TOPICS IN
PHOSPHORUS-FLUORINE
CHEMISTRY

"Everything's got a moral,
if only you can find it."

— Lewis Carroll

THESIS

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by

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DEDICATED TO THE PARENTS
THAT HAVE TOLERATED ME.

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if only you can find it."

- Lewis Carroll

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ABSTRACT

The reactions between primary amines and phosphorus pentafluoride were complex and yielded alkylammonium hexafluorophosphates, $RNH_3^+ PF_6^-$ (R = Me, Et, Bu^t), and bis(alkylamino)trifluorophosphoranes, $(RNH)_2PF_3$ (R = Me, Et, Bu^t). In addition a 2:1 adduct, $2MeNH_2.PF_5$, was formed in the reaction with methylamine whereas 1:1 adducts, $RNH_2.PF_5$ (R = Et, Bu^t), were produced with ethylamine and t-butylamine. The preparation of alkylaminotetrafluorophosphoranes, $RNHPF_4$ (R = Et, Bu^t), by the thermal decomposition of the 1:1 adducts was studied. Methylaminotetrafluorophosphorane could be prepared by the reaction between methylaminotrimethylsilane, $Me_3SiNHMe$, and phosphorus pentafluoride.

The formation of diazafluorodiphosphetidines from alkylaminofluorophosphoranes was studied. Phosphorus pentafluoride and phenyltetrafluorophosphorane reacted with $(MeNH)_2PF_3$ to give $(F_3PNMe)_2$ and $PhF(F_2PNMe)_2$ respectively, but the yield of these products was low.

The reaction between primary amines and phosphorus trifluoride proceeded by a two step process. Alkylaminodifluorophosphines, $RNHPF_2$ (R = Me, Et, Bu^t, Bu^n), were formed in the initial step. The nature of the subsequent step is believed to depend on the steric properties of the attacking amine. Bis(alkylamino)difluorophosphoranes, $(RNH)_2PF_2H$ (R = Me, Et, Bu^n), were usually isolated,

but the bulky t-butylamine produced bis(t-butylamino)fluorophosphine, $(Bu^tNH)_2PF$

The compounds isolated above were characterised by their n.m.r., i.r. and mass spectra. Several fragmentation modes for molecules of the type RNHP(F) are discussed. Infra-red correlations for the RNH-P group are also made. The bulk of the evidence suggests that the extra molecule of amine in $2MeNH_2.PF_5$ is co-ordinated to the 1:1 adduct by means of N---H hydrogen-bonding.

Several routes to produce PNP bridges were investigated. Difluorophosphino(tetrafluorophosphoranyl)methylamine, PF_2NMePF_4, was best prepared from the reaction between phosphorus pentafluoride and difluorophosphino(trimethylsilyl)methylamine, $Me_3SiNMePF_2$, which was itself prepared from the reaction between heptamethyldisilazane and chlorodifluorophosphine. A similar reaction between POF_3 and $Me_3SiNMePF_2$ only gave low yields of difluorophosphino(difluorophosphoryl)methylamine, $PF_2NMePOF_2$. The latter was more conveniently synthesized from chlorodifluoro phosphine and methylaminophosphoryl difluoride, $MeNHPOF_2$. The ease of reaction between $Me_3SiNMeX$ (X = P(F), $SiMe_3$) and a phosphorus-fluoride could be correlated with the Lewis basicity of the former and the Lewis acidity of the latter. The spectroscopic properties of the bridged compounds produced were examined.

Attempts to prepare PNS bridges by the above routes failed, and possible reasons for this are discussed. The products isolated

from the reaction of SOF_2 with either $MeNHPF_2$ or $Me_3SiNMePF_2$ included methylaminothiophosphoryl difluoride, $MeNHPSF_2$, and $MeNHPOF_2$, which were fully characterised.

The addition of $HPSF_2$ to alkenes took place at room temperature under the influence of U.V. light to give alkylphosphonothioic difluorides, $RPSF_2$ (R = Et, Pr^n, Bu^n), which were fully characterised. Evidence is presented which suggests that the ease of the U.V. induced addition of a phosphorus-halide to an alkene depends on the strength of the P-X (X = F, Cl, Br) bonds in the latter compound. It proved possible to isolate and characterise 2-bromoethylphosphonic difluoride, $BrC_2H_4POF_2$, from the reaction between ethylene and bromophosphoryl difluoride.

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* This includes a list of abbreviations used throughout the text.

CHAPTER I

THE REACTIONS OF PHOSPHORUS-FLUORIDES WITH AMINES.

INTRODUCTION

The preparation and characterisation of phosphorus-fluorine-nitrogen compounds has been the subject of much work in recent years. The first summary of this research is included in the comprehensive review on the fluorides of phosphorus written by Schmutzler in 1965 [1]. Since then, a sufficiently rapid growth has been experienced in the study of F-P-N compounds to warrant a new review [2], which has emphasized the swing in interest away from work on the derivatives of the more stable four co-ordinated phosphorus. The main new developments listed were, (a) the increased use of fluorophosphines as ligands in transition metal chemistry and (b)the preparation of pentaco-ordinated compounds,mainly with a view to examining their structure [3].

The chemistry of phosphorus pentafluoride is dominated by its behaviour as a Lewis acid, and many examples of 1:1 adducts are known [1]. The stability of the latter indicate that PF_5 is a slightly weaker Lewis acid than BF_3, probably because of crowding around the phosphorus atom in the hexa-co-ordinated state [1]. Adducts of PF_5 and nitrogen-containing Lewis bases were first studied stoichiometrically by Johnson [4] who found, on the basis of manometric measurements, that adducts of the type $nNH_3.PF_5$ (n=1-4) existed in the

NH_3-PF_5 system. A very recent study has indicated that $(NH_2)_2PF_3$ can also be isolated from this system; no evidence for the formation of NH_2PF_4 was given [5]. The adduct formed between PF_5 and trimethylamine has been confirmed to be a 1:1 adduct both in the solid state and in acetonitrile solution by ebulliometric and n.m.r. studies [6,7], despite allegations, on the basis of conductivity data and hydrolysis studies, that these adducts existed as ions in solution [8,9]. Dimethylamine likewise has been shown to form a 1:1 complex with PF_5 in toluene solution [10,11]; it is thermally stable at room temperature but decomposes when heated to 100-120°, forming dimethylaminotetrafluorophosphorane and dimethylammonium hexafluorophosphate,

$$2\ Me_2NH.PF_5 \xrightarrow{\Delta} Me_2NPF_4 + Me_2NH_2^+\ PF_6^-$$

Bis(dimethylamino)trifluorophosphorane can be prepared from the reaction of excess amine with either PF_5 or Me_2NPF_4; the latter reaction is thought to proceed via the unstable complex $Me_2NH.Me_2NPF_4$,

$$\begin{tikzcd}
2\ Me_2NPF_4 \arrow[r, "RT"] & (Me_2N)_2PF_3 + PF_5 \arrow[d, "Me_2NH"] \\
& Me_2NH.PF_5
\end{tikzcd}$$

Further reaction between $(Me_2N)_2PF_3$ and dimethylamine did not take place [11].

Sulphur tetrafluoride, which is isoelectronic with phosphorus pentafluoride, was found to react with dimethylamine to give mainly oils and solid products [12,13] from which none of the expected dimethylaminosulphur trifluoride, Me_2NSF_3, could be isolated. On the other hand SF_4 has been shown to react with methylamine to eliminate two moles of HF and form methyliminosulphur difluoride, $MeN{=}SF_2$ [14]. The reaction between PF_5 and methylamine in the presence of trimethylamine has been studied [15]; 2,2,2,4,4,4-hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosphacyclobutane (henceforth referred to as diazafluorodiphosphetidine) was isolated,

$$6\ PF_5 + 2\ MeNH_2 + 4\ Me_3N \longrightarrow (F_3PNMe)_2 + 4\ Me_3NH^+\ PF_6^-$$

During the course of the work presented here, Harris and Rudner published the results of their observations on the reactions of PF_5 with primary amines (aniline, 2,4-dimethylaniline, 2,6-dimethylaniline, 2,6-diethylaniline, o-phenylenediamine, n-propylamine, i-propylamine and t-butylamine) [16]. A wide range of products were formed under a variety of reaction conditions. Reactions were performed both in the presence and absence of solvents and/or triethylamine. They presented positive proof for the existence of diazadifluorodiphosphetidines, alkyl(aryl)aminotetrafluorophosphoranes ($RNHPF_4$), 1:1 alkyl(aryl)-amine-phosphorus pentafluoride adducts ($RNH_2.PF_5$), and alkyl(aryl)ammonium hexafluorophosphate salts ($RNH_3^+\ PF_6^-$), but only slight evidence for the existence of the further substituted fluorophosphoranes ,$(RNH)_nPF_{5-n}$ and alkylammonium salts of the monosubstituted hexafluorophosphate anion, $(RNHPF_5)^-$. Since then, further reactions have been performed between monoalkylamines and fluorophosphoranes. The latter include dialkyltrifluorophosphoranes [17,18], phenyltetrafluorophosphorane [19,20] and dialkylaminotetrafluorophosphoranes [21] which are found to undergo replacement of one fluorine atom by an amino group. Alkyltetrafluorophosphoranes lose either one or two fluorine atoms [17,18,22].

In contrast to PF_5, phosphorus trifluoride is only a very weak Lewis acid and it is the donor properties of this compound which are best known, especially where it is co-ordinated to a transition metal [1,23]. However, a study of the PF_3-Me_3N system has revealed that a 1:1 adduct, stable only in the non-gaseous state below room temperature, was formed [24]. It has been assumed that similar adducts were intermediates in the reaction of PF_3 with Me_2NH [25-7]. Both gas and liquid phase reactions have indicated that the main reaction is represented by the equation:

$$2\ PF_3 + 3\ Me_2NH \longrightarrow Me_2NPF_2 + Me_2NH_2^+\ HF_2^-$$

The dimethylaminodifluorophosphine formed was less susceptible to substitution than PF_3 and the temperature had to be raised to 50° to produce bis(dimethylamino)fluorophosphine [25]. The only published work dealing with the reaction of PF_3 and primary amines is that by Drozd and his co-workers [28]. They claim that alkylaminodifluorophosphines, $RNHPF_2$ ($R=Pr^n$, Pr^i), are among the products formed but evidence, to be presented later, tends to disagree with their conclusions. Nixon has investigated a route to $MeNHPF_2$ which involves cleavage of the P-C bond in trichloromethyldifluorophosphine with methylamine [29]:

$$MeNH_2 + CCl_3PF_2 \longrightarrow MeNHPF_2 + CCl_3H$$

An alternative synthesis involved the cleavage of the P-N bond in bis(difluorophosphino)methylamine with methylamine [29]:

$$MeNH_2 + (PF_2)_2NMe \longrightarrow 2\ MeNHPF_2$$

Methylamine was found to be capable of replacing all the fluorine atoms attached to phosphorus in $PF_3.BH_3$ according to the equation [30]:

$$2\ MeNH_2 + BH_3.(MeNH)_xPF_{3-x} \longrightarrow MeNH_3^+\,F^- + BH_3.(MeNH)_{x+1}PF_{2-x} \qquad (x = 0\text{–}2)$$

The actual extent to which this took place depended on the experimental conditions employed. Reaction of the adduct formed with trimethylamine resulted in the formation of the adduct $BH_3.Me_3N$ for x=0, but not for x=1; the $MeNHPF_2$ thus displaced was not characterised.

The reactions of primary amines with alkoxyfluorophosphines [31], dialkylaminodifluorophosphines [31] and alkyl(aryl)difluorophosphines [32-5] have been studied. Methyldifluorophosphine reacted with primary amines to produce low or non-existent yields of methyl(alkylamino)fluorophosphine, MePFNHR ($R = CH_2{=}CHCH_2$), along with the main product which was methyl(alkylamino)difluorophosphorane, $MePF_2(NHR)H$ ($R = Pr^i$, Bu^i, $CH_2{=}CHCH_2$, cyclohexyl). Alkoxyfluorophosphines and dialkylaminodifluorophosphines react similarly. On prolonged heating at 70° in the presence of a base, $MePF_2(NHR)H$ ($R = Pr^i$, Bu^i) dehydrofluorinated to MePF(NHR) [28]. In the reaction between phenyldifluorophosphine and isobutylamine, $PhPF(NHBu^i)$ was produced together with a distillable not very well characterised adduct, $PhPF(NHBu^i).HF$ [35].

RESULTS

REACTIONS BETWEEN PHOSPHORUS PENTAFLUORIDE AND PRIMARY AMINES.

Phosphorus pentafluoride reacts with methylamine in the liquid phase below room temperature to give a volatile liquid bis(methylamino)trifluorophosphorane, $(MeNH)_2PF_3$, and a solid mixture consisting of bis(methylamine)-phosphorus pentafluoride adduct, $2MeNH_2.PF_5$, and methylammonium hexafluorophosphate, $MeNH_3^+ PF_6^-$, which can be separated by sublimation. With ethylamine and t-butylamine a similar mixture of reaction products is obtained, from which di(alkylamino)trifluorophosphoranes, $(RNH)_2PF_3$ (R = Et, Bu^t), alkylamine-phosphorus pentafluoride adducts, $RNH_2.PF_5$ (R = Et, Bu^t), and alkylammonium hexafluorophosphates, $RNH_3^+ PF_6^-$ (R = Et, Bu^t), are isolated. Several primary amine adducts of PF_5 were reported to act as curing agents for epoxy resins, but synthetic and structural details were not given [36]; amines studied included ethylamine, isopropylamine, butylamine and benzylamine. Adducts reported by Harris et al. were isolated in some cases (with aniline, 2,6-dimethylaniline, and n-propylamine) but not in others (with 2,6-diethylaniline and isopropylamine) [16]. Evidence, to be presented later, suggests that $2MeNH_2.PF_5$ is the first authentic 2:1 adduct in which the PF_5 entity has been proved to remain intact. While amine salts of hexafluorophosphoric acid are well known, few reports of salts of primary amines existed prior to Harris' work. Ethylammonium hexafluorophosphate is mentioned in the patent literature as a herbicide [37] and t-butylammonium hexafluorophosphate has been reported by Harris et al. [16] and had its infra-red spectrum catalogued [38]. However, details concerning the preparative conditions were not reported for either compound. Harris has also cited tentative evidence for the existence of bis(arylamino)trifluorophosphoranes, but made little attempt to characterise them.

Thermal decomposition of the 1:1 adducts of ethylamine and t-butylamine with PF_5 gives a mixture of alkylaminotetrafluorophosphorane, $RNHPF_4$ ($R = Et, Bu^t$), and alkylammonium hexafluorophosphate:

$$2 \quad RNH_2.PF_5 \xrightarrow{\Delta} RNHPF_4 \quad + \quad RNH_3^+ \, PF_6^- \qquad (R = Et,\ Bu^t)$$

Harris reported that the compounds $RNHPF_4$ ($R = 2,4\text{-}Me_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}Et_2C_6H_3$, Pr^i) were among the reaction products of PF_5 and the appropriate primary amine.

The isolation of $MeNHPF_4$ by an analogous route is not possible, since the extra molecule of methylamine in the bis(methylamine)-phosphorus pentafluoride adduct reacts with the methylaminotetrafluorophosphorane immediately it is formed. Methylamine and bis(methylamino)trifluorophosphorane are, therefore, the only volatile adducts isolated. Thermal decomposition is in accordance with the equation:

$$3 \quad 2MeNH_2.PF_5 \xrightarrow{\Delta} (MeNH)_2PF_3 \ + \ 2 \quad MeNH_3^+ \, PF_6^- \ + \ 2 \quad MeNH_2$$

The mass spectrum obtained by placing the adduct directly on the instrument's probe is that of the products obtained by thermal decomposition. The spectrum shows that the high mass portion is almost identical with that of $MeNHPF_4$, while the low mass region (reproduced in Fig. 1.1) arises from the superpositioning of the mass spectra of $MeNHPF_4$ and $MeNH_2$. The line diagram for the methylamine spectrum is obtained from the data given by Gohlke et al. [39]. The preparation of $MeNHPF_4$ will be dealt with in Chapter 2, and its mass spectrum will be discussed in detail at the end of this chapter.

The alkylaminotetrafluorophosphoranes prepared are colourless liquids with an appreciable vapour pressure at room temperature. If stored over a long period, they decompose to form colourless crystals. The infra-red spectum of the volatile material, which remains after leaving $MeNHPF_4$ in a sealed tube for six months, reveals that some $(F_3PNMe)_2$ is also formed. Harris reported that arylaminotetrafluorophosphoranes, with their bulkier substituents, were more stable than alkylaminotetrafluorophosphoranes at room temperature [16]. No other evidence was found in the work presented above for the production of diazafluordiphosphetidines, $(F_3PNR)_2$, or alkylammonium alkylaminopentafluorophosphate salts, $RNH_3^+ (RNHPF_5)^-$.

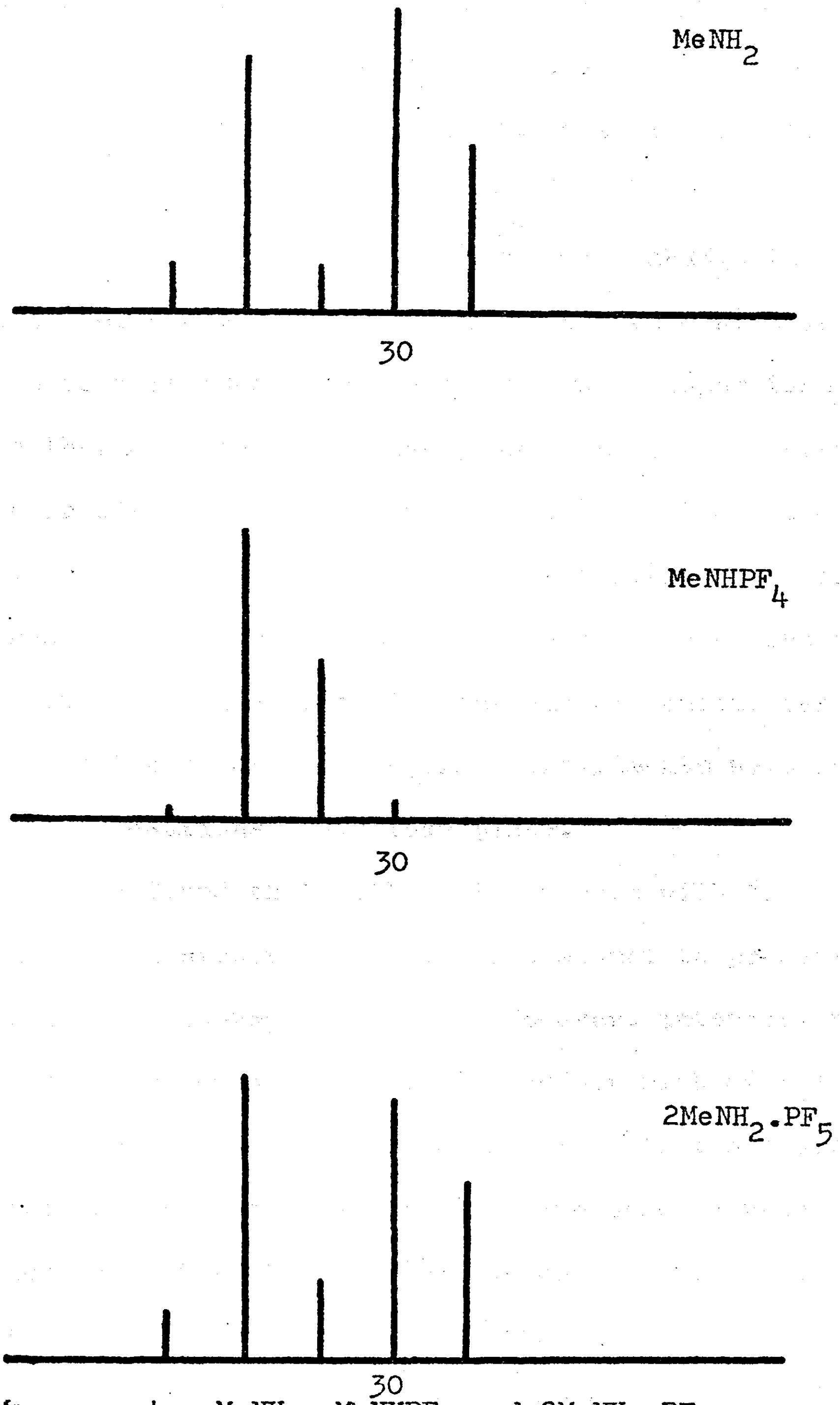


Fig. 1.1 Mass spectra $MeNH_2$, $MeNHPF_4$ and $2MeNH_2.PF_5$.

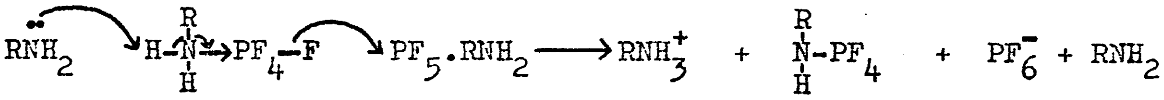
MECHANISM FOR REACTIONS.

On the basis of the previous work reported for the reactions of amines with phosphorus pentafluoride it is reasonable to assume that the amine initially interacts with the PF_5 to form an adduct:

$$n\ RNH_2 \quad + \quad PF_5 \xrightarrow{-78^\circ} nRNH_2.PF_5$$

In view of the discrepancy between the temperature at which the reaction is performed, and the much higher temperatures ($\sim 140^\circ$) required to thermally decompose these adducts, the next step is unlikely to involve simple disproportionation of the adduct. By the very nature of the manner in which the reaction is performed, amine is present in excess for most of the reaction; thus it appears likely that amine attack on the adduct constitutes the second stage of the reaction. Separate experiments were performed to see if these reactions would take place.

It is indeed found that methylamine reacts with the bis(methylamine)-phosphorus pentafluoride adduct to produce bis(methylamino)trifluorophosphorane. However, interaction of the ethylamine-phosphorus pentafluoride adduct with methylamine produces a mixture of the two compounds, bis(methylamino)trifluorophosphorane and bis(ethylamino)trifluorophosphorane, and not the mixed product $(EtNH)(MeNH)PF_3$ which is expected if the P-N bond remained intact. From steric considerations, nucleophilic attack on the adduct by free amine seems more likely to take place at the amino-proton than at the phosphorus atom. A concerted mechanism can be written:



$$\mathrm{R\ddot{N}H_2} \quad \mathrm{H\text{-}\overset{R}{\underset{H}{N}}\rightarrow PF_4\text{-}F} \quad \mathrm{PF_5\cdot RNH_2} \longrightarrow \mathrm{RNH_3^+} + \mathrm{\overset{R}{\underset{H}{N}}\text{-}PF_4} + \mathrm{PF_6^-} + \mathrm{RNH_2}$$

The alkylaminotetrafluorophosphoranes thus formed will be further attacked by another molecule of amine unless this is sterically impossible. A separate experiment shows that t-butylamine will react with t-butylaminotetrafluorophosphorane in agreement with the equation:

$$3\ \mathrm{RNHPF_4} + 2\ \mathrm{RNH_2} \longrightarrow 2\ \mathrm{(RNH)_2PF_3} + \mathrm{RNH_3^+\,PF_6^-}$$

This reaction is likely to proceed via a 1:1 adduct of amine and alkylaminotetrafluorophosphorane. These adducts are expected to be considerably less stable than those formed with PF_5 on account of the poor Lewis acidity of the fluorophosphorane. This reduction in Lewis acidity has previously been demonstrated for a series arylfluorophosphoranes [40].

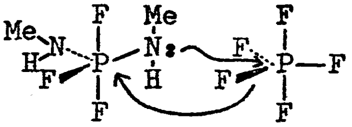
Trans-amination reactions have been reported before [41], and it is probably at this stage of the reaction that they are most likely to occur. Work has shown that a strongly basic amine and electron-withdrawing substituents on phosphorus, i.e. conditions promoting adduct formation, enhanced trans-amination rates in P(III)-N systems [41]. Thus it would prove instructive to observe if the product distribution could be predicted on the basis of the amine and the alkylaminotetrafluorophosphorane employed. While bis(alkylamino)trifluorophosphoranes were observed not to undergo further displacement of fluorine - a similar state of affairs to that noted for bis(dialkylamino)trifluorophosphoranes [10] - it has not yet been demonstrated whether or not trans-amination reactions involving trifluorophosphoranes are feasible.

The work reported by Harris et al. fits in well with the above general reaction scheme. Large yields of the 1:1 adduct were isolated by using a solvent, low reaction temperatures ($\sim 0^{\circ}$), and short reaction times, in order to minimize the contact between the adduct and the excess starting material. It appears that a high yield of adduct in the absence of a solvent could best be obtained by performing a gas phase reaction, in which the amine is added to the phosphorus pentafluoride.

DIAZAFLUORODIPHOSPHETIDINE FORMATION.

Harris et al. found that reactions carried out in the presence of excess PF_5 and a tertiary amine promoted the formation of diazafluorodiphosphetidine [16]. It is found that phosphorus pentafluoride reacts with methylaminotetrafluorophosphorane both in the presence and absence of triethylamine to form $(F_3PNMe)_2$. t-Butylaminotetrafluorophosphorane is more stable in the presence of PF_5 than the methylamino analogue and even at 40° this reaction is slow. Examination of the solid products showed no indication for the formation of $(F_3PNBu^t)_2$, which was isolated as a solid in the reaction between PF_5 and t-butylamine only when excess Et_3N was present [16].

