spectroscopic results, has a structure in which the pyrryl ring lies in the axial plane of the trigonal bipyramid about phosphorus. This however, is not the least sterically hindered position. An explanation for this might be a large amount of hydrogen bonding between the methyl group and the axial fluorine atoms which is possible when the ring lies in the axial plane thus holding the ring in this position. The use of pπ-dπ bonding between the nitrogen of the ring and the phosphorus atom can also be invoked as an explanation but the structure of the ring, which is aromatic, dictates that the lone pair of electrons on the nitrogen is involved in the π system of the ring. Therefore any pπ-dπ interaction between nitrogen and phosphorus might only be small. The main factor influencing the structure can only be hydrogen bonding.

The structures proposed for the trifluorophosphoranes 2-methyl- and 3-methyl-piperidylphenyl(methyl)trifluorophosphorane, from consideration of the spectroscopic results, in which the piperidyl ring lies in the axial plane of the trigonal bipyramid about phosphorus can also be explained by the preference of the ring to take up the position of least stereochemical hindrance. On introduction of a methyl or phenyl group into the equatorial plane the stereochemical requirements of the ring are altered and the least crowded plane becomes the axial plane. That the observation of magnetically non-equivalent fluorine atoms is made at room temperature can be explained by there not being any positional exchange of ligands, due to greater energy requirements, and a strong pπ-dπ interaction between phosphorus and nitrogen enhanced by the inductively electron withdrawing effect of the fluorine atoms attached to phosphorus. This effect is also present for the tetrafluorophosphoranes but even if the phosphorus-nitrogen bond rotation is effectively "frozen" no observation of magnetically nonequivalent axial or equatorial fluorine atoms will be made until the positional exchange process has been slowed down by reduction of temperature.

The presence of any hydrogen bonding in these trifluorophosphoranes might conveniently explain the high energy barrier to rotation in the case of the 2-methylpiperidyl trifluorophosphoranes as the methyl group of the heteroatom group would be sufficiently close enough to one of the axial fluorine atoms to bring about some hydrogen bonding. Such hydrogen bonding cannot be invoked in an explanation for the high energy barrier in the case of the 3-methylpiperidyltrifluorophosphoranes as the methyl group of the heteroatom group is too far removed from the axial fluorine atoms to be able to form any hydrogen bonds, yet the spectroscopic results are analogous. Therefore the main factors to be considered are the possibility of pπ-dπ bonding and the positioning of the ring in the position of least stereochemical hindrance. From these considerations one can also assume a similar structure for the analogous 4-methylpiperidylphenyl(methyl)trifluorophosphorane.

In contrast to the piperidyl trifluorophosphoranes no observation was made of magnetically non-equivalent axial or equatorial fluorine atoms between room temperature and

-100°C for 2-methylpyrrylphenyltrifluorophosphorane. This observation might be explained by a very low energy barrier to phosphorus-nitrogen bond rotation due to very little or no pπ-dπ interaction between phosphorus and nitrogen. This might be expected in view of the aromatic requirements of the pyrryl ring needing the use of the lone pair of electrons on the nitrogen atom and a decrease in electron withdrawal effect of the fluorine atoms attached to phosphorus compared to the pyrryltetrafluorophosphoranes. Therefore one cannot make any assumptions as to the structure of the pyrryltrifluorophosphoranes.

The proposed structure for the difluorophosphoranes 2-methyl- and 3-methyl-piperidyldiphenyldifluorophosphorane in which the piperidyl ring is situated in the axial plane of the trigonal bipyramid about phosphorus can also be explained by the piperidyl ring taking up the position of least stereochemical hindrance as the equatorial plane is somewhat crowded due to the presencs of two phenyl groups attached to phosphorus. Any pπ- dπ interaction between phosphorus and nitrogen would be of a smaller nature than for the corresponding tetra- and tri-fluorophosphoranes due to the decrease in the number of fluorine atoms attached to phosphorus and the subsequent decrease in their inductively electron withdrawing effect. For these difluorophosphoranes the possibility of any pseudorotation process is negligible and therefore on lowering the temperature, the phosphorus-nitrogen bond rotation is the only process which is being slowed down. The possibility of any hydrogen bonding can only be invoked for the case of 2-methyl substituted compounds as the methyl group in the 3-methyl substituted compounds is situated too far away from the fluorine atoms for any possible hydrogen bonding to take place. However the results for the two series of compounds are the same. By analogy a similar structure can be proposed for 4-methylpiperidyldiphenyldifluorophosphorane.

Since the subject of restricted bond rotation is of a complex nature it would probably be meaningless to make any comparison between mechanisms postulated for other phosphorus-heteroatom compounds where phosphorus shows coordination numbers of three, four and five. It is possible that in each case several factors are involved including $p\pi$-$d\pi$ interaction enhanced by inductively electron withdrawing groups; hydrogen bonding between the axial fluorine atoms and protons of a hydrocarbon group attached to the heteroatom, and stereochemical requirements of the molecule. For the tetrafluorophosphoranes one has to also consider the existence of a positional exchange process for the fluorine atoms.

Discussion

The preparation of these asymmetric and symmetric aminofluorophosphoranes proves to be no exception to the well documented routes to aminofluorophosphoranes involving the cleavage of a Si-N bond with fluorophosphoranes.[2, 18, 20, 21] The reaction presumably takes place via the formation of a Lewis acid-Lewis base adduct which breaks down forming the volatile by-product trimethylfluorosilane and the aminofluorophosphorane. The driving force is the formation of a strong Si-F bond compared to the weaker P-F bond. (See Chapter 1). As the Lewis acid nature of the fluorophosphoranes decreases in the order $PF_5 > PhPF_4 > MePF_4 > Ph_2PF_3 > Me_2PF_3$ and the Lewis base nature of the aminosilanes decreases from piperidyl to pyrryl the energy required to bring about a reaction becomes higher. It was noticed that no reaction took place when methyltetrafluorophosphorane was allowed to react with 2-methylpyrryltrimethylsilane and this can be explained by the non formation of an expected 1:1 adduct. The chemical properties are as expected for fluorophosphoranes.[1] The trifluorophosphoranes show a tendency to undergo a rearrangement to their ionic isomers in a fashion which has been observed for other aminofluorophosphoranes, [26, 106, 107] rearrangement proceeding according to the equation,

$$2RR'NPR''F_3 \longrightarrow [(RR'N)_2PR''F]^+[R''PF_5]^-$$

(where RR'N = 2-Me-, 3-Me-, 4-Me-piperidyl-; 2-Me- or 2,5-dimethylpyrryl; R'' = Me, Ph).

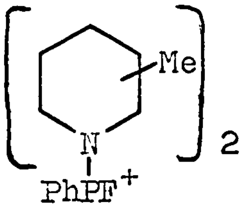
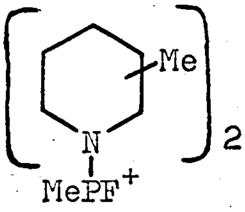
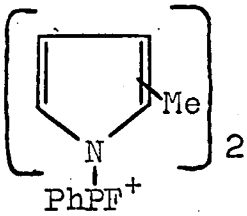
These rearranged products were characterised by ^{19}F n.m.r. spectroscopy. The reaction of phosphorus pentafluoride with the aminotrimethylsilanes show a tendency for the formation of ionic species due to the rearrangement of the covalent tetrafluorophosphoranes, as they are formed, to their ionic isomers. The rearrangements proceed according to the equation,

$$2RR'NPF_4 \longrightarrow [(RR'N)_2PF_2]^+[PF_6]^-$$

(where RR'N = 2-Me-, 3-Me-, 4-Me-piperidyl-; 2-Me-. or 2,5-dimethyl-pyrryl-). These ionic products were characterised by ^{19}F and ^{31}P n.m.r spectroscopy. Tables 2.7 and 2.8 list the n.m.r. data for the hexa- and penta-fluorophosphates, respectively.

Table 2.7

^{19}F Nuclear Magnetic Resonance Data for the Pentafluorophosphates

Compound	J (Hz)	δF p.p.m.
 $[PhPF_5]^-$	J_{PFa} 691 J_{PFe} 815 J_{FeFa} 39 $J_{PF(cat)}$ 1050	δFa + 60.7 δFe + 57.2 δF(cat) + 86.0
 $[MePF_5]^-$	J_{PFa} 673 J_{PFe} 843 J_{FeFa} 42 $J_{PF(cat)}$ 1033	δFa + 58.9 δFe + 47.2 δF(cat) + 83.1
 $[PhPF_5]^-$	J_{PFa} 653 J_{PFe} 825 J_{FeFa} 33 $J_{PF(cat)}$ 1011	δFa + 57.7 δFe + 47.2 δF(cat) + 82.0

No ^{31}P n.m.r. data was obtained.

All spectra made on solutions in acetonitrile.

δFa and δFe refer to axial and equatorial fluorine atoms respectively.

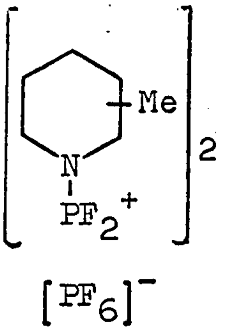
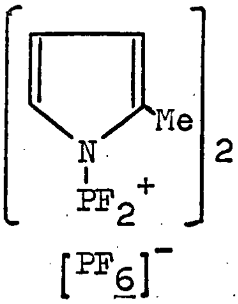
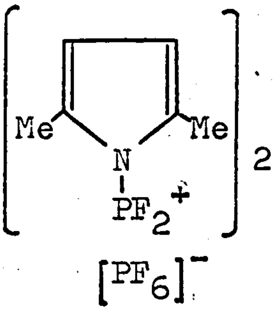
cat refers to the cation.

For the piperidyl compounds the orientation of the Me groups is 2, 3, or 4.

For the pyrryl compounds the orientation of the Me groups is 2-Methyl- or 2,5-Dimethyl-.

Table 2.8

^{19}F and ^{31}P N.m.r. Data for the Hexafluorophosphates

Compound	F p.p.m.	P p.p.m.	J (Hz)
	F(an) + 72.6	P(an) + 145.2	J_{PF}(an) 720
	F(cat) a	P(cat) a	J_{PF}(cat) a
	F(an) + 71.6	P(an) + 145.0	J_{PF}(an) 711
	F(cat)+ 76.4	P(cat)+ a	J_{PF}(cat) 1088
	F(an) + 71.2	P(an) + 145.0	J_{PF}(an) 710
	F(cat)+ 75.8	P(cat) -80.2	J_{PF}(cat) 1061

(a) Not observable from the spectrum because concentration of sample too small.

All spectra made on solutions in acetonitrile.

an. and cat. refer to the anion and cation, respectively.

For the piperidyl compounds the orientation of the Me groups is 2, 3, or 4.

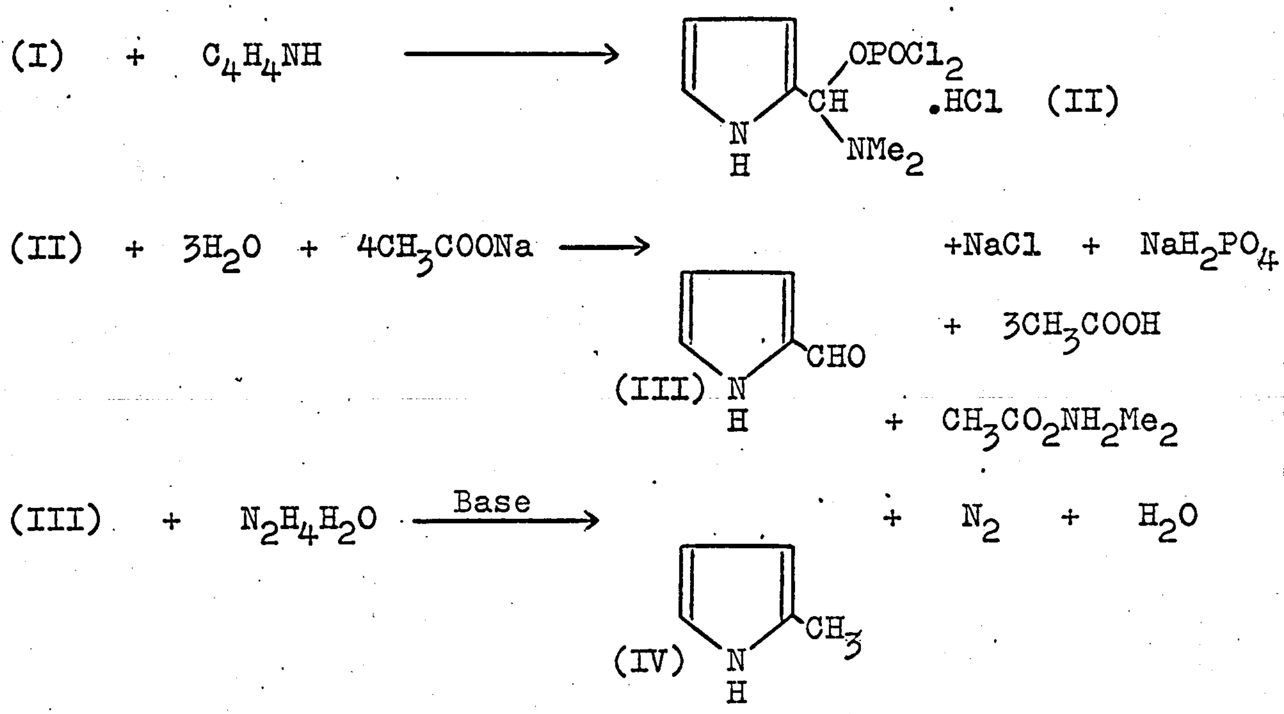
The ^{19}F and ^{31}P n.m.r. data for the hexafluorophosphates are in agreement with those reported in the literature. [1,,72] The ^{19}F n.m.r. spectra of the pentafluorophosphates show a second order AB_4X pattern of the type which has been observed for the ions $[PhPF_5]^-$, $[Me_2NPF_5]^-$, and $[MePF_5]^-$. [23,26,27] One observes a doublet of quintets which is attributed to the single fluorine atom coupling with the four remaining fluorine atoms and the phosphorus atom; a doublet of doublets attributed to four fluorine atoms, which are magnetically equivalent, coupling with the remaining fluorine atom and the phosphorus atom, and a doublet at higher field attributed to the fluorine atom of the cation which couples with the phosphorus atom of the cation. The results obtained are consistent with an octahedral structure in which four of the five fluorine atoms are situated in the equatorial plane. The fluorine atom opposite to the organo group has an environment differing from the remaining fluorine atoms.

Experimental

Since all the reactants and products containing P-F bonds are sensitive to moisture it was necessary to take the precautions described in the section on General Experimental Technique. All the fluorophosphoranes were prepared by reported methods. (See section on Experimental Technique). The methyl substituted piperidyl compounds were obtained as technical products from Fluka, Buchs, Switzerland, and the pyrrole derivatives were obtained from Cilag Chemie, Basel, Switzerland.

The silicon-nitrogen compounds 2-methyl-, 3-methyl- and 4-methyl-trimethylsilane were prepared in a manner similar to that reported for the preparation of phenyltrimethylsilyl ether.[96] The corresponding pyrryl silanes, however, were not prepared by the analogous method. 2-Methylpyrryltrimethylsilane was prepared from pyrrole via 2-formylpyrrole[130] which was reduced using hydrazine hydrate to give 2-methylpyrrole.[131] The magnesium bromide Grignard of 2-methylpyrrole was then allowed to react with trimethylchlorosilane affording 2-methylpyrroletrimethylsilane.[132] 2,5-Dimethylpyrryltrimethylsilane was prepared from the reaction of the magnesium bromide Grignard of 2,5-dimethylpyrrole with trimethylchlorosilane in a manner similar to that for the preparation of 2-methylpyrryltrimethylsilane.[132] The reactions proceed according to the equations,

$$Me_2NCHO + POCl_3 \longrightarrow Me_2NCHO.POCl_3 \quad (I)$$



$$(IV) + EtMgBr \longrightarrow \underset{(V)}{2\text{-}MeC_4H_3NMgBr}$$

$$(V) + Me_3SiCl \longrightarrow 2\text{-}Me\text{-}C_4H_3NSiMe_3 + MgCl_2 + MgBr_2$$

All the silyl compounds were characterised by their ^1H n.m.r. spectra. Attempts at preparing the pyrrylsilanes from the reaction of the pyrrole with trimethylchlorosilane in the presence of a tertiary amine proved unsuccessful presumably due to the decreased Lewis base nature of the amine.

Preparation of compounds -

2-Methylpiperidyltrimethylsilane: The preparation was carried out in a manner similar to the preparation of perfluorophenyltrimethylsilyl ether as described in Chapter 1. Trimethylchlorosilane (135.5 g., 1.26 mole) was allowed to react with 2-methylpiperidine (125.0 g., 1.26 mole) in the presence of triethylamine (128.0 g., 1.26 mole) in a 2l. three-necked flask using 1l. of sodium dried ether as solvent. The reaction mixture was allowed to reflux for 12 h. On cooling the reaction mixture to room temperature it was filtered to remove solid amine-hydrochloride. The filtrate was distilled first at atmospheric pressure to remove the ether and subsequently distilled under vacuum through a 12 in. Vigreux column affording a colourless liquid of b.p. 90°C/66 mm. and identified as 2-methylpiperidyltrimethylsilane. The weight collected (121.7 g.) represents 65% yield.

Found:	C, 63.7;	H, 12.0;	N, 8.1;	Si, 16.2%
Calc. for $C_9H_{21}NSi$	C, 63.2;	H, 12.3;	N, 8.2;	Si, 16.4%.

3-Methylpiperidyltrimethylsilane: The preparation was carried out in a manner similar to that described in the previous preparation. Distillation of the final residue afforded a colourless liquid of b.p. 108°C/120 mm. and identified as 3-methylpiperidyltrimethylsilane. Yield 70%

Found:	C, 63.3;	H, 12.6;	N, 8.0;	Si, 16.1%
Calc. for $C_9H_{21}NSi$	C, 63.2;	H, 12.3;	N, 8.2;	Si, 16.4%

<u>4-Methylpiperidyltrimethylsilane</u>: The preparation was carried out in a manner similar to that described for the preparation of 2-methylpiperidyltrimethylsilane. Distillation of the final residue afforded a colourless liquid of b.p. 106°C/120 mm. and identified as 4-methylpiperidyltrimethylsilane. Yield 67%.

Found:	C, 63.0;	H, 12.3;	N, 8.1;	Si, 16.3%
Calc. for $C_9H_{21}NSi$	C, 63.2;	H, 12.3;	N, 8.2;	Si, 16.4%.

<u>2-Methylpiperidyltetrafluorophosphorane</u>: Phosphorus pentafluoride (9.5 g., 0.08 mole) was condensed onto 2-methylpiperidyltrimethylsilane (12.9 g., 0.08 mole) in a glass reaction tube cooled to -196°C on a vacuum line. After condensation was completed the tube was sealed and placed in a cold bath at -78°C for 2 days. On opening the tube and connecting to a trap at -78°C, protected from atmospheric moisture at the open end with a silica gel drying tube, a volatile product was seen to boil off which collected in the trap. This volatile product was shown by ^1H n.m.r. to be trimethylfluorosilane, Me_3SiF, and the weight collected (5,2 g.) represented 71% reaction having taken place. The liquid remaining in the tube was distilled under vacuum affording a colourless liquid of b.p. 54°C/20 mm. and subsequently identified as 2-methylpiperidyltetrafluorophosphorane. The weight collected (10.1 g.) represents 61%

yield of 2-Me-$C_5H_9NPF_4$. An undistillable residue (6.3 g.) remained in the distillation flask and was shown to contain the hexafluorophosphate anion $[PF_6]^-$.

Found:	C, 35.0;	H, 5.8;	F, 37.3%
Calc. for $C_6H_{12}F_4NP$	C, 35.1;	H, 5.8;	F, 37.1%.

3-Methylpiperidyltetrafluorophosphorane: Phosphorus pentafluoride (10.3 g., 0.08 mole) was allowed to react with 3-methylpiperidyltrimethylsilane (14.0 g., 0.08 mole) in a manner similar to the preparation of 2-methylpiperidyltetrafluorophosphorane. Trimethylfluorosilane (6.1 g.) was formed representing 83% reaction having taken place. Vacuum distillation of the remaining liquid afforded a colourless liquid of b.p. 58°C/20 mm. and was subsequently identified as 3-methylpiperidyltetrafluorophosphorane. The weight collected (5.0 g.) represents 32% yield of 3-Me-$C_5H_9NPF_4$. An undistillable residue (11.0 g.) remained in the distillation flask and was shown to contain the hexafluorophosphate anion $[PF_6]^-$.

Found.	C, 35.2;	H, 5.7;	F, 37.0%
Calc. for $C_6H_{12}F_4NP$	C, 35.1;	H, 5.8;	F, 37.1%.

4-Methylpiperidyltetrafluorophosphorane: Phosphorus pentafluoride (6.2 g., 0.049 mole) was allowed to react with 4-methylpiperidyltrimethylsilane (8.5 g., 0.049 mole) in a manner similar to the preparation of 2-methylpiperidyltetrafluorophosphorane. Trimethylfluorosilane (3.8 g.) was formed representing 85% reaction having taken place. Vacuum distillation of the remaining liquid afforded a colourless liquid of b.p. 84°C/23 mm. and was subsequently identified as 4-methylpiperidyltetrafluorophosphorane. The weight collected (6.2 g.) represents 62% yield of 4-Me-$C_5H_9NPF_4$. An undistillable residue (3.8 g.) remained in the distillation flask and was shown to contain the hexafluorophosphate anion $[PF_6]^-$.

Found: C, 35.2; H, 5.8; F, 36.6%

Calc. for $C_6H_{12}F_4NP$ C, 35.1; H, 5.8; F, 37.1%.

2-Methylpiperidylphenyltrifluorophosphorane:[23, 133]

The preparation was carried out in a 25 ml. three necked flask fitted with a reflux condenser, thermometer and dropping funnel. The reflux condenser was attached to a weighed trap cooled to -78°C. Attached to the open end of the trap was a silica gel drying tube to protect the apparatus from atmospheric moisture. Phenyltetrafluorophosphorane (9.2 g., 0.05 mole) was placed in the flask and heated to 50°C. 2-Methylpiperidyltrimethylsilane (8.5 g., 0.05 mole) was placed in the funnel and slowly added to the stirred fluorophosphorane during a 0.5 h. period. An exothermic reaction was observed, the temperature rising to 60°C. The reaction mixture was heated at 60°C for another 0.5 h. during which a colourless volatile liquid collected in the trap, this was subsequently shown by ^{1}H n.m.r spectroscopy to be trimethylfluorosilane. The weight of trimethylfluorosilane collected (3.6 g.) represented 79% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 86°C/0.01 mm. and was subsequently identified as 2-methylpiperidylphenyltrifluorophosphorane. The weight collected (8.2 g.) represents 61% yield of 2-Me-$C_5H_9NPF_3Ph$. If the temperature in the distillation flask was allowed to exceed 90°C then the yield was found to decrease with the formation of a pentafluorophosphate species at the expense of the covalent trifluorophosphorane. (For analysis see reference 23).