In the reaction between bis(methylamino)trifluorophosphorane and PF_5 a small amount of $MeNHPF_4$ is isolated along with some solid products, showing that a methylamino group can exchange with a fluorine atom possibly via the intermediate adduct:



A small amount of $(F_3PNMe)_2$ and some $MeNHPF_4$ are also isolated on heating up the solid formed.

The products obtained from the reaction between bis(methylamino)-trifluorophosphorane and an approximately equimolar quantity of phenyltetrafluorophosphorane similarly show evidence for exchange processes occurring. Phenyl(methylamino)trifluorophosphorane, $PhPF_3(NHMe)$, and diazafluorodiphosphetidine, $(F_3PNMe)_2$, are both identified among the volatile products. Diphenyldiazafluorodiphosphetidine, $(PhF_2PNMe)_2$, is found along with $MeNH_3^+ PF_6^-$ and some $nMeNH_2.PF_5$ ($n = 1$ or 2) in the solid residue. A liquid which moves with difficulty under vacuum was identified as monophenyldiazafluorodiphosphetidine, $PhF(F_2PNMe)_2$, contaminated with $PhPF_3(NHMe)$. These products can be visualized as being derived via a series of loose adducts which are capable of eliminating HF and exchanging methylamino groups. The reactions are summarized by the following equations:-

$$2\ PhPF_4 + 2\ (MeNH)_2PF_3 \longrightarrow PhPF_3(NHMe) + PhF(F_2PNMe)_2 + MeNH_3^+\,PF_6^-$$

$$2\ PhPF_4 + 2\ (MeNH)_2PF_3 \longrightarrow (PhF_2PNMe)_2 + 2\ MeNH_2.PF_5$$

$$3\ PhPF_4 + 3\ (MeNH)_2PF_3 \longrightarrow (PhF_2PNMe)_2 + PhF(F_2PNMe)_2 + 2\ MeNH_3^+\,PF_6^-$$

Note that all the above equations require that the reactants are present in the ratio 1:1. Evidence for the existence of $PhF(F_2PNMe)_2$ is based on the following facts:-

(i) The volatility of the compound is intermediate between that of $(F_3PNMe)_2$ (m.p. -10°, b.p. 91.6°/757 mm. [42]) and $(PhF_2PNMe)_2$ (m.p. 162° [42]).

(ii) The ^1H n.m.r. spectrum (Fig. 1.2) shows (in addition to resonances due to the phenyl group) a doublet of doublets which is present in the region characteristic of MeNP groups, and is superimposed upon the N-methyl resonance of $PhPF_3(NHMe)$, a major impurity in the sample. The two coupling constants are 14.7 c/s and 12.0 c/s, close to those observed for $^3J(PH)$ in $(F_3PNMe)_2$ and $(PhF_2PNMe)_2$ respectively (see Table 1.1) indicating the existence of one kind of methyl group bonded to two phosphorus nuclei in different magnetic environments. For a cyclic compound this limits the ring size to one containing four atoms.

(iii) From the ^{19}F n.m.r. spectrum (Fig 1.3) two sets of resonances are picked out which are not related to $PhPF_3(NHMe)$. The chemical shifts nearly coincide with those found for the diphenyl- and non-substituted diazafluorodiphosphetidines

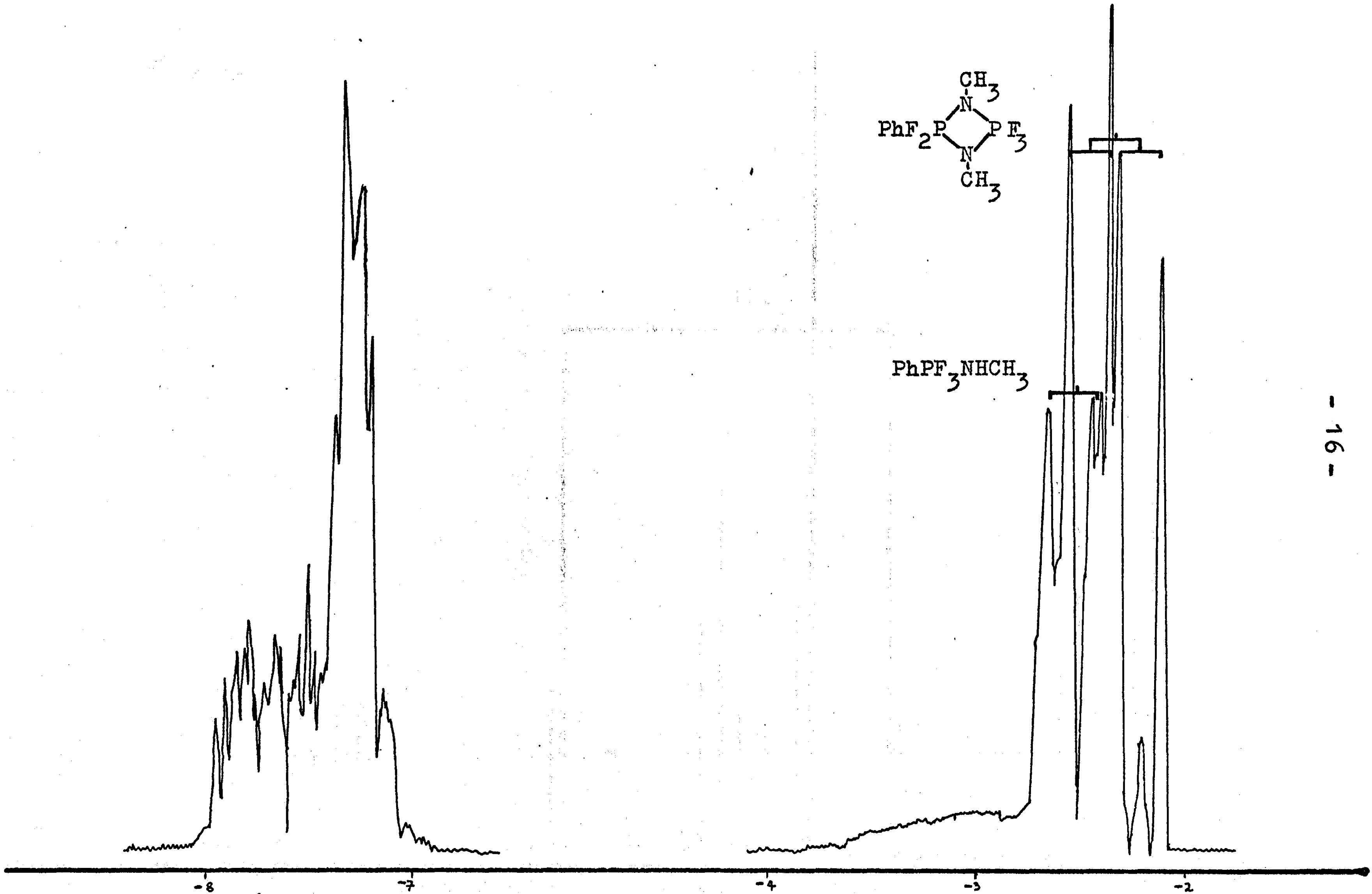


Fig. 1.2 ^{1}H n.m.r. of a mixture of PhPF$_3$NMeH and PhF(F$_2$PNMe)$_2$

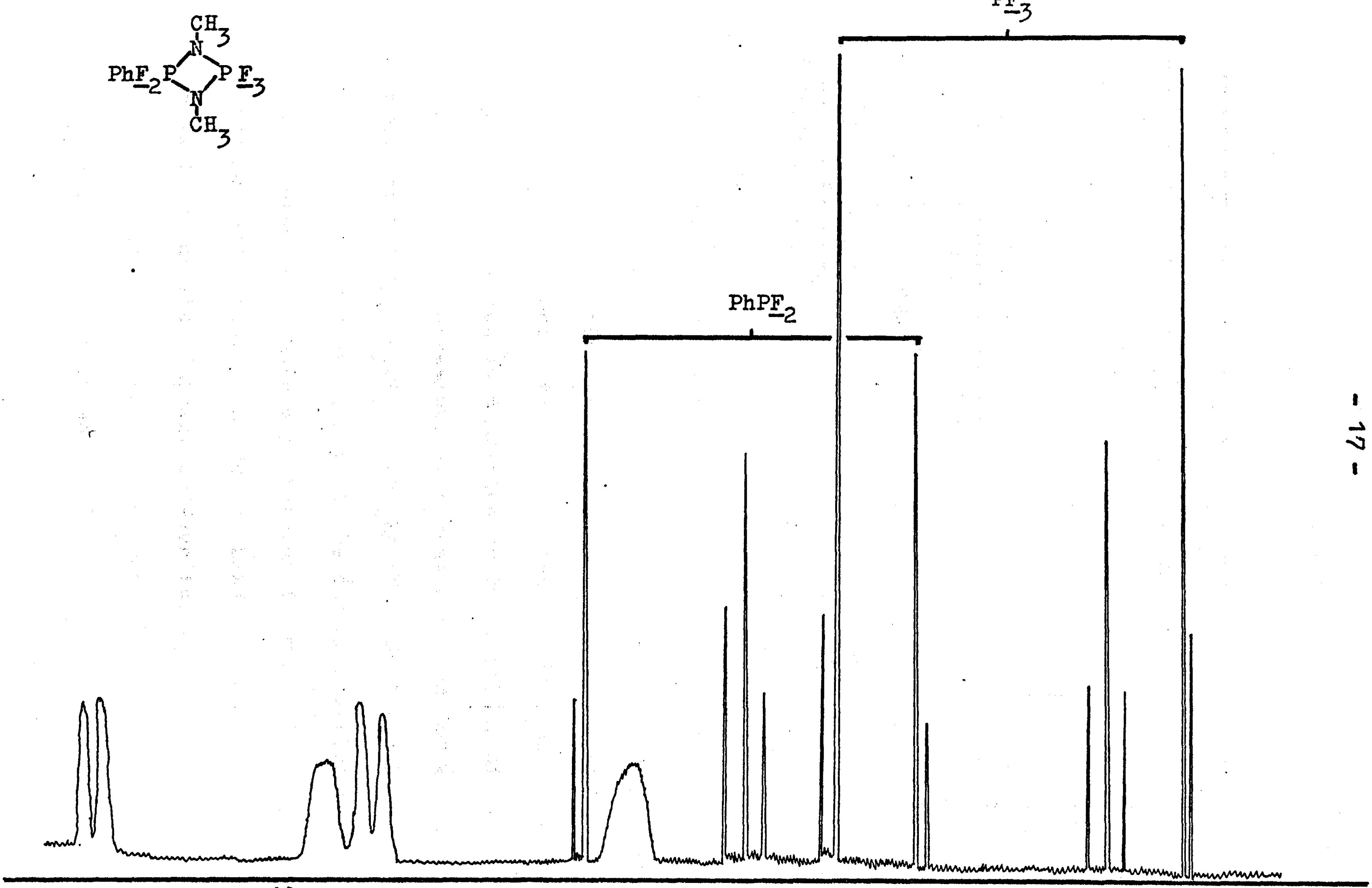


Fig. 1.3 ^{19}F n.m.r. of a mixture of $PhPF_3NMeH$ and $PhF(F_2PNMe)_2$

Table 1.1

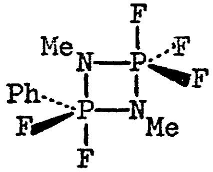
Compound	δ_{CH_3}	δ_{Ph}	δ_F	δ_P
Found *	-2.4 dd	-7.3	64.0,77.2	
$(F_3PNMe)_2$* [43]	-2.83 t		80.7	69.5
$(PhF_2PNMe)_2$* [3,42]	-2.46 t	-7.7	63.4	56.1

Compound	$^1J(PF)$	$J(PH)$	$^3J(PF)$	$^4J(FF)$	$^2J(PP)$
Found	~885,~914	14.7,12.0			
$(F_3PNMe)_2$	922	14.1	32	8.7	210
$(PhF_2PNMe)_2$	~900[a]	12.5			

[a] Obtained from ^{31}P n.m.r. spectrum.

respectively. Integration shows that the areas are in the ratio 2:3. The ^{19}F n.m.r. spectrum is then in agreement with that expected for a four-membered $(PN)_2$ ring containing one phosphorus atom which is connected to three fluorine atoms, and a second phosphorus atom which is connected to two fluorine atoms. The spectrum is not in agreement with that expected for a linear compound of the type X_2PF_2-NMe-PF_3X' (X,X' = Ph and NHMe) [3]. High resolution studies show that the two main resonances, which are associated with a particular fluorine atom environment, are further associated with smaller bands of peaks placed symmetrically about the midpoint between them. A further splitting of the two main resonances is also observed. This situation is reminiscent of that reported for $(F_3PNMe)_2$ [43].

The fluorine spectrum is then interpreted on the basis of the idealized structure given below:-



The room temperature ^{19}F spectra for the symmetrical molecules $(F_3PNMe)_2$ and $(PhF_2PNMe)_2$ indicated that the axial and equatorial fluorine atoms are indistinguishable on the n.m.r. time scale; mechanisms for this exchange process were considered by Harris and Woodman [43]. The same mechanism presumably operates for $PhF(F_2PNMe)_2$. On the basis of a first order treatment both sets of fluorine atoms should be coupled to two phosphorus atoms, and in addition both resonances should further be split by long-range F-F coupling. In $PhF(F_2PNMe)_2$ the $P\underline{F}_3$ group is split into a triplet (with the distance between the resonances, 7.6 c/s, being close to that anticipated for $^4J(FF)$) while the $PhP\underline{F}_2$ group is split into a distorted quartet. While a first order spectrum would be predicted from the fluorine spectrum parameters, since $\nu_o(\delta_{P\underline{F}_3} - \delta_{PhP\underline{F}_2})$ is large compared with $^4J(FF)$, those parameters that would be expected from the ^{31}P n.m.r. spectrum (using the data of Table 1.1) would indicate that $\nu_o(\delta_{\underline{P}F_3} - \delta_{\underline{P}F_2})$ is comparable with $^2J(PP)$, and this would produce an overall second order spectrum. As a result only approximate data for coupling constants in $PhF(F_2PNMe)_2$ are available.

While the evidence presented above is overwhelmingly in favour of the existence of $PhF(F_2PNMe)_2$, a ^{31}P n.m.r. spectrum of the products is obviously desirable. This is only the second monosubstituted derivative of diazafluorodiphosphetidine reported. Fluorination of $(Cl_3PNMe)_2$ gave a mixture of compounds $Cl_nF_{6-n}(PNMe)_2$ (n = 1-5), from which pure components have been isolated and characterised by means of analytical and i.r. studies [44]. Structural data for $(F_3PNMe)_2$ -comprising n.m.r. [43], i.r. [45-6] and an electron diffraction study [47]- and the crystal structure for $(PhF_2PNMe)_2$ [48] are all in good agreement with diazafluorodiphosphetidines possessing a similar stereochemistry, in which two slightly distorted trigonal bipyramids are linked together by means of a planar $(PN)_2$ ring. The phenyl group in $(PhF_2PNMe)_2$ occupies an equatorial site in the trigonal bipyramid [48]. The structure which has been proposed for $PhF(F_2PNMe)_2$, and has provided a satisfactory basis for explaining its n.m.r. spectra, is that which would be anticipated from the above structural data.

oOo

These results together with those of Harris et al. [16] emphasize that several competing reactions are taking place. For reactions in which steric effects are not of prime importance, the results of the reaction between primary amines and fluorophosphoranes (including PF_5) can be summarized:

(i) In the presence of excess primary amine, products are those resulting from the replacement of the maximum possible number of fluorine atoms by alkylamino groups. Dimers are not formed.
(ii) In the presence either of a tertiary base or excess fluorophosphorane, the products isolated are predominantly those resulting from intermolecular dehydrofluorination reactions.

REACTIONS BETWEEN PHOSPHORUS TRIFLUORIDE AND PRIMARY AMINES.

The reaction of PF_3 with methylamine at or below room temperature is found to be a two step process. In the first stage one fluorine atom is replaced by a methylamino group to form methylaminodifluorophosphine, $MeNHPF_2$, which possesses almost identical properties with those reported for the compound by Barlow et al. [29]. This is also the initial stage in the reaction of the other amines studied (ethylamine, n- and t-butylamine). The low stability reported for $MeNHPF_2$ at room temperature is confirmed and a mass spectrometrically pure compound was never obtained; $(F_2P)_2NMe$ is not however found to be present as an impurity, which indicates that there is no substantial equilibrium

$$2\ MeNHPF_2 \rightleftharpoons (PF_2)_2NMe + MeNH_2$$

as previously suggested [29]. An increase in the molecular weight of the alkylamino function is found to confer an increased stability on the molecule. The formation of a "pure" product is achieved only by using reaction conditions which favour minimum contact of the product with excess amine, i.e. gas or solution phase reactions are preferred.

In the presence of excess amine the reaction can follow two alternative pathways depending on the amine employed. Bis(alkylamino)-difluorophosphoranes, $(RNH)_2PF_2H$ (R = Me, Et, Bu^n), are obtained with methylamine, ethylamine and n-butylamine. The infra-red spectrum of $(MeNH)_2PF_2H$ is identical with that reported for a by-product in the initial synthesis of $MeNHPF_2$ [29]. The only other well authenticated difluorophosphorane containing two nitrogen ligands is $Me_2N(Bu^iNH)PF_2H$ [31]. The thermal stability of these difluorophosphoranes with respect to the re-formation of alkylaminodifluorophosphines is low, and again found qualitatively to be a function of their molecular weight. The stability of $(MeNH)_2PF_2H$ is such that no decomposition was recorded during the period required to take an n.m.r. spectrum but solids were found to precipitate in less than a day. Its stability is lower in the vapour phase; i.r. studies indicate the formation of $MeNHPF_2$ and a small quantity of PF_3 (vide infra). Both $(MeNH)_2PF_2H$ and $(EtNH)_2PF_2H$ are, therefore, only characterised by means of their i.r., n.m.r. and mass spectra. The reaction of t-butylaminodifluorophosphine with excess t-butylamine is found to be much slower than the analogous reaction with n-butylaminodifluorophosphine; bis(t-butylamino)fluorophosphine, $(Bu^tNH)_2PF$, is isolated from the reaction product and characterised as a low melting, easily sublimed solid, with a considerably greater thermal stability than the bis(alkylamino)difluorophosphoranes.

Alkyltrifluorophosphoranes were observed [32] to react with tertiary amines in accordance with the scheme:-

$$\begin{tikzcd}
RPF_3H + R'_3N \arrow[r] & {[R(HF_3)P \leftarrow NR'_3]} \arrow[r] & R'_3NH^+ F^- \arrow[d, "+ RPF_3H"] & + RPF_2 \\
 & & R'_3NH^+ (RPF_4H)^- &
\end{tikzcd}$$

While $(MeNH)_2PF_3$ is stable in pyridine at room temperature (pyridine is used as a solvent for n.m.r. spectra) it is found to react slowly with methylamine to precipitate solid products. On heating $(MeNH)_2PF_2H$ with Et_3N there is no evidence for dehydrofluorination to produce $(MeNH)_2PF$.

The products formed from the reaction of $MePF_2$ with alcohols are very similar to those formed from the reactions of $MePF_2$ with primary amines (vide supra) [49-51],

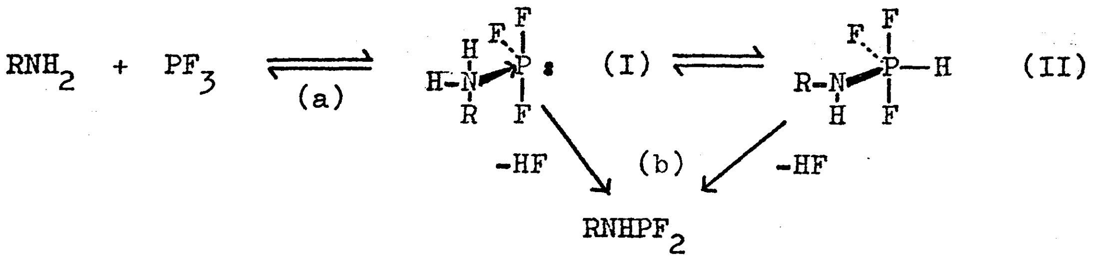
$$ROH + MePF_2 \longrightarrow MePF_2(OR)H$$

No previous reports related to the reaction of PF_3 with methanol exist, although PF_3 was observed by Moissan to react exothermally with ethanol [52]. The replacement of fluorine by alkoxy groups was later assumed to take place in these reactions [53]. Methanolysis of trifluorophosphine in iron carbonyl complexes gave a mixture of products, suggesting retention of P-Fe bonds and replacement of fluorine atoms by methoxy groups one at a time [54].

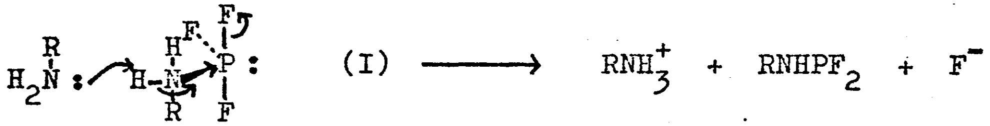
In the absence of a tertiary amine, methanol is found not to react with PF_3. In the presence of a tertiary amine, almost complete substitution of the fluorine atoms in PF_3 is found to take place, and none of the desired $(MeO)_2PF_2H$ can be isolated.

MECHANISM FOR REACTIONS.

Nucleophilic attack on P(III) is particularly facile compared with attack on a saturated carbon atom [55]. Presumably this is the initial step in all reactions between amines and tervalent phosphorus compounds. The transition state is formulated as a trigonal bipyramid in which the amine molecule and the lone pair of electrons attached to phosphorus both occupy equatorial positions (by analogy with the structures of other pentaco-ordinated compounds [56]). The stability of these complexes is low, and decomposition takes place either (a) to re-form the reactants (as was observed for the reaction between Me_3N and PF_3 [24]), or (b) to form new products by way of HF elimination. Hydrogen fluoride elimination can be visualized as taking place through two possible intermediates, I or II:-



I will probably be dehydrofluorinated by means of nucleophilic attack by a second amine molecule on the co-ordinated amine molecule, with displacement of F$^-$ from the axial position (as postulated in other nucleophilic substitution reactions at phosphorus [57]):-



Loss of HF from II probably takes place spontaneously, since a recent study by Goodrich et al. of the reaction between Me$_2$NPF$_4$ and Me$_3$SnH showed that dimethylaminotrifluorophosphorane, Me$_2$NPF$_3$H, was unstable at room temperature and readily decomposed to form Me$_2$NPF$_2$ as the only identifiable volatile product [58]. The similar postulation of five co-ordinate intermediates has recently played an important role in the rationalization of the hydrolysis rates of esters of phosphoric acid which contain five-membered rings [59].

The solids formed in these reactions were found to be insufficiently soluble in any normal solvent for their n.m.r. spectra to be recorded. By analogy with the reaction of dimethylamine and phosphorus trifluoride, which was followed stoichiometrically and produced only one volatile product, the majority of this solid product is assumed to be alkylammonium bifluoride [25],

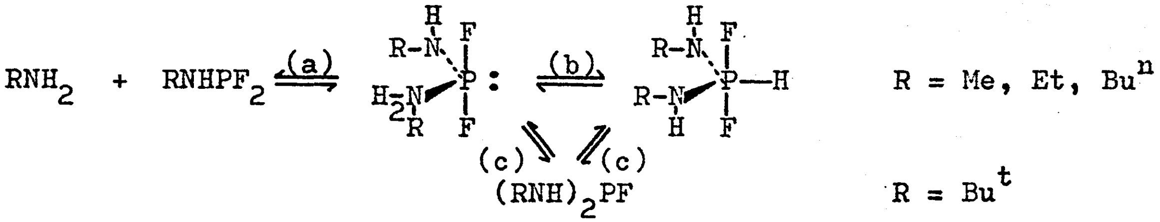
$$3\ RNH_2 + 2\ PF_3 \longrightarrow 2\ RNHPF_2 + RNH_3^+\ HF_2^-$$

However, more recent studies have indicated that some of the Me_2NPF_2 or PF_3 reacted further with the bifluoride ion to form the hydridopentafluorophosphate anion, $(HPF_5)^-$, [60]:-

$$Me_2NPF_2 + 2\ HF \longrightarrow PF_3 + Me_2NH_2^+\ F^-$$

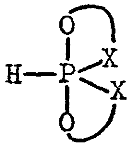
$$PF_3 + HF_2^- \longrightarrow (HPF_5)^-$$

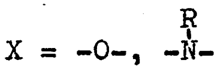
The second stage of the reaction between primary amines and PF_3 is also postulated to proceed via a trigonal bipyramidal intermediate which can decompose in three ways, (a) to reform the starting materials, (b) by means of an amino-proton migration to the phosphorus atom, or (c) by eliminating a molecule of HF. These routes are depicted below:-



Similar types of transition states have been used to rationalize the hydrolysis of PF_3 to form the unexpected hydridophosphoryl difluoride, $HPOF_2$ [61]. Effects controlling the direction of this reaction will now be considered.

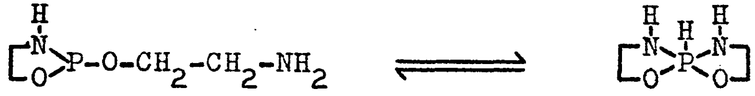
Besides the previously mentioned reactions of alkyl(aryl)-difluorophosphines to produce fluorophosphoranes [32-5], a substantial body of work has been recorded [62] on the preparation of spirophosphoranes with the general structure





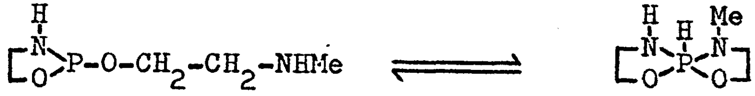
$X = -O-,\ -\overset{R}{N}-$

These were synthesized from $Me_2N\text{-}P\!<^{O}_{X}\!]$ by displacement of the dimethylamino group by an amino-alcohol. It appeared that the alcoholic end of the molecule was the better nucleophile. The P(III) compound so formed was then studied to examine the equilibrium $P(III) \rightleftharpoons P(V)$ [63]. The large difference in the ^{31}P chemical shifts of the P(III) and the P(V) states permitted an estimate of the equilibrium constant for the following two reactions:-



(III)

100 % δ_P +57



(IV)

90 % δ_P -137

10 % δ_P +63

The results shown are in agreement with the differences observed for the reaction of aminophosphines with amines, in that the P(V) state is favoured more for a primary than for a secondary amine. A general preference for a five as against a three co-ordinated compound can be justified by calculating the enthalpy changes in the above two equations. Bond energy data [Appendix 2] indicate that $D(P\text{-}N) + D(P\text{-}H) > D(N\text{-}H)$. If the energy required to re-hybridize the phosphorus atom is ignored, then the enthalpy for the reaction is found to be favourable. In going from methylamine to dimethylamine the N-H bond energy decreases, while the P-N bond energy only changes marginally on the introduction of more electron-donating groups onto the nitrogen atom. Since bond energy factors would appear, if anything, to favour stabilization of a pentaco-ordinated product containing a dialkylamino as against an alkylamino substituent some other factor must be operating which destabilizes this compound. Steric crowding is an important factor in determining the stability of pentaco-ordinated phosphorus derivatives. Thus spirophosphoranes are found to be more stable than their non-spiro analogues. While several factors will ultimately control the stability of the pentaco-ordinated molecule, it seems that the difference in stability between III and IV stems primarily from the large steric requirements of the methyl group as compared to the simple hydrogen atom. A similar reasoning will reconcile the different paths followed in the reaction of Bu^tNH_2 and Bu^nNH_2 with PF_3. The different steric requirements of the Bu^tNH- and the Bu^nNH- group are best emphasized by building Stuart models for the two possible pentaco-ordinated molecules, $(RNH)_2PF_2H$.

COMPARISON OF REACTIONS BETWEEN PRIMARY AMINES AND NON-METAL HALIDES.

The foregoing discussion has presented data to suggest that the RNHP grouping possesses considerable stability in some compounds where the phosphorus atom is bonded to fluorine. Thus alkylaminofluorophosphoranes are readily isolated under favourable reaction conditions. Disproportionation of $MeNHPF_4$ only takes place over a period of months (this may in fact be due to either kinetic or thermodynamic effects); while the solid product was not examined, a suitable equation for this process would be:-

$$3\ MeNHPF_4 \longrightarrow (F_3PNMe)_2 + MeNH_3^+\ PF_6^-$$

These results should be contrasted with those appertaining to the reactions of primary amines with other P(V) compounds, which contain a variety of ligands attached to the phosphorus atom [64-5]. A considerable bulk of work has indicated that the intermediate compounds $RNHPX_4$ are unstable with respect to disproportionation:-

$$RNHPX_4 \longrightarrow 1/n\ (X_3PNMe)_n + HX$$

The diazadiphosphetidines formed exist either as monomers or dimers,with electron-donating substituents attached to nitrogen and electron-withdrawing substituents attached to phosphorus favouring the latter species. It is found that a similar role is played by substituents attached to phosphorus in the analogous diazafluorodiphosphetidines,for an increase of m in $(Ph_mF_{3-m}PNMe)_n$ from one to two takes the structure from being a dimer to a monomer [42]. The reaction of PCl_3 with primary amines emphasizes the more facile cleavage of a P-Cl bond than a P-F bond, since in most reactions complete substitution of chlorine by nitrogen containing ligands has been reported [65]. It has, however, proved possible to isolate some compounds as representatives of $RNHPCl_2$, and it has recently been demonstrated that the latter is readily dehydrochlorinated by a tertiary amine at ambient temperatures [66],

$$Bu^tNHPCl_2 \xrightarrow{-\ HCl} \tfrac{1}{2}\ (ClPNBu^t)_2$$

Attempts to dehydrofluorinate $MeNHPF_2$ and produce an analogous product were reported to be fruitless [67].

One can apply a simplified, purely thermodynamic approach to explain the different stabilities found for these two systems. Both disproportionation reactions involve the cleavage of a P-X (X = F, Cl) bond and formation of a molecule of HX:-

$$RN\text{-}H \ + \ P\text{-}X \longrightarrow RN\text{-}P \ + \ H\text{-}X$$

Bond strength data [Appendix 2] indicate that the difference between P-F and P-Cl bond energies (46 kcal.) is larger than the difference between the H-F and the H-Cl bond energies (33 kcal.), which favours the elimination of a molecule of HCl more than a molecule of HF. There are several important assumptions which have been made in this approach:-

(i) Thermodynamic control for the system has been assumed and the possibility of kinetic control has so far not been considered.

The decomposition of $MeNHPF_4$ may be thermodynamically controlled, with the rate determining step in the decomposition process being that in which the adduct $P_dF_4N_dMeH.P_aF_4N_aHMe$ is formed. This will not only be weaker than the simple alkylamine-phosphorus pentafluoride adduct, due to (a) the decreased Lewis acidity of the phosphorus atom, P_a, due to electron donation by nitrogen, N_a, and (b) the decreased basicity at nitrogen, N_d, due to the electron withdrawal by P_d, but its formation will be hindered by steric interactions.

(ii) While HCl is liberated as a gas in the reactions of amines with PCl_5, alternative mechanisms for aiding the removal of HX are possible. Thus, in the decomposition of $MeNHPF_4$, the HF formed is probably removed by means of the reaction:-

$$MeNHPF_4 + 2\ HF \longrightarrow MeNH_3^+\ PF_6^-$$

Thermodynamic data are not available to estimate a value for the enthalpy change in such a reaction but there is no doubt that, in this particular instance, such an interaction would tend to aid the dehydrofluorination step.

(iii) Factors such as variations in P-N bond strengths have been ignored. The wide spread of values for this particular bond energy [Appendix 2] indicate that this is unlikely to be a correct assumption. In $(X_3PNMe)_2$ (X = F, Cl) the two P-N bonds possess different bond lengths [47,68] and presumably also different bond energies. In addition, a certain degree of (p-d)π-bonding in these systems has been postulated [69], and is likely to be more predominant in the fluoro- than the chloro-derivative. Small changes in bond energy may well play an important part in promoting particular break-down paths where overall enthalpy changes are small.

(iv) As an extension to the above topic, the nature of the products formed also has to be considered. This point will be illustrated by reference to other related systems. Alkylaminoborondifluoride, $RNHBF_2$, can decompose as shown:-

$$2\ RNHBF_2 \longrightarrow \tfrac{1}{2}\ (FBNR)_2 + RNH_2.BF_3$$

The extent to which this reaction proceeds is governed by the stability of the borazine that can be formed. For bulky alkyl groups (e.g. R = Bu^t) the borazine has not been identified and hence the parent compound is stable. On the other hand $RNHBF_2$ (R = Me, Et) have so far not been isolated [70], in spite of the great stability of the B-F bond. In sulphur-fluorine chemistry there is a dearth of compounds containing the unit RNH-S(F), which are spontaneously converted to RN=S groups [71]. While this reaction is aided by the weak S-F bond, there appears to be a particular stability for isolated multiple sulphur nitrogen bonds; thiazyl fluorides are less stable than phosphazenes and this is probably related to the inability of the former to delocalize charge throughout the ring.

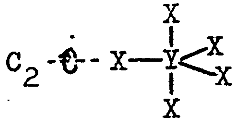
These observations emphasize the wide range of factors that are responsible for variations in the reactions of amines with non-metal halides. It appears that until the kinetic and thermodynamic aspects of these reactions have received greater attention, the chemist will have to refrain from his continual desire to systematize related topics, and be forced to treat each individual system separately.

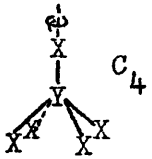
STRUCTURES OF PHOSPHORUS-FLUORIDES.

The evidence presented here in the form of n.m.r., i.r. and mass spectral data suggests that the structures of all the molecules encountered with in this chapter are normal, i.e. fluorophosphines are three co-ordinated, fluorophosphoranes are five co-ordinated, and adducts and anions are six co-ordinated. There is some difficulty in completely assigning the structure of $2MeNH_2.PF_5$, but the bulk of the evidence suggests that the extra molecule of amine is co-ordinated to the 1:1 adduct by means of N····H hydrogen-bonding.

PENTACO-ORDINATION.

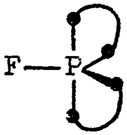
In the past ten years or so, much work has been carried out in order to determine the stereochemistry of fluorophosphoranes. The two idealized geometries for a five co-ordinated species are trigonal bipyramidal and square pyramidal. It has been pointed out that these geometries are strikingly similar [56], as can be shown by looking at the former down the C_2 axis, and the latter down the C_4 axis,





The energy difference between the two structures is likely to be small compared with lattice energy parameters and solvation energies in solution, and comparable with association energies in the liquid state. Structural discussions concerning pentaco-ordinated species must clearly be referred to a particular physical state [56].

Fluorophosphoranes are usually either gases or volatile liquids, and are ideal for structural studies. Up until now all evidence has been in agreement with (a) all these molecules adopting trigonal bipyramidal structures and (b) where more than one type of substituent is present, the least electronegative groups generally occupying the equatorial sites [3,72]. Griffiths has concluded from the different results found from electron diffraction and infra-red studies on CF_3PF_4 that at low pressures it possesses an axial CF_3 group, but that at high pressures (>3 torr) a configuration with an equatorial CF_3 group is favoured [73]. Another contradiction to this general rule is observed where steric factors dictate the geometry of fluorophosphoranes; two four- or five-membered heterocycles containing the same phosphorus atom as one of the hetero atoms force the fluorine atom in the tetra-substituted fluorophosphoranes to occupy an equatorial site [74-5],



This general concept has been extended to include phosphoranes containing no fluorine atoms; where five-membered rings are involved, they are best placed so as to span one equatorial and one apical position with the more electronegative atom in the ring occupying the latter site [59,76].

While gaseous electron diffraction studies [77] and infrared studies [78] indicated that PF_5 possesses D_{3h} symmetry, the original n.m.r. studies on the pure liquid showed two lines indicating that all fluorine atoms are magnetically equivalent and remain coupled to the central phosphorus atom [79]. These apparently conflicting results are explained by noting the different time scales for these techniques: 10^{-20}, 10^{-13} and 10^{-1}-10^{-9} sec. respectively [80]. Berry suggested that the fluorine atoms exchange at a rate slow compared with the time necessary to establish sharp vibrational levels and fast compared with the inverse line width associated with n.m.r. measurements [81]. There are four routes by which fluorine exchange can take place in PF_5:-

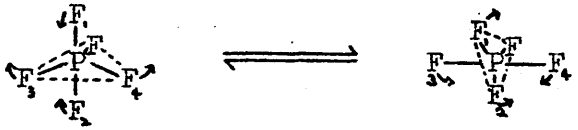
(i) Intermolecular exchange;

(ii) Exchange via bond cleavage (e.g. radical formation);

(iii) Intramolecular exchange;

(iv) Quantum mechanical tunnelling.

The first two mechanisms are ruled out in this particular case since PF coupling is maintained. Of the possible intramolecular exchange routes, Berry proposed that the most probable one on energy grounds, was that in which "internal pseudorotation" was involved; this mode is depicted below:-



The mechanism involves small shifts of F_1 and F_2, and F_3 and F_4 away from their equilibrium positions, with the pivot fluorine atom not moving at all; this proceeds via a tetragonal pyramidal intermediate state. The final route, that of quantum mechanical tunnelling, is a device for traversing potential energy barriers (in this case the energy required to produce the tetragonal pyramid) when the system does not possess enough kinetic energy to do this.

This work has been extended to explain how exchange takes place within other fluorophosphoranes, and at the same time more quantitative work has been performed,chiefly by Holmes et al., to evaluate the heights of the energy barriers involved [82-3]. More detailed vibrational potential functions based on normal co-ordinate analysis results have confirmed that Berry's mechanism represents the lowest energy path leading to exchange. In the specific case of PF_5, the most favourable exchange co-ordinate approximates one normal mode, the axial bending mode (ν_7), which was assigned in a recent gas phase Raman study to a peak occurring at 175 cm.$^{-1}$ [84]. Consideration of rates of tunnelling through the barrier and reaction over the barrier lead to the conclusion that the latter process assumes importance at all but the lowest temperatures. The results showed that pseudorotation is possible only when the co-ordinate governing exchange has a low frequency and a large amplitude motion, and hence a correspondingly small force constant, associated with a molecule of comparatively low reduced mass. In the condensed state there is evidence that intermolecular interactions serve to lower the barrier by allowing weakly held short-lived solvation complexes or specifically oriented collisional complexes to be formed [83].

Pseudorotation rates are generally obtained experimentally by performing a variable temperature n.m.r. study on the compound in question. The temperature at which n.m.r. signals for the individual axial and equatorial substituents begin to appear determines the activation energy for this process. These studies have ranged over a wide variety of pentaco-ordinated compounds and the effect of bulky groups, small rings and electronegativities on these rates has been examined [85-6]. Of special interest, is the generalisation that the activation energy increases with the increasing number of substituents in place of fluorine in fluorophosphoranes [72]. An activation energy for fluorine exchange in Et_2NPF_4, where equivalent fluorine atoms were observed at 25° and two sets of fluorine atoms were observed at -85°, was evaluated as lying in the range 6-12 kcal./mole [87]. A more recent study of the low temperature ^{31}P n.m.r. spectrum of Me_2NPF_4, which involved a detailed examination of line widths, indicated that the Berry mechanism, with simultaneous interchange of both axial and equatorial fluorine atoms rather than interchange of only one pair of axial and equatorial fluorine atoms, was operating [88].

N.M.R. SPECTRA OF RNHP(F) COMPOUNDS.

The existence of three nuclei, each of which possesses a nuclear spin quantum number, I, value equal to $\frac{1}{2}$ in RNHP(F) containing compounds usually results in sufficiently characteristic n.m.r. spectra to make identification of unknown compounds by this technique almost unambiguous. In addition, the nitrogen nucleus with spin I = 1 also possesses an electric quadrupole moment, which can interact with the fluctuating electric field gradients produced at the nucleus by other molecular degrees of freedom. In the absence of quadrupole relaxation, coupling of ^{14}N to nuclei of spin $\frac{1}{2}$ produces spectra for both sorts of nuclei which consist of simple multiplets. The electric quadrupole relaxation mechanism will only operate on the ^{14}N nucleus, and will affect the multiplets in two different ways [89]. As the relaxation rate increases the spectrum of the ^{14}N nucleus will broaden proportionately, and at high rates the multiplet will coalesce into a broad signal. The spectrum of the spin-$\frac{1}{2}$ nuclei will also reveal broadening of its multiplet which will finally coalesce into a broad signal, but at a faster relaxation rate this further sharpens into a single line. At intermediate relaxation rates theory shows that individual components of the multiplet in the spectrum of the spin-$\frac{1}{2}$ nuclei are broadened to different extents [89]. In the absence of broadening due to exchange effects, it has been shown that slow molecular motions are most effective for quadrupole relaxation [90]. Quadrupole relaxation rates depend to a large extent on the influence that the substituents attached to nitrogen have on the symmetry of the electron cloud at the ^{14}N nucleus; a high degree of asymmetry leads to complete decoupling of the ^{14}N nucleus [91].

In the compounds studied quadrupole relaxation most affects the appearance of the amino-proton's resonance, which in some cases cannot be detected. In view of work previously performed, an increase in temperature should reveal coupling between the amino-proton and the nitrogen nucleus [90]. A general broadening of peaks arising from alkyl-protons is also noted. The same phenomenon has also been observed in compounds with nitrogen bonded to phosphorus previously; no broadening of the analogous compounds, containing oxygen in place of nitrogen, was found [92].

N.M.R. SPECTRA OF ALKYLAMINOTETRAFLUOROPHOSPHORANES (Table 1.2).

The room temperature ^{19}F n.m.r. spectra of Bu^tNHPF_4 and $EtNHPF_4$ both show two broad resonances indicating that the axial and equatorial fluorine atoms are exchanging on the n.m.r. time scale by means of pseudorotation. The same explanation accounts for the absence of peaks in the ^{19}F n.m.r. spectrum of $MeNHPF_4$. These results show that the energy barrier for pseudorotation is increased in going from the t-butylamino- or ethylamino- to the methylamino- derivative of phosphorus pentafluoride. ^1H n.m.r. spectra show complex multiplets due to coupling with more than one nucleus. In $EtNHPF_4$ the methylene resonance shows a septet of broad lines which is attributed to the near coincidence of the values for $\frac{1}{2}J(PCH_2)$, $J(H_2CCH_3)$ and $J(H_2CNH)$;further coupling with fluorine is not resolved. The band heights agree well with the required 1:4:7:8:7:4:1 intensity ratio. A similar explanation has been put forward to account for the methylene multiplet in $PhP(NHEt)_2$; justification for these assignments was then obtained from homonuclear double-resonance experiments [93]. The two multiplets for the methyl resonance in $MeNHPF_4$ can be similarly rationalized.

The resonance arising from the methyl group in $EtNHPF_4$ is split into a triplet due to coupling with the methylene group;

each peak is then further split into a doublet. The resonance due to the methyl group in Bu^tNHPF_4 is also split into a doublet. This additional splitting could be ascribed to either (a) long-range coupling with the phosphorus atom, (b) long-range coupling with the amino-proton or (c) some mechanism which makes the methyl group magnetically nonequivalent. The first suggestion is favoured since results, both presented here and obtained from other sources [94-5] (one of which also showed evidence for additional splitting due to magnetic nonequivalence), suggest that long-range coupling over four bonds is possible in these systems. Provided that this assumption is correct, the following effects should be observed:-

(i) Irradiation at the phosphorus resonance should remove the double degeneracy of the methyl resonance.

(ii) Deuteration of the amino-proton should not effect the appearance of the methyl resonance.

(iii) No alteration in the appearance of the methyl resonance should be produced by using a 100 MHz n.m.r. machine, unless magnetic nonequivalence is the cause of the splitting.

The further long-range HF coupling observed for the methyl group in Bu^tNHPF_4 is unusual since it appears that coupling through five bonds has not previously been reported for analogous systems.

Table 1.2

Compound	δ^*_F	J(PF)	$\delta^*_{CH_3}$	$\delta^*_{CH_2}$	δ^*_{NH}	$J(PCH_2)$	$J(PCH_3)$
$\mathrm{MeNHPF_4}$[b]	n.o.	n.o.	-2.9 dy		~-3.0 v br		15.6
$\mathrm{MeNHPF_4}$[a]	74 br d	847					
$\mathrm{EtNHPF_4}$[b]	75 br d	800	-1.1 td	-3.0 y	n.o.	14.0	2.0
$\mathrm{Bu^tNHPF_4}$[b]	65 br d	830	-1.1 dp		-2.4 d		2.0

Compound	J(PNH)	$J(H_2CNH)$	$J(H_3CNH)$	$J(H_2CCH_3)$	$J(H_3CF)$	$^4J(H_2CF)$
$\mathrm{MeNHPF_4}$[b]	n.o.		3.4		1.7[h]	
$\mathrm{EtNHPF_4}$[b]	n.o.	7.0		7.1	n.o.	n.o.
$\mathrm{Bu^tNHPF_4}$[b]	15		n.o.		0.7[h]	

Compound	$\delta^*_{F_a}$	$\delta^*_{F_{a'}}$	$\delta^*_{F_e}$	$J(PF_a)$	$J(PF_{a'})$	$J(PF_e)$	$J(F_aF_e)$
$\mathrm{MeNHPF_4}$[c]	60	70	83	755	770	920	66.5, 69.3
$\mathrm{Bu^tNHPF_4}$[d]	54	55	76	767	808	940	~73

Compound	$J(F_{a'}F_e)$	$J(F_aF_{a'})$	$J(F_aCH_3)$	$J(F_{a'}CH_3)$	$J(F_eCH_3)$	$J(F_aNH)$	$J(F_{a'}NH)$
$\mathrm{MeNHPF_4}$[c]	65.4, 72.7	2.8	0	2.1[h],2.8[f]	2.1[h],2.1[f]	0	~21[h],27.6[f]
$\mathrm{Bu^tNHPF_4}$[d]	~76						~33[h],33.8[f]

Compound	$J(F_eNH)$	$\delta^*_{CH_3}$	δ^*_{NH}	J(PNH)	$J(PCH_3)$
$\mathrm{MeNHPF_4}$[c]	?	-2.7	-3.3 br t	~21	15.2
$\mathrm{Bu^tNHPF_4}$[d]		-1.2	-3.4 br dd	~13	

[a] +70°, [b] +33°

[c] -80°, [d] -50°.

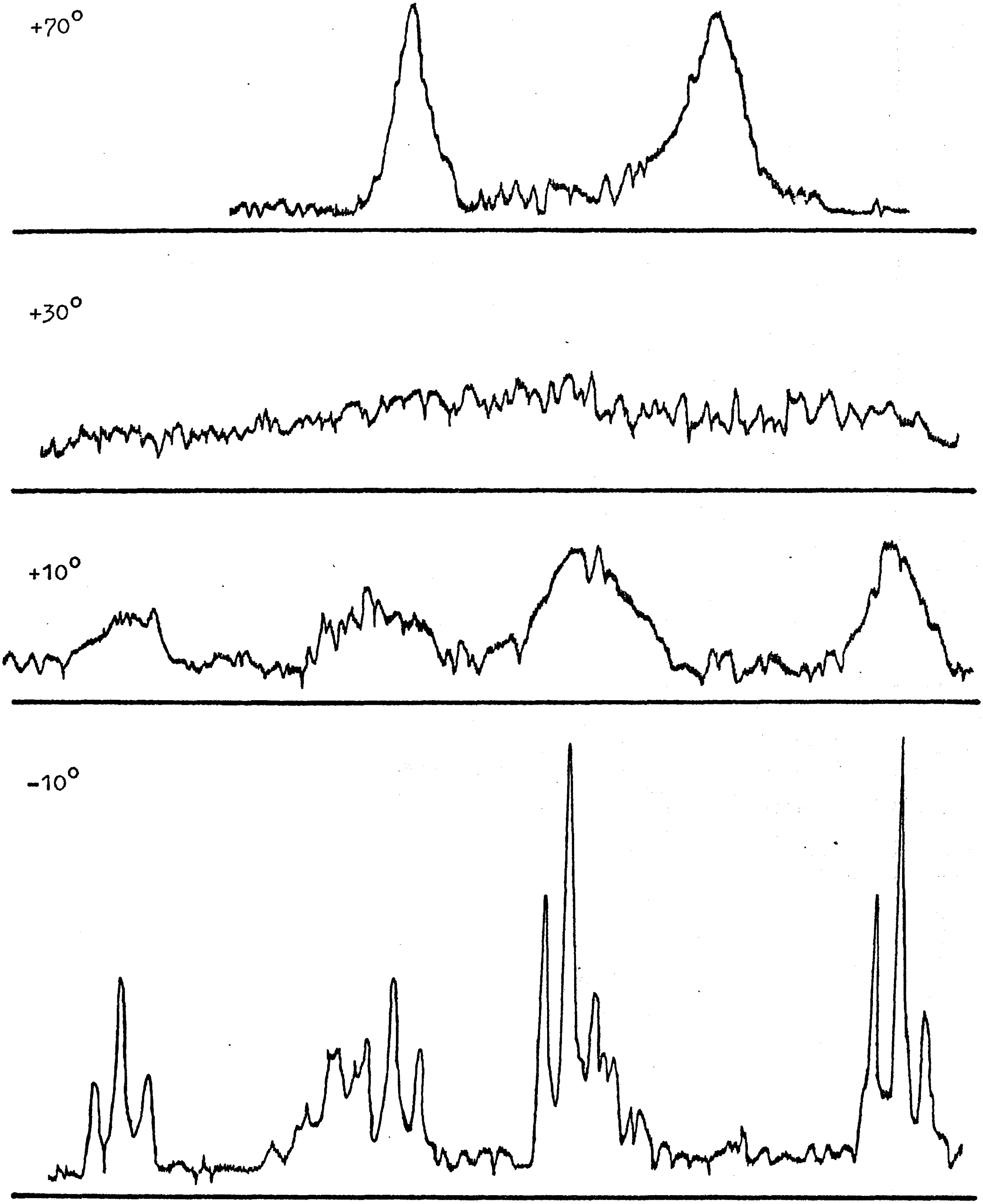
[f] ^{19}F n.m.r. spectrum

[h] ^1H n.m.r. spectrum

VARIABLE TEMPERATURE N.M.R. STUDIES OF $MeNHPF_4$ AND Bu^tNHPF_4.

Since the room temperature n.m.r. spectrum of $MeNHPF_4$ shows no signals, a variable temperature n.m.r. study was performed. Figs. 1.4 and 1.5 show how the ^{19}F n.m.r. spectrum depends on the temperature of the system (+70 - -80°). At the highest temperature studied, the spectrum of the neat liquid resembles that obtained for the other two tetrafluorophosphoranes at room temperature. On lowering the temperature to -40° three fluorine atom environments in the ratio 1:1:2 are produced. The spectrum remains essentially unchanged down to -80°, and its appearance does not depend on whether it is run as a neat liquid or in solution, which indicates that the nonequivalence of the fluorine atoms arise from some intramolecular process. A room temperature ^{19}F n.m.r. spectrum showing three fluorine atom environments was briefly mentioned for $2,6\text{-}Et_2C_6H_3NHPF_4$ [16].