3-Methylpiperidylphenyltrifluorophosphorane: Phenyltetrafluorophosphorane (9.2 g., 0.05 mole) was allowed to react with 3-methylpiperidyltrimethylsilane (8.5 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidylphenyltetrafluorophosphorane. Reaction was found to be exothermic and the volatile trimethylfluorosilane (3.4 g.) was formed representing 74% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 83°C/0.01 mm. and was subsequently identified as 3-methylpiperidylphenyltrifluorophosphorane. The weight collected (5.2 g.) represents 40% yield of $3\text{-Me-}C_5H_9NPF_3Ph$. The undistillable residue remaining in the distillation flask was shown to contain the pentafluorophosphate anion $[PhPF_5]^-$.

Found: C, 54.7; H, 6.4; F, 21.8; P, 11.3%

Calc. for $C_{12}H_{17}F_3NP$ C, 54.7; H, 6.4; F, 21.6; P, 11.7%.

4-Methylpiperidylphenyltrifluorophosphorane: Phenyltetrafluorophosphorane (15.5 g., 0.08 mole) was allowed to react with 4-methylpiperidyltrimethylsilane (14.8 g., 0.08 mole) in a manner similar to the preparation of 2-methylpiperidylphenyltrifluorophosphorane. The reaction was found to be exothermic and the volatile trimethylfluorosilane (6.8 g.) was formed representing 96% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 82°C/0.01 mm. and was subsequently identified as 4-methylpiperidylphenyltrifluorophosphorane.

The weight collected (16.8 g.) represents 80% yield of 4-Me-$C_5H_9NPF_3Ph$. The undistillable residue remaining in the distillation flask was shown to contain the pentafluorophosphate anion $[PhPF_5]^-$.

Found:	C, 54.7;	H, 6.4;	F, 21.6;	P, 11.7%
Calc. for $C_{12}H_{17}F_3NP$	C, 54.7;	H, 6.4;	F, 21.6;	P, 11.7%.

<u>2-Methylpiperidylmethyltrifluorophosphorane:</u> Methyltetrafluorophosphorane (9.0 g., 0.07 mole) was condensed onto 2-methylpiperidyltrimethylsilane (12.6 g., 0.07 mole) in a glass reaction tube at -196°C on a vacuum line. After condensation had been completed the tube was sealed and allowed to warm up to room temperature. The reaction was found to be exothermic noticed by rise in temperature of tube. The tube was then left at room temperature for 48 h. to allow completion of reaction. On opening the tube and connecting to a weighed trap cooled to -78°C a volatile product was seen to boil off and collected in the trap. This liquid was shown by ^1H n.m.r. to be trimethylfluorosilane and the weight collected (5.9 g.) represented 78% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 74°C/ 20 mm. which was subsequently identified as 2-methylpiperidylmethyltrifluorophosphorane. The weight collected (9.9 g.) represents 67% yield of 2-Me-$C_5H_9NPF_3Me$. An oily brown undistillable liquid remained in the distillation flask and was shown to contain the pentafluorophosphate anion $[MePF_5]^-$. As was noticed during the preparation of the phenyl derivatives if the temperature of the distillation was allowed to rise above 90°C then the ionic compound was

formed at the expense of the covalent trifluorophosphorane.

Found: C, 41.6; H, 7.4; F, 28.0; N, 6.9%

Calc. for $C_7H_{15}F_3NP$ C, 41.8; H, 7.5; F, 28.4; N, 6.9%.

3-Methylpiperidylmethyltrifluorophosphorane: Methyltetrafluorophosphorane (8.5 g., 0.07 mole) was allowed to react with 3-methylpiperidyltrimethylsilane (11.3 g., 0.07 mole) in a manner similar to the preparation of 2-methylpiperidylmethyltrifluorophosphorane. The reaction was found to be exothermic and the reactants were left for 48 h. to allow for the completion of the reaction. On opening the tube and connecting to a trap at -78°C trimethylfluorosilane was seen to boil off and collected in the trap. The weight collected (5.9 g.) represented 83% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 67°C/15 mm. which was subsequently identified as 3-methylpiperidylmethyltrifluorophosphorane. The weight collected (10.8 g.) represents 80% yield of 2-Me-$C_5H_9NPF_3Me$. The undistillable residue remaining in the distillation flask was found to contain the pentafluorophosphate anion $[MePF_5]^-$.

Found: C, 40.4; H, 7.5; F, 28.1; N, 6.9%

Calc. for $C_7H_{15}F_3NP$ C, 41.8; H, 7.5; F, 28.4; N, 6.9%.

4-Methylpiperidylmethyltrifluorophosphorane: Methyltetrafluorophosphorane (7.6 g., 0.056 mole) was allowed to react with 4-methylpiperidyltrimethylsilane (10.6 g., 0.056 mole) in a manner similar to the preparation of 2-methylpiperidylmethyltrifluorophosphorane. The reaction was found to be exothermic and the reactants were left for 48 h. to allow for completion of the reaction. The volatile by -

product trimethylfluorosilane was formed and the weight collected (3.8 g.) represented 75% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 69°C/17 mm. which was subsequently identified as 4-methylpiperidylmethyltrifluorophosphorane. The weight collected (10.1 g.) represents 83% yield of 4-Me-$C_5H_9NPF_3Me$. The undistillable residue remaining in the flask was found to contain the pentafluorophosphate anion $[MePF_5]^-$

Found:	C, 42.0;	H, 7.4;	F, 28.3;	N, 6.9%
Calc. for $C_7H_{15}F_3NP$	C, 41.8;	H, 7.5;	F, 28.4;	N, 6.9%.

2-Methylpiperidyldiphenyldifluorophosphorane: The reaction was carried out in a 25 ml. three necked flask fitted with a reflux condenser, thermometer and addition funnel. The reflux condenser was attached to a weighed trap cooled to -78°C. Attached to the open end of the trap was a silica gel drying tube to protect the apparatus from atmospheric moisture. Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) was placed in the flask and heated to 50°C. 2-methylpiperidyltrimethylsilane (8.5 g., 0.05 mole) was placed in the addition funnel and added to the stirred fluorophosphorane over a 0.5 h. period. The reaction was found to be exothermic, the temperature rising about 10°C. The reaction mixture was heated for a further 2 h. at 80°C to complete the reaction. A volatile product collected in the trap and was shown by ^1H n.m.r. to be trimethylfluorosilane. The weight collected (4.3 g.) represented 93% reaction having taken place. The remaining reaction residue, which solidified on cooling to room temperature, was distilled

under vacuum affording a colourless liquid of b.p. 166°C/0.05mm. which solidified on cooling to give a white crystalline solid and was subsequently identified as 2-methylpiperidyldiphenyldifluorophosphorane. There was very little forecut and very little residue. The weight collected (14.7 g.) represents 93% yield of 2-Me-$C_5H_9NPF_2Ph_2$. The compound was further purified by sublimation at 100°C/0.03 mm. using a water-cooled finger to collect the compound.
(For analysis see Reference 23)

3-Methylpiperidyldiphenyldifluorophosphorane:
Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) was allowed to react with 3-methylpiperidyltrimethylsilane (8.5 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidyldiphenyldifluorophosphorane. The reaction was found to be exothermic and the raction mixture was heated at 80°C for 2 h. in order to complete the reaction. The volatile by-product trimethylfluorosilane was formed and the weight collected (4.2 g.) represented 92% reaction having taken place. Distillation of the higher-boiling fraction afforded a colourless liquid of b.p. 165°C/0.05 mm. which solidified on cooling giving a white crystalline solid and was subsequently identified as 3-Methylpiperidyldiphenyldifluorophosphorane. The weight collected (14.8 g.) represents 92% yield of 3-Me-$C_5H_9NPF_2Ph$.

Found:	C, 67.3; H, 6.8; F, 11.8%
Calc. for $C_{18}H_{22}F_2NP$	C, 67.3; H, 6.8; F, 11.8%.

4-Methylpiperidyldiphenyldifluorophosphorane:
Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) was allowed to react with 4-methylpiperidyltrimethylsilane (8.5 g., 0.05 mole) in a manner similar to the preparation

of 2-methylpiperidyldiphenyldifluorophosphorane. The reaction was found to be exothermic and the reaction mixture was heated at 80°C for 2 h. to complete the reaction. The volatile by-product trimethylfluorosilane was formed and the weight collected (4.3 g.) represented 93% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 155°C/0.05 mm. which solidified on cooling and was subsequently identified as 4-methylpiperidyldiphenyldifluorophosphorane. The weight collected (11.3 g.) represents 71% yield of $4\text{-Me-}C_5H_9NPF_2Ph$

Found:	C, 67.5;	H, 6.9;	F, 12.0;	N, 4.4%
Calc. for $C_{18}H_{22}F_2NP$	C, 67.3;	H, 6.8;	F, 11.8;	N, 4.3%.

<u>2-Methylpyrryltrimethylsilane</u>: The preparation of 2-methylpyrryltrimethylsilane was carried out in a manner similar to that described by Nagy et.al.[132] for the preparation of 2,5-dimethylpyrryltrimethylsilane via the formation of the magnesium bromide Grignard and its further reaction with trimethylchlorosilane. A 0.65 mole reaction affords 67.3 g. (66% yield) of 2-methylpyrryltrimethylsilane b.p. 77°C/26 mm.

<u>2-Methylpyrryltetrafluorophosphorane</u>: Phosphorus pentafluoride (6.3 g., 0.05 mole)was allowed to react with 2-methylpyrryltrimethylsilane (7.6 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidyltetrafluorophosphorane. The volatile by-product trimethylfluorosilane was formed and the weight collected (4.2 g.) represented 91% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 76°C/25 mm. which solidified on cooling giving a white crystalline

solid and was subsequently identified as 2-methylpyrryltetrafluorophosphorane. The weight collected (5.7 g.) represents 62% yield of 2-Me-$C_4H_3NPF_4$. An undistillable oil remained in the flask and was shown to contain the hexafluorophosphate anion, $[PF_6]^-$ which was presumably formed at the expense of covalent tetrafluorophosphorane.

<u>2-Methylpyrrylphenyltrifluorophosphorane</u>: Phenyltetrafluorophosphorane (9.2 g., 0.05 mole) was allowed to react with 2-methylpyrryltrimethylsilane (7.6 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidylphenyltrifluorophosphorane. No exothermic reaction was observed the reaction mixture having to be heated at 100°C for 3 h. in order to induce any reaction. The volatile byproduct trimethylfluorosilane was formed and the weight collected (4.2 g.) represented 92% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 79°C/0.05 mm. which was subsequently identified as 2-methylpyrrylphenyltrifluorophosphorane. The weight collected (10.3 g.) represents 83% yield of 2-Me-$C_4H_3NPF_3Ph$. The undistillable residue remaining in the flask was found to contain the pentafluorophosphate anion $[PhPF_5]^-$. It was found that if the temperature of the reaction mixture on distillation was allowed to rise above 100°C then the yield of the covalent trifluorophosphorane was reduced and the corresponding yield of the ionic species was increased.

<u>Attempted Preparation of 2-Methylpyrrylmethyltrifluorophosphorane</u>: Methyltetrafluorophosphorane (8.1 g., 0.06 mole) was allowed to react with 2-methylpyrryltrimethylsilane

(9.2 g., 0.06 mole) in a manner similar to the preparation of 2-methylpiperidylmethyltrifluorophosphorane. However, no reaction took place even when the reaction mixture had been heated at 100°C for 24 h. in a sealed tube. This might presumably be due to the difficulty in formation of any Lewis acid-Lewis base adduct, owing to the decreased Lewis base character of the pyrrylsilylamine compared to the corresponding piperidylsilylamines. Recovery of starting materials was effected in 100% yield.

Attempted Preparation of 2-Methylpyrryldiphenyldifluorophosphorane: Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) was allowed to react with 2-methylpyrryltrimethylsilane (7.6 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidyldiphenyldifluorophosphorane. However, The reaction was found not to be exothermic and the reaction mixture had to be heated at 150°C for 12 h. to induce any reaction. The volatile by-product trimethylfluorosilane was formed and the weight collected (3.9 g.) represented 85% reaction having taken place. Due to the extreme reaction conditions it proved impossible to isolate any pure difluorophosphorane from the reaction mixture although evidence for its possible existence was obtained from ^{19}F n.m.r. analysis of the reaction mixture. The reaction mixture appeared to polymerise and attempts at distillation and sublimation afforded no product.

2,5-Dimethylpyrryltetrafluorophosphorane: Phosphorus pentafluoride (9.5 g., 0.07 mole) was allowed to react with 2,5-dimethylpyrryltrimethylsilane (12.6 g., 0.07 mole) in a manner similar to the preparation of 2-methylpiperidyltetrafluorophosphorane. The volatile by-product trimethylfluorosilane was formed and the weight collected (5.8 g.) represented 90% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 95°C/20 mm. which was subsequently identified, by ^{19}F n.m.r. analysis, as 2,5-dimethylpyrryltetrafluorophosphorane The weight collected (1.4 g.) represents 10% yield of $2,5\text{-}Me_2C_4H_2NPF_4$. The remaining undistillable residue was found to solidify on cooling to room temperature. This residue was recrystallised from acetonitrile affording a white crystalline solid which was subsequently identified as bis(2,5-dimethylpyrryl)difluorophosphonium hexafluorophosphate. The weight collected (13.8 g.) represents 88% yield of $[(2,5\text{-}Me_2\text{-}C_4H_2N)_2PF_2]^+[PF_6]^-$. The reaction was repeated several times but in all cases the main phosphorus-fluorine compound formed was the ionic species in yields of 85-95%. The ionic compound is presumably formed from the rearrangement of the covalent tetrafluorophosphorane.

<u>2,5-Dimethylpyrrylphenyltrifluorophosphorane</u>: Phenyltetrafluorophosphorane (9.2 g., 0.05 mole) was allowed to react with 2,5-dimethylpyrryltrimethylsilane (8.3 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidylphenyltrifluorophosphorane. No exothermic reaction took place, the reaction mixture having to be heated at 80°C for five hours to induce any reaction. The volatile by-product trimethylfluorosilane was formed and the weight collected (4.1 g.) represented 89% reaction having taken place. Distillation of the higher boiling fraction afforded a colourless liquid of b.p. 95°C/0.05 mm. which was subsequently identified as 2,5-dimethylpyrrylphenyltrifluorophosphorane.

The weight collected (8.4 g.)represents 63% yield of $2,5\text{-}Me_2C_4H_2NPF_3Ph$. An undistillable oil remained in the flask which was shown to contain the pentafluorophosphate anion $[PhPF_5]^-$.

Attempted Preparation of 2,5-Dimethylmethyltrifluorophosphorane: Methyltetrafluorophosphorane (8.1 g., 0.06 mole) was allowed to react with 2,5-dimethylpyrryltrimethylsilane (11.1 g., 0.06 mole) in a manner similar to the preparation of 2-methylpiperidylmethyltrifluorophosphorane. However, no reaction took place even when the reaction mixture had been heated at 90°C for 12 h. The starting materials were recovered in 100% yield.

Attempted Preparation of 2,5-Dimethylpyrryldiphenyldifluorophosphorane: Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) was allowed to react with 2,5-dimethylpyrryltrimethylsilane (8.3 g., 0.05 mole) in a manner similar to the preparation of 2-methylpiperidyldiphenyldifluorophosphorane. No exothermic reaction was observed and the reaction mixture was heated at 150°C for 12 h. in order to induce any reaction. The volatile by-product trimethylfluorosilane was formed and the weight collected (4.2 g.) represented 91% reaction having taken place. The ^{19}F n.m.r. spectrum of the reaction mixture showed evidence for the existence of a new phosphorus-fluorine compound and the data indicate that it is probably a difluorophosphorane. However, it was only present in very small concentrations and could not be isolated from the reaction mixture. Attempts at isolating any pure product, either by vacuum distillation or sublimation proved unsuccessful.

CHAPTER III

ALKOXY- AND ARYLOXY- SUBSTITUTED DERIVATIVES OF TRIMERIC PHOSPHONITRILIC FLUORIDE

CHAPTER III

ALKOXY- AND ARYLOXY- SUBSTITUTED DERIVATIVES OF TRIMERIC PHOSPHONITRILIC FLUORIDE

Studies into the replacement of chlorine atoms in trimeric phosphonitrilic chloride, $(PNCl_2)_3$, by hydroxy, alkoxy and aryloxy groups have been well documented. The hydrolysis of $(PNCl_2)_3$ was thought to produce the hydroxyphosphonitrilic compound $[(HO)_2PN]_3$ but the product is probably the cyclophosphazinic acid $[HOP(:O)NH]_3$.[134] The hydroxy compound $(OH)(NH_2)Cl_4P_3N_3$ [135] was obtained from the hydrolysis, under controlled conditions, of the trimeric phosphonitrile $(NH_2)Cl_5P_3N_3$ and retains the structure of the parent ring compound; however, a tautomeric cyclotriphosphazadiene structure cannot be ruled out. Hydrolysis of the pentaphenylchlorophosphonitrile $ClPh_5P_3N_3$ affords the hydroxy phosphonitrile $HOPh_5P_3N_3$, but there is also the possibility of the tautomeric cyclotriphosphazadiene being formed. The ammonolysis of phenyltetrachlorophosphorane, $PhPCl_4$, resulted in the isolation of the partially hydrolysed product $Ph_3Cl(OH)_2P_3N_3$,[137] presumably formed due to the presence of moisture in the reaction mixture.

Attempts to prepare alkoxy or aryloxy cyclo phosphonitriles by the direct reaction of alcohols or phenols with chlorocyclophosphonitriles failed.[138, 139] The hexaethoxy derivative $[(EtO)_2PN]_3$ was reported by this route but was shown later not to be this compound on grounds of its physical properties. It was reported as a water soluble oil but later reported as a stable water-insoluble compound.[140, 141]

Successful replacement of chlorine in chlorocyclophosphonitriles has been achieved by the reaction of alcohols or phenols with chlorocyclophosphonitriles in the presence of a tertiary amine or alkaline base as acid scavenger according to the equation,

$$(Cl_2PN)_n \quad + \quad 2nROH \xrightarrow[\text{or KOH}]{\text{pyridine}} [(RO)_2PN]_n \quad + \quad n\,pyHCl \text{ or } KCl$$

(where R = Me, Et, nPr, nBu, Ph, $(CH_2)_2NH_2$, $(CH_2)_4NH_2$, $4\text{-}NO_2\text{-}C_6H_4$, $CF_3C_6H_4$, $3\text{-}PhO\text{-}C_6H_4$, $PhCH_2$.).[4, 9-12] It was found more convenient to use alkali metal alkoxides in order to obtain alkoxy and aryloxy substituted cyclophosphonitriles reactions taking place according to the equation,

$$(Cl_2PN)_3 \quad + \quad 6NaOR \longrightarrow [(RO)_2PN]_3 \quad + \quad 6NaCl. \qquad ^{4,\ 10}$$

(where R = Me, Et, nPr, iPr, $CH_2CH{=}CH$, nBu, C_6H_{11}, $CH_2{=}CH_2OH$, $(CH_2)_4OH$, $CH_2{=}CH_2OCH_2CH_2OH$, $CH_2CH(OH)CH_2OH$, $CH_2(CF_2)_mCF_2H$; m = 1, 3, 5, 7, 9; $CH_2(CF_2)_mCF_3$; m = 0,2; Ph, $4\text{-}MeO\text{-}C_6H_4$, $4\text{-}F\text{-}C_6H_4$, $4\text{-}Cl\text{-}C_6H_4$, $4\text{-}Br\text{-}C_6H_4$, $4\text{-}NO_2\text{-}C_6H_4$, $4\text{-}HO\text{-}C_6H_4$, $PhCH_2$.).

By using stoichiometric amounts of the reagents partially substituted chloroalkoxy-(aryloxy) derivatives have been obtained, of the trimeric chlorophosphonitrile.

$$(Cl_2PN)_3 \quad + \quad \underset{\text{or NaOR}}{nROH\ (Py)} \longrightarrow (RO)_nCl_{6-n}P_3N_3 \qquad ^{4,\ 10}$$

n = 1 R = Me, nBu, $CH_2CH{=}CH_2$, Ph, $4\text{-}Br\text{-}C_6H_4$, $4\text{-}NO_2\text{-}C_6H_4$;

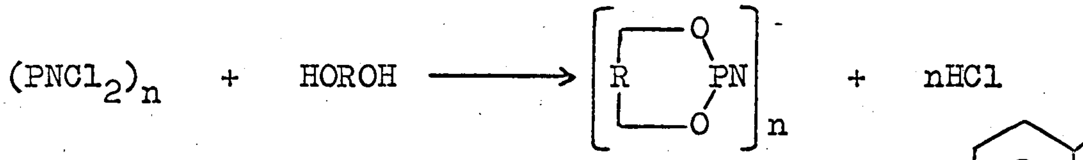
n = 2 R = nBu, Ph, $4\text{-}Br\text{-}C_6H_4$;

n = 3 R = nBu, Ph, $4\text{-}Br\text{-}C_6H_4$, $4\text{-}NO_2\text{-}C_6H_4$, $1\text{-}C_{10}H_7$, $2\text{-}C_{10}H_7$;

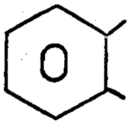
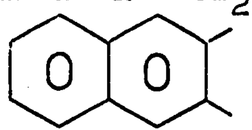
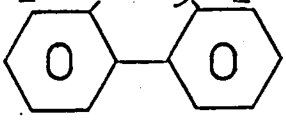
n = 4 R = $CH_2(CF_2)_4F$, Ph, $4\text{-}Br\text{-}C_6H_4$;

n = 5, R = Ph, $4\text{-}Br\text{-}C_6H_4$, $4\text{-}NO_2\text{-}C_6H_4$.

A complete study of the substitution pattern of the reaction of phenol with $(PNCl_2)_3$ has been undertaken.[142-144] The reaction of diols with phosphonitrilic chlorides has been found to produce spiro derivatives according to the equation,



(4, 11)

(where R = CH_2CH_2, $CH\text{-}CH_3CH_2$, $(CH_2)_2C(CH_2ONO_2)_2$,




In partially substituted products the remaining chloro groups have been successfully substituted by amino or other organo-functional groups [4, 9-12] thus affording large synthetic possibilities.

Acetoxime was found to react with trimeric phosphonitrilic chloride to produce the monosubstitited product,[145] $(Me_2C{=}NO)Cl_5P_3N_3$. Attempts to use the same reactions for the synthesis of siloxy derivatives had mixed results. Trimeric phosphonitrilic chloride reacts with $Ph_2Si(OH)_2$ to give a readily hydrolysable polymer,[146] but with Et_3SiOH, Ph_3SiOH and Ph_3SiONa no siloxy derivatives could be obtained.[147] However, the reaction of $Et_3SiOSiEt_3$ with $(PNCl_2)_3$ afforded the siloxy derivative $(Et_3SiO)_2Cl_4P_3N_3$.[147] Recently it has been reported that the reaction of hexabutoxy phosphonitrile $(BuO)_6P_3N_3$ with chlorosilanes affords a siloxy derivative,[148] according to the equation,

$$[(nBuO)_2PN]_3 + 3\,xClSiR_3 \longrightarrow [NP(OSiR_3)_x(OnBu)_y]_3 + 3x\,nBuCl.$$

(where R = Me, Ph; x + y = 2).

Hydrolysis of these products produced the hydroxy compound $P_3N_3(OnBu)_5OH$.[148]

As yet there are no examples of alkoxy and aryloxy substituted trimeric phosphonitrilic fluorides and no examples of Si-O bond cleavage reactions by halophosphonitriles have been reported. The cleavage of the Si-N bond of the silylamine Me_3SiNMe_2 by cyclo-phosphonitrilic fluorides has been reported[57] and it was found that the reactions proceed smoothly to give as the main product the mono-substituted derivative.

Reactions have since been carried out between the trimeric phosphonitrilic fluoride $(PNF_2)_3$ and the Lewis base silyl ethers $ROSiMe_3$ (where R = Me, Et, Ph or C_6F_5), producing a series of compounds of the type $ROP_3N_3F_5$.

Synthesis

The substituted trimeric fluorophosphonitriles were prepared by the cleavage of the Si-O bond of the silyl ethers by trimeric phosphonitrilic fluoride, $(PNF_2)_3$, the reaction proceeding according to the equation,

$$(PNF_2)_3 \quad + \quad ROSiMe_3 \longrightarrow P_3N_3F_5OR \quad + \quad Me_3SiF.$$

(where R = Me, Et, Ph, C_6F_5).

The reaction of methyltrimethyl ether, $MeOSiMe_3$, with the phosphonitrile was found to be exothermic whereas all the other reactions were carried out in sealed glass reaction tubes at high temperatures. All the reactions gave an almost quantitative yield of the volatile by-product trimethylfluorosilane, Me_3SiF, which was identified from its ^1H n.m.r. spectrum. All compounds were purified by vacuum distillation and the yields are in the range 41-61%. The low yields might be explained by the high vapour pressure of the products. Characterisation was carried out by n.m.r., mass spectral, infrared spectroscopy and elemental analysis.

Properties

In contrast to the starting material, $(PNF_2)_3$, which is a colourless crystalline solid of low melting point and boiling point these new alkoxy and aryloxy cyclo fluorophosphonitriles are colourless liquids of relatively high boiling points. The stability to hydrolysis of the new compounds is greater than for other phosphorus-fluorine compounds in which P is present in coordination number four. [1]

Nuclear Magnetic Resonance Data

The ^{19}F and ^{31}P n.m.r. spectra of the substituted trimeric phosphonitrilic fluorides are complicated in nature, the complication arising from the presence of several different magnetic nucleii whose chemical shift differences are small. The fluorine atoms, although chemically equivalent are all magnetically non-equivalent and this is also the case for the phosphorus atoms. The spin system being considered for these compounds can be classified as an $[A(X)_2]_2BY$ spin system, (where A and X are the phosphorus and fluorine atoms, respectively, of the two PF_2 units and B and Y are the single phosphorus and fluorine atom, respectively, of the single PF unit). By simple first order analysis of the ^{19}F n.m.r. spectra one can obtain approximate chemical shifts and coupling constants for the PF_2 and PF units of the cyclic structures. The quoted values of J_{PF} are not simple coupling constants over one P-F bond but the sum of several coupling constants made up from spin-spin coupling over several bonds. From the n.m.r. data one can establish that substitution has taken place as the environment of the PF unit is different from that of the PF_2 unit. Table 3.1 shows the n.m.r. data for the new compounds.

Table 3.1

^{19}F N.m.r. Data for Substituted Trimeric Phosphonitrilic Fluorides

Compound	PF unit		PF_2 unit	
$C_6F_5OP_3N_3F_5$	δF	+ 64.0	δF	+ 68.6
	J_{PF}	956	J_{PF}	789
$PhOP_3N_3F_5$	δF	+ 67.0	δF	+ 69.8
	J_{PF}	904	J_{PF}	872
$EtOP_3N_3F_5$	δF	+ 66.4	δF	+ 71.4
	J_{PF}	932	J_{PF}	910
$MeOP_3N_3F_5$	δF	+ 67.1	δF	+ 69.6
	J_{PF}	912	J_{PF}	868

^{19}F N.m.r. Data for the Aromatic Region of the Pentafluorophenoxy Derivative

Compound	δF ortho	δF meta	δF para
$C_6F_5OP_3N_3F_5$	+ 153.4	+ 161.2	+ 157.2

δF values given in p.p.m.; J values given in Hz.

The ^{19}F n.m.r. spectrum of the aromatic region of the pentafluorophenoxy substituted derivative shows the existence of three distinct fluorine atom environments, although the spin system is not of a first order nature (See Chapter 1).

Spin-spin coupling occurs between all the fluorine atoms of the pentafluorophenyl ring. The highly positive chemical shifts of these fluorine atom resonances are consistent with data reported for other compounds containing the C_6F_5 group.[86, 87] There is no evidence for any spin-spin coupling between the phosphorus atom of the PF unit and the fluorine atoms of the pentafluorophenyl ring.

Mass Spectral Data

Mass spectra have been obtained for all the compounds prepared. Figures 3.1, 3.2, and 3.3 show Relative Abundance Diagrams for the compounds $MeOP_3N_3F_5$, $EtOP_3N_3F_5$, and $PhOP_3N_3F_5$, respectively. Tables 3.2, 3.3 and 3.4 show the main fragments observable from the spectra of the compounds $MeOP_3N_3F_5$, $EtOP_3N_3F_5$ and $PhOP_3N_3F_5$, respectively. Although the mass spectrum of the compound $C_6F_5OP_3N_3F_5$ was obtained the presence of extraneous peaks made complete analysis difficult, however, Table 3.5 shows the main fragments observable from the spectrum.

The molecular ions were observed for all the compounds investigated and in high percentage relative to the basis peak. The basis peak was formed by cleavage of the P-O bond with loss of the alkoxy or aryloxy group and formation of the positive ion $P_3N_3F_5^+$. The fragmentation pattern of each molecule is characterised by P-O bond cleavage and then successive cleavage of P-F bonds of the resulting ion. Cleavage of P-N bonds with loss of P-N units was also observed causing ring contraction. Such fragmentation patterns have been observed for other halocyclophosphonitriles, fluoro,[149] chloro,[150, 151] chloro-bromo,[151] and bromo.[152, 153]

Fig. 3.1 Mass Spectral Relative Abundance Diagram.

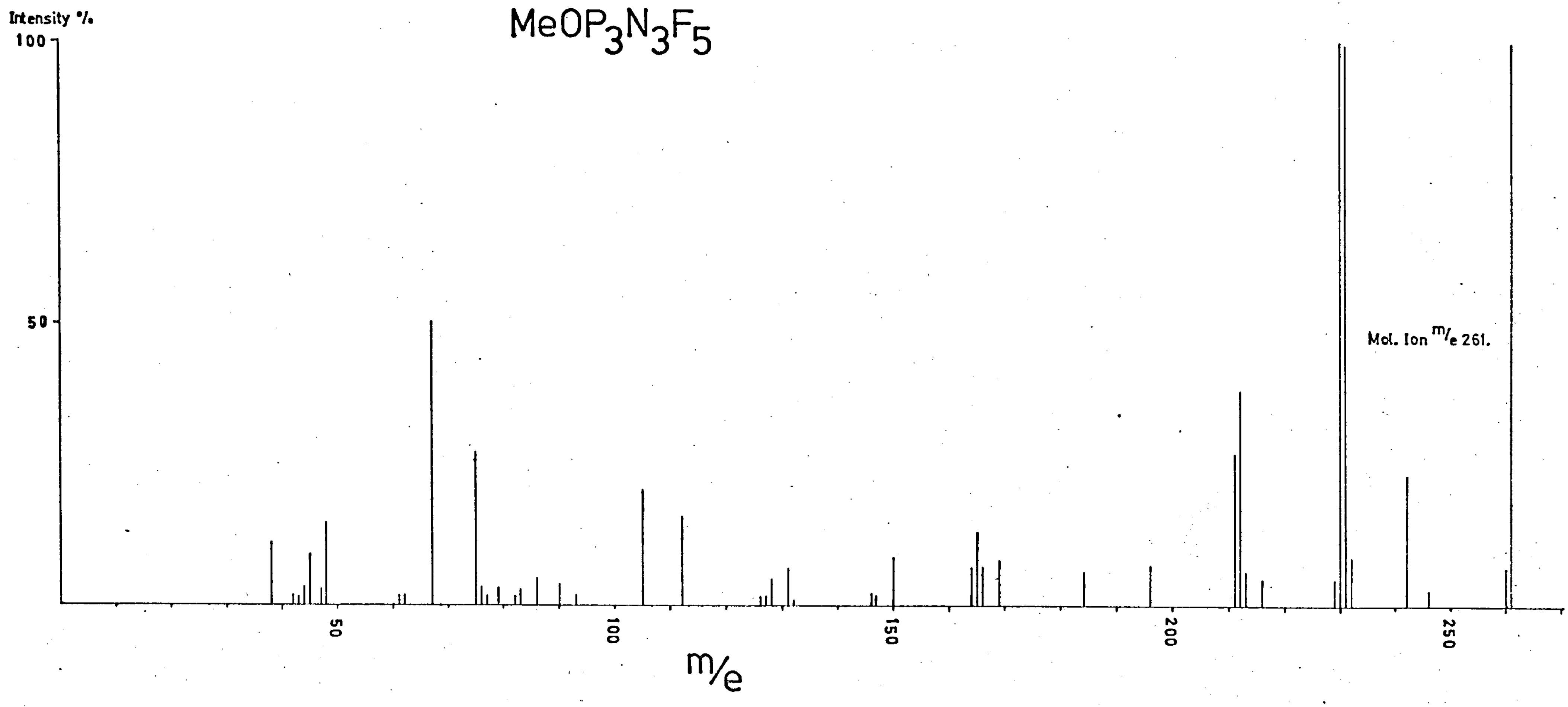


Table 3.2

Mass Spectral Data for $MeOP_3N_3F_5$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
261	100.0	$CH_3OP_3N_3F_5$ (Mol. Ion.)
260	6.4	$CH_2OP_3N_3F_5$
246	2.3	$OP_3N_3F_5$
230	100.0	$P_3N_3F_5$ (Basis Peak.)
211	25.8	$P_3N_3F_4$
192	<1.0	$P_3N_3F_3$
135	<1.0	P_3N_3
216	4.6	$P_3N_2F_5$
197	<1.0	$P_3N_2F_4$
135	<1.0	P_3N_3
121	<1.0	P_3N_2
90	2.3	P_2N_2
76	8.7	P_2N
45	8.7	PN
31	1.5	P
261	100.0	$CH_3OP_3N_3F_5$
242	23.0	$CH_3OP_3N_3F_4$
211	25.8	$P_3N_3F_4$

Fig. 3.2 Mass Spectral Relative Abundance Diagram.

$EtOP_3N_3F_5$

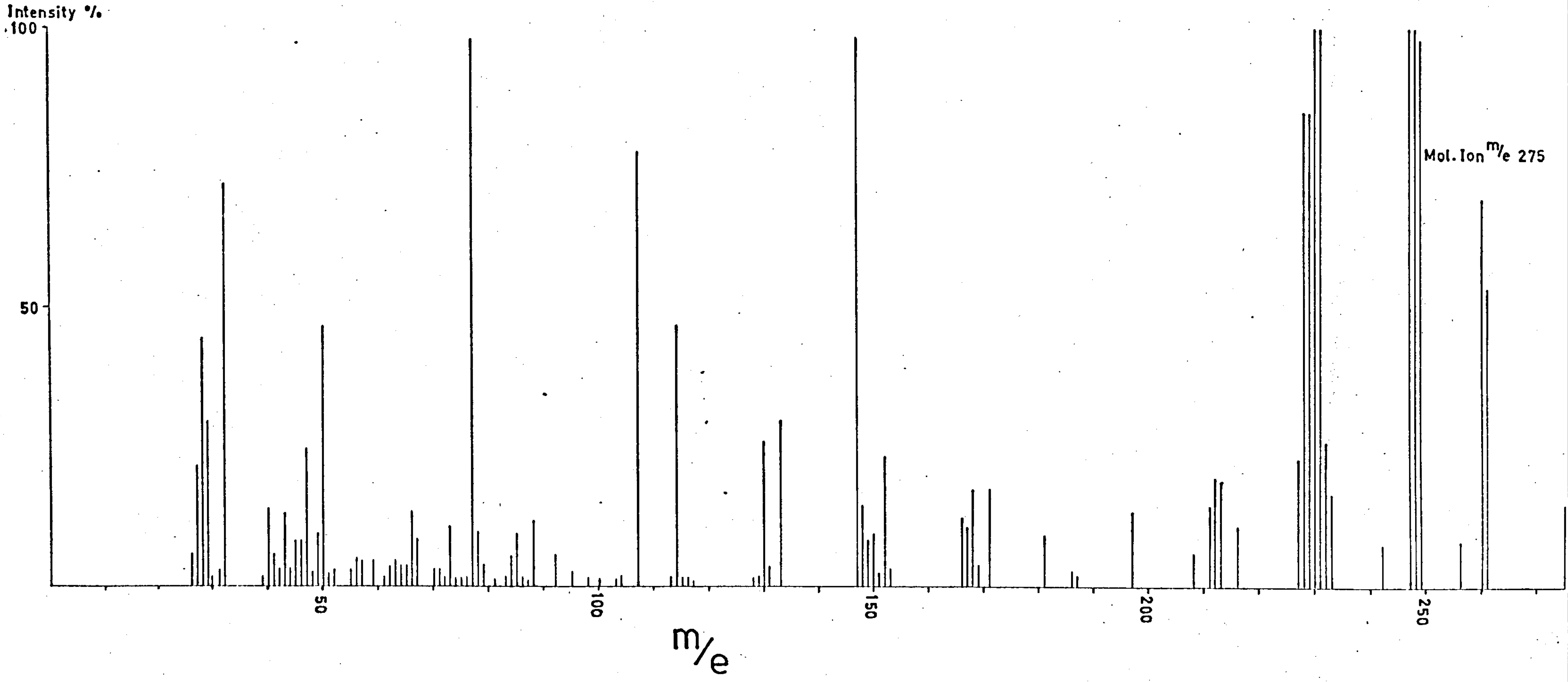


Table 3.3

Mass Spectral Data for $EtOP_3N_3F_5$, Molecular Fragments

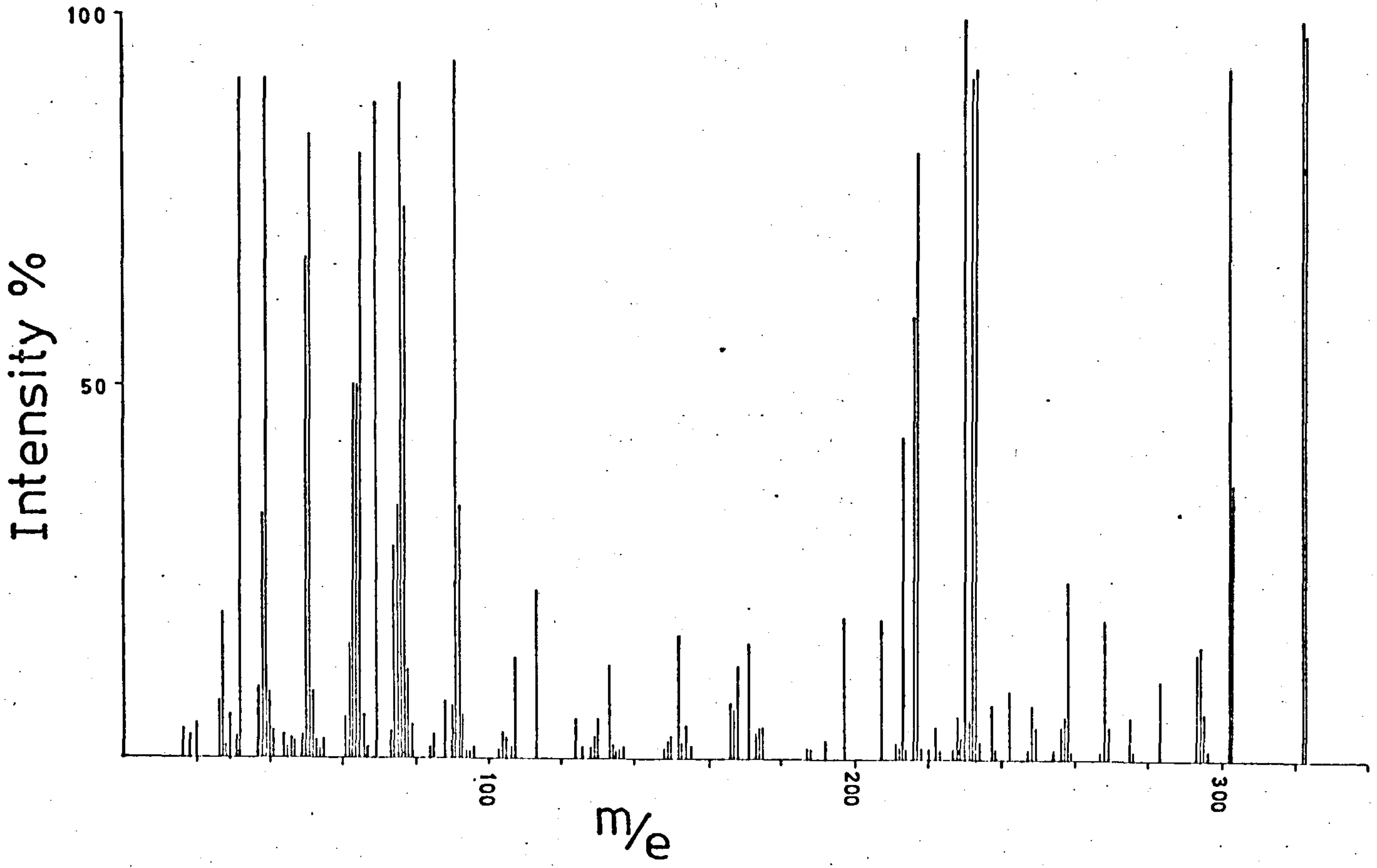
m/e	relative abundance %	possible positive ion fragment
275	14.8	$CH_3CH_2OP_3N_3F_5$ (Mol. ion.)
260	69.9	$CH_2OP_3N_3F_5$
246	1.0	$OP_3N_3F_5$
230	100.0	$P_3N_3F_5$
211	14.4	$P_3N_3F_4$
192	2.0	$P_3N_3F_3$
173	1.2	$P_3N_3F_2$
154	<1.0	P_3N_3F
135	<1.0	P_3N_3
216	10.6	$P_3N_2F_5$
197	13.8	$P_3N_2F_4$
178	1.0	$P_3N_2F_3$
159	1.5	$P_3N_2F_2$
140	<1.0	P_3N_2F
121	<1.0	P_3N_2
135	<1.0	P_3N_3
121	<1.0	P_3N_2
90	<1.0	P_2N_2
76	15.0	P_2N
45	8.0	PN or CH_3CH_2O
31	26.0	P
275	14.8	$CH_3CH_2OP_3N_3F_5$ (Mol. ion.)
256	8.3	$CH_3CH_2OP_3N_3F_4$

Table 3.3 cont.

m/e	relative abundance %	possible positive ion fragment
45	8.0	CH_3CH_2O or PN
44	3.0	CH_2CH_2O
43	12.9	$CHCH_2O$
42	3.0	CHCHO or CCH_2O
29	29.8	CH_3CH_2
28	44.1	CH_2CH_2
27	21.3	$CHCH_2$
26	5.3	CHCH

Fig. 3.3 Mass Spectral Relative Abundance Diagram.

$PhOP_3N_3F_5$



Mol. Ion m/e 323.

Table 3.4

Mass Spectral Data for $C_6H_5OP_3N_3F_5$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment	
323	98.3	$C_6H_5OP_3N_3F_5$	(Mol. ion.)
322	100.0	$C_6H_4OP_3N_3F_5$	
321	36.0	$C_6H_4OP_3N_3F_5$	
246	1.2	$OP_3N_3F_5$	
230	100.0	$P_3N_3F_5$	(Basis Peak.)
211	2.2	$P_3N_3F_4$	
192	2.6	$P_3N_3F_3$	
173	3.7	$P_3N_3F_2$	
154	4.5	P_3N_3F	
135	1.1	P_3N_3	
216	60.0	$P_3N_2F_5$	
197	19.0	$P_3N_2F_4$	
178	1.1	$P_3N_2F_3$	
159	1.1	$P_3N_2F_2$	
140	5.3	P_3N_2F	
121	$<$1.0	P_3N_2	
135	1.1	P_3N_3	
121	$<$1.0	P_3N_2	
90	7.5	P_2N_2	
76	90.8	P_2N	

Table 3.4 cont.

m/e	relative abundance %	possible positive ion fragments
45	1.5	PN
31	3.0	P
323	98.3	$C_6H_5OP_3N_3F_5$ (Mol. ion.)
304	5.0	$C_6H_5OP_3N_3F_4$
303	37.5	$C_6H_4OP_3N_3F_4$
302	93.7	$C_6H_3OP_3N_3F_4$
77	74.3	C_6H_5
76	90.8	C_6H_4
75	34.0	C_6H_3
74	28.5	C_6H_2
93	6.0	C_6H_5O
92	34.0	C_6H_4O
91	93.7	C_6H_3O
90	9.5	C_6H_2O

Table 3.5

Mass Spectral Data for $C_6F_5OP_3N_3F_5$, Molecular Fragments

m/e	relative abundance %	possible positive ion fragment
413	m	$C_6F_5OP_3N_3F_5$ (Mol. ion.)
394	w	$C_6F_5OP_3N_3F_4$
246	w	$OP_3N_3F_5$
230	v.st	$P_3N_3F_5$
211	w	$P_3N_3F_4$
192	w	$P_3N_3F_3$
173	w	$P_3N_3F_2$
154	st	P_3N_3F
135	m	P_3N_3
216	v.st	$P_3N_2F_5$
197	st	$P_3N_2F_4$
178	m	$P_3N_2F_3$
159	w	$P_3N_2F_2$
140	m	P_3N_2F
121	m	P_3N_2
166	v.st	$P_2N_2F_4$
147	w	$P_2N_2F_3$
128	m	$P_2N_2F_2$
109	st	P_2N_2F
90	m	P_2N_2

Table 3.5 cont.

m/e	relative abundance %	possible positive ion fragment
135	m	P_3N_3
121	m	P_3N_2
90	m	P_2N_2
76	m	P_2N
45	m	PN
31	m	P
183	m	C_6F_5O
167	m	C_6F_5
334	m	C_6F_5-C_6F_5

Due to the presence of extraneous peaks the relative intensity of the peaks could not be accurately measured although it can be clearly seen that the strongest peak is formed by the loss of the C_6F_5O- group and formation of the positive ion $P_3N_3F_5$.

w = weak, m = medium, st = strong, v = very.