Nonequivalence of axial fluorine atoms was first reported to occur in RPF_3NHR' [18,96-7], and has since been found to be present in R_2PF_2NHR' [18], $RPF_2(NHR')H$ [18], $R_2N(R'NH)PF_3$ [98-9] and several alkylthio- and arylthio-substituted fluorophosphoranes [100]. In all cases the asymmetry arises from a slowing down of free rotation about the P-N or P-S bond with respect to the n.m.r. time scale. The spectrum for Me_2NPF_4 was reported to show separate resonances for axial and equatorial fluorine



<u>Fig. 1.4</u> ^{19}F n.m.r. spectrum of $MeNHPF_4$ +70 - -10°

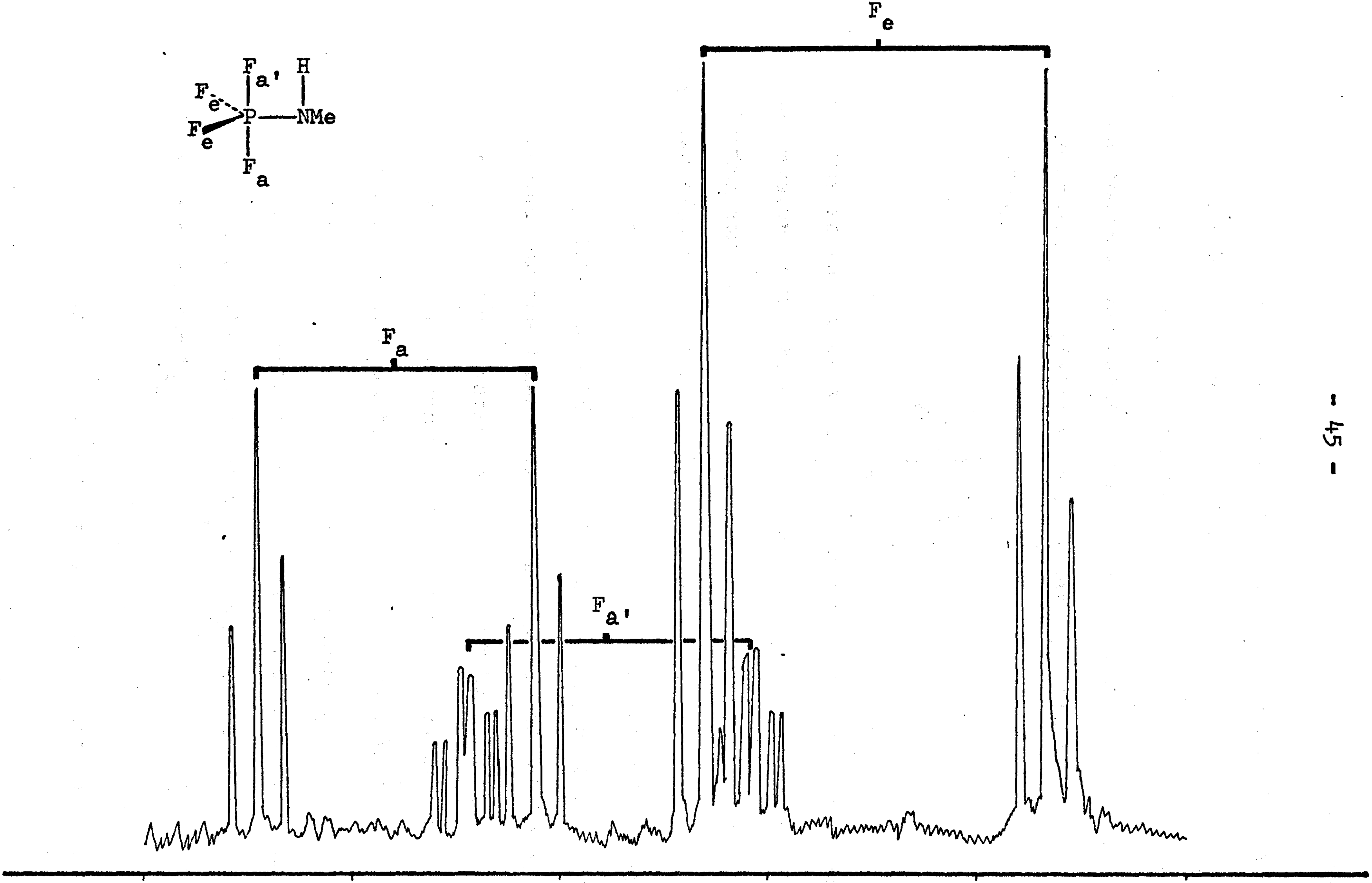
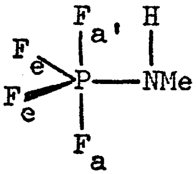


Fig. 1.5 ^{19}F n.m.r. spectrum of $MeNHPF_4$ at -80°

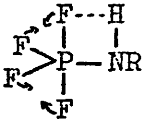
atoms only below -80°; nonequivalence of the individual axial fluorine atoms was not observed [3].

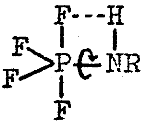
The n.m.r. spectrum of $MeNHPF_4$ is interpreted by assuming that the compound can adopt a structure in which one of the fluorine atoms, $F_{a'}$, preferentially interacts with the amino-proton,



The changes in the appearance of the spectrum found on lowering the temperature thus arise from a combination of two effects, (a) slowing down of fluorine exchange processes and (b) an increased importance attached to hindered rotation about the P-N bond. Let us assume first that the nitrogen atom is hybridized in such a way that the C-NH-P skeleton is planar, as has been observed for the C_2N-P skeleton in Me_2NPF_2 [101]. Then, at temperatures where rotation around the P-N bond is slow, the two axial fluorine atoms will both be magnetically non-equivalent and the two equatorial fluorine atoms will be magnetically equivalent. The two axial fluorine atoms thus produce two different sets of resonances. In common with all fluorophosphoranes the values of δ_{F_a} and $\delta_{F_{a'}}$ are both less than that obtained for δ_{F_e}.

It appears that hydrogen-bonding between the amino-proton and $F_{a'}$ increases the energy required for both rotation about the P-N bond and pseudorotation. The pseudorotation rate has been shown earlier to depend on the ease with which axial fluorine atoms can be deformed from their equilibrium positions. The diagram below shows that both these processes are severely restricted:-





It is somewhat surprising that in $EtNHPF_4$ and Bu^tNHPF_4, where larger alkyl groups are involved, that these effects are less pronounced; this anomaly may be due to a change in the acidity of the amino-proton, which would be expected to decrease on replacing the methyl group by a more electron-donating alkyl group. It would be interesting to see whether the inclusion of a group in the alkyl substituent to which the amino-proton could also hydrogen-bond (e.g. a carbonyl group) would appreciably affect the appearance of the n.m.r. spectrum.

Since the axial fluorine atom at higher field is further split into a doublet by coupling with the amino-proton, it is tempting to assign these resonances to the fluorine atom to which it is closest alligned. The value of $^3J(F_a,NH)$ (27.6 c/s) is larger than that generally observed for coupling through three bonds, and its increased magnitude may be a direct result of through-space coupling. The amino-proton produces a broad triplet in the low temperature ^1H n.m.r. due to almost equal coupling of the proton with both the phosphorus atom and $F_{a'}$. In $(NH_2)_2PF_3$ the values for $^3J(F_{a'}NH)$ and J(PNH) were both reported to be ~20 c/s while that for $^3J(F_eNH)$ was only 1.7 c/s [5]. Coupling of the methyl group with $F_{a'}$ but not with F_a is observed in the ^{19}F spectrum of $MeNHPF_4$. Similar coupling between only one of the axial fluorine atoms and the protons on the alkylthio group was observed in alkylthiotetrafluorophosphoranes [100]. A recent study of OH---F hydrogen-bonding (in this case no direct H---F coupling was observed) in ortho-trifluoromethylphenol indicated that the resonance due to the co-ordinated CF_3 group lay to a lower field than that due to the unco-ordinated CF_3 group [102]. The direction and magnitude of the shift was shown to be that expected on the basis of the Karplus and Das theory for chemical shifts [103], in which only the p orbitals on fluorine are considered to affect the value of δ_F. Both NH---F and OH---F bonding should result in a decrease in fluorine p orbital symmetry, as the result of the 2p orbital on fluorine overlapping with the 1s orbital on hydrogen which will affect the fluorine paramagnetic screening term. Since the shift of electrons is in the same direction in both cases, one might expect a similar direction of shift between the hydrogen-bonded and nonhydrogen-bonded fluorine atoms. That this is not so may simply be a consequence of the fact that changes of electron density within the P-F bond have been overlooked.

A closer examination of the ^{19}F spectrum of $MeNHPF_4$ reveals that the fine structure associated with the two outside bands is different from that associated with the middle band of all the triplet resonances; the left-hand triplet arising from $F_{a'}$ is reproduced in Fig. 1.6. There are two explanations for this phenomenon:-

(i) If the C-NH-P skeleton is not completely planar, as previously assumed, then both equatorial fluorine atoms will be magnetically nonequivalent. While different chemical shifts are not observed for these two fluorine atoms, they do appear to couple to the other magnetic nuclei to different extents. The content of Fig. 1.6 shows how the resonance for $F_{a'}$ can be interpreted as arising from two different values for $J(F_{a'}F_e)$. The triplet resonance due to the equatorial fluorine atoms (after coupling to the phosphorus atom) shows a broad central band and two outer bands, which are further split into sextets. Coupling with protons is indicated, but it is not possible to decide whether the peaks are produced from one or two types of equatorial fluorine atom. HF coupling constants derived from both the ^{19}F and ^{1}H n.m.r. spectra are self-consistent. Coupling constants calculated on the assumption of nonequivalent equatorial fluorine atoms are given in Table 1.2.

It was hoped that the low temperature study of Bu^tNHPF_4 would reveal a simpler ^{19}F n.m.r. spectrum since long-range

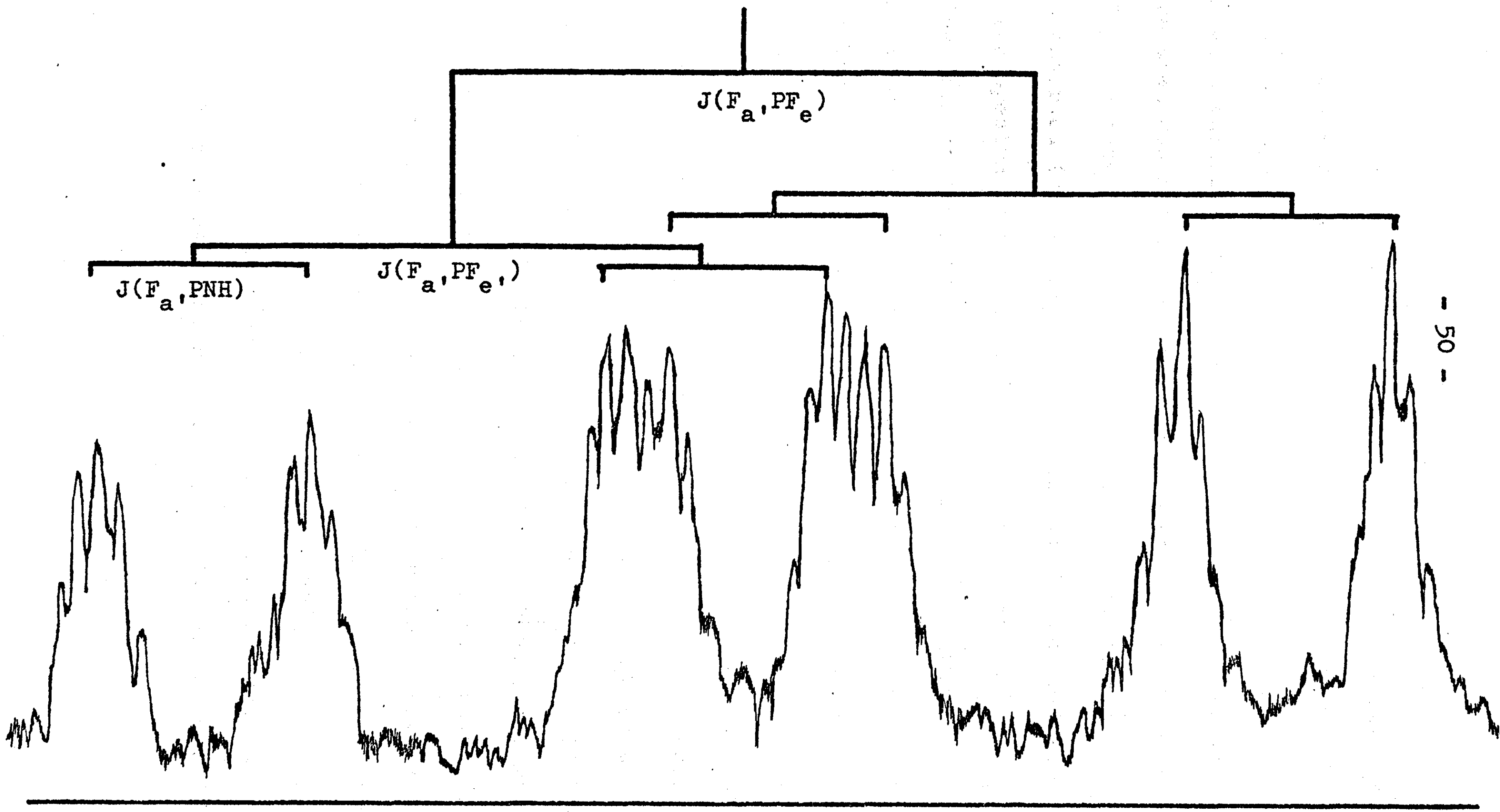


Fig. 1.6 Left-hand triplet arising from $F_{a'}$ in $MeNHPF_4$

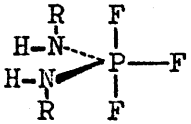
hydrogen fluorine coupling should not be resolvable. However, even at the lowest temperature obtained (-50°, the m.p. of the compound) a slight broadening was observed due to fluorine exchange; a suitable solvent (e.g. toluene) for studies at lower temperatures was not found. The low temperature spectrum of Bu^tNHPF_4 indicates that there are three fluorine atom environments, as was observed for $MeNHPF_4$; one notable difference between these two spectra is the dissimilar magnitude of $(\delta_{F_{a'}} - \delta_{F_a})$.
(ii) The fine structure can alternatively be explained as arising from a second order effect. The AB_2 spin system has been analysed [104]. For small values of $J/\nu_o\delta$ (i.e. for situations which can closely be represented by an AX_2 spin system) both the central line of the 'A' triplet and the two lines associated with the B nucleus are split to different extents into doublets. The two outside lines of the triplet also possess different intensities. The equatorial fluorine resonance in the spectrum of $(NH_2)_2PF_3$, examined by Lustig et al. [5], showed a central band which was split into a doublet by means of the above effect.

Methylaminotetrafluorophosphorane (which can either be considered to represent an ABCDX or an ABC_2X spin system, depending on whether or not the C-NH-P grouping is planar) might similarly be expected to produce a splitting in the central band of the triplet resonances. Lustig et al. were able to produce a partial computer calculated spectrum which indicated a splitting similar to that obtained in practice, by employing the coupling constants calculated on the basis of a first order analysis [5].

Without similarly using a computer it is not possible to state categorically whether or not the equatorial fluorine atoms are magnetically equivalent in $MeNHPF_4$ on the basis of the work presented here. Since it is regarded as somewhat strange that the equatorial fluorine atoms should possess different values of J(FF) but possess the same chemical shift, the second explanation is favoured.

N.M.R. SPECTRA OF BIS(ALKYLAMINO)TRIFLUOROPHOSPHORANES (Table 1.3).

The ^{19}F n.m.r. spectra of these compounds indicate that all the fluorophosphoranes studied here have the structure:-



There is evidence for restricted rotation around the P-N bonds in both $(MeNH)_2PF_3$ and $(EtNH)_2PF_3$ since the axial fluorine atoms produce two peaks which are very broad at room temperature. As the equatorial fluorine atom produces sharp peaks this phenomenon cannot be associated with a pseudorotational process. On the other hand in $(Bu^tNH)_2PF_3$ the axial fluorine atoms produce much sharper peaks which indicate that coupling to the equatorial fluorine atom and both amino-protons takes place. The ^1H n.m.r.

Table 1.3

Compound	$\delta^*_{F_a}$	$\delta^*_{F_e}$	$J(PF_a)$	$J(PF_e)$	$J(F_aF_e)$
$(MeNH)_2PF_3$ [a]	62 br d	78	703	868	41.2
$(EtNH)_2PF_3$ [b]	62 br d	76	694	875	41.7
$(Bu^tNH)_2PF_3$ [b]	47 br ddt	69	726	897	47.7

Compound	$J(F_aCH)$	$J(F_eCH)$	$J(F_aPNH)$	$\delta^*_{CH_3}$	$\delta^*_{CH_2}$
$(MeNH)_2PF_3$	1.6^h	$1.6^h, 1.9^f$	n.o.	-2.6 ddq	
$(EtNH)_2PF_3$	n.r.	n.o.	n.o.	-1.2 t	-3.1 y
$(Bu^tNH)_2PF_3$			$16.7^h, 16.1^f$	-1.1 s	

Compound	δ^*_{NH}	$J(H_2CCH_3)$	$J(PNCH)$	$J(HNCH)$	$J(PNH)$
$(MeNH)_2PF_3$	-3.6 br		13.7	4.8	n.o.
$(EtNH)_2PF_3$	n.o.	6.8	13.6	6.8	n.o.
$(Bu^tNH)_2PF_3$	-2.5 br dt				13.3

[a] In Me_3N. [b] Neat. [h] Obtained from ^1H n.m.r. [f] Obtained from ^{19}F n.m.r.

spectrum also indicates that the amino-protons are coupled equally to both axial fluorine atoms in $(Bu^tNH)_2PF_3$, i.e. free rotation around the P-N bonds is present in this compound.

A variable temperature n.m.r. study was performed on $(MeNH)_2PF_3$ (Fig. 1.7). The high temperature spectrum shows that the resonances due to the axial fluorine atoms become much

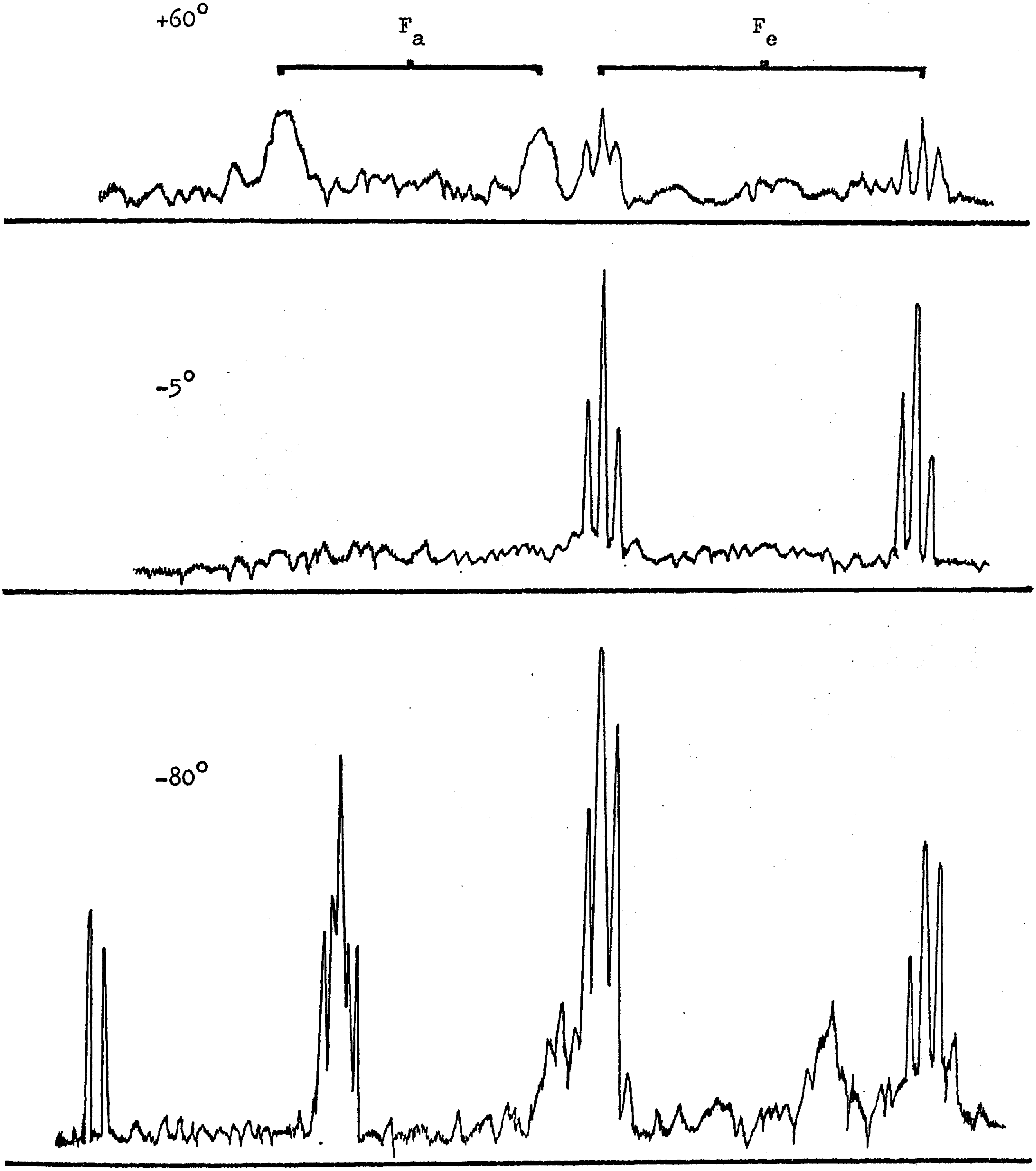
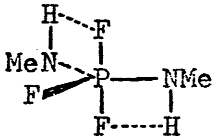


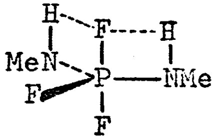
Fig. 1.7 ^{19}F n.m.r. spectrum of $(MeNH)_2PF_3$ +60 - -80°

sharper, i.e. rotation around the P-N bond becomes easier, and the appearance of these resonances approaches that expected for a compound in which rotation around all bonds is unhindered. On reducing the temperature, the broad doublet divides into more than one set of peaks. One might have expected that at low temperatures $(MeNH)_2PF_3$ would adopt a structure in which each amino-proton is hydrogen-bonded to a different axial fluorine atom (I), which would render both axial fluorine atoms magnetically equivalent:-

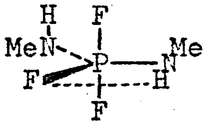
(I)



(II)



(III)



The spectrum shows that no such simple state of affairs exists since a change in the appearance of the equatorial fluorine atom resonance is also observed. As there is only one equatorial fluorine atom in each molecule this suggests that at low temperatures $(MeNH)_2PF_3$ may exist in more than one configuration. Both equatorial fluorine atoms in I and II, for example, exist in different magnetic environments and a mixture of these two species would produce a complex fluorine spectrum. In both of these configurations hydrogen-bonding to axial fluorine atoms only is considered. Different configurations in which hydrogen-bonding to equatorial fluorine atoms takes place can be envisaged (e.g. III). Although experiments were not carried out to study solvent effects, it might prove possible to alter the ratio of molecules in these various configurations by a suitable choice of solvent.

In the presence of a base (Me_3N or pyridine) the peaks in both the fluorine and proton spectra of $(RNH)_2PF_3$ are found to sharpen considerably. In $(MeNH)_2PF_3$, for example, the methyl resonance changes from being two broad peaks (in which only coupling with phosphorus can be resolved) in the liquid state to one which reveals further coupling with the amino-protons and the fluorine atoms; at the same time the equatorial fluorine atom resonance exhibits a further septet fine structure due to coupling with the protons in the two methyl groups. This effect, also observed in the other RNHP(F) compounds, may be ascribed to a reduction in the rate of amino-proton exchange. The septet fine structure for the methyl resonance in $(EtNH)_2PF_3$ arises from multiple overlap as explained for $EtNHPF_4$.

N.M.R. SPECTRA OF BIS(ALKYLAMINO)DIFLUOROPHOSPHORANES (Table 1.4).

N.m.r. studies show that these molecules contain one hydrogen and two fluorine atoms, since their ^{19}F n.m.r. spectra consist of two sets of doublets, with the smaller coupling constant corresponding to the separation between the triplets in the doublet of triplets, arising from the proton that is directly bonded to phosphorus, in the ^1H n.m.r. spectra. Fig. 1.8,

Table 1.4

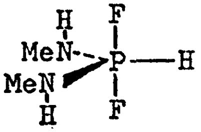
Compound	δ^*_F	J(PF)	$\delta^*_{CH_3}$	$\delta^*_{NCH_2}$	$\delta^*_{CCH_2}$
$(MeNH)_2PF_2H$	62 br dd	655	-2.3 ddt		
$(EtNH)_2PF_2H$	60 br dd	660	-1.1 t	-3.0 y	
$(Bu^nNH)_2PF_2H$	59 br dd	658	-0.9 comp.	-2.9 x	-1.4 comp.