For all mass spectral measurements the ionising potential was 70 e.v.

The temperature of the samples at the inlet was 100°C for all measurements.

Infra-Red Data

Tables 3.6, 3.7 and 3.8 list the infrared data for the compounds $MeOP_3N_3F_5$, $EtOP_3N_3F_5$ and $PhOP_3N_3F_5$, respectively The spectra are characterised by a P-N stretch at about 1285 cm^{-1} which has been reported by other authors for halophosphonitriles.[9, 154-156] There is, however, very little change in the value of P-N for the compounds reported here contrasting to the values reported for other phosphonitriles, $(PNR_2)_3$ (where R = Me, Ph, Br, NMe_2, Cl, OMe, F).[9] There is possibly very little effect by the alkoxy or aryloxy group on the basic P-N ring vibrations.

The PF_2 symmetric and asymmetric stretching frequencies are to be found in the 870-956 cm^{-1} region.[155] The PF stretching frequency of the PFR group is to be found at about 846 cm^{-1} [155] and the POC stretching frequencies are to be found at ν_sPOC 830-740 cm^{-1} and ν_{as}POC 1050-970 cm^{-1}.[188]

Table 3.6

Infra-Red Data for $MeOP_3N_3F_5$

a. 2% solution in CCl_4; 0.1 mm. path length; KBr cell.

Wave No. cm^{-1}		Assignment	Wave No. cm^{-1}		Assignment
850	s	ν PF	1080	s	
892	s	$\nu_s PF_2$	1192	m	
910	w		1285	s	ν PN
950	s	$\nu_{as} PF_2$	1454	w	
963	s		2850	w	
979	m		2955	w	
1012	m	ν_{as} POC			

Table 3.6 cont.

b. Neat Sample; 0.025 mm. path length; NaCl cell

Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
730 w	ν_sPOC	2180 w br	
1190 s		2856 m	
1455 s		2960 m	ν CH_3
1550 w br		3010 w br	
1890 w br		3580 v w	
1996 m			

Table 3.7

Infra Red Data for $EtOP_3N_3F_5$

a. 2% solution in CCl_4; 0.1 mm. path length; KBr cell

Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
846 s	ν PF	1010 m	ν_{as} POC
870 s	ν_s PF_2	1070 w	
950 s	ν_{as} PF_2	1170 w	
970 w sh		1285 s	ν PN
990 v w		1376 w	

b. Neat Sample; 0.025 mm. path length; NaCl cell

Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
730 m	ν_s POC	1620 w br	
1168 s		1860 w br	
1206 w		2000 m	
1375 m		2180 w br	
1400 m		2910 m	

Table 3.7 cont.

Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
1450 m		2940 m	
1474 m		2990 s	ν CH_3
1545 w br		3580 w	

Table 3.8

Infra Red Data for $PhOP_3N_3F_5$

a. 2% solution in CCl_4; 0.1 mm. path length; KBr cell

Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
684 s		1008 m	
846 s	ν PF	1030 m	
864 s		1068 w	
872 s	ν_s PF_2	1160 m	
905 v w		1190 s	ν CO
956 s	ν_{as} PF_2	1285 s	ν PN
964 s		1492 s	
995 w		1596 w br	

b. Neat Sample; 0.025 mm. path length; NaCl cell

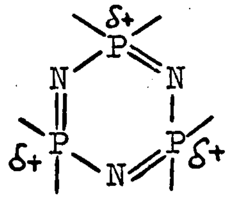
Wave No. cm^{-1}	Assignment	Wave No. cm^{-1}	Assignment
684 s		1070 m	
728 w	ν_s POC	1460 m	
770 m		1492 m	
905 m		1596 s	
1010 s		3030 w br	
1040 s			

For the reported infrared data the symbols used have the following meaning, w = weak, m = medium, s = strong, v = very and sh = shoulder.

Discussion

All the reactions were found to proceed smoothly giving an almost quantitative yield of the volatile by-product trimethylfluorosilane, Me_3SiF, and affording as the main phosphorus-fluorine product the mono-substituted derivative of trimeric phosphonitrilic fluoride. Apart from the pentafluorophenoxy derivative which has only been characterised by mass spectral analysis, due to the presence of other phosphorus-fluorine compounds, the compounds have been fully characterised. It proved difficult to isolate the compound $C_6F_5OP_3N_3F_5$ from its reaction mixture because all the species present had similar boiling points in the range 85-90°C.

The reactions probably proceed via nucleophilic attack of the O atom of the Lewis base silyl ether on the four-coordinate phosphorus atom of the P-N ring with the formation of a loose adduct which subsequently breaks down to give Me_3SiF and the substituted phosphonitrilic fluoride. The driving force of these reactions is believed to be the formation of a strong Si-F bond in the by-product compared to the P-F bond in the starting compound. One might envisage the structure of the phosphonitrilic fluoride as being,



in which there is pπ-dπ bonding between the nitrogen lone pair of electrons and an empty d-orbital of phosphorus. The slightly positive nature of the phosphorus arises from the greater electronegativity of nitrogen compared to phosphorus and the inductively electron withdrawing effect of the fluorine atoms attached to phosphorus. Attempts at preparing the analogous alkylthio and arylthio substituted phosphonitrilic fluorides by the reaction of the corresponding thiosilyl ethers with trimeric phosphonitrilic fluoride have proved unsuccessful and this might be explained either by the decreased nucleophilicity of the silylthio ethers compared to silyl ethers, or the possibility of greater steric hindrance to approach of the sulphur atom to the phosphorus atom. Thio-substituted derivatives of trimeric phosphonitrilic fluoride have, however, been reported [58] from the reaction of the alkali metal mercaptide, NaSEt, with trimeric phosphonitrilic fluoride, the reaction proceeding according to the equation,

$$(PNF_2)_3 \quad + \quad nNaSEt \longrightarrow P_3N_3(SEt)_nF_{6-n} \quad + \quad nNaF.$$

The reaction is exothermic in ether or dioxan at -20°C. In this case the sulphur atom of the mercaptide is more electronegative than the sulphur atom of the corresponding silylthio ethers. Also, there is a decrease in steric hindrance on approach of a mercaptide ion, EtS^-, compared to the approach of a silylthio ether which is a large bulky entity.

The reaction of silyl ethers with trimeric phosphonitrilic fluoride is exothermic for the reaction of $(PNF_2)_3$ with $MeOSiMe_3$ but the other reactions were conducted in sealed tubes at high temperatures. This observation falls in with the expectation of decreased nucleophilicity at the oxygen atom of the silyl ether as the alkyl or aryl groups are changed. The expected decrease in nucleophilicity at oxygen is in the order $C_6F_5 < Ph < Et < Me$. The increase in size of the alkyl or aryl group is also another factor to be considered in which as the size increases then so the possibility of steric hindrance increases.

In proposing the above structure for the phosphonitrilic fluoride trimer one would expect there to be possibility of multisubstitution as the fluorine atoms are all chemically equivalent. This is in fact the case although in every case the main product formed was the mono-substituted one. Multisubstitution was found to take place to a small extent, as indicated by n.m.r. analysis of the product remaining. after isolation of the mono-substituted product, but it proved difficult to isolate any of these multi-substituted products.

In comparison to reactions of silyl ethers with fluorophosphoranes in which alkylsilyl ethers react to give phosphoryl compounds and alkyl fluorides and arylsilyl ethers react to give multi-substituted products, the reaction of silyl ethers with trimeric phosphonitrilic fluoride is found to be a route to the mono-substituted derivative in which a stable P-O-R bond is formed.

Experimental

The silyl ethers were prepared by the reaction of the corresponding alcohols with trimethylchlorosilane in the presence of triethylamine as acid acceptor using sodium dried ether as a solvent.[96] The reaction takes place according to the equation,

$$ROH + Me_3SiCl + Et_3N \longrightarrow ROSiMe_3 + [Et_3NH]^+Cl^-$$

(where R = Me, Et, Ph, C_6F_5).

The experimental procedure is as described in Chapter I for the preparation of pentafluorophenyltrimethylsilyl ether.

Trimeric phosphonitrilic fluoride was prepared [157] by the fluorination of the corresponding chloride using sodium fluoride as fluorinating agent and acetonitrile as solvent. The chloride was obtained as a technical product from B.A.S.F., Ludwigshafen, Germany.

All the necessary precautions were taken to exclude atmospheric moisture from the reactions, as described in the section on General Experimental Technique.

Preparation of Compounds -

Methoxypentafluorocyclotriphosphonitrile: The reaction was carried out in a 25 ml. three necked flask fitted with a reflux condenser, thermometer and dropping funnel. Attached to the condenser, by means of P.V.C. tubing was a weighed trap cooled to -78°C. A drying tube was attached to the open end of the trap to protect the apparatus from atmospheric moisture. Solid trimeric phosphonitrilic fluoride (9.3 g., 0.037 mole) was placed in the flask and methyltrimethylsilyl ether (4.2 g., 0.037 mole) was placed in the dropping funnel. Over a ten minute period the silyl ether was added to the phosphonitrilic fluoride. An exothermic reaction was observed the temperature rising about 10°C and after addition had been completed the reaction mixture was heated at 60°C for a further 0.5 h. A colourless volatile liquid collected in the trap and was subsequently identified, by

^{1}H n.m.r. analysis, as trimethylfluorosilane, Me_3SiF, and the weight collected (3.1 g.) represents 91% reaction having taken place. Distillation of the higher boiling fraction under vacuum through a 10 in. Vigreux column afforded a colourless liquid of b.p. 75°C/185 mm. which was subsequently identified as methoxypentafluorocyclotriphosphonitrile. The weight collected (4.1 g.) represents 43% yield of $MeOP_3N_3F_5$.

Found:	C, 4.8;	H, 1.1;	F, 36.3%
Calc. for $CH_3F_5N_3OP_3$	C, 4.7;	H, 1.2;	F, 36.4%.

<u>Ethoxypentafluorocyclotriphosphonitrile</u>: Ethyltrimethylsilyl ether (4.2 g., 0.035 mole) and **trimeric phosphonitrilic fluoride** (8.9 g., 0.035 mole) were charged into a glass reaction tube which was then sealed under vacuum. The tube was then heated at -100°C for 6 h. The tube was then allowed to cool to room temperature and then opened and connected to a trap cooled to -78°C. A volatile product collected in the trap which was identified as trimethylfluorosilane and the weight collected (4.9 g.) represented 80% reaction having taken place. Distillation of the higher-boiling fraction under vacuum through a 10 in. Vigreux column afforded a colourless liquid of b.p. 72°/100 mm. which was subsequently identified as ethoxypentafluorocyclotriphosphonitrile. The weight collected (5.1 g.) represents 52.5% yield of $EtOP_3N_3F_5$.

Found:	C, 8.8;	H, 1.8;	F, 34.4%
Calc. for $C_2H_5F_5N_3OP_3$	C, 8.7;	H, 1.8;	F, 34.6%.

Phenoxypentafluorocyclotriphosphonitrile: Phenyltrimethylsilyl ether (5.6 g., 0.033 mole) was allowed to react with trimeric phosphonitrilic fluoride (8.3 g., 0.033 mole) in a manner similar to the preparation of ethoxypentafluorocyclotriphosphonitrile. The reaction tube was heated at 100°C for 10 h. The volatile by-product trimethylfluorosilane was found to be formed and the weight collected (1.6 g.) represented 80% reaction having taken place. Distillation of the higher boiling fraction under vacuum through a 10 in. Vigreux column afforded a colourless liquid of b.p. 88°C/27 mm. which was subsequently identified as phenoxypentafluorocyclotriphosphonitrile. The weight collected (6.8 g.) represents 65% yield of $PhOP_3N_3F_5$.

Found:	C, 22.4;	H, 1.5;	F, 29.4%
Calc. for $C_6H_5F_5N_3OP_3$	C, 22.3;	H, 1.5;	F, 29.4%.

Pentafluorophenoxypentafluorocyclotriphosphonitrile: Pentafluorophenyltrimethylsilyl ether (8.1 g., 0.033 mole) was allowed to react with trimeric phosphonitrilic fluoride 8.3 g., 0.033 mole) in a manner similar to the preparation of ethoxypentafluorocyclotriphosphonitrile. The sealed tube was heated at 150°C for 24 h. The volatile by-product trimethylfluorosilane was formed and the weight collected (2.4 g.) represented 83% reaction having taken place. Distillation of the higher boiling fraction under vacuum through a 10 in. Vigreux column afforded a colourless liquid of b.p. 85-90°C/20 mm which was subsequently shown to contain the monosubstituted compound pentafluorophenoxypentafluorocyclotriphosphonitrile. The mass spectrum indicated the presence of the monosubstituted compound and the absence of ions of higher molecular weight.

CHAPTER IV

THE REACTIONS OF TRIFLUOROPHOSPHORANES WITH SECONDARY AMINES AND THE SYNTHESIS OF DIALKYLAMINOALKYL(ARYL)DIFLUOROPHOSPHORANES

CHAPTER IV

THE REACTIONS OF TRIFLUOROPHOSPHORANES WITH SECONDARY AMINES AND THE SYNTHESIS OF DIALKYLAMINOALKYL(ARYL)DIFLUOROPHOSPHORANES

It has been well established that phosphorus pentafluoride is a Lewis acid [158] whose acceptor properties are comparable to that of boron trifluoride. It was thus expected that derivatives of phosphorus pentafluoride, for instance, those containing hydrocarbon substituents, alkyl or aryl, should also possess some Lewis acid character. Lewis acid character of the tetrafluorophosphoranes has since been established [2, 25, 26, 105] from the direct aminolysis of alkyl(aryl)tetrafluorophosphoranes with secondary aliphatic amines resulting in the formation of both alkyl(aryl)pentafluorophosphates , and alkyl(aryl)dialkylaminotrifluorophosphoranes according to the equations,

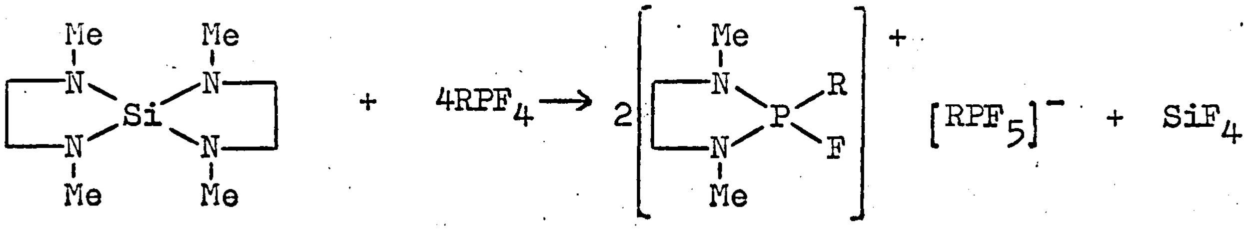
$$RPF_4 + 2R'_2NH \longrightarrow RPF_3NR'_2 + [R'_2NH_2]^+[F]^-$$

$$[R'_2NH_2]^+[F]^- + RPF_4 \longrightarrow [R'_2NH_2]^+[RPF_5]^-$$

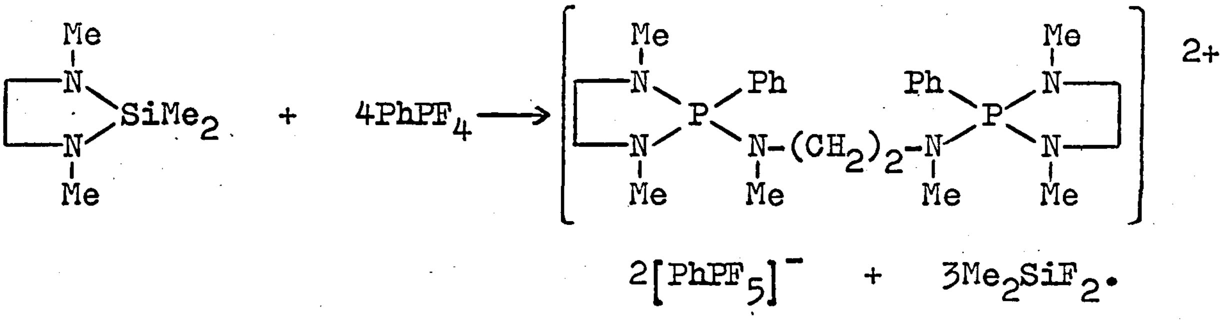
(where R = Me, Et, Ph; R' = Me, Et)

The formation of this ionic phosphorus-fluorine compound thus establishes a Lewis acid character for the tetrafluorophosphoranes. The reaction of phenyltetrafluorophosphorane with pyridine has also been studied [159] and a stable 1:1 adduct was isolated indicating Lewis acid character for phenyltetrafluorophosphorane.

The reactions of tetrafluorophosphoranes with spirosilazanes [160] were expected to give rise to heterocyclic difluorophosphoranes but these difluorophosphoranes have an apparently pronounced donor character and are obtained as their 1:1 adducts with the tetrafluorophosphorane. The reactions proceed according to the equations,



(where R = Et, Ph)



Reactions occur readily between phosphorus pentafluoride or alkyl(aryl)tetrafluorophosphoranes and silicon-nitrogen bonded compounds [2, 5] and this is clearly a function of the Lewis acid (acceptor) strength of the fluorophosphorane. However, a limit is reached with diphenyltrifluorophosphorane, Ph_2PF_3, which reacts readily with Me_2NSiMe_3 [2, 24] whereas other hydrocarbon trifluorophosphoranes are unreactive.

The formation of adducts involving oxygen donors and fluorophosphoranes has also been well established for phosphorus pentafluoride and tetrafluorophosphoranes. [1, 2]

In further investigations into the possibility of hydrocarbon trifluorophosphoranes behaving as Lewis acid acceptors the aminolysis reactions of tetrafluorophosphoranes were extended to trifluorophosphoranes in order to see if this was a useful route to diorganotetrafluorophosphates, $[R_2PF_4]^-$ and dialkylaminodialkyl(aryl)difluorophosphoranes $R_2PF_2NR'_2$. However, the reactions of secondary aliphatic amines with hydrocarbon trifluorophosphoranes [27] proved to be a useful route to dialkylaminodialkyl(aryl)difluorophosphoranes but these were the only phosphorus-fluorine compounds formed. The expected dialkylammonium diorganotetrafluorophosphate was not formed, instead the only ionic compound formed was a dialkylammonium bifluoride $[R'_2NH_2]^+[HF_2]^-$

Synthesis

The preparation of these new difluorophosphoranes is achieved by the aminolysis of alkyl(or aryl)trifluorophosphoranes, $R^1R^2PF_3$, with the secondary amines R^3_2NH using sodium dried ether as a solvent. The reactions take place according to the equation,

$$2R^1R^2PF_3 \quad + \quad 3R^3_2NH \longrightarrow 2R^1R^2PF_2NR^3_2 \quad + \quad [R^3_2NH_2]^+[HF_2]^-$$

(where $R^1 = R^2 =$ Me, Ph; or $R^1 =$ Ph, $R^2 =$ Me; $R^3 =$ Me, Et).

The reactions were found to be mildly exothermic and a white solid seperated out of the reaction mixtures and was subsequently identified, by ^{19}F n.m.r. as a dialkylammonium bifluoride. No evidence was obtained for the formation of any other phosphorus-fluorine compound apart from the new difluorophosphoranes. All the compounds prepared were characterised by ^1H, ^{19}F, ^{31}P n.m.r. and elemental analysis. Yields are in the range 42-58%.

Properties

All of the new dialkylaminodialkyl(aryl)difluorophosphoranes are colourless liquids of high boiling point and all show a stability to hydrolysis comparable to other fluorophosphoranes.[2] There is no tendency for any of these compounds to rearrange to give ionic compounds as has been observed for dialkylaminoalkyl(aryl)trifluorophosphoranes. (Ref. 2, 26, 105, 106) This is also consistent with the behaviour of other amino difluorophosphoranes[2] (Chapter 2).

Nuclear Magnetic Resonance Data

The ^{19}F and ^{31}P n.m.r. data for the dialkylaminodialkyl(aryl)difluorophosphoranes $R^1R^2PF_2NR^3_2$ are listed in Table 4.1 and the ^1H n.m.r. data are listed in Table 4.2. These data suggest that the molecules are of a trigonal bipyramidal structure with the two fluorine atoms occupying the axial positions of the trigonal bipyramid. The low fluorine chemical shifts (in the range 14.4 to 40.1 p.p.m.) and the small PF coupling constants (in the range 654 to 730 Hz.) are characteristic of axial fluorine atoms in difluorophosphoranes.[2] The positive phosphorus chemical shifts (in the range 27.0 to 54.0 p.p.m.) are characteristic of pentacoordinate phosphorus compounds.[72] The variation of δP can be explained by the electronegative effects of the groups attached to phosphorus, i.e. the greater the electronegativity of the groups the higher the chemical shift.

The ^{19}F n.m.r. spectra of the solid products, as solutions in acetonitrile, confirmed the absence of any phosphorus-fluorine species. A single broad resonance at ca + 130 p.p.m. from CCl_3F was observed in each case and is attributed to the fluorine resonances of the dialkylammonium bifluorides.

Table 4.1

^{19}F and ^{31}P N.m.r. Data for Dialkylaminodialkyl(aryl)difluorophosphoranes

Compound	δF p.p.m.	δP p.p.m.	J_{PF} (Hz)
$Me_2PF_2NMe_2$ [a]	+ 14.4	+ 27.0	654
$Me_2PF_2NEt_2$	+ 18.0	+ 27.1	663
$MePhPF_2NEt_2$	+ 28.2	+ 39.7	693
$Ph_2PF_2NMe_2$ [a]	+ 35.8	+ 54.0	709
$Ph_2PF_2NEt_2$	+ 40.1	+ 50.1	730

a. Preparation carried out by R.Schmutzler.

Table 4.2

^{1}H n.m.r. Data for Dialkylaminodialkyl(aryl)difluorophosphoranes

Compound	δH(NMe)	δH(PMe)	δH(N.CH$_2$C)	δH(N.C.CH$_3$)
$Me_2PF_2NMe_2$ [a]	- 2.69	- 1.45		
$Me_2PF_2NEt_2$		- 1.45	- 3.02	- 1.06
$MePhPF_2NEt_2$		- 1.69	- 3.10	- 1.09
$Ph_2PF_2NMe_2$ [a]	- 2.80			
$Ph_2PF_2NEt_2$			- 3.10	- 1.10

a. Preparation carried out by R.Schmutzler.