Compound	δ^*_{NH}	$\delta^*_{P\underline{H}}$	J(FPNCH)	$J(H_2CCH_3)$	J(PNCH)
$(MeNH)_2PF_2H$	-3.2 br	-6.5 dt	1.5 ^{h}		13.9
$(EtNH)_2PF_2H$	-2.5 br	-6.7 dt	n.r.	7.1	14.2
$(Bu^nNH)_2PF_2H$	n.o.	-6.7 dt	n.r.		~12.2

Compound	J(HNCH)	J(PH)	J(FPH)	$J(H_2CCH_2)$
$(MeNH)_2PF_2H$	5.0	837	118 ^{h}	
$(EtNH)_2PF_2H$	7.1	845	117 ^{h}	
$(Bu^nNH)_2PF_2H$	6.1	844	118 ^{h}	~6.1

^{h} Obtained from ^{1}H n.m.r. spectrum.

showing both the ^{1}H and ^{19}F spectra for $(MeNH)_2PF_2H$, clarifies the point. The structure of these molecules is then represented by:-



The broadening of the axial fluorine atom resonance is likely to be due to the onset of hindered rotation around the P-N bonds.

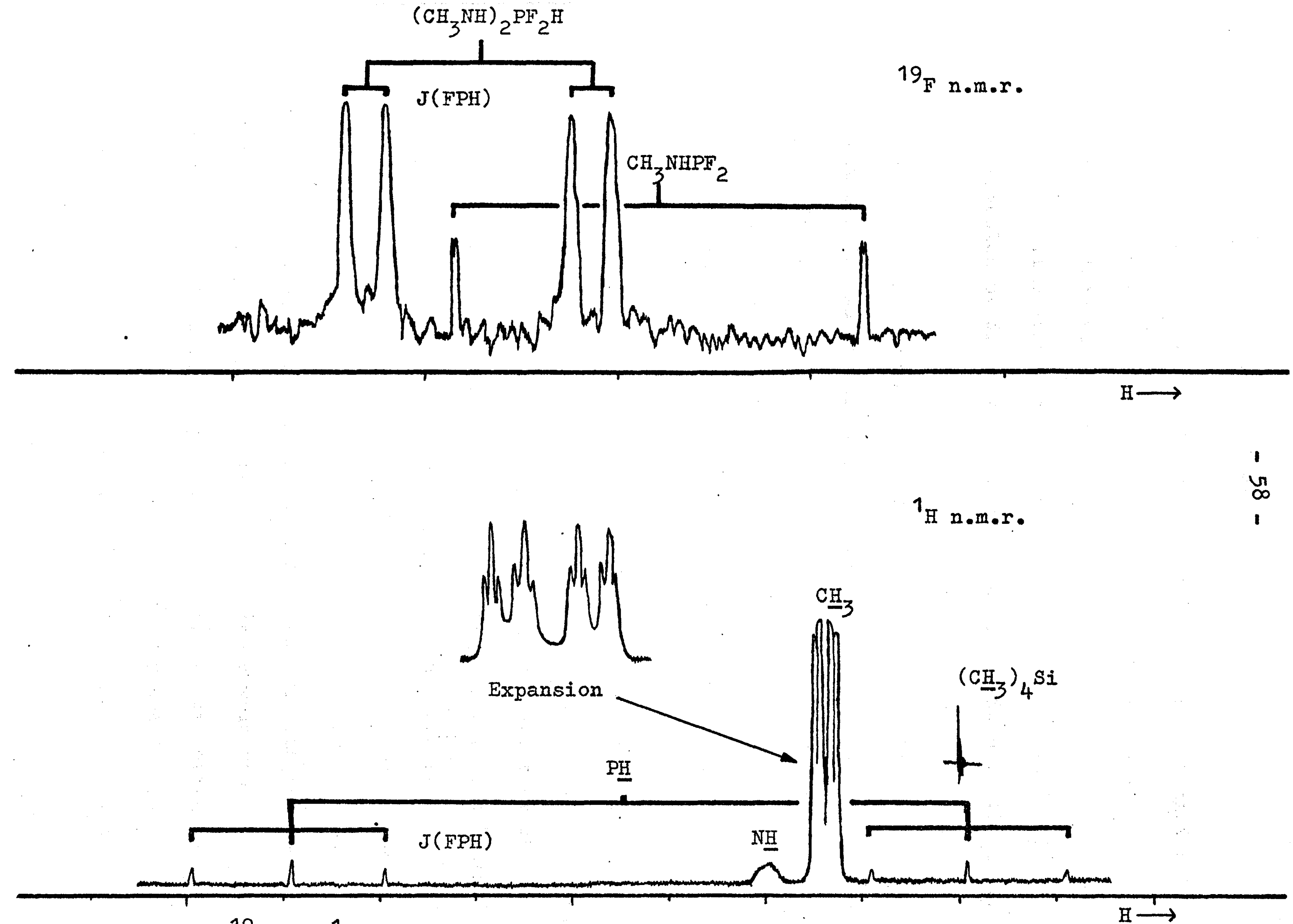


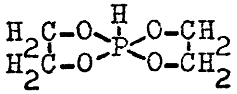
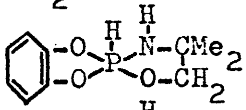
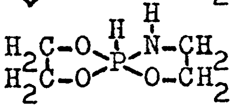
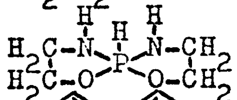
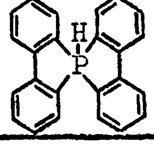
Fig. 1.8 ^{19}F and ^1H n.m.r. spectra of $(MeNH)_2PF_2H$ in pyridine (not shown)

The variable temperature n.m.r. spectra were not studied but those for Me_2PF_2NHMe and $MePF_2(NH^iPr)H$ revealed that this process did take place at low temperatures [18].

The fine structure for the methyl resonance in $(MeNH)_2PF_2H$ is revealed by dissolving the compound in pyridine. The septet for the methylene resonance in $(EtNH)_2PF_2H$ and the sextet for the N-methylene resonance in $(Bu^nNH)_2PF_2H$ arise from multiple peak overlap as explained previously. The remainder of the alkyl group in $(Bu^nNH)_2PF_2H$ gives a complex proton resonance.

While little interpretation has been given to the type of coupling involved in directly bonded PH systems [105], some data have been collected which suggest that the value of J(PH) depends on both the oxidation state of phosphorus and the electronegativities of the elements to which the phosphorus atom is attached [51,62]. These workers have suggested, with the aid of Bent's hypothesis [106] that the s orbital of an atom is concentrated into the hybrid orbitals which are directed towards the least electronegative substituent, that an increase in the value of J(PH) may be connected with an increase in the s-nature of the P-H bond. Table 1.5 gives a list of J(PH) values for various phosphoranes, which emphasizes that the trend holds for a wide range of compounds. A scattering associated with the differing inductive effects of the substituents attached to N,C and O, and anisotropic effects associated with the aromatic rings is also evident. A

Table 1.5

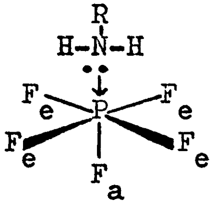
Compound	$^1J(PH)$	$^1J(PF_a)$	Σx [a]	References
HPF_4	1075	n.o. [b]	15.92	[107]
$ArPF_3H$	~900	~820	~14.50	[87,108]
RPF_3H	~860	~800	~14.50	[58]
$(RNH)(R'O)PF_2H$	~820	~660	~14.44	[31]
H_2PF_3	841-908	n.o. [b]	14.14	[107]
$(Me_2N)(Bu^iNH)PF_2H$	c	712	~14.04	[31]
$(RNH)_2PF_2H$	~840	~660	~14.04	
$RPF_2(OR')H$	~850	~750	~14.00	[51]
	829		~13.76	[62]
$RPF_2(NHR')H$	~750	~620	~13.50	[18,33,35]
	830		~13.36	[62]
	780		~13.36	[62]
Me_2PF_2H	733	535	~13.06	[135]
	732		~12.96	[62]
	482		~10.20	[109]

[a] Σx, Sum of electronegativities of groups bonded to phosphorus (not hydrogen); use Pauling-type values [110]. [b] Unobserved because of pseudorotation. [c] Not given.

rough correlation between $J(PF_a)$ and the electronegativities of the atoms attached to phosphorus has also been noted [51]. It has been reported that the increasing value of $J(PF_a)$ may reflect changes in the P-F bond distance or an increased s-character of the axial phosphorus orbital [72]. Since the s-characters of both the P-H and P-F bonds are unlikely to increase simultaneously, the former explanation seems more valid. The contents of Table 1.5 show that the values of J(PH) and $J(PF_a)$ for the compounds with general formula $(RNH)_2PF_2H$ follow the general trends.

N.M.R. SPECTRA OF ALKYLAMINE-PHOSPHORUS PENTAFLUORIDE ADDUCTS (Table 1.6).

The n.m.r. spectra of the alkylamine-phosphorus pentafluoride adducts were obtained in deuterioacetonitrile solutions. The ^{19}F n.m.r. spectra of $2MeNH_2.PF_5$, $EtNH_2.PF_5$ and $Bu^tNH_2.PF_5$ indicate that all adducts have the same structure in solution:-



While δ_{F_a} is larger than δ_{F_e} for all the adducts considered, the closeness of these two values produces second order effects in the ^{19}F n.m.r. spectra, which makes further coupling between the equatorial fluorine atoms and the other magnetic nuclei on the organic residue impossible to resolve. An analysis for the

Table 1.6

Compound	$\delta^{**}_{F_a}$	$\delta^{**}_{F_e}$	$J(PF_a)$	$J(PF_e)$	$J(F_eF_a)$
$2MeNH_2.PF_5$ [a]	80	64	759	780	55
$EtNH_2.PF_5$ [a]	79	62	758	785	56
$Bu^tNH_2.PF_5$ [a]	78	54	758	802	55
PF_6^- [a]	72		710		

Compound	$\delta^{**}_{CH_3}$	$\delta^{**}_{CH_2}$	δ^{**}_{NH}	$J(PNCH)$	$J(HCNPF_e)$	$J(H_2CCH_3)$
$2MeNH_2.PF_5$	-2.6 dp -2.5 s		-6.3	12.5	1.1 h	
$EtNH_2.PF_5$	-1.2	-3.0 x	-5.8	14.6	n.r.	7.3
$Bu^tNH_2.PF_5$	-1.3		-5.9			
$MeNH_3^+ PF_6^-$	-2.6		-6.0			
$EtNH_3^+ PF_6^-$	-1.2 t	-3.0 q	-6.0			7.3
$Bu^tNH_3^+ PF_6^-$	-1.2		-5.8			

[a] CD_3CN solution. [h] Observed from ^1H n.m.r. spectrum.

AB_4X system is given in Appendix 3 together with a diagram which reproduces part of a typical n.m.r. spectrum. While $J(F_eF_a)$ remains constant, the value of $(\delta_{F_a} - \delta_{F_e})$ is found to be both solvent and concentration dependent. In common with work performed on XSF_5 derivatives [111], $J(F_eF_a)$ remains practically constant and δ_{F_a} is found to be less dependent than δ_{F_e} on the nature of the complexed amine. The values of δ_{F_e} and δ_{F_a} lie on either side of the reported chemical shift of PF_6^- [1]; however, evidence from many sources suggests that this cannot be reliably correlated with changes in the electronegativity of the substituents attached to the central atom [104].

The methyl groups in the ^1H n.m.r. spectrum for $2MeNH_2.PF_5$ show two sets of resonances; one, a doublet of quintets, is due to the co-ordinated methylamine and the other, a singlet of variable intensity, which is situated to slightly higher field arises from the free methylamine molecule; this chemical shift difference is as predicted for complexed and uncomplexed amine. The addition of excess methylamine led to an increase in the height of the singlet - which confirms this assignment. If the solvent is pumped off the acetonitrile solution of the 2:1 adduct, then some excess methylamine can be detected in the volatile material by its vapour phase i.r. spectrum [112]. The ^1H but not the ^{19}F n.m.r. spectrum is consistent with the alternative formulation $MeNH_3^+$ $(MeNHPF_5)^-$ for this compound. Evidence thus suggests that, in solution, $2MeNH_2.PF_5$ contains one labile and one complexed amine molecule.

N.M.R. SPECTRA OF ALKYLAMMONIUM HEXAFLUOROPHOSPHATES (Table 1.6).

The ^1H spectra of RNH_3^+ PF_6^- ($R = Me, Et, Bu^t$) are identical with those obtained for other alkylammonium salts [113]. The ^{19}F n.m.r. spectra show that the PF_6^- anion is present and its chemical shift is independent of the nature of the cation [1].

N.M.R. SPECTRA OF ALKYLAMINOFLUOROPHOSPHINES (Table 1.7).

The room temperature ^1H and ^{19}F n.m.r. spectra of $MeNHPF_2$ are essentially in agreement with those reported previously [29]. At -80° an improved resolution is obtained for the ^{19}F n.m.r. spectrum (Fig. 1.9) and the broad resonance due to the methyl protons in the ^1H spectrum is resolved into a triplet of triplets (Fig. 1.9), resulting from almost identical values for J(HNCH) and J(PNCH), and further splitting arising from long-range HF coupling. In addition, the amino-proton in the low temperature spectrum appears as a broad ill-resolved doublet downfield of the methyl resonance. The room temperature spectrum for the amino-proton only shows a broad resonance (not observed in [29]), which is slightly closer to the methyl resonance than in the low temperature spectrum; there is some slight evidence for this being further coupled to the phosphorus and nitrogen nuclei.
An explanation is required for the appearance of the methyl resonance:-

(i) Restricted rotation around the P-N bond can surely be ruled out as taking place at room temperature, since it has recently been shown that very low temperatures were required to "freeze out" the two possible rotational isomers in the closely related

Table 1.7

Compound	δ_F	J(PF)	J(FPNH)	δ_{CH_3}	δ_{NH}
$\mathrm{MeNHPF_2}$**[a]	71	1193	10.4[f]	-2.6	-4.0 br
$\mathrm{EtNHPF_2}$**	67	1195	10.8[f]	-1.1 t	n.o.
$\mathrm{Bu^nNHPF_2}$**	67	1193	10.9[f]	-0.9	n.o.
$\mathrm{Bu^tNHPF_2}$**	61	1195	12.4[f]	-1.3	-4.1 br
$\mathrm{(Bu^tNH)_2PF}$ *[b]	54	1013	4.6[f]	-1.3[c]	-2.8

Compound	δ_{NCH_2}	δ_{CH_2}	J(PNH)	$J(H_2CCH_3)$	J(HNCH)
$\mathrm{MeNHPF_2}$			46		5.8
$\mathrm{EtNHPF_2}$	-2.9 x		n.o.	7.1	7.1
$\mathrm{Bu^nNHPF_2}$	-3.0 p	~-1.3	n.o.		6.9
$\mathrm{Bu^tNHPF_2}$			n.o.		
$\mathrm{(Bu^tNH)_2PF}$			n.o.		

Compound	J(PNCH)	J(PNCCH)	$J(H_2CCH_2)$	J(FPNCH)
$\mathrm{MeNHPF_2}$	5.8			2.0[h],2.1[f]
$\mathrm{EtNHPF_2}$	7.1			2.0[f]
$\mathrm{Bu^nNHPF_2}$	6.9		6.9	1.8[h],1.9[f]
$\mathrm{Bu^tNHPF_2}$		0.5		
$\mathrm{(Bu^tNH)_2PF}$		0.9		

[a] -80°. [b] +60°. [c] Further fine structure discernible. [h] Obtained from ^{1}H n.m.r. spectrum. [f] Obtained from ^{19}F n.m.r. spectrum.

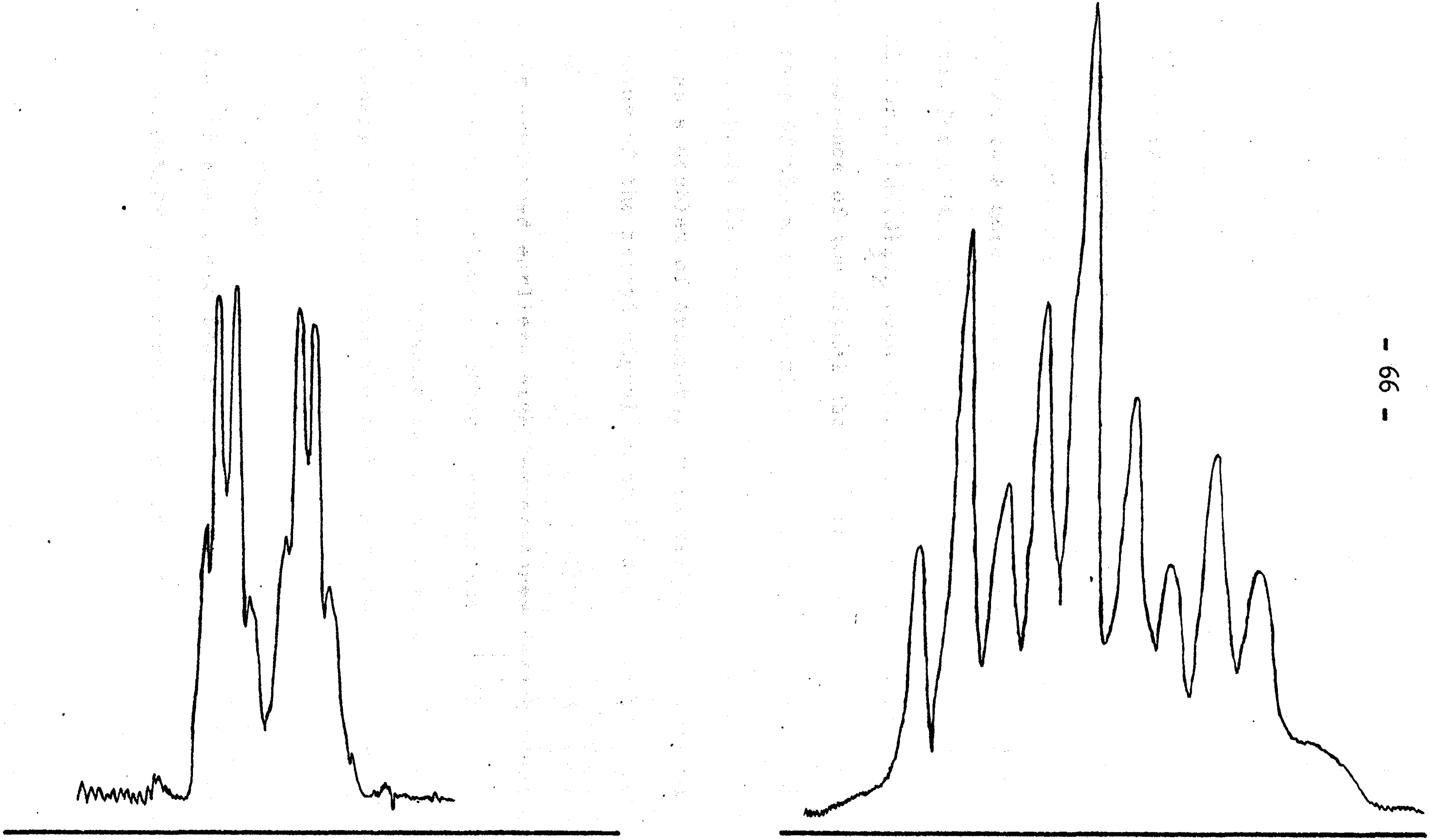


Fig. 1.9 ^{19}F n.m.r. spectrum $MeNHPF_2$, ^{1}H n.m.r. spectrum $C\underline{H_3}NHPF_2$

compound $MeNHP(CF_3)_2$ [114]. The room temperature n.m.r. spectrum then does not show the existence of two isomers whose population is temperature dependent, such that only one of these is favoured at low temperatures.

(ii) A second order effect due to the closer proximity of the amino-proton resonance in the room temperature n.m.r. spectrum would lead to a more complicated methyl signal than would be expected for a first order analysis. Distortions of the methyl signal for $MeNHP(CF_3)_2$ were shown to depend on this effect [114]. The appearance of the signal should then depend on the operating frequency of the n.m.r. machine. Deuteration of the amino-proton should simplify the methyl signal which would be expected to appear as a doublet of triplets. This will also remove any broadening of the methyl signal which is due to amino-proton exchange.

(iii) As explained earlier, high temperatures favour coupling of the nitrogen nucleus to other magnetic nuclei; the nitrogen nucleus is observed to broaden the amino-proton signal and might also significantly broaden the methyl signal. Heteronuclear decoupling of the ^{14}N nucleus would eradicate all such effects if they are present.

The ^{19}F n.m.r. spectra of $EtNHPF_2$, Bu^tNHPF_2 and Bu^nNHPF_2 as well as $MeNHPF_2$ show coupling to both the phosphorus nucleus and the amino-proton. It should be noticed that the products of the reaction between PF_3 and isopropylamine or n-propylamine, reported by Drozd et al. [28], have values of 1280 and 1247 c/s for J(PF), and +69 and +67 p.p.m. for δ_F respectively; these values do not coincide with those found here for either $RNHPF_2$ or $(RNH)_2PF_2H$. The ^1H n.m.r. spectra of $RNHPF_2$ (R = Et, Bu^t, Bu^n) are assigned as for the other alkylamino derivatives of phosphorus. A solution of $EtNHPF_2$ in pyridine reveals a complex structure for each component of the sextet arising from multiple overlap of lines due to near coincidence of J-values.

It is of interest to note that studies of the ^{19}F n.m.r. spectra of $RNHPF_2$, $RNHPF_4$, $(RNH)_2PF_3$, $(RNH)_2PF_2H$ and $RNH_2.PF_5$ show that the value of δ_F decreases along the series:-

$$Me > Et \approx Bu^n > Bu^t$$

This is in the opposite direction to that expected if δ_F were determined purely on the basis of the inductive effect of the group attached to fluorine [115], and is presumably a consequence of a greater degree of (p-d)π-bonding in the P-F bonds when the phosphorus atom is attached to electron-donating groups.

Both the ^1H and ^{19}F n.m.r. spectra of $(Bu^tNH)_2PF$ are determined at 60° and confirm the absence of any P-H bond. On the basis of previous work, the value observed for δ_F is unexpectedly low; the anticipated drop in the value of J(PF) on substituting a Bu^tNH group for a fluorine atom in Bu^tNHPF_2 is, however, observed [92].

INFRA-RED SPECTRA OF ALKYLAMINOFLUOROPHOSPHINES (Table 1.8 and Fig.1.10).

The infra-red spectrum of $MeNHPF_2$ agrees well with that originally reported for this compound [29], except that the peak at 892 cm.$^{-1}$, which was assigned to the P-N stretching mode, is not reproduced and presumably owes its existence to the presence of an impurity; PF_3 [116] and $(PF_2)_2NMe$ [117] both produce intense peaks in this region. This leaves no obvious candidate for the P-N stretching mode, which was reported to produce a band of medium intensity in Me_2NPF_2 at 704 cm.$^{-1}$ [27] and in $MeNHP(CF_3)_2$ [118] at ~790 cm.$^{-1}$, and a band of low intensity at 853 cm.$^{-1}$ in $MeNHP(CF_3)Cl$ [119]. The assignment of phosphorus-nitrogen stretching frequencies is notoriously unsuccessful; the difficulty in obtaining satisfactory correlations stems from the large degree to which these modes are coupled with other ones [120-1]. It is, however, possible that this mode is obscured by the very intense absorptions arising from the symmetric and asymmetric stretching modes. The two absorptions are also very intense in the spectra of the other alkylaminodifluorophosphines, and remain substantially unaffected by changes in the nature of the alkyl group attached to nitrogen.

The PF_2 bending mode in $RNHPF_2$ is shifted from ~550 cm.$^{-1}$ for R = Me, Et, Bu^n to 585 cm.$^{-1}$ for R = Bu^t; this is in line with shifts observed elsewhere (vide infra) for PF bending modes where the phosphorus atom is attached to a Bu^tNH group.