All chemical shifts in p.p.m.

All measurements made on neat liquids.

Table 4.2 cont.

Compound	J_{HP}	J_{HF}	J_{HH}
$Me_2PF_2NMe_2$ [a]	10.0 (MeNP) 17.5 (MeP)	2.6 (MeN.F) 13.1 (Me.F)	
$Me_2PF_2NEt_2$	19.0 (MeP)	12.7 (Me.F)	7.5 (NCH_2CH_3)
$MePhPF_2NEt_2$	17.0 (MeP)	13.0 (Me.F)	
$Ph_2PF_2NMe_2$ [a]	10.0 (MeNP)	2.5 (MeN.F)	
$Ph_2PF_2NEt_2$	b	b	7.0 (NCH_2CH_3)

a. Preparation carried out by R.Schmutzler.

b. Not measured.

All coupling constants in Hz.

Discussion

The preparation of these new dialkylaminodialkyl(aryl)-difluorophosphoranes is analogous to the preparation of dialkylaminoalkyl(aryl)trifluorophosphoranes from the reaction of tetrafluorophosphoranes with secondary amines. However there is no formation of any phosphorus-fluorine ionic compounds which thus indicates that in this series of reactions the Lewis acid character of the trifluorophosphoranes is less than that of the corresponding tetrafluorophosphoranes. This might be expected in view of the decrease in the number of electronegative ligands attached to phosphorus.

The reactions presumably take place via the formation of 1:1 adducts which break down under the reaction conditions to give the difluorophosphorane and hydrogen fluoride which then forms the bifluoride salt with the secondary amine. The reactions proceed, presumably, according to the equations,

$$R_2PF_3 + R'_2NH \longrightarrow R_2PF_3.R'_2NH$$

$$R_2PF_3.R'_2NH \longrightarrow R_2PF_2NR'_2 + HF$$

$$R'_2NH + 2HF \longrightarrow [R'_2NH_2]^+[HF_2]^-.$$

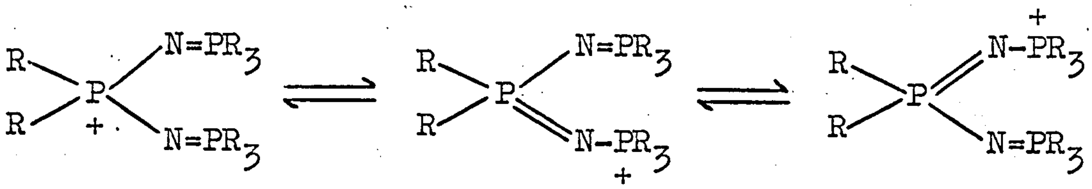
This is probably the same reaction route for the reactions of tetrafluorophosphoranes with secondary amines; however, the tetrafluorophosphorane, having a stronger Lewis acid acceptor strength, is able to abstract a fluoride ion from the hydrogen fluoride before the hydrogen fluoride is able to react with the secondary amine.

Although the reactions discussed here do not lead to the formation of any diorganotetrafluorophosphates it has since been established that the reaction of caesium fluoride with dialkyl(aryl)trifluorophosphoranes in acetonitrile produces stable tetrafluorophosphates.[27] The reactions are all exothermic and proceed according to the equation,

$$R^1R^2PF_3 + CsF \longrightarrow Cs^+[R^1R^2PF_4]^-$$

(where $R^1 = R^2 = Ph$; or $R^1 = Me$, $R^2 = Ph$).

It was noted that no reaction took place between caesium fluoride and dimethyltrifluorophosphorane. The tetrafluorophosphate anion $[Me_2PF_4]^-$ has, however, been prepared from the reaction of dimethyltrifluorophosphorane with N-trimethylsilylphosphinimines $Me_3SiN{=}PR_3$ (where R = Me, Ph, iPr).[161] The cation is thought to be of the type $[Me_2P(N{=}PR_3)_2]^+$. The same reaction was found to take place for other trifluorophosphoranes, Ph_2PF_3, and $PhMePF_3$. It is believed that these ionic compounds are stabilised by resonance forms of the cation, of the type,



Chan and Willis[162] have prepared a series of caesium fluorophosphates with the general formula $Cs^+[(CF_3)_nPF_{6-n}]^-$ (where n = 1, 2, 3) from the reaction of the appropiate fluorophosphorane with caesium fluoride. Compounds of the type $[Me_3Sn]^+[(CF_3)_nPF_{6-n}]^-$ have also been prepared[162, 163] from the reaction of Me_3SnCF_3 with $(CF_3)_nPF_{5-n}$. The formation of these ionic compounds might be expected in view of the greater Lewis acid acceptor properties of perfluoromethyl fluorophosphoranes, compared to the analogous hydrocarbon fluorophosphoranes. The perfluoromethyl group is more electronegative than the methyl group and has an electronegativity close to that of fluorine. The results of the work reported here are in agreement with the following order of decreasing acceptor strength of the fluorophosphoranes; $PF_5 > ArPF_4 > RPF_4 > Ar_2PF_3 > ArRPF_3 > R_2PF_3$ this evidence being borne out by evidence obtained from various reactions of fluorophosphoranes with nucleophiles.[2] It must, however, be remembered that several factors play a part in determining whether or not ionic phosphorus-fluorine compounds can be formed.

As has been indicated the acceptor strength of the fluorophosphoranes employed plays an important part in determining the formation of an ionic compound. It has also been seen that the choice of cation is important and determines whether certain ionic fluorophosphates can be produced. The stability of the cation must also be considered and its existence in resonance forms adds to its stability. Other factors which might be considered are size of cation, solubility, crystal lattice energy and ion sizes. All these factors must be considered when the possibility arises for the formation of an ionic phosphorus-fluorine compound.

Experimental

As all starting materials and products containing P-F bonds are sensitive to moisture it was necessary to take all the precautions described in the section on General Experimental Technique. All the trifluorophosphoranes were prepared by known literature methods. (General Experimental Technique).

Preparation of Compounds -

Diethylaminodiphenyldifluorophosphorane: The reaction was carried out in a 25 ml. three necked flask fitted with a reflux condenser, thermometer and dropping funnel. To the open end of the condenser was attached a drying tube to protect the apparatus from atmospheric moisture. Diethylamine (4.4 g., 0.06 mole) was added dropwise over a 0.5 h. period to a stirred solution of diphenyltrifluorophosphorane (12.1 g., 0.05 mole) and ether (40 ml.). A mildly exothermic reaction was observed and precipitation of a white solid commenced as soon as addition had started. The reaction mixture was refluxed for a further 1 h. after which it was allowed to cool down to room temperature and filtered in a dry-box. The precipitate was identified as diethylammonium bifluoride, $[Et_2NH_2]^+[HF_2]^-$. The filtrate was distilled at atmospheric pressure to remove the ether and the higher boiling fraction was distilled under high vacuum through a short Vigreux column affording a colourless liquid of b.p. 115°C/0.1 mm. which was subsequently identified as diethylaminodiphenyldifluorophosphorane. The weight collected (5.7 g.)represents 58% yield of $Et_2NPF_2Ph_2$.

Found:	C, 65.0;	H, 6.8;	N, 4.7%
Calc. for $C_{16}H_{20}F_2NP$	C, 65.2;	H, 6.9;	N, 4.6%.

Methylphenyldiethylaminodifluorophosphorane: Methylphenyltrifluorophosphorane (6.0 g., 0.03 mole) in 20ml. of sodium dried ether was allowed to react with diethylamine (3.2 g., 0.045 mole) in a manner similar to the preparation described in the previous experiment. The reaction was found to be exothermic and a white solid was precipitated. The reaction mixture was refluxed for 1 h. and on cooling down to room temperature the reaction mixture was filtered to remove the solid product. The white solid was identified as diethylammonium bifluoride. The filtrate was distilled at atmospheric pressure to remove the ether and the higher boiling fraction was distilled under vacuum through a short Vigreux column affording a colourless liquid of b.p. 60°C/1 mm. which was subsequently identified as diethylaminomethylphenyldifluorophosphorane. The weight collected (4.0 g.) represents 53% yield of Et_2NPF_2MePh.

Found:	C, 57.4;	H, 7.7;	N, 6.0%
Calc. for $C_{11}H_{18}F_2NP$	C, 58.2;	H, 7.4;	N, 5.8%.

Diethylaminodimethyldifluorophosphorane: Dimethyltrifluorophosphorane (11.8 g., 0.1 mole) in 20 ml. of sodium dried ether was allowed to react with diethylamine

(10.8 g., 0.15 mole) in 20 ml. of sodium dried ether in a manner similar to the preparation of diethylaminodiphenyldifluorophosphorane. The reaction was found not to be exothermic but on refluxing for 1 h. a white solid was seen to separate out of the solution. On cooling the reaction mixture to room temperature it was filtered and the filtrate distilled at atmospheric pressure to remove the ether. Distillation of the higher boiling fraction under vacuum through a short Vigreux column afforded a colourless liquid of b.p. 68°C/70 mm. which was subsequently identified as diethylaminodimethyldifluorophosphorane. The weight collected (7.1 g.) represents 42% yield of $Et_2NPF_2Me_2$.

Found:	C,	42.1;	H,	9.3;	N,	8.2%
Calc. for $C_6H_{16}F_2NP$	C,	41.9;	H,	9.4;	N,	8.1%.

The preparation of $Me_2NPF_2Me_2$ and $Me_2NPF_2Ph_2$ were first carried out by Schmutzler [24] in which an excess of Me_2NH was passed through an ethereal solution of the corresponding trifluorophosphoranes. Purification was carried out by filtration followed by distillation of the filtrate affording the two difluorophosphoranes as colourless liquids of high boiling point.

CHAPTER V

ATTEMPTED PREPARATION OF BIS(DIALKYLAMINO)ARYL(OR ALKYL) DIFLUOROPHOSPHORANES

CHAPTER V

ATTEMPTED PREPARATION OF BIS(DIALKYLAMINO)ARYL(OR ALKYL) FLUOROPHOSPHORANES

The preparation of diaminotrifluorophosphoranes has been reported in the reaction of phosphorus pentafluoride with silicon-nitrogen compounds,[2, 18] primary amines,[16] and secondary amines.[13, 14] The reaction of phosphorus trifluoride with primary amines affords diaminofluorophosphoranes of the type $(RNH)_2PF_2H$[17] (where R = Me, Et, nBu). A mixed diaminotrifluorophosphorane of the type $(Et_2N)(Me_2N)PF_3$ has been reported[2] in the reaction of Et_2NPF_4 with Me_2NSiMe_3. The diaminotrifluorophosphoranes $(R_2N)(R'NH)PF_3$ (where R = Me Et; R' = nBu, Me) have been prepared from the reaction of dialkylaminotetrafluorophosphoranes with the corresponding primary amine.[101] All the reactions take place smoothly between 25 and 40°C giving yields in the range 40-60% The compounds were characterised by ^{19}F n.m.r. spectroscopy.

It has been reported in the literature[25, 28, 164] that only one fluorine atom can be replaced by an amino group if a primary or secondary amine is allowed to react with an alkyl (or aryl) tetrafluorophosphorane, however, it has been recently reported[102] that the reactions of methyltetrafluorophosphorane with primary amines afford methyldiaminodifluorophosphoranes of the type $(RNH)_2PF_2Me$.

In view of these reports the reactions of aryl(alkyl) tetrafluorophosphoranes with secondary amines have been studied in the hope of being able to prepare bis(dialkylamino)-

aryl(alkyl)difluorophosphoranes containing two secondary amino groups. This was tried out by two different methods, neither of which produced the expected diamino-fluorophosphoranes.

A. The Reaction of Phenyltetrafluorophosphorane with Dimethylamine

Phenyltetrafluorophosphorane and dimethylamine in a 1:2 molar ratio were allowed to react together in a sealed tube at 60°C for 12 h. The tube was then opened and the reaction mixture was distilled affording four products:

(i). $PhPF_3NMe_2$ which was identified from its ^{19}F n.m.r. spectrum by comparison to the spectrum of an authentic sample,

(ii). $[Me_2NH_2]^+ [PhPF_5]^-$ which was identified from its ^{19}F n.m.r. spectrum by comparison to the spectrum of an authentic sample,

(iii). $[PhPF(NMe_2)_2]^+[PhPF_5]^-$ which was identified from its ^{19}F n.m.r. spectrum by comparison to the spectrum of an authentic sample.

(iv). Excess dimethylamine was also found to be present.

The reaction of phenyltetrafluorophosphorane with dimethylamine in the ratio 1:1 produces the trifluorophosphorane $PhPF_3NMe_2$ and dimethylammonium phenylpentafluorophosphate, $[Me_2NH_2]^+[PhPF_5]^-$, the reaction proceeding according to the equation,

$$2PhPF_4 + 2Me_2NH \longrightarrow [Me_2NH_2]^+[PhPF_5]^- + PhPF_3NMe_2.$$

This is a reported method of preparation of dialkylamino-alkyl(or aryl)trifluorophosphoranes. 25, 26, 165 Under the reaction conditions the trifluorophosphorane is able to rearrange to its ionic isomer according to the equation,

$$2PhPF_3NMe_2 \longrightarrow [PhPF(NMe_2)_2]^+[PhPF_5]^- .$$

This is the known general behaviour of several aminoalkyl(aryl)trifluorophosphoranes of the type R_2NPF_3R', (where R = Me, Et; R' = Me, Et, Ph). 2, 18, 25, 105

The corresponding reaction of methyltetrafluorophosphorane with dimethylamine, in which a 1:2 molar ratio was allowed to react together in a glass reaction tube at 100°C for 12 h. also failed to produce any disubstituted amino compound. In this case a solid residue was seen to form in the tube which was subsequently shown to contain the two ionic compounds $[Me_2NH_2]^+[MePF_5]^-$ and $[MePF(NMe_2)_2]^+[MePF_5]^-$ with evidence for trace amounts of $MePF_3NMe_2$. There was no evidence for the formation of any disubstituted amino compound. This reaction presumably proceeds by the same route as indicated for the reaction of phenyltetrafluorophosphorane with dimethylamine. The compounds were identified by n.m.r. analysis.

Nuclear Magnetic Resonance Data

Table 5.1 lists the ^{19}F and ^{31}P n.m.r. data for the products obtained from the reaction of phenyltetrafluorophosphorane with dimethylamine. Table 5.2 lists the ^{19}F and ^{31}P n.m.r. data for the products obtained from the reaction of methyltetrafluorophosphorane with dimethylamine.

The n.m.r. data for the two trifluorophosphoranes are consistent with data already obtained and reported for these compounds [2] and are indicative of a trigonal bipyramidal structure about phosphorus with the axial positions occupied by fluorine atoms. The positive phosphorus chemical shift for $PhPF_3NMe_2$ is consistent with a five-coordinate phosphorus atom. [72]

The n.m.r. data obtained for the ionic phosphorus-fluorine compounds are consistent with data already reported for these compounds. [1] The negative phosphorus chemical shifts for the cationic species are consistent with a four-coordinate phosphorus atom [72] and the highly positive phosphorus chemical shifts for the anionic species are consistent with a six-coordinate phosphorus atom. [72]

Table 5.1

^{19}F N.m.r. Data for the Products from the Reaction of Phenyltetrafluorophosphorane with Dimethylamine

Compound		δF p.p.m.	J_{PF} (Hz)
$PhPF_3NMe_2$ [a]		δF_a + 40.8	J_{PFa} 820
		δF_e + 68.2	J_{PFe} 956
$[Me_2NH_2]^+[PhPF_5]^-$		see data below	
$[(Me_2N)_2PFPh]^+$	Cation	δF + 87.5	J_{PF} 1048
$[PhPF_5]^-$ [b]	Anion	δF_a + 59.8	J_{PFa} 698
		δF_e + 58.0	J_{PFe} 814
			J_{FaFe} 33

Fa and Fe refer to axial and equatorial fluorine atoms, respectively.

a. cf. Ref. 2 b. cf. Ref. 1

Table 5.1 cont.

^{31}P N.m.r. Data for the Products from the Reaction of Phenyltetrafluorophosphorane with Dimethylamine

Compound	δP p.p.m.	J_{PF} (Hz)
$PhPF_3NMe_2$ [a]	δP + 54.1	J_{PFa} 820
		J_{PFe} 956
$[Me_2NH_2]^+[PhPF_5]^-$	see data below	
$[(Me_2N)_2PFPh]^+$	Cation δP − 56.0	J_{PF} 1048
$[PhPF_5]^-$ [b]	Anion δP + 136.5	J_{PFa} 698
		J_{PFe} 814

Fa and Fe refer to the axial and equatorial fluorine, atoms respectively.

a. cf. Ref. 2; b. cf. Ref. 1

Table 5.2

N.m.r. Data for the Products from the Reaction of Methyl tetrafluorophosphorane with Dimethylamine

Compound	δF p.p.m.	δP p.p.m.	J_{PF} (Hz)
$MePF_3NMe_2$ [a]	δFa + 28.0	c	J_{PFa} 810
	δFe + 68.8		J_{PFe} 960
			J_{FaFe} 55
$[Me_2NH_2]^+[MePF_5]^-$	see data below		
$[MePF(NMe_2)_2]^+$	δF + 82.2	δP − 70.0	J_{PF} 1030
$[MePF_5]^-$ [b]	δFa + 57.8	δP + 126	J_{PFa} 670
	δFe + 45.9		J_{PFe} 835

a. cf. Ref. 2; b. cf. Ref. 26 and 106; c. not measured

B. The Reaction of Diethylaminophenyltrifluorophosphorane with Dimethylamine and Diethylamine

Diethylaminophenyltrifluorophosphorane was allowed to react with dimethylamine, Me_2NH, and diethylamine, Et_2NH, in sealed tubes at 100°C for 12 h. In both cases starting materials were recovered in 100% yield, no reaction having taken place. ^{19}F n.m.r. analysis of the reaction mixtures showed the presence of $PhPF_3NEt_2$, no other P-F species being present. Table 5.3 shows the n.m.r. data obtained from the reaction mixtures. The choice of $PhPF_3NEt_2$ was made on the grounds that of the known dialkylaminoalkyl(aryl)trifluorophosphoranes it is the only one which does not, under the influence of heat, rearrange to its ionic isomer.[2]

Table 5.3

^{19}F N.m.r. Data form Reaction Mixtures of $PhPF_3NEt_2$ with Dimethylamine and Diethylamine

Compound	δF p.p.m.	P p.p.m.	J (Hz)
$PhPF_3NEt_2$ [a]	δFa + 43.0	δP + 52.1	J_{PFa} 816
	δFe + 66.0		J_{PFe} 966
			J_{FaFe} 55

a. cf. Ref. 2

Fa and Fe refer to axial and equatorial F atoms resp.

The n.m.r data are consistent with a phosphorus-fluorine compound in which phosphorus has a coordination number of five and the structure is of a trigonal bipyramidal type in which the axial positions are occupied by fluorine atoms.

Discussion

It would seem from the observations made that a bis(dialkylamino)alkyl(aryl)difluorophosphorane with two secondary amino groups, $(R_2N)_2PF_2R'$, cannot be made under the conditions described in this report. The already reported diaminoalkylfluorophosphoranes[102] contain at least one primary amino group. In the reactions described in this chapter there is the possibility of several competing reactions taking place:

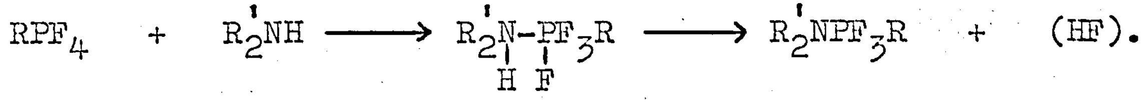
a. The formation of an ionic compound at the expense of the mono-substituted aminofluorophosphorane.

b. Further reaction of the mono-substituted compound with more amine to give the di-substituted compound.

c. No reaction taking place and recovery of starting materials.

For the reaction of phenyltetrafluorophosphorane with dimethylamine and methyltetrafluorophosphorane with dimethylamine the prefered reaction route is a. On the other hand no reaction takes place between diethylaminophenyltrifluorophosphorane and secondary amines

The formation of the mono-substituted aminofluorophosphorane takes place via the formation of a Lewis acid-Lewis base adduct which, under the reaction conditions, breaks down to give the mono-substituted product according to the equation,



$$RPF_4 + R'_2NH \longrightarrow R'_2\underset{H}{\underset{|}{N}}-\underset{F}{\underset{|}{P}}F_3R \longrightarrow R'_2NPF_3R + (HF).$$

This sort of mechanism would also be necessary for further reaction of the amine to produce a disubstituted amino product and is the proposed mechanism for the formation of bis(dialkylamino)trifluorophosphoranes $(R_2N)_2PF_3$[13]

and $(RNH)_2PF_3$.[16] However, there is an obvious decrease in Lewis acid (acceptor) character of the fluorophosphorane on further substitution and for the case of compounds of the type R_2NPF_3R' there may be a sufficient decrease in the Lewis acid character so as to prevent formation of an adduct with a Lewis base. This contrasts to the results obtained for the aminolysis of hydrocarbon trifluorophosphoranes. (Chapter 4) The introduction of an amino group might be expected to have a greater effect in decreasing the Lewis acid character of a fluorophosphorane than a hydrocarbon group in view of the formation of a possible $p\pi-d\pi$ bond between the phosphorus and the nitrogen.

Another point to be considered is the expectation that secondary amines have a greater Lewis base character than primary amines and thus a greater ability to form adducts with Lewis acids; however, this appears not to be so. Therefore one might explain the results on grounds of the stereochemistry of the molecules concerned. Monosubstitution takes place easily but the approach of a second amine molecule might be sterically hindered by the groups already attached to the phosphorus atom of the fluorophosphorane. Obviously a smaller primary amine molecule has a better chance of approach than a larger secondary amine molecule.

Thus formation of dialkylaminoalkyl(aryl)trifluorophosphoranes might well be dependent on the Lewis acid (acceptor) strength of the fluorophosphorane employed and the stereochemical nature of the reactants used.

CHAPTER VI

THE CHEMICAL REACTIVITY OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE AND DIETHYLAMINOTETRAFLUOROPHOSPHORANE

CHAPTER VI

THE CHEMICAL REACTIVITY OF DIMETHYLAMINOTETRAFLUOROPHOSPHORANE AND DIETHYLAMINOTETRAFLUOROPHOSPHORANE

Preparation

Both of these tetrafluorophosphoranes can be conveniently prepared from the reaction of phosphorus pentafluoride with the corresponding dialkylaminotrimethylsilane according to the equation,

$$R_2NSiMe_3 \quad + \quad PF_5 \longrightarrow R_2NPF_4 \quad + \quad Me_3SiF.$$

(where R = Me, Et).[18, 21]

They may also be prepared from the reaction of phosphorus pentafluoride with the corresponding secondary amines according to the equation,

$$2R_2NH \quad + \quad PF_5 \longrightarrow R_2NPF_4 \quad + \quad [R_2NH_2]^+[PF_6]^-.$$

(where R = Me, Et).[13, 14]

It was, however, thought that these two aminofluorophosphoranes might also be obtained from the reaction of phosphorus pentafluoride with the corresponding dialkyamino-dimethylsilanes $(R_2N)_2SiMe_2$. This was found to be a feasible route to diethylaminotetrafluorophosphorane but not for the preparation of dimethylaminotetrafluorophosphorane. The reaction of PF_5 with $(Et_2N)_2SiMe_2$ produced an almost quantitative yield of the volatile by-product dimethyldifluorosilane which was identified from its ^1H n.m.r. and the expected diethylaminotetrafluorophosphorane in high yield. This fluorophosphorane was identified from its ^{19}F and ^{31}P n.m.r. spectra and the data compared with that obtained from a sample prepared from an independent method.[18, 21] The corresponding reaction of PF_5 with $(Me_2N)_2SiMe_2$ produced an almost quantitative yield of the volatile by-product dimethyldifluorosilane, but instead of producing the expected dimethylaminotetrafluorophosphorane an ionic compound was formed which was subsequently identified, by ^1H, ^{19}F, ^{31}P n.m.r. and elemental analysis, as $[(Me_2N)_3PF]^+[PF_6]^-$.

The reactions are postulated as proceeding according to the following equations,

$$(Et_2N)_2SiMe_2 \quad + \quad 2PF_5 \longrightarrow 2Et_2NPF_4 \quad + \quad Me_2SiF_2,$$

and,

$$(Me_2N)_2SiMe_2 \quad + \quad 2PF_5 \longrightarrow 2Me_2NPF_4 \quad + \quad Me_2SiF_2$$

$$(Me_2N)_2SiMe_2 \quad + \quad PF_5 \longrightarrow (Me_2N)_2PF_3 \quad + \quad Me_2SiF_2$$

$$\begin{tikzcd}
Me_2NPF_4 + (Me_2N)_2PF_3 \arrow[r] & {[(Me_2N)_2PF_2]^+[Me_2NPF_5]^-} \arrow[d] \\
 & {[(Me_2N)_3PF]^+[PF_6]^-}
\end{tikzcd}$$

Nuclear Magnetic Resonance Data

Table 6.1 shows the n.m.r. data obtained for the products from the reaction of PF_5 with the silanes $(R_2N)_2SiMe_2$ (where R = Me, Et). ^{19}F and ^{31}P n.m.r. data for the covalent diethylaminotetrafluorophosphorane, Et_2NPF_4, are consistent with data obtained for other tetrafluorophosphoranes.[2]

The ^{19}F n.m.r. data for tris(dimethylamino)fluorophosphonium hexafluorophosphate $[(Me_2N)_3PF]^+[PF_6]^-$ are consistent with four and six-coordinate phosphorus-fluorine compounds.[1] The fluorine atom of the cation has a large chemical shift and a large coupling constant to phosphorus.

The hexafluorophosphate ion has a characteristic chemical shift of + 71.0 p.p.m and characteristic coupling constant to phosphorus of ca 710 Hz. The negative phosphorus chemical shift for the cation is consistent with a four-coordinate phosphorus atom,[72] and the highly positive ^{31}P chemical shift for the anion is consistent with a six-coordinate phosphorus atom.[72]

Table 6.1

^{19}F and ^{31}P N.m.r. Data for Diethylaminotetrafluorophosphorane and Tris(dimethylamino)fluorophosphonium hexafluorophosphate

Compound	δF p.p.m	δP p.p.m	J (Hz)
Et_2NPF_4 [a]	δF + 66.5	δP + 70.9	J_{PF} 860
$[(Me_2N)_3PF]^+$ [b]	δF + 75.0	δP - 39.8	J_{PF} 952
$[PF_6]^-$	δF + 71.5	δP + 144.0	J_{PF} 708
^1H n.m.r. Anion	δH - 3.2	J_{HP} 12.2	J_{HF} 2.8

a. cf. Ref. 2.

b. N.m.r. measurements made on solutions in acetonitrile.

Experimental

Bis(dimethylamino)dimethylsilane and bis(diethylamino)-dimethylsilane were prepared from the reaction of dimethyldichlorosilane with the corresponding secondary amine in the presence of a tertiary amine as acid acceptor, according to the equation,

$$2R_2NH + Me_2SiCl_2 + 2R'_3N \longrightarrow (R_2N)_2SiMe_2 + 2R'_3NH^+Cl^-$$

(where R = Me, Et; R' = pyridine, Et).

Preparation of Compounds -

Diethylaminotetrafluorophosphorane: Bis(diethylamino)-dimethylsilane (8.4 g., 0.041 mole) was allowed to react with phosphorus pentafluoride (10.5 g., 0.084 mole) in a manner similar to that described for the reaction of PF_5 with other silylamines. (Chapter 2) A volatile product was formed which was identified as dimethyldifluorosilane and the weight collected (3.2 g.) represented 82% reaction having taken place. Distillation of the higher boiling fraction at atmospheric pressure through a 10 in. Vigreux column afforded a colourless liquid of b.p. 98°C which was subsequently identified as diethylaminotetrafluorophosphorane. The weight collected (11.9 g.)represents 83% yield of Et_2NPF_4.

Tris(dimethylamino)fluorophosphonium hexafluorophosphate: Bis(dimethylamino)dimethylsilane (27.0 g., 0.18 mole) was allowed to react with phosphorus pentafluoride (48.5 g., 0.38 mole) in a manner similar to that described in the previous experiment. The volatile by-product dimethyldifluorosilane was formed. The remaining solid residue was recrystallised three times from an acetonitrile/benzene mixture affording a white crystalline solid which was found to stable up to 250°C. The solid product was identified by n.m.r. analysis as tris(dimethylamino)fluorophosphonium hexafluorophosphate. The weight collected (32.9 g.) represents 81% yield of $[(Me_2N)_3PF]^+[PF_6]^-$ based on the amount of bis(dimethylamino)-dimethylsilane used.

Analysis Calc. for $C_6H_{18}F_7N_3P_2$

Found: C, 21.9; H, 5.5; F, 41.0; N, 12.8; P, 18.8%

Calc: C, 22.0; H, 5.5; F, 40.7; N, 12.8; P, 18.9%.

Thermal Stability of Aminofluorophosphoranes.

Experiments were carried out with the aminofluorophosphoranes, Me_2NPF_4, $(Me_2N)_2PF_3$, Et_2NPF_4 and $(Et_2N)_2PF_3$ in which samples of each were heated in sealed tubes at 120°C for 48 h. The following observations were made.

A. Dimethylaminotetrafluorophosphorane

After 48 h. it was observed that the tube contained about 80% solid and 20% liquid. N.m.r analysis of the solid in acetonitrile showed the presence of an ionic species postulated as being bis(dimethylamino)difluorophosphonium hexafluorophosphate $[(Me_2N)_2PF_2]^+[PF_6]^-$. The liquid was found by comparison to an authentic sample to be unchanged dimethylaminotetrafluorophosphorane Me_2NPF_4.[2]

B. Bis(dimethylamino)trifluorophosphorane

After 48 h. it was observed that the tube contained about 80% solid and 20% liquid. N.m.r. analysis of the solid in acetonitrile showed the presence of an ionic species postulated as being tetrakis(dimethylamino)phosphonium hexafluorophosphate, $[(Me_2N)_4P]^+[PF_6]^-$. The liquid was found by comparison to an authentic sample to be unchanged bis(dimethylamino)trifluorophosphorane, $(Me_2N)_2PF_3$.[2]

C. Diethylaminotetrafluorophosphorane

After 48 h. it was **observed** that the tube contained about 30% solid and 70% liquid. N.m.r. analysis of the solid in acetonitrile showed the presence of an ionic species postulated as being bis(diethylamino)difluorophosphonium hexafluorophosphate, $[(Et_2N)_2PF_2]^+[PF_6]^-$. The liquid was found by comparison to an authentic sample to be unchanged diethylaminotetrafluorophosphorane, Et_2NPF_4.[2]

D. Bis(diethylamino)trifluorophosphorane

After 48 h. it was observed that no reaction had taken place. N.m.r. analysis of the liquid confirmed the presence of unchanged bis(diethylamino)trifluorophosphorane. The n.m.r. data was consistent with that already reported for the trifluorophosphorane.[2]

One can therefore postulate the thermal rearrangement of these aminofluorophosphoranes as proceeding via the following equations,

$$2R_2NPF_4 \longrightarrow (R_2N)_2PF_3 \quad + \quad PF_5 \longrightarrow [(R_2N)_2PF_2]^+[PF_6]^-$$

(where R = Me, Et).

$$2(R_2N)_2PF_3 \longrightarrow (R_2N)_4PF \quad + \quad PF_5 \longrightarrow [(R_2N)_4P]^+[PF_6]^-$$

(where R = Me)

Phosphorus pentafluoride being a strong Lewis acid will accept a fluoride ion and readily form a hexafluorophosphate ion.[158] The reaction schemes postulated here are to some extent confirmed by later experiments.

Nuclear Magnetic Resonance Data

N.m.r. data for the ionic compounds obtained are shown in Table 6.2 and are characteristic for ionic phosphorus-fluorine compounds.[1, 72] The low phosphorus chemical shifts for the cations are characteristic for four-coordinate phosphorus and the high phosphorus chemical shift for the anion is characteristic of a six coordinate phosphorus atom.[72]

Data for the unreacted aminofluorophosphoranes are consistent with data already reported.[2]

Table 6.2

N.m.r. Data for Aminophosphonium Hexafluorophosphates

Compound	Anion		Cation		
$[(Me_2N)_2PF_2]^+[PF_6]^-$	δF	+ 72.2	δF	+ 84.5	
	δP	+ 144.4	δP	- 20.6	
	J_{PF}	715	δH	- 3.0	
			J_{PF}	1056	
			J_{PH}	12.5	
			J_{HF}	2.5	
$[(Me_2N)_4P]^+[PF_6]^-$	δF	+ 72.4	δP	- 36.9	
	δP	+ 144.0	δH	- 2.6	
	J_{PF}	712	J_{PH}	9.5	
$[(Et_2N)_2PF_2]^+[PF_6]^-$	δF	+ 72.0	δF	+ 82.9	
	δP	+ 144.0	δP	a	
	J_{PF}	715	δH	- 1.2	$(N.C.CH_3)$
			δH	- 3.3	$(N.CH_2C)$
			J_{PF}	1072	
			J_{PH}	11	
			J_{HF}	3	
			J_{HH}	7	

δ values p.p.m. J values Hz.

a. δP not observable from the spectrum due to small conc.

All measurements made on solutions in acetonitrile.

For the PF_2 cations one observes in the ^{31}P spectra a triplet which is accounted for by the single phosphorus resonance coupling with the two magnetically equivalent fluorine atoms. The phosphorus resonance for R_4P cation ($R = Me_2N$) is just a single peak, no coupling to any other magnetic nucleii.

Reaction of Dimethylaminofluorophosphoranes with Phosphorus Pentafluoride

A series of experiments were carried out in which phosphorus pentafluoride was allowed to react with the aminofluorophosphoranes $(Me_2N)_nPF_{5-n}$ (where n = 1, 2, 3). It was expected, due to the greater Lewis acid acceptor properties of PF_5, [158] that the aminofluorophosphoranes would readily donate a fluoride ion and thus form aminophosphonium hexafluorophosphates of the type $[(Me_2N)_nPF_{4-n}]^+$ $[PF_6]^-$. Ionic phosphorus-fluorine compounds of this type were found to be formed, the ease of reaction increasing as n increased. This increase in the ease of reaction can be explained by the decrease in the Lewis acid acceptor properties of the aminofluorophosphoranes or, conversely, the increase in the donor properties as n increases. This falls in line with the now accepted decrease in Lewis acid character of substituted fluorophosphoranes. [2] Factors affecting the formation of ionic compounds are discussed later.

Reaction of Dimethylaminotetrafluorophosphorane with Phosphorus Pentafluoride

Dimethylaminotetrafluorophosphorane, Me_2NPF_4, and phosphorus pentafluoride were allowed to react together in a sealed tube over a two week period at room temperature. The two reactants were present in a 1:1 ratio. On opening the tube a large amount of unreacted PF_5 was noticed and subsequent investigation of the remaining contents of the tube confirmed the presence of mostly unreacted Me_2NPF_4. An oily brown residue was also present amounting to about 10% of total reaction mixture and ^{19}F and ^{31}P n.m.r. analysis indicated the presence of an ionic species which was postulated as being methylaminotrifluorophosphonium hexafluorophosphate $[Me_2NPF_3]^+[PF_6]^-$.

Reaction of Bis(dimethylamino)trifluorophosphorane with Phosphorus Pentafluoride

Bis(dimethylamino)trifluorophosphorane, $(Me_2N)_2PF_3$, and phosphorus pentafluoride in a 1:1 ratio were allowed to react together in a sealed tube at room temperature. After 1 h. the reaction mixture was found to have solidified. On opening the tube there was no evidence of any excess PF_5. N.m.r. analysis of the solid product confirmed the presence of an ionic species which was postulated as being bis(dimethylamino)difluorophosphonium hexafluorophosphate $[(Me_2N)_2PF_2]^+[PF_6]^-$. The n.m.r data were found to be identical to those of the ionic product obtained from the thermal rearrangement of dimethylaminotetrafluorophosphorane. This reaction confirms the mechanism proposed for the thermal rearrangement of dimethyaminotetrafluorophosphorane.

Reaction of Tris(dimethylamino)difluorophosphorane with Phosphorus Pentafluoride

Tris(dimethylamino)difluorophosphorane, $(Me_2N)_3PF_2$, and phosphorus pentafluoride in a 1:1 ratio were allowed to react together in a sealed tube at room temperature. The reaction was found to be exothermic and after 0.5 h. the reaction mixture was found to be solid. On opening the tube there was no evidence of any excess PF_5. Investigation of the solid product confirmed the presence of an ionic species which was postulated, by n.m.r. analysis, as being tris(dimethylamino)fluorophosphonium hexafluorophosphate $[(Me_2N)_3PF]^+[PF_6]^-$. The n.m.r. data were found to be identical to the data of the ionic product obtained from the reaction of bis(dimethylamino)dimethylsilane with phosphorus pentafluoride. The reaction discussed here might confirm the existence of a difluorophosphorane intermediate in the reaction of $(Me_2N)_2SiMe_2$ with PF_5. However, this would imply the reaction of the monosubstituted product, Me_2NPF_4, with more $(Me_2N)_2SiMe_2$ affording the difluorophosphorane $(Me_2N)_2PF_2$ and this seems unlikely in view of the vigorous reaction conditions employed if the disubstituted compound $(Me_2N)_2PF_3$ is to be prepared by such a reaction.[2]

Nuclear Magnetic Resonance Data

N.m.r. data for these phosphorus-fluorine ionic compounds are shown in Table 6.3. The data are consistent with such ionic compounds.[1, 72] The negative phosphorus chemical shifts for the cations are indicative of four-coordinate phosphorus atoms and the multiplet nature of the resonances indicate the number of fluorine atoms associated with each cation. The cation $[(Me_2N)_2PF_2]^+$ shows a low field triplet made up of a phosphorus resonance coupling with the two magnetically equivalent fluorine atoms. The cation $[(Me_2N)_3PF]^+$ shows a low field doublet made up of the phosphorus resonance coupling with the single fluorine atom. The highly positive phosphorus chemical shift for the anion of ca. 140 p.p.m. is indicative of the hexafluorophosphate ion, PF_6^-.

Experimental

All the reactions were carried out as described for the reactions of silylamines with phosphorus pentafluoride in Chapter 2. The aminofluorophosphoranes were prepared using known literature methods as indicated in the section on General Experimental Technique.

The ionic compounds obtained were recrystallised from acetonitrile/benzene mixtures affording colourless crystalline solids. The compounds were found to be stable up to about 250°C.

The corresponding reaction of diethylaminotetrafluorophosphorane with phosphorus pentafluoride did not, however, produce any of the expected ionic phosphorus-fluorine compound, even when the reaction mixture had been heated at 100°C for 12 h.

Table 6.3

N.m.r. Data for Aminophosphonium Hexafluorophosphates

Compound	Anion		Cation	
$[Me_2NPF_3]^+[PF_6]^-$	δF	+ 71.5	δF	+ 55.7
	δP	+ 144.8	δP	a
	J_{PF}	710	J_{PF}	1054
$[(Me_2N)_2PF_2]^+[PF_6]^-$ b	δF	+ 72.1	δF	+ 84.7
	δP	+ 144.3	δP	- 20.6
	J_{PF}	710	δH	- 3.0
			J_{PF}	1046
			J_{HP}	12.5
			J_{HF}	2.5
$[(Me_2N)_3PF]^+[PF_6]^-$ c	δF	+ 72.2	δF	+ 86.3
	δP	+ 144.4	δP	- 40.1
	J_{PF}	718	δH	- 2.7
			J_{PF}	954
			J_{HP}	10
			J_{HF}	d

δ values p.p.m. and J values Hz.

a. δP not observable from the spectrum because concentration of sample too small.

b. Compare data with those in Table 6.2.

c. Compare data with those in Table 6.1.

d. J_{HF} not resolvable.

All measurements made on solutions in acetonitrile.

Reactions of Aminotetrafluorophosphoranes with Si-N Compounds

The reactions of the fluorophosphoranes R_nPF_{5-n} with Si-N bonded compounds have been extensively investigated.[2] A review of such reactions appears in the introduction to this thesis.

The reactions to be discussed here are the reactions of dimethyl- and diethyl- aminotetrafluorophosphoranes with the disilazanes $R'N(SiMe_3)_2$ (where $R' = Me, Ph$). It was hoped that the reactions would produce the hitherto unknown diazadiphosphetidines $(R_2NPF_2\text{-}NR')_2$ (where R = Me, Et; R' = Me, Ph). This proved to be an adequate route for the diazadiphosphetidine $(Et_2NPF_2\text{-}NMe)_2$ which was formed in good yield but inadequate for the preparation of the other phosphetidines. In the other reactions a mixture of products was found to be formed, including trace amounts of phosphetidines, the monomeric amino-fluorophosphine imides, rearranged products and ionic products.

Experimental

The fluorophosphoranes were prepared from methods already described in this chapter. The two disilazanes were prepared by known literature methods, $MeN(SiMe_3)_2$ [166] and $PhN(SiMe_3)_2$.[167] All precautions were taken in handling starting materials and products as described in the section on General Experimental Technique.

Reaction of Diethylaminotetrafluorophosphorane with N-Methylhexamethyldisilazane

Diethylaminotetrafluorophosphorane (8.9 g., 0.05 mole) was allowed to react with N-methylhexamethyldisilazane (8.7 g., 0.05 mole) in a Monel cylinder at 150°C for 6 h.

On cooling to room temperature the cylinder was opened and attached to a weighed trap cooled to -78°C. A volatile product collected in the trap which was subsequently identified, by ^1H n.m.r., as trimethylfluorosilane. The weight collected (7.1 g.)represented 80% reaction having taken place. Distillation of the higher boiling fraction under vacuum afforded a colourless liquid of b.p. 102°C/0.2 mm. which was subsequently identified as 1,1,3,3-difluoro-1,3-diethylamino-N,N'-dimethyl-1,2,3,4-diazadiphosphetidine. The weight collected (5.0 g.) represents 59% yield of $(Et_2NPF_2-NMe)_2$.

Found:	N, 16.0; P, 18.4%
Calc. for $C_{10}H_{26}F_4N_4P_2$	N, 16.3; P, 18.1%.

It was noticed that in a repeat of this reaction when it was carried out in a glass reaction tube at 150°C for 3 h. the main product formed was bis(diethylamino)trifluorophosphorane, $(Et_2N)_2PF_3$. This compound was identified by comparison of its ^{19}F and ^{31}P n.m.r. data with those of an authentic sample.[2] The formation of this trifluorophosphorane could conceivably be from the thermal rearrangement of diethylaminotetrafluorophosphorane, discussed previously in this chapter.

Reaction of Diethylaminotetrafluorophosphorane with N-Phenylhexamethyldisilazane

Diethylaminotetrafluorophosphorane (8,9 g., 0.05 mole) was allowed to react with N-phenylhexamethyldisilazane (11.8 g., 0.05 mole) in a manner similar to that described in the previous reaction. The volatile by-product trimethylfluorosilane was found to be formed and the weight collected (8.1 g.) represented 88% reaction having taken place.

The semi-solid residue remaining was filtered in a dry box and the solid was washed several times with dry benzene, the washings being added to the filtrate. The filtrate was distilled first at atmospheric pressure to remove the benzene and then under vacuum affording a colourless liquid of b.p. 93°C/0.05 mm. This liquid was found to solidify on standing and was subsequently identified, by n.m.r. analysis, as a mixture of the phosphetidine $(Et_2NPF_2-NPh)_2$ and the monomeric form of this compound the amino-fluorophosphine imide $Et_2NPF_2{=}NPh$. The solid product removed by filtration was found to contain the hexafluorophosphate anion $[PF_6]^-$ but it proved difficult to ascertain the nature of the cation.

Repeated attempts to prepare the phosphetidine were not successful. In all attempts the main product formed was the ionic compound, the phosphetidine and its monomer being formed only in very small yields (ca. 5%) or not at all.

Reaction of Dimethylaminotetrafluorophosphorane with N-Methylhexamethyldisilazane

Dimethylaminotetrafluorophosphorane (7.5 g., 0.05 mole) was allowed to react with N-methylhexamethyldisilazane (8.7 g., 0.05 mole) in a manner similar to the reactions described previously. The volatile by-product trimethylfluorosilane was formed and the weight collected (7.7 g.) represented 85% reaction having taken place. The remaining reaction mixture was found to contain three products;

(i). An ionic species identified as containing the hexafluorophosphate ion $[PF_6]^-$ in about 80% yield. The cation was not identified.

(ii). Bis(dimethylamino)trifluorophosphorane, $(Me_2N)_2PF_3$, which was identified by comparison of its ^{19}F and ^{31}P n.m.r.

data to those of an authentic sample.[2] The formation of this trifluorophosphorane could conceivably be from the thermal rearrangement of dimethylaminotetrafluorophosphorane, discussed previously in this chapter.