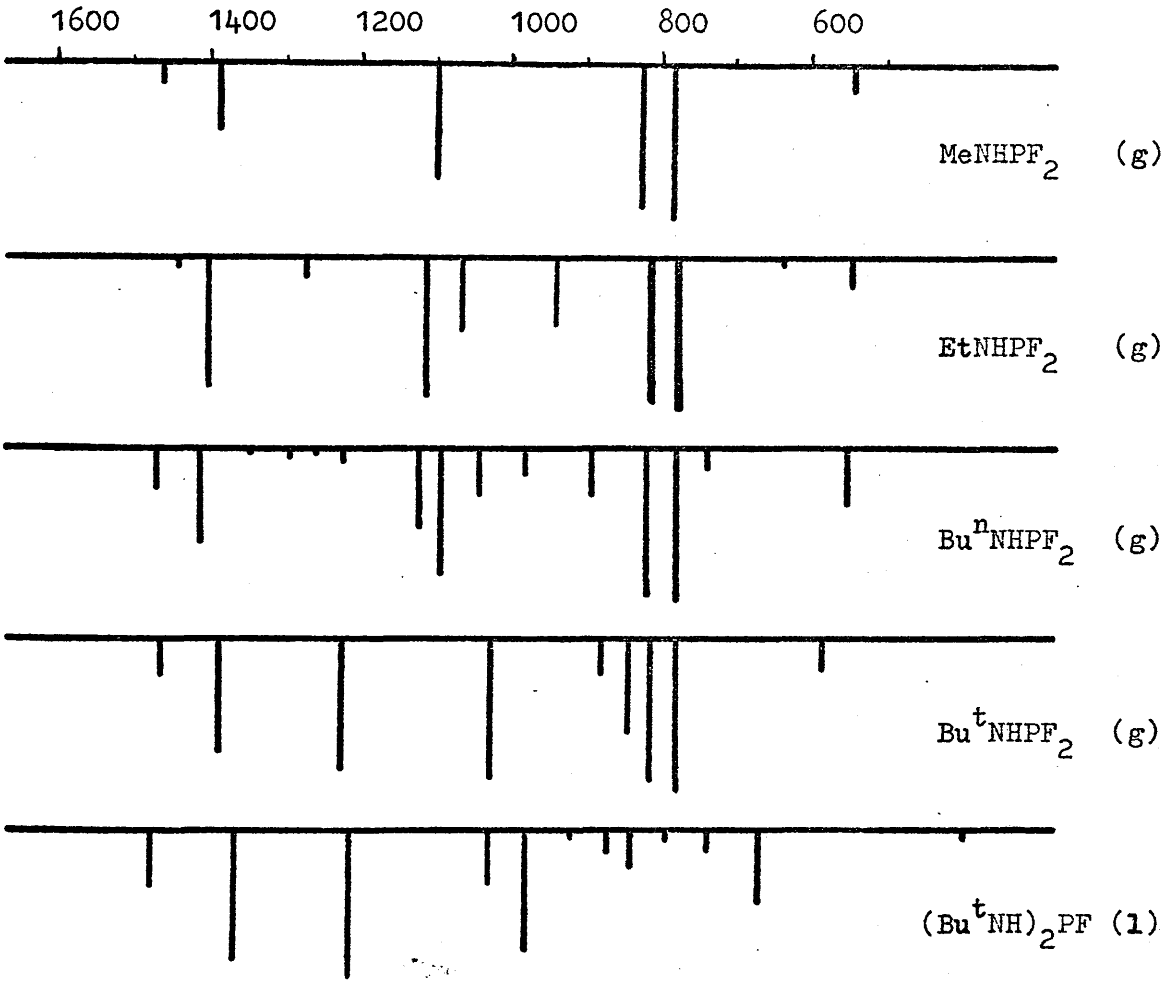


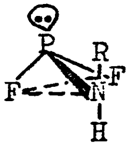
Fig. 1.10 I.r. spectra alkylaminofluorophosphines 500-1600 cm.$^{-1}$

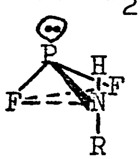
In the region 3367-3465 cm.$^{-1}$ there are two peaks associated with the N-H stretching mode while only one is expected. The highest N-H stretching frequency is observed in the methyl analogue; a successive lowering of the frequency, as the alkyl group becomes more branched at the α-carbon atom, is noted (Me, 3465; Et, 3440; Bu^n, 3442; Bu^t, 3406 cm.$^{-1}$). The second peak, which is considerably less intense, is always at a frequency ~40 cm.$^{-1}$

$(Bu^tNH)_2PF$	Bu^tNHPF_2	Bu^nNHPF_2	$EtNHPF_2$	$MeNHPF_2$	Assignments
3342 w	3406 w	3442 w	3440 w	3465 m	ν_{NH}
3278 w,br	3367 vw	3412 vw,sh	3400 vw,sh	3425 w,sh	
2968 vs	2975 s	2973 m	2975 m	3022 w,sh	ν_{CH}
2905 m	2920 m	2948 m	2940 w	2973 s	
2870 m	2888 m	2889 m	2890 w,sh	2925 sh	
			2830 vw	2840 m	
1467	1479	1468	1440 sh	1460	$\delta_{as.CH_3}$
1364	1387 br*	1410	1404	1382	δ_{NH}
1217 br	1228	1346	1271		
		1297			
		1256			
		1219			
		1120			
1030 sh	1027	1089	1113	1095	ν_{CN}
979 br	868 sh	1039	1066		
920	845 sh	980	940		
869		890			
835	817	817	813	823	$\nu_{as.PF_2}$
796					
741	782	777	775	789	$\nu_{sym.PF_2}$
670 br		739 sh	638		
497 br	585	550	544	548	$\delta_{sym.PF_2}$
	* Three bands in liquid.				

Table 1.8 (All frequencies in $cm.^{-1}$) Assignments for $MeNHPF_2$.

lower than the main peak. Nyquist has made an extensive study of compounds in which the RNHP(X) (X = S,O) group was present over the region associated with the N-H stretching mode [122]. He found that two peaks were present in these analogues which, he concluded, were associated with two configurations resulting from restricted rotation around the P-N bond. A dependence of peak frequency on the nature of R was also observed, and is identical with that reported here. A thorough study in this region of the i.r. spectrum of $MeNHP(CF_3)_2$ has shown peaks to be present at 3465 and 3430 cm.$^{-1}$, with the peak at the higher frequency possessing the lower intensity; hydrogen-bonding and combination band effects have been considered, and rejected, as explanations for this effect [118]. In the light of the n.m.r. studies on the latter compound (vide supra) two isomers seem to be present in $RNHPF_2$:-





Rotational barriers in analogous compounds of ~9 kcal./mole were calculated for this process [114]. It has been suggested that the main contributing cause to the rotational barrier is that due to $(p\text{-}d)\pi$-bonding [123]. The relative intensity data would tend to suggest that either (a) different isomers predominate in the fluorophosphine and trifluoromethylphosphine derivative, or (b) the effect that fluorine atoms have in the above two isomers of $MeNHPF_2$ on the value of ν_{NH} is opposite to the effect that the CF_3 groups exert on ν_{NH} in the two isomers of $MeNHP(CF_3)_2$.

In a recent i.r. study of $MeNHPSCl_2$ and its deuterated analogues [124], bands at 1465 and 1455 (w), 1428 (vw) and 1370 cm.$^{-1}$ (m) were assigned to $\delta_{as.CH_3}$, $\delta_{sym.CH_3}$ and δ_{NH} respectively. The bands at 1460 and 1382 cm.$^{-1}$ in $MeNHPF_2$ are therefore assigned to $\delta_{as.CH_3}$ and δ_{NH} respectively, in contrast to the previous assignments by Barlow et al. [29]. A band in the 2760-2820 cm.$^{-1}$ region, which is considered to result from an overtone of $\delta_{sym.CH_3}$ in Fermi resonance with one of the CH stretching modes, has previously been correlated with the presence of an unshared pair of electrons on nitrogen [125]. A similar prominent band is also observed in the spectra of $(MeNH)_{5-n}PF_n$ (n = 3, 4) and $(MeNH)_2PF_2H$, while this region is virtually devoid of peaks for compounds in which no -NMe- group is present.

Peaks are observed in the spectra of $EtNHPF_2$ and Bu^tNHPF_2 close to 1095 cm.$^{-1}$, which is the C-N stretching frequency for $MeNHPF_2$. However, a similar peak is absent in the spectrum of Bu^tNHPF_2. Similar differences between the methyl and ethyl, and t-butyl analogues of $(RNH)_xPF_{5-x}$ (x = 1, 2) are observed in this region. Since the C-N stretching frequency for primary amines drops by about 50 cm.$^{-1}$ in going from compounds containing a $-CH_2N$ group to those containing a $\geq$CN group [126], the strong band at 1027 cm.$^{-1}$ in Bu^tNHPF_2 is assigned to ν_{CN}. Strong peaks, similar to the one at 1228 cm.$^{-1}$ for Bu^tNHPF_2, are also present in this region for $(Bu^tNH)_xPF_{5-x}$ (x = 1, 2) and $(Bu^tNH)_2PF$, and are generally considered characteristic of a t-butyl group [127]. Similar comparisons between the i.r. spectra of phosphorus-fluorides containing the same alkylamino group reveal skeletal modes belonging to the EtNH and Bu^nNH groups.

The i.r. spectrum of $(Bu^tNH)_2PF$ bears a resemblance to that of Bu^tNHPF_2. The two peaks at 817 and 782 cm.$^{-1}$, associated with the two PF_2 stretching modes in the latter compound, are replaced by one broad band at 670 cm.$^{-1}$. A value of 745 cm.$^{-1}$ was assigned to ν_{PF} in a gaseous sample of $(Me_2N)_2PF$ [26]. The large discrepancy in these values compared with the close relationship found for the stretching modes in the difluorophosphines is partly explained by a substantial shift in frequencies between the liquid and vapour state for certain modes, which has been previously observed for fluorophosphines (26-7); a liquid phase i.r. spectrum was recorded for Bu^tNHPF_2, and significant changes were found in the positions of the ν_{PF_2} and ν_{NH} modes. The frequency of the symmetric and asymmetric PF_2 stretching modes drop by 35 and 21 cm.$^{-1}$ respectively (and so turn the shoulder at 845 cm.$^{-1}$in the gas phase spectrum into a prominent peak). Only the peak associated with ν_{NH}, due to the rotational isomer which absorbs at a higher frequency, is shifted to lower frequency (by 16 cm.$^{-1}$). The relative abundance of the two isomers (based on peak heights) becomes almost equal. There are also two bands in the ν_{NH} region for $(Bu^tNH)_2PF$, but these are of a completely different nature and are reminiscent of band shapes associated with a moderate degree of intermolecular hydrogen-bonding [122].

INFRA-RED SPECTRA OF FLUOROPHOSPHORANES.

Since the evidence for fluorophosphoranes adopting a trigonal bipyramidal structure, in which the equatorial sites are occupied by the least electronegative substituents, is overwhelming [3] , assignments will be made by assuming that this state of affairs still prevails.

One strong narrow peak is present for all compounds in the N-H stretching region. Its exact position is dependent more on the nature of the alkyl group to which the nitrogen atom is attached than the nature of the fluorophosphorane. Since, even where restricted rotation around the P-N bond is present, the environment of the amino-proton is the same for each isomer, no splitting of this peak would be expected. Restricted rotation has been shown earlier to be enhanced by intramolecular hydrogen-bonding. Since this effect would increase the non-linearity of the PF_2(a) unit, the intensity of the i.r. band arising from the symmetric stretching mode of this group should be greater than that expected. This mode is i.r. forbidden for PF_5 [78], but a weak band assigned to this mode has been reported in the spectra of $MePF_4$ [128] and Me_2PF_3 [129]. The axial bending mode, which has been assigned to a weak band at 175 $cm.^{-1}$ in the Raman spectrum of PF_5 [84], would be expected to occur at a higher frequency for molecules in which internal hydrogen-bonding is present. Other effects should be less noticeable.

The major changes between the i.r. spectra of gaseous and liquid samples of methylfluorophosphoranes were reported to occur in the position of the PF stretching frequencies [3]; the axial stretching frequencies being lowered by as much as 60 cm.$^{-1}$ in the liquid state. In alkylaminofluorophosphoranes a slight lowering in the frequency of the NH and PF stretching modes is noted. For example, in $(EtNH)_2PF_3$ ν_{NH} drops from 3480 cm.$^{-1}$to 3460 cm.$^{-1}$ (and no change which can be associated with intermolecular hydrogen-bonding is found) and the bands at 891 and 797 cm.$^{-1}$ shift to 878 and 785 cm.$^{-1}$ respectively.

INFRA-RED SPECTRA OF ALKYLAMINOTETRAFLUOROPHOSPHORANES (Table 1.9 and Fig. 1.11).

The i.r. spectrum of $MeNHPF_4$ is very simple. The 450-1000 cm.$^{-1}$ region is reproduced in Fig. 1.12. Assignments for the peaks in this spectrum have been made on the basis of the complete analyses for $MePF_4$ [128] and $ClPF_4$ [130] and the partial analysis for Me_2NPF_4 [10,12]. Many of these bands show a pronounced fine structure. However, without an exact knowledge of the principal moments of inertia for this molecule, which control the contours of these bands, previous work has indicated that little knowledge can be gleaned from this extra information [130].

Two bands occur in the 1400-1500 cm.$^{-1}$ range for $MeNHPF_4$ as well as for $(MeNH)_2PF_3$ and $(MeNH)_2PF_2H$. That at 1478 cm.$^{-1}$ has a counterpart in Me_2NPF_4 at 1464 cm.$^{-1}$ and is assigned to the

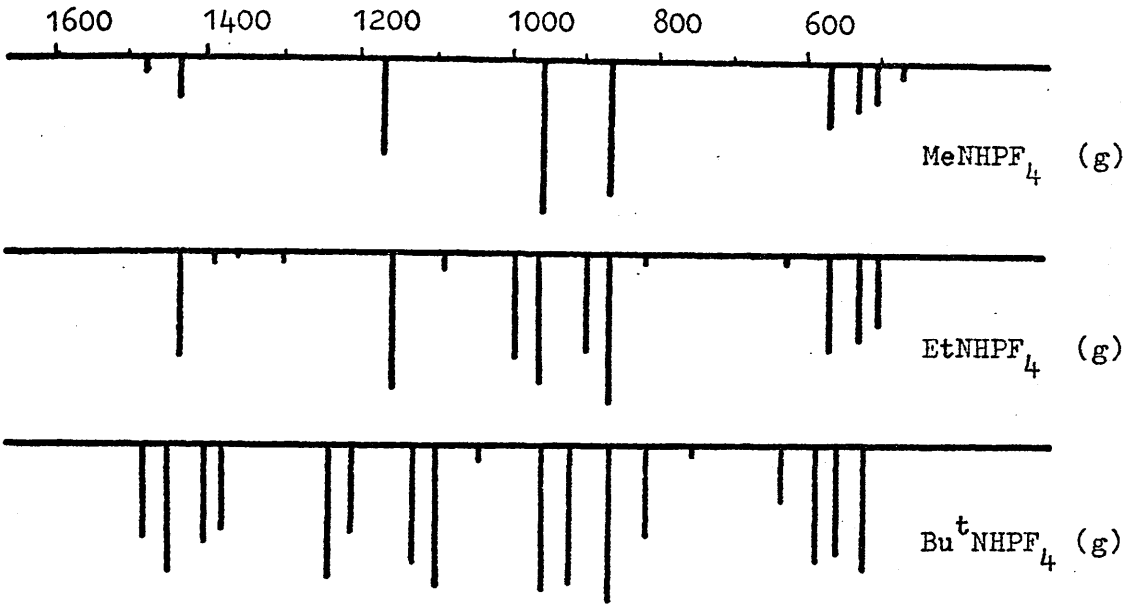


Fig. 1.11 I.r. spectra of alkylaminotetrafluorophosphoranes 450-1600 cm.$^{-1}$.

asymmetric deformation mode of the methyl group. The symmetric deformation mode occurs at 1300 cm.$^{-1}$ in Me_2NPF_4 so that the band at 1440 cm.$^{-1}$ in $MeNHPF_4$ is assigned to the NH deformation mode (although some coupling with other modes is to be expected [124]) in spite of the fact that this is 60 cm.$^{-1}$ higher than the corresponding mode for $MeNHPF_2$. Increases are also found in the values for ν_{NH} and ν_{CN}. The assignment for δ_{NH} could be confirmed by a deuteration study; a large drop in frequency would be expected for CH_3NDPF_4 but not CD_3NHPF_4.

Only two peaks are found in the PF stretching region (700-1000 cm.$^{-1}$) for $MeNHPF_4$. Three PF stretching modes are expected: these are the asymmetric and symmetric PF_2(e) and the

Bu^tNHPF_4	$EtNHPF_4$	$MeNHPF_4$	Assignments
3468 w	3479 m	3495 m	ν_{NH}
3016 m	2986 m	3003 w	ν_{CH}
2982 m	2942 m	2964 w	
2933 w	2918 w	2921 vw	
2892 w	2895 w,sh	2855 vw	
1476		1478	$\delta_{as.CH_3}$
1450	1442	1440	δ_{NH}
1403	1390		
1378	1356		
1238	1300		
1214			
1127	1161	1171	ν_{CN}
1098	1088		
1044	986		
956	959	962	$\nu_{as.PF_2(e)}$ & ?
918	900	954	ν_{PN}
		875 R	$\nu_{as.PF_2(a)}$ &
863	865	867 Q	$\nu_{sym.PF_2(e)}$
815	815	860 P	
760	626		
		573 R	$\nu_{sym.PF_2(a)}$
634	567	567 Q	
582		560 P	
561		541 R	$\delta_{o.o.p.NPF_2(e)}$
520	533	533 Q	
		524 P	
		513 R	$\delta_{i.p.PF_2(e)}$
	500 sh	504 Q	
		496 P	
		479 R	ρ_{PF_4}
		473 Q	
		466 P	

Table 1.9 (All frequencies in $cm.^{-1}$) Assignments for $MeNHPF_4$.

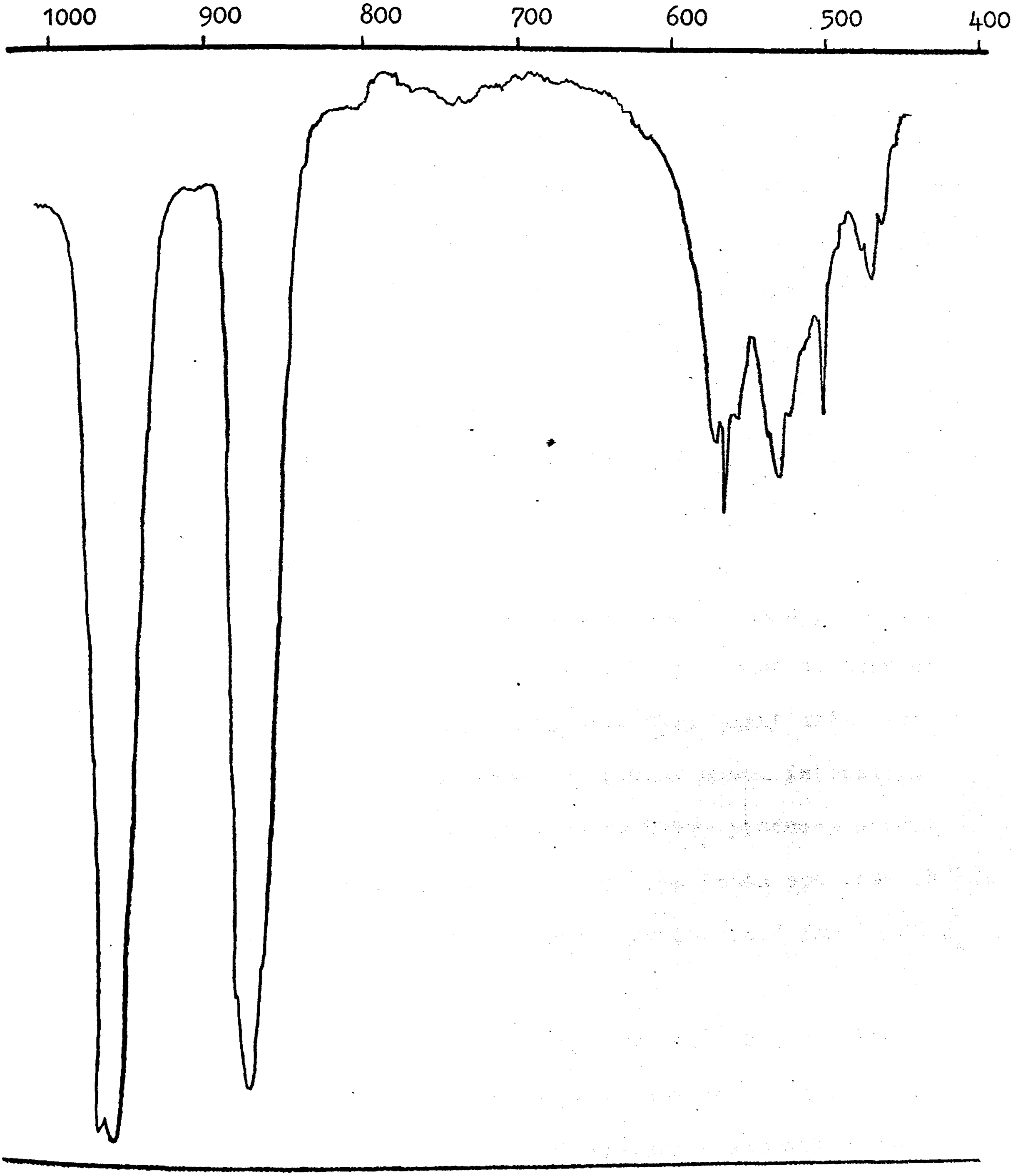


Fig. 1.12 I.r. spectrum $MeNHPF_4$ 450-1000 cm.$^{-1}$

asymmetric PF_2 (a) stretching modes. All three modes give strong peaks in HPF_4 (1024,1016;880 cm.$^{-1}$ [131]), $ClPF_4$ (921,895;903 cm.$^{-1}$), $MePF_4$ (1009,932;843 cm.$^{-1}$), CF_3PF_4 (986,909;892 cm.$^{-1}$ [132]), and $MeSPF_4$ (960,899;874 cm.$^{-1}$ [133]). Hence the band centred at 958 cm.$^{-1}$ is assigned to the asymmetric PF_2 (e) stretching mode and that at 867 cm.$^{-1}$ to both the symmetric PF_2 (e) and asymmetric PF_2 (a) stretching modes. In Me_2NPF_4 there are similarly two strong bands at 950 cm.$^{-1}$ and 882 cm.$^{-1}$, and one set of workers has reported that the latter band is a doublet [10], which encourages the assignments given here. There is disagreement over the assignment of ν_{PN} in Me_2NPF_4 which is reported as a weak peak at either 817 cm.$^{-1}$ [10] or 703 cm.$^{-1}$ [12]. There is no peak in this region of the spectrum for $MeNHPF_4$ which could correspond to this mode, but the slight asymmetry of the band centred at 958 cm.$^{-1}$ (see Fig. 1.12) suggests that this might arise from the juxtapositioning of two peaks of almost equal intensity. The corresponding PC stretching mode in $MePF_4$ produces a weak band in the i.r. but an intense band in its Raman spectrum [128]. Bands close to 960 and 870 cm.$^{-1}$ are also obtained for Bu^tNHPF_4 and $EtNHPF_4$.

There are four bands in the 450-600 cm.$^{-1}$ region which is reminiscent of the same region in $MePF_4$ and very similar to that in Me_2NPF_4. The PF_2 (a) symmetric stretching vibration was assigned to the band at 701 cm.$^{-1}$ in Me_2NPF_4 [11]; this seems unlikely in view of assignments for other molecules. The most likely band to be associated with this mode in $MeNHPF_4$ is that at 567 cm.$^{-1}$ (cf. PF_5, 640 cm.$^{-1}$ [78]; $ClPF_4$, 691 cm.$^{-1}$; HPF_4, 640 cm.$^{-1}$ [131]; $MePF_4$, 596 cm.$^{-1}$). The remaining three bands must arise from bending modes of the NPF_4 skeleton; they are tentatively assigned on the basis of the i.r. study for $MePF_4$.

INFRA-RED SPECTRA OF BIS(ALKYLAMINO)TRIFLUOROPHOSPHORANES (Table 1.10 and Fig. 1.13).

The i.r. spectrum for $(MeNH)_2PF_3$ shows only a few strong peaks, which exhibit a much less pronounced fine structure than those obtained in the spectrum of $MeNHPF_4$. The peaks in $(MeNH)_2PF_3$ above 1000 cm.$^{-1}$ are assigned as for $MeNHPF_4$ and those below 1000 cm.$^{-1}$ on the basis of the complete analyses for Me_2PF_3 [129] and Cl_2PF_3 [78,84,134]. There are three strong bands in the 700-1000 cm.$^{-1}$ region for $(Me_2N)_2PF_3$ (at 870,830 and 755 cm.$^{-1}$) [10,11] and only two for $(MeNH)_2PF_3$ (at 905 and 807 cm.$^{-1}$). Two bands are expected to arise in this region from the PF_3 stretching modes: these are the PF (e) stretching and asymmetric PF_2 (a) stretching modes. The band at 905 cm.$^{-1}$ in $(MeNH)_2PF_3$ is then assigned to the former and that at 807 cm.$^{-1}$ to the latter mode. In $(Me_2N)_2PF_3$ the band at 870 cm.$^{-1}$ is then unambiguously assigned to the PF (e) stretching mode. This leaves one of the two bands at 830

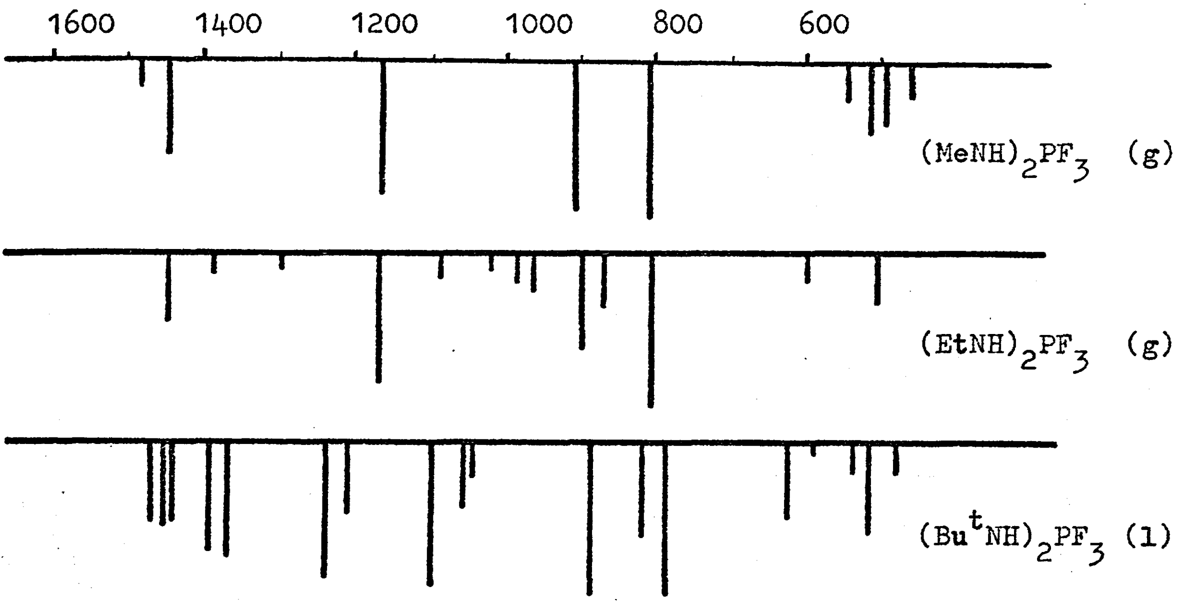


Fig. 1.13 I.r spectra of bis(alkylamino)trifluorophosphoranes 450-1600 cm.$^{-1}$.

or 775 cm.$^{-1}$ to be associated with the asymmetric PF_2 (a) stretching mode. By analogy with the PC_2 grouping in Me_2PF_3, two bands are expected which mainly originate from the PN_2 grouping. The other band in $(Me_2N)_2PF_3$ is then assigned to the asymmetric PN_2 stretching mode. A band of considerable intensity would be predicted to be present in the Raman spectrum at a lower frequency corresponding to the symmetric PN_2 stretching mode.

In $(MeNH)_2PF_3$ the band at 905 cm.$^{-1}$ is about twice as broad as that at 807 cm.$^{-1}$, which in turn possesses a similar band width to the three bands obtained for $(Me_2N)_2PF_3$. It seems likely then that this band also includes a peak due to the

$(Bu^tNH)_2PF_3$	$(EtNH)_2PF_3$	$(MeNH)_2PF_3$	Assignments
3459 m	3480 w	3499 m	ν_{NH}
3003 m	2980 m	2961 m,sh	ν_{CH}
2966 s	2938 w	2950 m,sh	
2934 m	2905 w	2910 w,sh	
2869 m		2840 w	
1468		1481	$\delta_{as.CH_3}$
1450			
1436			
1392	1441	1444	δ_{NH}
1367	1384		
1235	1296		
1206			
1094	1157	1162	ν_{CN}
1053	1084		
1037 sh	1018 sh		
	990		
	960		
882	891	905 br	$\nu_{PF(e)}$ ν_{PN}
812	864		
782	797	807	$\nu_{as.PF_2(a)}$
619	593	540	$\nu_{sym.PF_2(a)}$
587	502 br	507	skeletal modes
532		485	
508		450	
472			

Table 1.10 (All frequencies in $cm.^{-1}$) Assignments for $(MeNH)_2PF_3$.

asymmetric PN_2 stretching mode. It might prove possible to detect a splitting of this band by running i.r. spectra in various solvents since, as mentioned previously, the PF stretching modes are more dependent than the others on their physical state. In $(EtNH)_2PF_3$ and $(Bu^tNH)_2PF_3$ the peaks due to the PF_3 modes, which are clearly visible in this region, possess similar band widths. It seems reasonable to assign the peak at 864 cm.$^{-1}$ in $(EtNH)_2PF_3$ and at 812 cm.$^{-1}$ in $(Bu^tNH)_2PF_3$ to the PN_2 asymmetric stretching mode. In $(Et_2N)_2PF_3$ a new peak appears in this region at 730 cm.$^{-1}$ [11]. The band at 775 cm.$^{-1}$ in $(Me_2N)_2PF_3$ [11] is then assigned to the asymmetric PN_2 stretching mode and that at 830 cm.$^{-1}$ to the asymmetric PF_2 (a) stretching mode, which makes the drop in frequency of the former band for both alkylamino and dialkylamino derivatives very similar on changing the nature of the alkyl groups attached to nitrogen. The dependence of the value for the asymmetric PF_2 (a) stretching mode in X_nPF_{5-n} on both X and n is presented in Table 1.11.

The i.r. spectrum of $(MeNH)_2PF_3$ shows one band at 540 cm.$^{-1}$, assigned to the symmetric PF_2 (a) stretching mode, and a further broad band at $\sim$500 cm.$^{-1}$ which is partially resolved into three peaks, but it is possible that more are in fact present. No confident assignments can, therefore, be made in this region.

Table 1.11 Asymmetric and symmetric PF_2 (a) stretching modes (cm.$^{-1}$)

X	Cl		Me		NMe_2		NMeH	
	as.	sym.	as.	sym.	as.	sym.	as.	sym
XPF_4	903	691	843	596	800	580 [a]	867	567
X_2PF_3	925	665	755	540	830	[b]	807	540
X_3PF_2	867	633 [c]	670 690 [f]	500 [c] 543 [f]	740 [d]	[b]	745 [e]	540 [e]

[a] Assigned here. [b] Not given. [c] Raman. [d] [136]. [e] $(MeNH)_2PF_2H$.
[f] Me_2PF_2H [135].

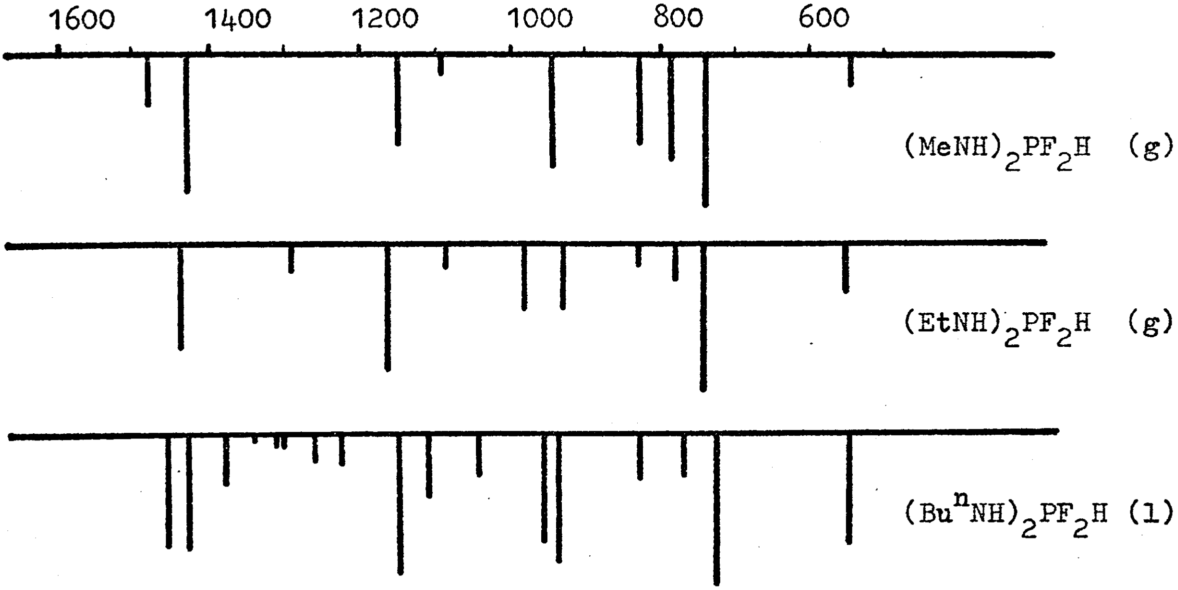


Fig. 1.14 I.r. Spectra of bis(alkylamino)difluorophosphoranes 500-1600 cm.$^{-1}$.

INFRA-RED SPECTRA OF BIS(ALKYLAMINO)DIFLUOROPHOSPHORANES (Table 1.12 and Fig. 1.14).

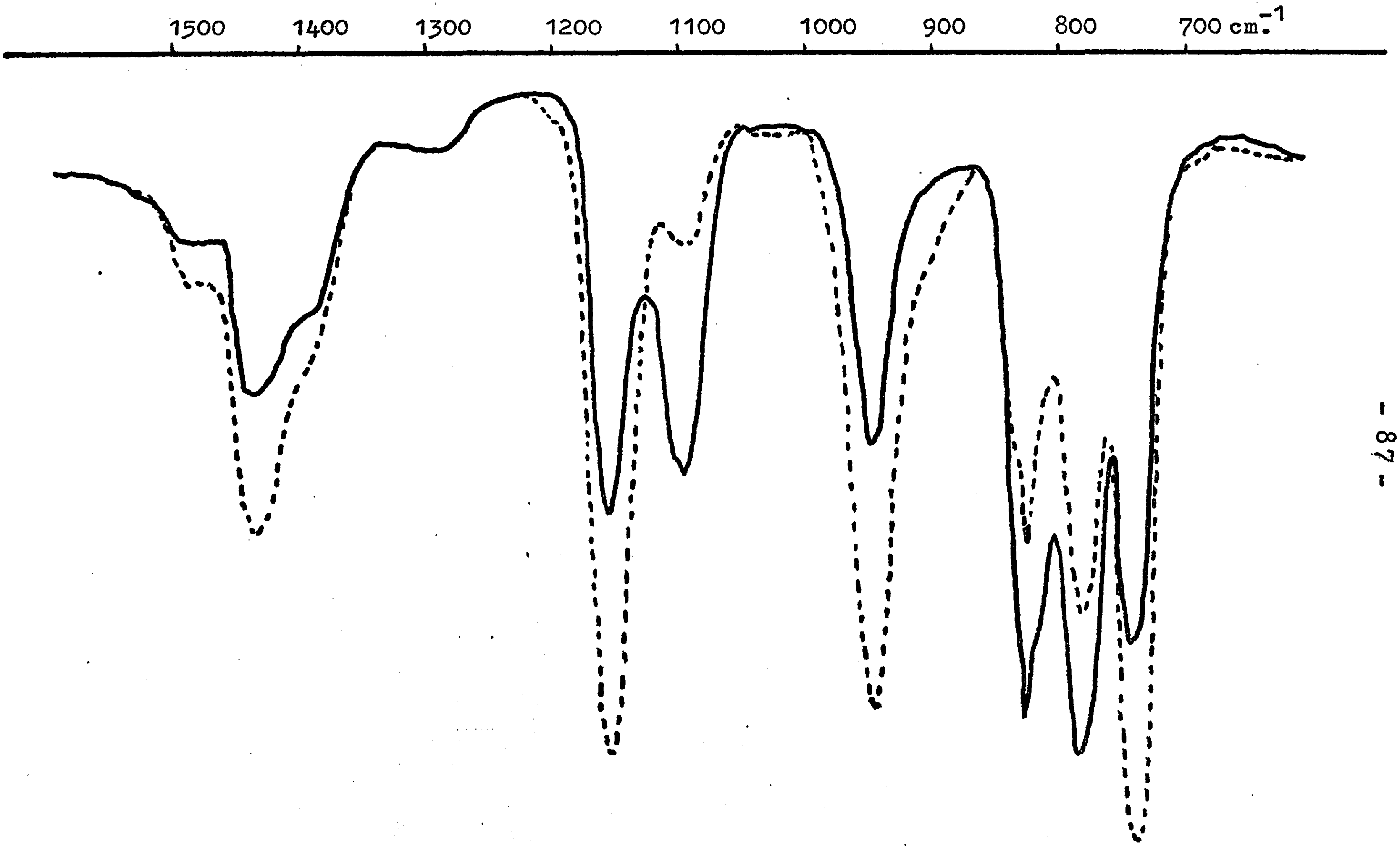
Owing to the low stability of these compounds, i.r. spectra could only be obtained from impure gaseous samples of (MeNH)$_2$PF$_2$H and (EtNH)$_2$PF$_2$H; band intensities are thus unreliable and weak bands might well have been missed. Fig. 1.15 shows the difference recorded in the i.r. spectrum of (MeNH)$_2$PF$_2$H in the 700-1500 cm.$^{-1}$ range over a 15 minute period. Peak intensities for the liquid film spectrum of (Bu^{n}NH)$_2$PF$_2$H, which is more stable with respect to decomposition, are more reliable

Two peaks are observed in the PH stretching region, while only one peak is expected. Previous work has similarly shown two

$(Bu^nNH)_2PF_2H$	$(EtNH)_2PF_2H$	$(MeNH)_2PF_2H$	Assignments
3495 m	3475 m	3493 m	ν_{NH}
2958 s	2975 s	2959 s	ν_{CH}
2933 s	2895 m	2838 m	
2875 m			
2740 vw			
2496 w	2502 w	2502 w	
2414 m	2423 m	2429 s	ν_{PH}
1455		1480	$\delta_{as.CH_3}$
1432	1435	1430	δ_{NH}
1381			
1343			
1311			
1300	1296		
1262			
1224			
1148	1154	1150	ν_{CN}
1109	1080	1090	? imp.
1045			
955	978		
939	925	944	$\nu_{as.PN_2}$
830	815	826	}? imp.
773	775	786	
718	737	745	$\nu_{as.PF_2}$ (a)
552 br	545	540	$\nu_{sym.PF_2}$ (a)

Table 1.12 (All frequencies in cm.$^{-1}$) Assignments for $(MeNH)_2PF_2H$.

bands in Me_2PF_2H [135] and $MePF_3H$ [58] as well as HPF_4 [131]; the lower more intense peak was always assigned to ν_{PH}. The band at the higher frequency, which is about one fifth as intense as that at the lower frequency, is presumably due to a combination band, whose intensity is enhanced by Fermi resonance with ν_{PH}, since this area is usually devoid of any other peaks. The value



<u>Fig. 1.15</u> I.r. spectrum $(MeNH)_2PF_2H$ (---), and with decomposition products 15 mins. later (——)

of ν_{PH} alters to a small extent on changing the nature of the substituents in the pentaco-ordinated derivatives, but there is no direct dependence of ν_{PH} on the electronegativities of the substituents, which is in line with work reported for other series of PH derivatives [120].

The strong band at 745 cm.$^{-1}$ in $(MeNH)_2PF_2H$ which rapidly decreases in intensity on standing is assigned to the asymmetric PF_2 (a) stretching mode. The two bands at 826 and 786 cm.$^{-1}$ which increase in intensity on standing along with that at 1090 cm.$^{-1}$ are the positions of the most prominent bands in the spectrum of $MeNHPF_2$. It is, however, uncertain whether less intense bands may in fact be present near these positions. Since $(MeNH)_2PF_2H$ only possesses a small vapour pressure, low temperature studies on the gas phase would be impracticable but one on the liquid phase might clear up this point.

A very intense band at 944 cm.$^{-1}$ is at a slightly higher frequency than the asymmetric PN_2 stretching mode in $(MeNH)_2PF_3$. Little change is reported in the values of the corresponding asymmetric PC_2 stretching mode on replacing one fluorine atom in Me_2PF_3 by a hydrogen atom [135]. This leaves no band which can be definitely assigned to a PH deformation mode, which is expected to fall in the 800-1150 cm.$^{-1}$ range [120]; no previous assignments have been made for this mode in other molecules of the type HPX_4. In order to establish whether such a band does exist, an infra-red study on $(MeND)_2PF_2D$ should be performed. It is quite probable that this mode will not be a pure bending mode, but will also to some extent involve motion of nearby atoms in the molecule.

The band at 540 $cm.^{-1}$ is assigned to the PF_2 (a) stretching mode although other skeletal deformation modes will also be present in this region. The assignment is supported by the corresponding values found for the same mode in similar compounds (see Table 1.11).

INFRA-RED SPECTRA OF ALKYLAMMONIUM HEXAFLUOROPHOSPHATES.

The major i.r. absorptions observed in the spectra of the alkylammonium hexafluorophosphate salts are given in Table 1.13. The infra-red spectrum for a KBr wafer of $Bu^tNH_3^+ PF_6^-$ has been catalogued elsewhere [38]; the peak positions are totally inconsistent with the values presented here. In a totally symmetric environment the hexafluorophosphate anion possesses only two infra-red active fundamentals; both gave rise to strong absorption bands at 830 ± 10 and 550 ± 2 $cm.^{-1}$ in alkali metal salts, which also exhibited feeble peaks arising from some of the "forbidden" fundamentals [137].

All three salts studied here exhibit very strong absorptions in these two regions. In addition the band at ~745 $cm.^{-1}$ may

$MeNH_3^+ PF_6^-$	$EtNH_3^+ PF_6^-$	$Bu^tNH_3^+ PF_6^-$
3415 ms	3386 w	3286 s
3315 s	3306 s	3249 m
3265 ms	3257 m	3215 m
3208 vw	3206 w	3182 m
3010 vw	2997 w	2980 w
		2890 w
All spectra show weak bands down to 2400 cm.$^{-1}$.		
1610 m	1607 ms	1612 s
1506 ms	1500 s	1498 s
	1479 m	1482 ms
	1466 w	
1437 ms	1406 m	1415 ms
1378 ms		1388 s
1306 vw	1340 w	1300 s
1262 w	1220 m	1215 w
	1191 ms	
	1123 w	
1100 w	1104 w	1088 w
	1045 m	
	960 s	969 m
		949 m
830 vs br	830 vs br	830 vs br
742 w sh	750 m sh	749 m
563 vs	563 vs	550 vs

Table 1.13 Major bands in i.r. spectra of alkylammonium hexafluorphosphates (all frequencies in cm.$^{-1}$).

correspond to one of the i.r. inactive fundamentals. The bands at ~3300 and ~1600 cm.$^{-1}$ are characteristic of the NH_3^+ stretching and the NH_3^+ asymmetric bending modes respectively [127]. Bands below the 1380-1510 cm.$^{-1}$ region, which is the characteristic region for the CH_3 bending and the NH_3^+ symmetric bending modes, either arise from overtones of the PF_6^- anion or skeletal modes of the cation.

INFRA-RED SPECTRA OF ALKYLAMINE-PHOSPHORUS PENTAFLUORIDE ADDUCTS (Table 1.14).

Large differences are observed between the infra-red spectra of $2MeNH_2.PF_5$ and $RNH_2.PF_5$ ($R = Et, Bu^t$) in the region associated with the NH_2 stretching and bending modes. Both $EtNH_2.PF_5$ and $Bu^tNH_2.PF_5$ show two sharp peaks centred at ~3270 cm.$^{-1}$, as has been observed in the i.r. spectra of other alkylamine-phosphorus pentafluoride adducts [16]. However, in $2MeNH_2.PF_5$ there is only one intense peak in this region, while there are also several medium to weak peaks extending down to 2500 cm.$^{-1}$ which are not associated with CH stretching modes. The NH_3^+ stretching modes and the NH_3^+ bending modes for $MeNH_3^+ F^-$ occur at a lower frequency (200-400 cm.$^{-1}$) and a higher frequency (~100 cm.$^{-1}$) respectively than those for the other alkylammonium salts, as the result of the appreciably greater degree of hydrogen-bonding (N-H---F) present in the former compound [138]. The frequency difference between the strong peaks which are present in the NH deformation region for $2MeNH_2.PF_5$ and $RNH_2.PF_5$ ($R = Et, Bu^t$) amounts to about 50 cm.$^{-1}$. There is thus substantial evidence for the presence of hydrogen-bonding in $2MeNH_2.PF_5$.

The PF bending and stretching modes occur at about the same frequency as for the hexafluorophosphate salts; however, the lower symmetry of these adducts produces several bands in both regions. Since the P-N stretching mode is also likely to fall

$2MeNH_2.PF_5$	$EtNH_2.PF_5$	$Bu^tNH_2.PF_5$
3332 ms	3306 s	3287 s
3294 vw	3266 s	3248 s
	3138 vw	3117 w
	3023 vw	3036 m
2988 w	3014 w	2989 m
2858 w	2967 vw	2964 m
2740 m br	2926 vw	2899 m
2588 w	2903 vw	
2504 m		
2103 w		
1655 w	1640 w	1645 vw
1613 s		
1545 w	1574 s	1565 s
	1516 vw	1483 m
1477 m	1474 m	1475 w sh
1455 w		1450 w
1433 w	1400 s	1415 w
	1388 s	1384 s
		1370 s
1292 vw	1317 m	
		1223 m
		1207 m
1150 vw		1197 m
1137 w	1112 m	
	1099 m	
1024 w	1030 w	1048 w
1003 m		
994 m		
943 m		934 w
866 vs	880 vs br	875 vs
845 vs	830 vs br	835 s
833 vs		819 s
803 vs		787 s
	755 vw	761 vw
704 w	716 m	708 w
	620 w	637 w
547 s		548 m
537 m	544 vs	533 m
523 m	520 vs	525 m

Table 1.14 Infra-red spectra of alkylamine-phosphorus pentafluoride adducts (all frequencies in cm.$^{-1}$).

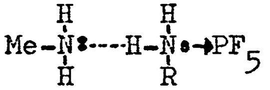
in the region associated with the PF stretching modes, it is not possible to make any definite statement about changes in symmetry in the 1:1 and 2:1 adducts. The spectra indicate that the differences between $EtNH_2.PF_5$ and $Bu^tNH_2.PF_5$ are as large as those between the 1:1 and the 2:1 adducts in this particular region.

There are four structures which the 2:1 adduct can be considered to adopt in the solid state:-

(i) A seven co-ordinated structure (I).

(ii) A salt-like structure, $MeNH_3^+ (MeNHPF_5)^-$ (II).

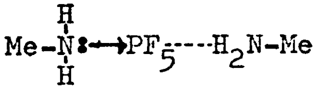
(iii) A structure in which hydrogen-bonding is through the nitrogen atom,



$$Me-\overset{H}{\underset{H}{N}}\!:\cdots H-\overset{H}{\underset{R}{N}}\!:\rightarrow PF_5 \qquad (III)$$

(Note that this is the transition state previously postulated to be formed in the reaction between the 1:1 adducts and excess amine.)

(iv) A structure in which hydrogen-bonding is through the fluorine atoms,

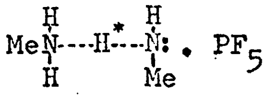


$$Me-\overset{H}{\underset{H}{N}}\!:\rightarrow PF_5\cdots H_2N-Me \qquad (IV)$$

Heptaco-ordinated phosphorus is unknown and exceedingly unlikely to be formed. If structure II is present, hydrogen-bonding would be through either (a) the NH_3 or (b) the NH hydrogen atoms interacting with the fluorine atoms or (c) the nitrogen atom on the MeNH group interacting with the protons on the cation. Since there is no substantial evidence for hydrogen-bonding in $MeNH_3^+ PF_6^-$, the first type of interaction (type (a)) can be ruled out. The type of interaction represented by (b) seems unlikely since, if it were present, appreciable hydrogen-bonding would be expected to be present in the 1:1 adducts. The magnitude of this type of hydrogen-bonding could be studied by preparing a series of salts containing the $(MeNHPF_5)^-$ anion. The third type of interaction (type (c)) in its extreme form leads to III, which contains the type of bonding which was postulated to be present in boron trifluoride adducts with the general formula $2L.BF_3$ [139].

There is some evidence that hydrogen-bonding through a fluorine atom has a greater effect on the NH fundamentals than when it is through a nitrogen atom [140]. However, the number of molecules studied was small, and the values of the NH modes do not appear to discriminate between these two types of bonding. If hydrogen-bonding were through H---F bonds, as in IV, one would expect (a) two strong peaks in the 3270 cm.$^{-1}$ region due to the unaffected co-ordinated amine, (b) some influence on the positions of the PF_5 stretching and bending modes to be apparent, and (c) the larger number of available sites for hydrogen-bonding to produce adducts containing more than two methylamine molecules.

I.r. evidence is thus compatible with a structure:-



$$\mathrm{Me}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{N}}}\text{---}\mathrm{H}^{*}\text{---}\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{N}}}\!:\ .\ \mathrm{PF_5}$$

but it does not appear to be possible to define exactly where H* lies. Both n.m.r. evidence, which shows that in solution dissociation takes place to form a free molecule of amine and the 1:1 adduct, and mass spectral evidence, which indicates that methylamine is easily lost, are in agreement with a structure as indicated in III. However, this evidence does not completely rule out structure IIc as being that adopted by $2MeNH_2.PF_5$ in the solid state; only a neutron diffraction study on a single crystal of the compound could positively identify the position of H* and give an unambiguous structural assignment.

MASS SPECTRA OF RNHP(F) COMPOUNDS.

Major fragments in mass spectra are best rationalized by bearing in mind that the most stable ion products are those which are formed by the most favourable reaction pathways [141]. The abundance of a particular ion will depend, not only on the rates of all reactions producing this ion, but also on the rates of all its decomposition reactions. It is the relative stability of the ionic rather than the radical species formed which controls the fragmentation pattern for a particular species and hence the ion product distribution obtained. Initial ionisation of organic molecules preferentially proceeds through the loss of an electron from a heteroatom containing non-bonding outer shell electrons; if no heteroatom is present then the electron has to be removed from a particular bond [142]. Djerassi has found that the best way of rationalizing bond cleavages is to assume preferential localization of the charge at specific sites in the molecular ion as well as fragment ions which are undergoing decomposition [142]. This is despite the very high energies used in mass spectrometers (70 eV v ~15 eV for ionizing an atom) which might lead one to expect an indiscriminate cleavage of bonds. In fact relative abundances of particular ions correlate well with those factors which control common ground-state reactions [141].

While organic compounds decompose almost exclusively to form fragments bearing positive charges, the high electronegativity of fluorine and the other halogen atoms, which leads to the ready formation of stable complex anions, could also lead to the possible formation of stable negatively charged species in the mass spectrometer. Negative ion mass spectrometric studies have shown that inorganic halides do indeed produce a range of anions of varying stability [143]. Without recourse to a mass spectrometer which is capable of detecting negative ions, it is not possible to estimate the extent to which such species are formed in the break-down of the phosphorus-fluorides studied here.

Table 1.15 lists all the ions that were mass measured, and Table 1.16 gives all the metastable transitions observed in the mass spectra of RNHP(F) compounds.

Table 1.15 Mass measurements of ions obtained from RNHP(F) compounds.