(iii). A small amount of an oily liquid which could possibly be the phosphine imide $Me_2NPF_2=NMe$ being characterised by a large fluorine chemical shift and coupling constant between phosphorus and fluorine. The values of δF and J_{PF} are consistent with four-coordinate phosphorus-fluorine compounds.[2] The possibility of this compound being the dimeric form (phosphetidine) is ruled out in view of the simple doublet nature of the ^{19}F n.m.r. spectrum. (See later)

Reaction of Dimethylaminotetrafluorophosphorane with N-Phenylhexamethyldisilazane

Dimethylaminotetrafluorophosphorane (7.5 g., 0.05 mole) was allowed to react with N-phenylhexamethyldisilazane (11.8 g., 0.05 mole) in a manner similar to that described in the previous reactions. The volatile by-product trimethylfluorosilane was formed in about 90% yield. The remaining residue of the reaction mixture was found to contain the hexafluorophosphate anion $[PF_6]^-$ although the identity of the cation was not established. Repeats of this experiment all produced the ionic compound and in no case was any other compound identified.

Nuclear Magnetic Resonance Data

The n.m.r. data obtained for the reaction products are listed in Table 6.4. The data obtained for the phosphetidines are consistent with data reported for other phosphetidines.[2, 18, 168] The n.m.r. data obtained for the ionic species

δF + 71.5; δP + 144.0 p.p.m. and J_{PF} 715 Hz. are characteristic of hexafluorophosphate, $[PF_6]^-$, however no n.m.r. data were obtained for the associated cation.

Table 6.4

N.m.r. Data for Amino-Fluoro-1,2,3,4-Diazadiphosphetidines and Amino-Fluoro-Phosphine Imides

Compound		δ p.p.m.		J (Hz)	
$(Et_2NPF_2\text{-}NMe)_2$		δF	+ 67.5	J_{PP}	136
		δP	+ 38.8	$^1J_{PF}$	± 833
		δH	- 1.2 ($N.C.CH_3$)	$^3J_{PF}$	∓ 13
		δH	- 2.5 (NCH_3)	J_{PH}	13
		δH	- 3.3 ($N.CH_2.C$)	J_{HH}	7
$(Et_2NPF_2\text{-}NPh)_2$	c	δF	+ 74.4	J_{PP}	140
		δP	a	$^1J_{PF}$	± 840
				$^3J_{PF}$	∓ 15
$(Et_2NPF_2{=}NPh)$	b, c	δF	+ 74.4	J_{PF}	1032
$(Me_2NPF_2{=}NMe)$		δF	+ 69,9	J_{PF}	916

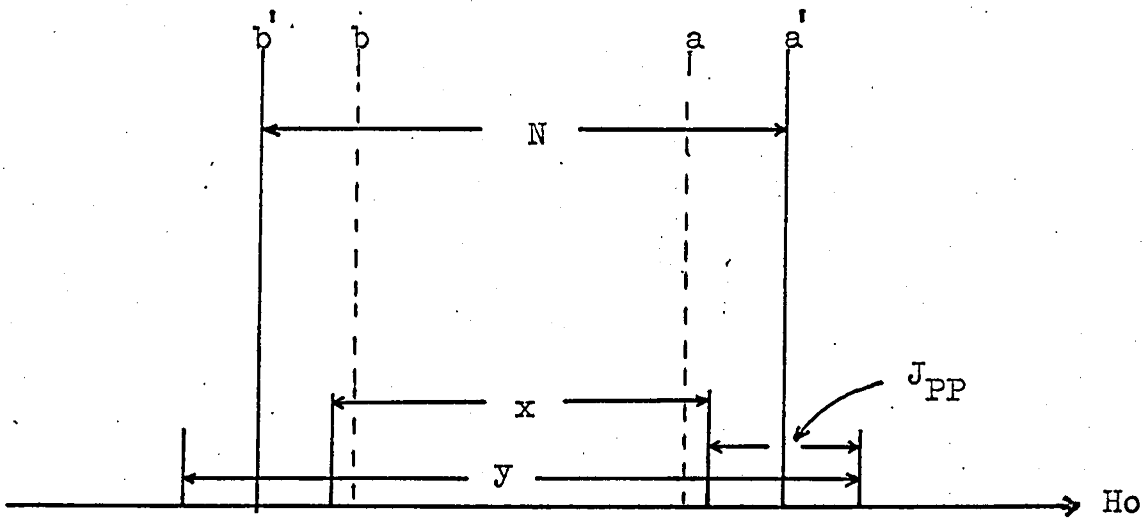
a. Insufficient sample to run a ^{31}P n.m.r. spectrum.

b. Data compares to those obtained for the product of the reaction of diethylaminodifluorophosphine, Et_2NPF_2, with phenyl azide, PhN_3, in which the phosphine imide $Et_2NPF_2{=}NPh$ was isolated.[169]

c. N.m.r. measurement made on solution in benzene.

Four-membered ring systems containing five-coordinate phosphorus bonded to fluorine have previously been reported by a number of workers.[5, 20, 21, 29, 103, 170-176] X-ray crystallographic studies of the compound $(PhPF_2\text{-}NMe)_2$[73] and Infrared studies of the compound $(F_3P\text{-}NMe)_2$[177, 178] have confirmed that, for these compounds, there is a trigonal-bipyramidal environment about the phosphorus atom and that the axial positions are occupied by one fluorine atom and one ring nitrogen atom. This is presumably the structure of the compounds reported here and the n.m.r. data support penta-coordination about phosphorus. The observation of apparently magnetically equivalent fluorine atoms when one would expect two distinct fluorine atom environments may be explained by a quasi-pseudorotational process involving the fluorine atoms and the diethylamino group, thus one observes an average of the fluorine atom environments. The possible involvement of a P-N bond in such a pseudorotational process is ruled out due to the great stress which would be invoked on the ring involving a change of the P-N-P bond angle from 90° to 120° and back to 90°. This implies a large energy barrier to rotation. Low temperature ^{19}F n.m.r. studies of $(Et_2NPF_2\text{-}NMe)_2$ were not successful in distinguishing between the two fluorine environments which suggests a very low barrier to rotation. Such a low energy barrier to rotation favours a process involving the fluorine atoms and the amino group only.

The ^{19}F n.m.r. spectral form is that of a basic doublet accompanied by several other lines of smaller intensity, the whole spectrum being symmetrical about the middle. The general spin system of fluoro-diazadiphosphetidines is classified as $AX_nX'_nA'$ (where A and X refer to phosphorus and fluorine, respectively),[109, 179] and full spectral analyses have been carried out for several such compounds.[168, 179, 180] The fluoro-diazadiphosphetidines reported here are classified as $AX_2X'_2A'$ spin systems and the spectral form is that shown in the following figure.



Making the assumption that there is no spin-spin coupling $J_{XX'}$ ($J_{F_1F_3}$, the coupling constant between the fluorine atoms bonded to one phosphorus atom and the fluorine atoms bonded to the other phosphorus atom) then the large coupling constant N is the summation of two coupling constants $J_{AX} + J_{AX'}$ (${}^1J_{PF} + {}^3J_{PF}$). The coupling constant between the two A nucleii J_{AA} (J_{PP}) can be obtained directly from the spectrum, as is shown in the figure. If all the lines are well resolved then the value $L = \sqrt{xy}$ is equal to the difference between the coupling constants J_{AX} and $J_{AX'}$. Thus knowing the values of N and L the relevant coupling constants can be ascertained.

The spin states of the two phosphorus atoms causes the spectral form to change in such a way that;

$F_2\alpha\alpha F_2$ causes shift of line a to a';

$F_2\beta\beta F_2$ causes shift of line b to b' ;

$F_2\alpha\beta F_2$ and $F_2\beta\alpha F_2$ cause the appearance of the extra lines.

The distance between a and b represents the phosphorus-fluorine coupling constant that would be expected for a normal five-coordinate phosphorus-fluorine compound containing two fluorine atoms, i.e. difluorophosphoranes.

Reaction of Aminotetrafluorophosphoranes with Si-S Compounds

The reactions of the fluorophosphoranes R_nPF_{5-n} (where $n = 0, 1, 2$; R = Me, Et, Ph) with the silylthio ethers $R'SiMe_3$ have been studied and a series of compounds of the type $R_nP(SR')F_{4-n}$ have been prepared.[31, 32] However, the corresponding reactions of the aminotetrafluorophosphoranes Me_2NPF_4 and Et_2NPF_4 with trimethylsilyl thioethers produced, in all cases, ionic compounds containing the hexafluorophosphate anion $[PF_6]^-$. The hexafluorophosphate ion was characterised by its n.m.r. data $\delta F + 72.0$; $\delta P + 144.0$ p.p.m.; J_{PF} 715 Hz.[1,72] It proved difficult to ascertain the identity of the cation though it is believed that the reactions proceed in a manner similar to the reaction of dimethylaminotetrafluorophosphorane with phenyltrimethylsilyl ether[36,39] in which a trifluorophosphorane intermediate is formed and then rearranges to its stable ionic isomer according to the equations,

$$R'SSiMe_3 + R_2NPF_4 \longrightarrow R_2NPF_3SR' + Me_3SiF$$

$$\begin{aligned} 2R_2NPF_3SR' &\longrightarrow [(R_2N)_2PFSR']^+[R'SPF_5]^- \\ &\quad\text{or}\quad [(R'S)_2PFNR_2]^+[R_2NPF_5]^- \\ &\qquad\qquad\downarrow \\ &\qquad [(R_2N)_2P(SR')_2]^+[PF_6]^- \end{aligned}$$

(where R = Me, Et; R' = Me, Et).

Reactions of Aminotetrafluorophosphoranes with Si-O Compounds

The aminotetrafluorophosphoranes Me_2NPF_4 and Et_2NPF_4 have been shown to react with pentafluorophenyltrimethylsilyl ether (Chapter 1) to give covalent stable difluorophosphoranes of the type $R_2NPF_2(OC_6F_5)_2$.

The corresponding reaction of the aminotetrafluorophosphoranes with phenyltrimethylsilyl ether produces an ionic compound and the yield is influenced by the presence of trace amounts of sodium fluoride.[36, 39] The reaction proceeds according to the equation,

$$2PhOSiMe_3 \quad + \quad 2R_2NPF_4 \longrightarrow [(R_2N)_2P(OPh)_2]^+[PF_6]^- + 2Me_3SiF.$$

Discussion

In assessing the results obtained it would seem reasonable to consider one distinct process which is involved: Thermal rearrangement to give ionic compounds.

It has been found that halofluorophosphoranes and fluorophosphoranes substituted by heteroatom-containing groups show a tendency to rearrange to give ionic compounds. The latter sometimes decompose thermally with the formation of more stable fluorophosphoranes and sometimes three-coordinate or ionic phosphorus species. Table 6.5 lists compounds which are known to rearrange to give ionic compounds.

From electronegativity considerations it would seem feasible that the most stable anion would contain the largest number of fluorine atoms, e.g. $[PF_6]^-$ and, correspondingly, the most stable cation would contain the least number of fluorine atoms, e.g. $[R_4P]^+$, (where R = Alk, Aryl, or hetero-

Table 6.5

Rearrangement of Fluorophosphoranes to give Ionic Species

$2X_2PF_3$ (X = Cl, Br)	$\longrightarrow$	$[X_4P]^+[PF_6]^-$	158, 181, 182
$2Cl_3PF_2$	$\longrightarrow$	$[PCl_4]^+[PF_4Cl_2]^-$	183
X_4PF (X = Cl, Br)	$\longrightarrow$	$[PX_4]^+F^-$	184, 185, 186
$2R_2NPR'F_3$	$\longrightarrow$	$[(R_2N)_2PR'F]^+[R'PF_5]^-$	24, 26, 187
(where R = Me; R' = Me, Et, Ph)			
$2R_2NPR'F_3$	$\longrightarrow$	$[(R_2N)_2PR'F]^+[R'PF_5]^-$	This work
(where R_2 = 4-Me-piperidyl-, 2,5-dimethyl-pyrryl; R = Me, Ph)			
$2RR'NPR''F_3$	$\longrightarrow$	$[(RR'N)_2PFR'']^+[R\ PF_5]^-$	This work 23
(where RR' = 2-Me-, 3-Me-piperidyl, 2-Me-pyrryl; R'' = Me, Ph; or R = $PhCH_2$ and R' = Me, R'' = Ph)			
$2MeBzNPF_4$	$\longrightarrow$	$[(MeBzN)_2PF_2]^+[PF_6]^-$	23
$2RR'NPF_4$	$\longrightarrow$	$[(RR'N)_2PF_2]^+[PF_6]^-$	This work
$2R_2NPF_4$	$\longrightarrow$	$[(R_2N)_2PF_2]^+[PF_6]^-$	This work
(where R = Me, Ph)			
$2Me_2NPF_3OPh$	$\longrightarrow$	$[(Me_2N)_2P(OPh)_2]^+[PF_6]^-$	36, 39
$2Me_2NPF_3OC_6F_5$	$\longrightarrow$	$[(Me_2N)_2P(OC_6F_5)_2]^+[PF_6]^-$	This work
$2(PhO)_2PF_3$	$\longrightarrow$	$[(PhO)_4P]^+[PF_6]^-$	23, 36
$2R_2NPF_3SR'$	$\longrightarrow$	$[(R_2N)_2P(SR')_2]^+[PF_6]^-$	This work
(where R = Me, Et; R' = Me, Et, Ph)			

atom group). Therefore the stability of the anions would decrease in the order $[PF_6]^- > [RPF_5]^- > [R_2PF_4]^-$ etc., and the the stability of the corresponding cation would be in the order $[R_4P]^+ > [R_3PF]^+ > [R_2PF_2]^+$ etc. For a theoretical sequence of phosphorus-fluorine ionic compounds, ,therefore, the stability would be in the order, $[R_4P]^+[PF_6]^- > [R_3PF]^+[RPF_5]^- >$ $[R_2PF_2]^+[R_2PF_4]^- > [RPF_3]^+[R_3PF_3]^-$.

All the observed results are consistent with theoretical considerations. The formation of a stable phosphorus-carbon bonded pentafluorophosphate, $[MePF_5]^-$ or $[PhPF_5]^-$, seems, however, to contradict the theoretical predictions. This may be explained by the need for P-C bond cleavage in the formation of any hexafluorophosphate and that such a bond cleavage, under the reaction conditions of the rearrangements discussed, is not possible in view of the larger P-C bond energy compared to that of P-O, P-N, P-F, P-Cl, P-Br, and P-S bonds. Therefore, for hydrocarbon phosphorus-fluorine compounds one would expect the formation of hydrocarbon-pentafluorophosphates. From the results observed the tendency is for a larger number of trifluorophosphoranes to rearrange, compared to tetra- and di-fluorophosphoranes.

Results obtained from the studies on aminofluorophosphoranes fit in with the previously observed results although it has been noticed that Me_2NPF_4 in its chemical reactivity shows a greater tendency towards formation of ionic compounds than Et_2NPF_4.

The reaction of phosphorus pentafluoride with bis(dimethylamino)dimethylsilane produces an ionic P-F compound and its formation can be explained by the formation of the two amino-fluorophosphoranes Me_2NPF_4 and $(Me_2N)_2PF_3$ which then undergo intermolecular fluorine atom exchange resulting in the formation of the ionic compound $[(Me_2N)_3PF]^+[PF_6]^-$ which is, from theoretical considerations, the most stable ionic compound expected to be formed in such a reaction mixture. The corresponding reaction of bis(diethylamino)dimethylsilane with phosphorus pentafluoride, however, produces, as the main product, the covalent phosphorus-fluorine compound, Et_2NPF_4 in high yield.

The thermal stability of dimethylamino-substituted fluorophosphoranes has been found to be lower than for the corresponding diethylamino-substituted fluorophosphoranes. Dimethylaminotetrafluorophosphorane and bis(dimethylamino)-trifluorophosphorane show a tendency to undergo intramolecular exchange affording ionic compounds and this rearrangement occurs to about 90%. Diethylaminotetrafluorophosphorane and bis(diethylamino)trifluorophosphorane, however, prefer to remain in the covalent state, although in the case of diethylaminotetrafluorophosphorane rearrangement does take place to a small degree. These observations can also be explained by the aminofluorophosphoranes preferring to exist as ionic isomers. However, the question arises why diethyl-amino-substituted fluorophosphoranes do not behave in a manner similar to dimethylamino-substituted fluorophosphoranes. The difference in P-N bond energies of the respective aminofluorophosphoranes is probably only minimal and thus not of great influence on the possible formation of ionic compounds. There is an obvious difference in the size of a dimethylamino-group and a diethylamino-group and therefore stereochemical hindrance might be considered as a possible explanation of the observed differnce in behaviour, the possibility of a dimethylamino group being accommodated by a phosphorus atom to a better degree than a diethylamino group.

It has been found that in the reactions of aminofluorophosphoranes with Si-S bonded compounds a tendency of formation of ionic compounds is observed in all cases. This might be explained by the formation of the most stable possible phosphonium cation $[(R_2N)_2P(SR')_2]^+$ (where R = Me, Et; R' = Me, Et). In this case the phosphonium cation readily accommodates two diethylamino groups which contrasts to previous results obtained from the thermal rearrangement of diethylamino-substituted fluorophosphoranes. The fluorophosphonium cation formed in the case of thermal rearrangements is, from previously mentioned theoretical considerations, not as stable as the cation formed from the reactions of dialkylamino-substituted fluorophosphoranes with Si-S bonded compounds and it might be expected that when the possibility arises for the formation of the most stable cation then reactions involving diethylaminotetrafluorophosphorane will also show a tendency towards the formation of ionic compounds. Similar results were also observed for the reactions of aminofluorophosphoranes with Si-O bonded compounds.

In view of the previously observed results it was not surprising to find that the reactions of dialkylamino-substituted fluorophosphoranes with Si-N bonded compounds gave varying results. Diethylaminotetrafluorophosphorane showed a tendency towards forming covalent products whereas dimethylaminotetrafluorophosphorane showed a tendency towards forming ionic products. The high reaction temperatures employed to induce reactions would aid in the thermal rearrangement of these aminofluorophosphoranes, and thus the ionic compounds detected in the reaction mixtures involving Me_2NPF_4 might very well be its ionic rearrangement product. Due to the greater thermal stability of Et_2NPF_4 the possibility of forming covalent products is greater.

The reactions of the aminofluorophosphoranes $(Me_nN)_nPF_{5-n}$ (where n = 1, 2, 3) with phosphorus pentafluoride are also consistent with the previously mentioned theoretical considerations. As the value of n increases so the Lewis acid character of the aminofluorophosphoranes decreases and the strong Lewis acid, phosphorus pentafluoride, has a greater chance of abstracting a fluoride and forming the stable hexafluorophosphate anion $[PF_6]^-$. The corresponding cation also becomes more stable as n increases and the stability of the ionic species can be envisaged as being in the order, $[(Me_2N)_3PF]^+[PF_6]^-$ $[(Me_2N)_2PF_2]^+[PF_6]^-$ $[(Me_2N)PF_3]^+[PF_6]^-$. This order is borne out by the experimental findings in which it was observed that the ease of reaction increased as n increased. The reaction of Me_2NPF_4 with PF_5 is very slow and only a small amount of the ionic compound is formed. The reaction of $(Me_2N)_2PF_3$ with PF_5 is faster and goes in 100% yield. The reaction of $(Me_2N)_3PF_2$ with PF_5 is very fast, exothermic and also goes in 100% yield.

In explaining the reactivities of these dialkylamino-substituted fluorophosphoranes one must take into account the thermal stability of these compounds; their respective Lewis acid characters; the stability of the cation and anion when an ionic compound is formed; lability of groups;

the size of possible ions formed, whether it is sterically possible to form such an ion or not and crystal lattice energies.

CHAPTER VII

CONCLUSIONS AND FUTURE WORK

CHAPTER VII

CONCLUSIONS AND FUTURE WORK

The cleavage reactions of Si-O bonded Lewis bases by the Lewis acid fluorophosphoranes have been shown to be a useful route to the preparation of compounds of the type $(RO)_{3-n}PR'_nF_2$ (where R = Ph C_6F_5; R' = Me, Ph, Me_2N, Et_2N; n = 0, 1, 2). The interesting feature of these reactions is the tendency towards multisubstitution in which all the available equatorial fluorine atoms are replaced by aryloxy groups. This contrasts to the analogous reactions involving the cleavage of Si-N and Si-S bonded compounds which are characterised by monosubstitution. The corresponding reactions of fluorophosphoranes with alkylsilyl ethers, in contrast, do not form any stable alkoxy fluorophosphoranes, instead the tendency is towards the formation of stable phosphoryl compounds and the elimination of an alkyl fluoride.

Cleavage reactions of Si-N bonded Lewis bases with fluorophosphoranes have been shown to produce new asymmetric aminofluorophosphoranes of the type $RR'NPR''_nF_{4-n}$ (where n = 0, 1, 2; RR' = 2-Me- and 3-Me-piperidyl, 2-Me- pyrryl; R'' = Me, Ph) and new symmetric aminofluorophosphoranes of the type $R_2NPR'_nF_{4-n}$ (where R_2 = 4-Me-piperidyl, 2,5-dimethylpyrryl; R' = Me, Ph; n = 0, 1, 2). These reactions proved to be no exception to the well documented reactions of Si-N bonded compounds with fluorophosphoranes, although the reaction of $MePF_4$ with pyrrylsilylamines did not take place, presumably due to decreased Lewis base character of the silylamine and thus its inability to form an intermediate adduct with $MePF_4$.

All the new trifluorophosphoranes show a tendency, as has been observed for other aminofluorophosphoranes, to rearrange intermolecularly to give stable ionic compounds.

New dialkylaminodialkyl(aryl)difluorophosphoranes of the type $RR'PF_2NR''_2$ (where $R = R' =$ Me, Ph; $R =$ Me and $R' =$ Ph; $R'' =$ Me, Et) have been prepared from the direct aminolysis of dialkyl(aryl)trifluorophosphoranes.

Trigonal bipyramidal structures about the phosphorus atom have been assigned to all the new fluorophosphoranes in which the two axial positions are occupied by fluorine atoms and the hydrocarbon and heteroatom groups occupy the equatorial positions.

The tetrafluorophosphoranes all undergo a pseudorotation process at room temperature but this process can be slowed down sufficiently at low temperatures to permit observation of rigid structures. The observation made for the fluorophosphoranes $RR'NPR''_nF_{4-n}$ was, apart from the expected magnetic non-equivalence of axial and equatorial fluorine atoms, of magnetic non-equivalence of either axial or equatorial fluorine atoms. This observation is accounted for by freezing of the P-N bond rotation, relative to the n.m.r. time scale. The cause of the comparitively high energy barrier to rotation may be due to either $p\pi$-$d\pi$ bonding between the nitrogen lone pair of electrons and an empty d orbital on phosphorus; a small amount of hydrogen bonding between protons on the hydrocarbon group attached to nitrogen and the axial fluorine atoms, or steric hindrance induced by the presence of large groups attached to phosphorus forcing the ring into a definite position.

The cleavage reactions of Si-O bonded compounds by trimeric phosphonitrilic fluoride, $(PNF_2)_3$, have been found to be a route to the monosubstituted trimeric phosphonitrilic fluorides $P_3N_3F_5OR$ (where R = Me, Et, Ph, C_6F_5). The tendency is for monosubstitution to take place although the presence of multisubstituted products is evident. The analogous reactions of Si-S bonded compounds with trimeric phosphonitrilic fluoride, however, do not lead to the formation of the analogous thio substituted compounds.

Attempts at preparing bis(dialkylamino)alkyl(aryl)-difluorophosphoranes by the aminolysis of alkyl(aryl)tetrafluorophosphoranes proved unsuccessful. The explanation for this is believed to be, either a tendency for the intermediate product to undergo intermolecular rearrangement to give a stable ionic product or stereochemical restriction to formation of a second amine-phosphorane adduct necessary for further substitution to take place.

The chemical reactivities of dialkylaminofluorophosphoranes have been studied and it was shown that dimethylaminofluorophosphoranes show a greater tendency towards the formation of ionic products whereas diethylaminofluorophosphoranes tend towards the formation of covalent products. A possible explanation for these observations is that in considering the formation of ionic compounds account must be taken of stability of ions formed; lability of groups concerned and thermal stability of the aminofluorophosphoranes.

It is hoped in the near future to be able to undertake extensive studies on the asymmetric aminofluorophosphoranes reported here and by means of n.m.r. measurements to calculate the energy barrier to rotation about the P-N bond. It would also seem reasonable to undertake extensive vibrational, electron diffraction and X-ray crystallographic studies to ascertain whether a tetragonal pyramid does not feature in the stereochemistry of these new fluorophosphoranes.

X-ray crystallographic studies are at the moment being carried out on the new aryloxy difluorophosphoranes described in Chapter 1.

Further studies are to be carried out into substitution of fluorine atoms in phosphonitrilic fluorides to ascertain whether further substitution takes place geminally or non geminally. These studies are then to be extended to the analogous tetrameric phosphonitrilic fluoride $(PNF_2)_4$.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. R. Schmutzler, in "Advances in Fluorine Chemistry", ed. M. Stacey, J. C. Tatlow and A. G. Sharpe, Butterworths, London, 1965, vol. 5, p. 31.
2. R. Schmutzler, in "Halogen Chemistry", ed. V. Gutmann, Academic Press, London and New York, 1967, vol. 2, p. 31.
3. Zh. M. Ivanova and A. V. Kirsanov, Zhur. obshchei Khim., 1962, 32, 2592.
4. I. Haiduc, "The Chemistry of Inorganic Ring Systems", Wiley Interscience, London, 1970, Part 2, p. 624.
5. R. E. Dunmur and R. Schmutzler, J. Chem. Soc. (A), 1971, 1289.
6. R. E. Dunmur, Ph. D. Thesis, University of Loughborough, 1970.
7. G. O. Doak and R. Schmutzler, Chem. Comms., 1970, 476
8. G. O. Doak and R. Schmutzler, J. Chem. Soc. (A), 1971, 1295.
9. N. L. Paddock, Quart. Rev., 1964, 18, 168.
10. R. A. Shaw, Record of Chemical Progress, 1967, 28, 243.
11. H. R. Allcock,"Heteroatom Ring Systems and Polymers", Academic Press, New York and London, 1967.
12. R. A. Shaw, Endeavour, 1968, 27, 74.
13. D. W. A. Sharp, D. H. Brown and G. W. Fraser, Chem and Ind., 1964, 367.
14. D. W. A. Sharp, D. H. Brown and G. W. Fraser, J. Chem. Soc. (A), 1966, 171.
15. G. W. Fraser, Ph. D. Thesis, University of Strathclyde, Glasgow, 1965.
16. J. S. Harman and D. W. A. Sharp, J. Chem. Soc. (A), 1970, 1138.
17. J. S. Harman and D. W. A. Sharp, J. Chem. Soc. (A), 1970, 1935.

18. R. Schmutzler, Angew. Chem., 1964, 76, 893. Angew. Chem. Internat. Edn. Engl., 1964, 3, 753.
19. G. C. Demitras, Ph. D. Dissertation, University of Pennsylvania, Philadelphia, Pa., 1964. Chem. Abs., 1966, 64, 9227.
20. G. C. Demitras, R. A. Kent and A. G. McDiarmid, Chem. and Ind., 1964, 1712.
21. G. C. Demitras and A. G. McDiarmid, Inorg. Chem., 1967, 6, 1903
22. F. Ramirez and C. P. Smith, Tetrahedron Letters, 1966, 30, 3651.
23. S. C. Peake, Ph. D. Thesis, University of Loughborough, 1970.
24. R. Schmutzler, Unpublished Results.
25. R. Schmutzler and G. S. Reddy, Inorg. Chem., 1965, 4, 191.
26. G. S. Reddy and R. Schmutzler, Inorg. Chem., 1966, 5, 164.
27. M. J. C. Hewson, S. C. Peake and R. Schmutzler, J. Chem. Soc. (A), 1970, 2364.
28. R. Schmutzler, Angew. Chem., 1964, 76, 570. Angew. Chem. Internat. Edn. Engl., 1964, 3, 513.
29. R. Schmutzler, Chem. Comms., 1965, 19.
30. S. Z. Ivin, K. V. Karavanov, V. V. Lysenko and I. D. Shelakova, Zhur. obshchei Khim., 1967, 37, 1341.
31. S. C. Peake and R. Schmutzler, J. Chem. Soc. (A), 1970, 1049.
32. S. C. Peake and R. Schmutzler, Chem. Comms., 1968, 665.
33. I. L. Knunyants, V. V. Tyuleneva, E. Ya. Pervova and R. N. Sterlin, Izvest. Akad. Nauk S.S.S.R., Ser. khim. 1964, 1797.
34. K. D. Crosbie, G. W. Fraser and D. W. A. Sharp, Chem. and Ind., 1968, 428.

35. G. I. Drozd, S. Z. Ivin and M. A. Sokal'skii, Zhur. obshchei Khim., 1969, 39, 1177.
36. M. Fild, M. J. C. Hewson, S. C. Peake and R. Schmutzler, Inorg. Chem., 1971, 10, in press.
37. R. A. Mitsch, J. Amer. Chem. Soc., 1967, 89, 6297.
38. M. Eisenhut and R. Schmutzler, Unpublished Results.
39. S. C. Peake and R. Schmutzler, Chem. and Ind., 1968, 1482.
40. R. Schmutzler, J. Chem. Soc., 1964, 4551.
41. U. Niedereuther, L. Beslier and R. Schmutzler, Unpublished Results.
42. S. C. Peake and R. Schmutzler, Unpublished Results.
43. O. Schlak and R. Schmutzler. Unpublished Results.
44. J. R. Van-Wazer, in "Phosphorus and its Compounds", Interscience, New York, 1958, p. 71.
45. H. Rose, Ann. Chem., 1834, 11, 131.
46. H. N. Stokes, J. Amer. Chem. Soc., 1895, 17, 275.
47. H. N. Stokes, Chem. Ber., 1895, 28, 437.
48. H. N. Stokes, J. Amer. Chem. Soc., 1896, 18, 629.
49. H. N. Stokes, J. Amer. Chem. Soc., 1896, 18, 780.
50. H. N. Stokes, J. Amer. Chem. Soc., 1897, 19, 782.
51. H. N. Stokes. Z. anorg. allg. Chem., 1899, 19, 36.
52. T. Moeller and F. Y. Tsang, Chem. and Ind. 1962, 361.
53. C. W. Allen, I. C. Paul and T. Moeller, J. Amer. Chem. Soc., 1967, 89, 6361.
54. C. W. Allen and T. Moeller, Inorg. Chem., 1968, 7, 2177.
55. C. W. Allen, F. Y. Tsang and T. Moeller, Inorg. Chem., 1968, 7, 2183.
56. J. Emsley and N. L. Paddock, J. Chem. Soc. (A), 1968, 2590.
57. N. L. Paddock and T. Chivers, Chem. Comms. 1969, 337.
58. H. W. Roesky, E. Niecke and O. Glemser, Z. Naturforsch., 1969, 24b, 1187.

59. H. W. Roesky and E. Niecke, Inorg. Nuclear Chem. Letters, 1968, 4, 463.

60. W. M. Douglas, M. Cooke, M. Lustig and J. K. Ruff, Inorg. Nuclear Chem. Letters, 1970, 6, 409.

61. M. Kilpatrick and M. L. Kilpatrick, J. Phys. Coll. Chem., 1949, 53, 1371.

62. M. Becke-Goehring, Fortschr. Chem. Forsch., 1968, 10, 207.

63. H. R. Allcock, Chem. Eng. News, 1968, 46, 68.

64. F. Seel and J. Langer, Angew. Chem., 1956, 68, 461.

65. F. Seel and J. Langer, Z. anorg. allg. Chem., 1958, 295, 316.

66. B. W. Fitzsimmons, C. Hewlett and R. A. Shaw, J. Chem. Soc., 1964, 4459.

67. B. W. Fitzsimmons and R. A. Shaw, Proc. Chem.Soc., 1961, 258.

68. W. Lange and E. Müller, Ber. dt. Chem. Ges., 1930, 63, 1058.

69. M. W. Dougill, J. Chem. Soc., 1963, 3211.

70. H. M. McGeachin and F. R. Tromans, J. Chem. Soc., 1961, 4777.

71. S. C. Peake and R. Schmutzler, Chem. Comms., 1968, 1662.

72. J. F. Nixon and R. Schmutzler, Spectrochim. Acta., 1964, 20, 1835.

73. J. W. Cox and E. R. Corey, Chem.Comms., 1967, 123.

74. E. L. Muetterties, W. Mahler and R. Schmutzler, Inorg. Chem., 1963, 2, 613.

75. R. K. Harris and C. M. Woodman, Mol. Phys., 1966, 10, 437.

76. R. Keat and R. A. Shaw, in "Organophosphorus Chemistry", Specialist Periodical Report, Chemical Society, London, 1970, vol. 1, p. 214.

77. R. Keat, in "Organophosphorus Chemistry", Specialist Periodical Report, Chemical Society, London, 1971, vol. 2, p. 191.

78. R. Schmutzler, Chem. and Ind., 1962, 1868.

79. R. Schmutzler, Inorg. Chem., 1964, 3, 410.

80. I. P. Komkov, S. Z. Ivin, K. V. Karavanova and L. Ye. Simonov, Zhur. obshchei Khim., 1962, 32, 301.

81. R. Schmutzler, Inorg. Synth., 1967, 9, 63.

82. R. Schmutzler, Inorg. Chem., 1964, 3, 421.

83. R. Schmutzler, (to E. I. Dupont de Nemours & Co. Inc.) U. S. P. 3,246,032/1966. Chem. Abs., 1966, 64, 19678.

84. L. Kolditz, K. Lehmann, W. Wieker and A. R. Grimmer, Z. anorg. allg. Chem., 1968, 360, 259.

85. M. Eisenhut and R. Schmutzler, Chem. Comms. 1971, in press.

86. M. Fild and R. Schmutzler, J. Chem. Soc., (A), 1969, 840.

87. M. Fild and O. Glemser, in "Fluorine Chemistry Reviews", New York, 1969, vol. 3, p. 129.

88. J. H. Letcher, and J. R. Van-Wazer, in "Topics in Phosphorus Chemistry", ed. M. Grayson and E. J. Griffith, Interscience, London and New York, 1967, vol. 5, p. 169.

89. A. J. Downs and R. Schmutzler, Spectrochim. Acta., 1967, 23, 681.

90. J. M. Miller, J. Chem. Soc., (A), 1967, 828.

91. A. T. Rake and J. M. Miller, J. Chem. Soc. (A), 1970, 1881.

92. W. A. Sheppard, J. Amer. Chem. Soc., 1970, 92, 5419.

93. S. B. Hartley, W. S. Holmes, T. K. Jacques, M. F. Mole and J. C. McCoubrey, Quart. Rev., 1963, 17, 204.

94. G. M. Kosolapoff, "Organophosphorus Compounds", Wiley, New York, 1950, p. 121.

95. R. F. Hudson, in "Organic Chemistry", A Series of Monographs Vol. 6, "Structure and Mechanism in Organo-Phosphorus Chemistry", ed. A. T. Blomquist, Academic Press, London, New York, 1965, p. 135.

96. J. L. Speier, J. Amer. Chem. Soc., 1952, 74, 1003.

97. H. W. Roesky and M. Lustig, Inorg. Chem., 1970, 9, 1289.

98. M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov and S. Z. Ivin, Zhur. strukt. Khim., 1967, 8, 1097.

99. V. V. Sheluchenko, M. A. Sokal'skii, M. A. Landau, G. I. Drozd and S. S. Dubov, Zhur. strukt. Khim., 1969, 10, 142.

100. M. A. Sokal'skii, G. I. Drozd, M. A. Landau and S. S. Dubov, Zhur. strukt. Khim., 1969, 10, 1113.

101. G. I. Drozd, M. A. Sokal'skii, M. A. Landau and S. Z. Ivin, Zhur. obshchei Khim., 1969, 39, 1888.

102. G. I. Drozd, S. Z. Ivin, M. A. Landau and V. V. Sheluchenko, Zhur. obshchei Khim., 1968, 38, 1654.

103. J. J. Harris and B. Rudner, J.Org. Chem., 1968, 33, 1392.

104. J. S. Harman and D. W. A. Sharp, Inorg. Chem., 1971, 10, 1538.

105. R. Schmutzler, J. Amer. Chem. Soc., 1964, 86, 4500.

106. R. Schmutzler, J. Chem. Soc., 1965, 5630.

107. J. A. Pople, W. G. Schneider and H. J. Bernstein, in "High Resolution Nuclear Magnetic Resonance", McGraw Hill, New York, 1959, p. 103.

108. K. B. Wiberg and B. J. Nist in "Interpretation of N.M.R. Spectra", W. A. Benjamin Inc., New York, 1962.

109. J. W. Emsley, J. Feeney and L. H. Sutcliffe, in "High Resolution N.M.R. Spectroscopy", Pergamon Press, 1967, vol.,1, p. 310.

110. R. M. Lyndon-Bell and R. K. Harris, in "Nuclear Magnetic Resonance Spectroscopy", Nelson, 1969, p. 60.

111. R. S. Berry, J. Chem. Phys., 1960, 32, 933.

112. E. L. Muetterties, W. Mahler, K. J. Packer and R. Schmutzler, Inorg. Chem., 1964, 3, 1298.

113. F. N. Tebbe and E. L. Muetterties, Inorg. Chem., 1968, 7, 172.

114. G. Binsch, in "Topics in Stereochemistry", ed. E. L. Eliel and N. L. Allinger, Interscience, London and New York, 1969, vol. 3, pp 97-192.

115. H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys., 1953, 21, 279.

116. E. L. Muetterties and W. D. Phillips, J. Amer. Chem. Soc., 1959, 81, 1084.

117. W. Mahler and E. L. Muetterties, J. Chem. Phys. 1960, 33, 636.

118. R. R. Holmes and Sr. R. M. Deiters, Inorg. Chem. 1968, 7, 2229.

119. E. L. Muetterties and R. A. Schunn, Quart. Rev., 1966, 20, 245.

120. E. L. Muetterties, Inorg. Chem., 1965, 4, 769.

121. L. S. Bartell and K. W. Hansen, Inorg. Chem., 1965, 4, 1775.

122. A. J. Downs and R. Schmutzler, Spectrochim. Acta., 1965, 21, 1927.

123. L. S. Bartell and K. W. Hansen, Inorg. Chem., 1965, 4, 1777.

124. J. E. Griffiths, J. Chem. Phys., 1968, 49, 1307.

125. E. A. Cohen and C. D. Cornwell, Inorg. Chem., 1968, 7, 398.

126. R. R. Holmes and M. Fild, J. Chem. Phys., 1970, 53, 4161.

127. M. Fild and R. R. Holmes., Inorg. Chem., 1971, 10, 1109.

128. A. H. Norbury, S. C. Peake and R. Schmutzler, Spectrochim. Acta., 1971, 27, 151.

129. M. J. C. Hewson, S. C. Peake and R. Schmutzler, Unpublished Results.

130. R. M. Silverstein, E. Ryskiewicz and C. Williard, Org. Synth., 36, 75.

131. A. J. Castro, J. F. Deck, M. T. Hugo, E. J. Lowe, J. P. Marsch and R. J. Pfeiffer, J. Org. Chem., 1963, 28, 857.

132. J. Nagy, P. Hencsei and E. Gergö, Z. anorg. allg. Chem., 1969, 367, 295.

133. M. J. C. Hewson, S. C. Peake and R. Schmutzler, Chem. Comms. 1971, in press.

134. M. Yokoyama, H. Cho and M. Sakuma, Kogyo. Kagaku. Zasshi., 1963, 66, 422.

135. A. M. Ficquelmont, Ann. Chim. (Rome), 1939, 12, 169.

136. C. D. Schmulbach and V. R. Miller, Inorg. Chem., 1966, 5, 1621.

137. H. Bode and H. Bach, Chem. Ber., 1942, 75, 215.

138. D. Lipkin, U.S. Pat., 2,109,491 (1938). Chem. Abs., 1938, 32, 3144.

139. D. Lipkin, U.S. Pat., 2,192,921 (1940). Chem. Abs., 1940, 34, 4836.

140. M.Yokoyama, Nippon Kagaku. Zasshi., 1959, 80, 1192.

141. B. W. Fitzsimmons and R. A. Shaw, Chem. and Ind., 1961, 109.

142. D. Dell, B. W. Fitzsimmons and R. A. Shaw, J. Chem. Soc., 1965, 4070.

143. K. Hills and R. A. Shaw, J. Chem. Soc., 1964, 130.

144. V. B. Tolstoguzov, V. V. Pisarenko, and V. V. Kireev, Zhur. neorg. Khim., 1965, 10, 712.

145. M. R. Pitina, T. M. Ivanova and N. T. Shvetsov-Shilovskii, Zhur. obshchei.Khim. 1967, 37, 2076.

146. S. M. Zhivukhin, V. B. Tolstoguzov and S. I. Belykh, Zhur. neorg. Khim., 1964, 9, 134.

147. S. M. Zhivukhin, V. B. Tolstoguzov and A. I. Ivanov, Zhur. neorg. Khim., 1962, 7, 2192.

148. S. I. Belykh, S. M. Zhivukhin, V. V. Kireev and G. S. Koleonikov, Russ. J. Inorg. Chem., 1969, 14, 668.

149. C. E. Brion and N. L. Paddock, J. Chem. Soc. (A), 1968, 392.

150. C. E. Brion and N. L. Paddock, J. Chem. Soc. (A), 1968, 388.

151. G. E. Coxon, T. F. Palmer and D. B. Sowerby, Inorg. Nuclear Chem. Letters, 1966, 2, 215.

152. G. E. Coxon, T. F. Palmer and D. B. Sowerby, J. Chem. Soc. (A), 1967, 1568.

153. G. E. Coxon and D. B. Sowerby, J. Chem. Soc. (A), 1967, 1566.

154. N. L. Paddock and A. C. Chapman, J. Chem. Soc., 1962, 635.

155. J. Emsley, J. Chem. Soc. (A), 1970, 109.

156. S. Lanoiux, J. Inorg. Nuclear Chem., 1971, 33, 279.

157. C. W. Tulloch and D. D. Coffmann, J. Org. Chem., 1960, 25, 2016.

158. E. L. Muetterties, T. A. Bither, M. W. Farlow and D. D. Coffmann, J. Inorg. Nuclear Chem., 1960, 16, 52.

159. E. L. Muetterties and W. Mahler, Inorg. Chem., 1965, 4, 119.

160. R. Schmutzler, Inorg. Chem., 1968, 7, 1327.

161. W. Stadelmann, O. Stelzer and R. Schmutzler, Z. anorg. allg. Chem., 1971, in press.

162. S. S. Chan and C. J. Willis, Canad. J. Chem., 1968, 46, 1237.

163. J. Jander, M. Börner and M. Engelhardt, Annalen, 1969, 726, 19.

164. S. Z. Ivin, K. V. Karavanov, V. V. Lysenko and T. N. Losina, Zhur. obshchei Khim., 1966, 36, 1246.

165. R. Schmutzler, (to E. I. Dupont de Nemours & Co., Inc.), U.S. Pat., 3,300,503 (1967).

166. S. W. Kantor and R. C. Osthoff, Inorg. Synth., 1957, 5, 58.

167. E. W. Abel and G. R. Wiley, J. Chem. Soc., 1964, 1528.

168. R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray and R. Schmutzler, Ber. Bunsengesellschaft Phys. Chem., 1971, in press.

169. R. J. Singer and R. Schmutzler, Unpublished Results.

170. E. S. Kozlov and B. S. Drach, Zhur. obshchei Khim., 1966, 36, 760.

171. B. S. Drach and I. N. Zhmurova, Zhur. obshchei Khim., 1967, 37, 892.

172. M. Becke-Goehring, H. J. Wald and H. Weber, Naturwiss., 1968, 55, 491.

173. M. Becke-Goehring and H. Weber, Z. anorg. Chem., 1969, 365, 185.

174. M. Becke-Goehring and H. J. Wald, Z. anorg. Chem., 1969, 371, 88.

175. M. Becke-Goehring, Chem.-Ztg., 1970, 94, 179.

176. R. Schmutzler, (to E. I. Dupont de Nemours & Co., Inc.), U.S. Pat., 3,287,406 (1966).

177. A. J. Downs, Chem. Comms., 1967, 628.

178. M. P. Yagupsky, Inorg. Chem., 1967, 6, 1770.

179. P. Diehl, R. K. Harris and R. G. Jones, in "Progress in N.M.R. Spectroscopy", Pergamon Press, Oxford and New York, 1967, vol. 3.

180. R. K. Harris and C. M. Woodman, Mol. Phys., 1966, 10, 437.

181. T. Kennedy and D. S. Payne, J. Chem. Soc., 1960, 4126.

182. T. Kennedy and D. S. Payne, J. Chem. Soc., 1959, 1228.

183. L. Kolditz, Z. anorg. Chem., 1956, 284, 144.

184. R. R. Holmes, J. Chem. Educ., 1963, 40, 125.

185. J. M. Hulme, L. A. Liberish, D. W. Pound and G. S. Hartley, Britsh Pat., 700,322 (1955).

186. L. Kolditz and K. Bauer, Z. anorg. Chem., 1959, 302, 241.

187. M. Murray and R. Schmutzler, Z.Chem., 1968, 8, 241.

188. N. B. Colthup, L. H. Daly and S. E. Wiberly, in "Introduction to Infrared and Raman Spectroscopy", Academic Press, London and New York, 1964, p. 301.

189. H. Koop and R. Schmutzler, J. Fluorine. Chem., 1971, in press.