Bu^tNHPF_4:-

Mass		
Found	Calc.	Ion
165.0285	165.0286	$C_2{}^{13}CH_7NPF_4^+$
164.0250	164.0252	$C_3H_7NPF_4^+$
144.0188	144.0190	$C_3H_6NPF_3^+$
135.9941	135.9939	$CH_3NPF_4^+$
127.9883	127.9877	$C_2H_2NPF_3^+$
118.0033	118.0033	$CH_4NPF_3^+$
115.9872	115.9877	$CH_2NPF_3^+$
103.9876	103.9877	$H_2NPF_3^+$
102.9792	102.9799	$HNPF_3^+$
84.9653	84.9655	POF_2^+

Bu^nNHPF_2:-

Mass		
Found	Calc.	Ion
126.0285	126.0284	$C_3H_7NPF_2^+$
124.0251	124.0253	$C_4H_7PF_2^+$

$(MeNH)_2PF_3$:-

Mass		
Found	Calc.	Ion
148.0371	148.0377	$C_2H_8N_2PF_3^+$
129.0388	129.0393	$C_2H_8N_2PF_2^+$
118.0031	118.0033	$CH_4NPF_3^+$

$(MeNH)_2PF_2H$:-

Mass		
Found	Calc.	Ion
130.0498	130.0462	$C_2H_9N_2PF_2^+$
129.0396	129.0384	$C_2H_8N_2PF_2^+$
127.0243	127.0237	$C_2H_6N_2PF_2^+$
111.0456	111.0487	$C_2H_9N_2PF^+$
110.0367	110.0409	$C_2H_8N_2PF^+$
100.0119	100.0128	$CH_5NPF_2^+$
80.0048	80.0065	CH_4NPF^+
77.9891	77.9909	CH_2NPF^+
60.0016	60.0003	CH_3NP^+
50.9803	50.9800	HPF^+

$(Bu^tNH)_2PF$:-

Mass		
Found	Calc.	Ion
195.1376	195.1382	$C_7{}^{13}CH_{20}N_2PF^+$
194.1351	194.1348	$C_8H_{20}N_2PF^+$
179.1114	179.1113	$C_7H_{17}N_2PF^+$
83.0178	83.0174	$H_5N_2PF^+$
65.9910	65.9909	H_2NPF^+
65.9672	65.9671	POF^+ *

* Less intense peak

Table 1.16 Metastable transitions obtained for RNHP(F) compounds.

m_1	Transition				m_2	m^*	
						calc.	found
		$MeNHPF_4$					
137	$CH_4NPF_4^+$	$\longrightarrow$	$CH_3NPF_4^+$	+ H	136	135.0	135.0
118	$CH_4NPF_3^+$	$\longrightarrow$	$CH_2NPF_3^+$	+ H_2	116	114.0	114.1
		Bu^tNHPF_4					
164	$C_3H_7NPF_4^{+\,\Delta}$	$\longrightarrow$	$C_3H_6NPF_3^{+\,\Delta}$	+ HF	144	126.5	126.5
164	$C_3H_7NPF_4^{+\,\Delta}$	$\longrightarrow$	$H_2NPF_3^{+\,\Delta}$	+ C_3H_5F	104	66.0	66.0
		Bu^tNHPF_2					
126	$C_3H_7NPF_2^+$	$\longrightarrow$	$C_3H_6NPF^+$	+ HF	106	89.2	89.1
41	$C_3H_5^+$	$\longrightarrow$	$C_3H_3^+$	+ H_2	39	37.1	37.1
	or $C_2H_3N^+$	$\longrightarrow$	C_2HN^+	+ H_2			
106	$C_3H_6NPF^+$	$\longrightarrow$	$C_3H_6N^+$	+ PF	56	29.6	29.5
57	or $C_3H_7N^+$	$\longrightarrow$	$C_2H_3N^+$	+ CH_4	41	29.5	
	or $C_4H_9^+$	$\longrightarrow$	$C_3H_5^+$	+ CH_4			
126	$C_3H_7NPF_2^+$	$\longrightarrow$	$C_3H_7N^+$	+ PF_2	57	25.8	25.8
		Bu^nNHPF_2					
141	$C_4H_{10}NPF_2^+$	$\longrightarrow$	$C_4H_7PF_2^{+\,\Delta}$	+ NH_3	124	109.1	109.0
98	$CH_3NPF_2^+$	$\longrightarrow$	CH_2NPF^+	+ HF	78	62.1	62.1
43	$C_2H_5N^+$	$\longrightarrow$	$C_2H_3N^+$	+ H_2	41	39.0	39.1
	or $C_3H_7^+$	$\longrightarrow$	$C_3H_5^+$	+ H_2			
41	$C_2H_3N^+$	$\longrightarrow$	C_2HN^+	+ H_2	39	37.1	37.1
	or $C_3H_5^+$	$\longrightarrow$	$C_3H_3^+$	+ H_2			

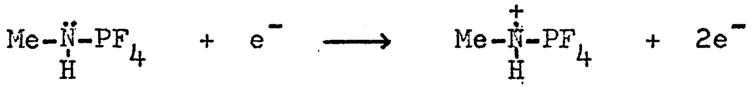
Table 1.16 (cont.)

m_1	Transition	m_2	m^* calc.	m^* found
	$(Bu^tNH)_2PF$			
194	$C_8H_{20}N_2PF^{+\Delta} \longrightarrow C_7H_{17}N_2PF^{+\Delta} + CH_3$	179	165.4	165.3
151	$C_6H_{15}NPF^+ \longrightarrow C_4H_{10}NPF^+ + C_2H_5$ or $C_5H_{13}N_2PF^+ \longrightarrow C_4H_{10}NPF^+ + CH_3N$ or $C_5H_{13}N_2PF^+ \longrightarrow C_3H_8N_2PF^+ + C_2H_5$	122	98.6	98.5
123	$C_3H_9N_2PF^+ \longrightarrow C_3H_6NPF^+ + NH_3$	106	91.4	91.3
122	$C_4H_{10}NPF^+ \longrightarrow C_4H_7PF^+ + NH_3$ or $C_3H_8N_2PF^+ \longrightarrow C_3H_5NPF^+ + NH_3$	105	90.4	90.4
41	$C_2H_3N^+ \longrightarrow C_2HN^+ + H_2$ or $C_3H_5^+ \longrightarrow C_3H_3^+ + H_2$	39	37.1	37.2
57	$C_3H_7N^+ \longrightarrow C_2H_3N^+ + CH_4$ or $C_4H_9^+ \longrightarrow C_3H_5^+ + CH_4$	41	29.5	29.5
123	$C_3H_9N_2PF^+ \longrightarrow C_3H_8N^+ + HNPF$	58	27.4	27.3
	$(MeNH)_2PF_3$			
118	$CH_4NPF_3^{+\Delta} \longrightarrow CH_2NPF_3^+ + H_2$	116	114.0	114.1
118	$CH_4NPF_3^{+\Delta} \longrightarrow CH_3NPF_2^+ + HF$	98	81.5	81.4
	$(EtNH)_2PF_2H$			
114	$C_2H_7NPF_2^+ \longrightarrow H_3NPF_2^+ + C_2H_4$	86	64.9	64.9
98	$CH_3NPF_2^+ \longrightarrow CH_2NPF^+ + HF$	78	62.1	62.2
86	$H_3NPF_2^+ \longrightarrow PF_2^+ + NH_3$	69	55.3	55.3
94	$C_2H_6NPF^+ \longrightarrow H_2NPF^+ + C_2H_4$	66	46.4	46.3

$^\Delta$ Confirmed by mass measurement (Table 1.15).

MASS SPECTRUM OF METHYLAMINOTETRAFLUOROPHOSPHORANE (Table 1.17 and Fig. 1.16).

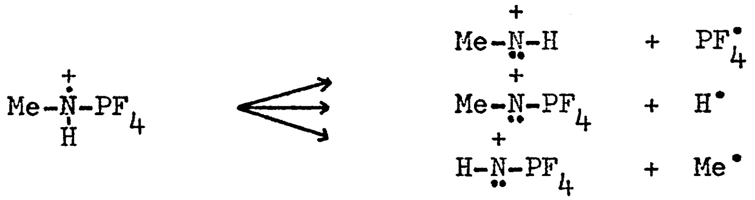
The mass spectrum of $\mathrm{MeNHPF_4}$ shows a simple break-down pattern with little evidence for any rearrangement processes taking place. The ionization step is most likely to involve the removal of an electron from the nitrogen lone pair,



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{\bullet\bullet}{\mathrm{N}}}-\mathrm{PF}_4 \quad + \quad e^- \longrightarrow \mathrm{Me}-\underset{\mathrm{H}}{\overset{+}{\overset{\bullet}{\mathrm{N}}}}-\mathrm{PF}_4 \quad + \quad 2e^-$$

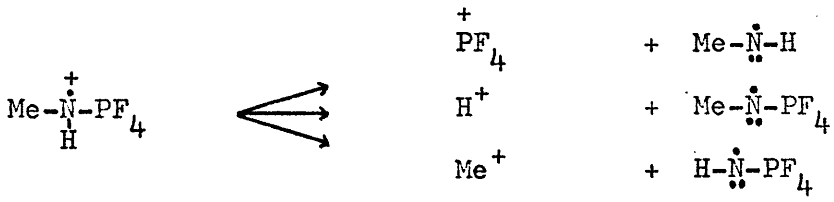
since fluorine is the only other atom present which possesses any non-bonding electrons and its ionization potential is a lot higher than that of nitrogen (see Appendix 2 for values of ionization potentials).

Cleavage of the molecular ion can take place at the nitrogen atom, either with charge retention on the nitrogen atom,



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{+}{\overset{\bullet}{\mathrm{N}}}}-\mathrm{PF}_4 \quad \begin{array}{lll} \nearrow & \mathrm{Me}-\underset{\bullet\bullet}{\overset{+}{\mathrm{N}}}-\mathrm{H} \quad + \quad \mathrm{PF}_4^{\bullet} & (1) \\ \rightarrow & \mathrm{Me}-\underset{\bullet\bullet}{\overset{+}{\mathrm{N}}}-\mathrm{PF}_4 \quad + \quad \mathrm{H}^{\bullet} & (2) \\ \searrow & \mathrm{H}-\underset{\bullet\bullet}{\overset{+}{\mathrm{N}}}-\mathrm{PF}_4 \quad + \quad \mathrm{Me}^{\bullet} & (3) \end{array}$$

or charge transfer to one of the other atoms,



$$\mathrm{Me}-\underset{\mathrm{H}}{\overset{+}{\overset{\bullet}{\mathrm{N}}}}-\mathrm{PF}_4 \quad \begin{array}{lll} \nearrow & \overset{+}{\mathrm{PF}}_4 \quad + \quad \mathrm{Me}-\underset{\bullet\bullet}{\overset{\bullet}{\mathrm{N}}}-\mathrm{H} & (4) \\ \rightarrow & \mathrm{H}^{+} \quad + \quad \mathrm{Me}-\underset{\bullet\bullet}{\overset{\bullet}{\mathrm{N}}}-\mathrm{PF}_4 & (5) \\ \searrow & \mathrm{Me}^{+} \quad + \quad \mathrm{H}-\underset{\bullet\bullet}{\overset{\bullet}{\mathrm{N}}}-\mathrm{PF}_4 & (6) \end{array}$$

Rearrangement processes will be favoured if the energy required for the above cleavage reactions is large. In fact fragments corresponding to all these processes except (3) and (5) are noted (H^+ is not seen because mass spectra are seldom

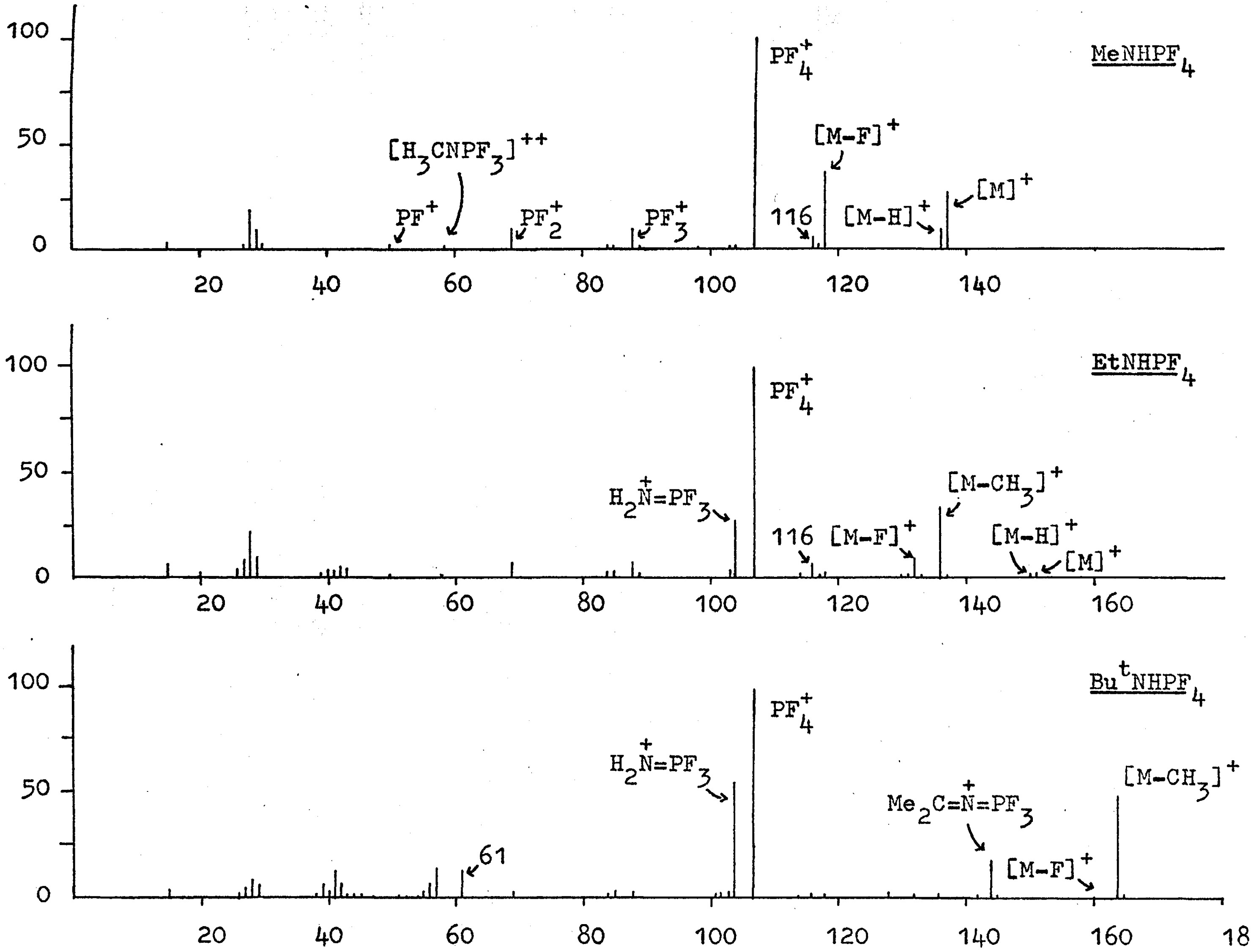


Fig. 1.16 Mass spectra of alkylaminotetrafluorophosphoranes.

Table 1.17 Mass spectra alkylaminotetrafluorophosphoranes (m/e value, relative abundance, ion - respectively)

$MeNHPF_4$:

137, 27, $CH_4NPF_4^+$; 136, 8, $CH_3NPF_4^+$; 118, 37, $CH_4NPF_3^+$; 117, 2, $CH_3NPF_3^+$ 116, 6, $CH_2NPF_3^+$; 107, 100, PF_4^+; 104, 2, POF_3^+ and $H_2NPF_3^+$; 103, 2, $HNPF_3^+$; 98, tr, $CH_3NPF_2^+$; 89, 1, HPF_3^+; 88, 9, PF_3^+; 85, 2, POF_2^+ and $H_2NPF_2^+$; 84, 2, $HNPF_2^+$; 69, 10, PF_2^+; 58.5, 2, $CH_3NPF_3^{++}$; 51, tr, HPF^+; 50, 2, PF^+; 30, 2, CH_4N^+; 29, 9, CH_3N^+; 28, 19, CH_2N^+; 27, 1, CHN^+; 19, tr, F^+; 15, 2, CH_3^+ and HN^+.

$EtNHPF_4$:

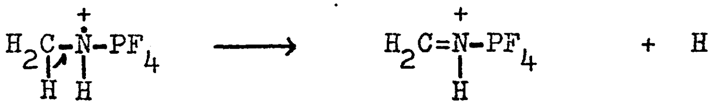
151, 1, $C_2H_6NPF_4^+$; 150, 1, $C_2H_5NPF_4^+$; 137, 1, $CH_4NPF_4^+$; 136, 33, $CH_3NPF_4^+$; 132, 11, $C_2H_6NPF_3^+$; 131, tr, $C_2H_5NPF_3^+$; 130, tr, $C_2H_4NPF_3^+$; 118, 2, $CH_4NPF_3^+$; 117, tr, $CH_3NPF_3^+$; 116, 5, $CH_2NPF_3^+$; 114, 1, $CNPF_3^+$; 107, 100, PF_4^+; 104, 25, $H_2NPF_3^+$; 103, 3, $HNPF_3^+$; 89, 1, HPF_3^+; 88, 6, PF_3^+; 85, 2 $H_2NPF_2^+$; 84, 2, $HNPF_2^+$; 69, 6, PF_2^+; 58.5, tr, $CH_3NPF_3^{++}$; 58, 1, $CH_2NPF_3^{++}$ and $CHNP^+$; 57.5, tr, $CHNPF_3^{++}$; 50, 1, PF^+; 43, 3, $C_2H_5N^+$; 42, 3, $C_2H_4N^+$; 41, 2, $C_2H_3N^+$; 40, 3, $C_2H_2N^+$; 39, 1, C_2HN^+; 29, 8, $C_2H_5^+$ and CH_3N^+; 28, 21, $C_2H_4^+$ and CH_2N^+; 27, 6, $C_2H_3^+$ and CHN^+; 26, 2, $C_2H_2N^+$ and CN^+; 15, 4, CH_3^+ and HN^+.

Bu^tNHPF_4:

165, 2, $C_2{}^{13}CH_7NPF_4^{+\Delta}$; 164, 67, $C_3H_7NPF_4^{+\Delta}$; 160, tr, $C_4H_{10}NPF_3^+$; 145, 1, $C_3H_7NPF_3^+$; 144, 18, $C_3H_6NPF_3^{+\Delta}$; 142, 1, $C_3H_4NPF_3^+$; 136, 2, $CH_3NPF_4^{+\Delta}$; 130, 1, $C_2H_4NPF_3^+$; 128, 1, $C_2H_2NPF_3^{+\Delta}$; 118, 1, $CH_4NPF_3^{+\Delta}$; 116, 2, $CH_2NPF_3^{+\Delta}$; 114, 1, $C_2H_7NPF_2^+$ and $CNPF_3^+$; 107, 100, PF_4^+; 104, 54, $H_2NPF_3^{+\Delta}$; 103, 2, $HNPF_3^{+\Delta}$; 88, 2, PF_3^+; 85, 1, $POF_2^{+\Delta}$; 84, 1, $HNPF_2^+$; 71.5, 1, $C_3H_5NPF_3^{++}$; 69, 2, PF_2^+; 61, 11, CH_4NP^+ and $C_3H_6F^+$;.... peaks mainly due to organic residue.

$^{\Delta}$ Confirmed by mass measurement (Table 1.15).

scanned down to $m/e = 1$, due to the inevitability that H^+ will be present). It is not, however, possible to state positively that these ions are derived from the processes given above without some more definite proof. The most conclusive evidence that a particular fragment ion is at least partially derived by means of a particular path, is that furnished by the observation of a metastable ion; these are ions which decompose after nearly complete acceleration from the ion source but before complete mass analysis (i.e. ions having a life time $\sim 10^{-6}$ sec.). One metastable ion found in the mass spectrum of $MeNHPF_4$ corresponds to the loss of a hydrogen atom from the molecular ion. In view of previous work reported on the mass spectra of amines [39], it is proposed that $[M-H]^+$ is not formed by cleavage of a N-H bond, as depicted in equation (2) but through cleavage of a C-H bond:-



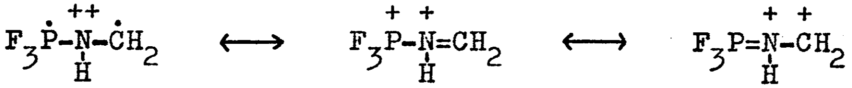
$$H_2\underset{H}{C}-\overset{+}{\underset{H}{N}}-PF_4 \longrightarrow H_2C=\overset{+}{\underset{H}{N}}-PF_4 + H^{\bullet} \qquad (7)$$

A similar process to that given above is found for other methylamino derivatives, and has also been reported to occur on electron bombardment of Me_2NPF_4 [144] and Me_2NPF_2 [144-5] (where no amino-protons are present). A comparison of the mass spectra of Me_2NPX_2 ($X = F, Cl, Br$) indicated that this was not a favoured process for other halophosphines ($X = Cl, Br$) due to the decreased stability of the P-N bond in these compounds [145]. Cleavage of the N-H rather than a C-H bond would be predicted on the basis of bond energy data, but the latter process is favoured because the cation so formed contains an additional bond to nitrogen.

Cleavage of the C-N bond in amines has been observed not to take place to any significant degree [39] which is in agreement with the non-production of the $HNPF_4^+$ ion in the mass spectrum of methylaminotetrafluorophosphorane.

The most abundant peak in this mass spectrum is that due to PF_4^+, which is presumably formed by means of process (4). This ion was also found to be the most abundant one in the spectra of a number of tetrafluorophosphoranes [146]. Its high stability is anticipated since the analogous PCl_4^+ ion is a chemically stable entity. The relatively low P-N bond energy also favours the formation of a PF_4^+ ion.

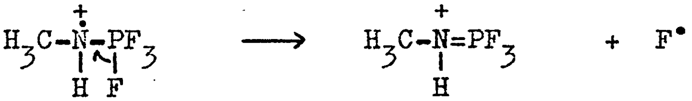
McLafferty has found that many of the most prominent peaks in the mass spectra of organic compounds are generally derived from ions which possess no unpaired electrons [141]. Those odd-electron ions which are present in high abundance are generally formed by particularly favourable fragmentation paths. Other PF_n^+ ions (n = 1-3) are also formed in the mass spectrum of $MeNHPF_4$ and other tetrafluorophosphoranes, and it is apparent that the abundance of PF_2^+ is larger than that of both $PF_3^{+\bullet}$ and $PF^{+\bullet}$. The relative abundance of doubly charged species is often found to follow the reverse trend, i.e. formation of PF^{++} and PF_3^{++} is favoured with respect to $PF_2^{++\bullet}$ formation. In general, multiply charged ions are infrequently observed and only found for highly stabilized molecules [141]. The particularly intense peak at m/e = 58.5 is assigned to the species $(F_3PNH\text{-}CH_2)^{++}$ rather than $(F_3PNCH_3)^{++}$ because of the greater chance of stabilizing the charge on the former species:-



$$F_3\dot{P}\text{-}\overset{++}{\underset{H}{N}}\text{-}\dot{C}H_2 \longleftrightarrow F_3\overset{+}{P}\text{-}\overset{+}{\underset{H}{N}}{=}CH_2 \longleftrightarrow F_3P{=}\overset{+}{\underset{H}{N}}\text{-}\overset{+}{C}H_2$$

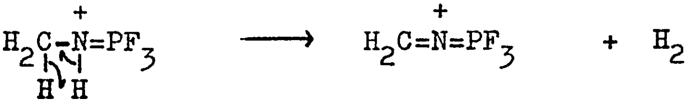
Multiply charged ions were also reported to be particularly prevalent in the break-down of phosphoronitrilic fluorides [147].

An alternative route by which the molecular ion can break down involves cleavage of bonds not directly attached to nitrogen. That involving C-H bond cleavage has already been mentioned. The high intensity of the peak corresponding to cleavage of a P-F bond is explained by the stability of the ion so formed,



$$H_3C\text{-}\overset{\dot{+}}{\underset{H}{N}}\text{-}\underset{F}{P}F_3 \longrightarrow H_3C\text{-}\overset{+}{\underset{H}{N}}{=}PF_3 + F^{\bullet} \qquad (8)$$

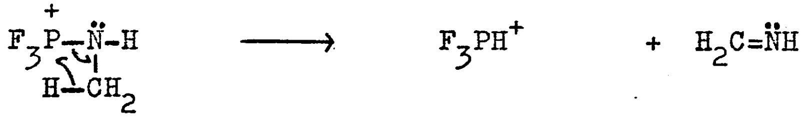
Charge retention on the fluorine atom is not favoured due to its high ionization potential. The peak at m/e = 19 in the spectra of fluorine containing compounds is always of low intensity. A metastable ion shows that the $CH_3NHPF_3^+$ ion so formed is capable of losing a molecule of hydrogen. The most likely mechanism for this process is:-



$$\underset{H}{H_2C}\text{-}\overset{+}{\underset{H}{N}}{=}PF_3 \longrightarrow H_2C{=}\overset{+}{N}{=}PF_3 + H_2 \qquad (9)$$

If this mechanism is correct, loss of HD, and not H_2, from $MeNDPF_4$ would be anticipated.

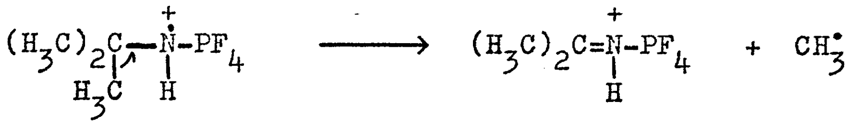
Ions in which the P-N-C skeleton remains intact but contain fewer than three fluorine atoms attached to the phosphorus atom are only observed in low abundance. The small peak at m/e = 89 is due to HPF_3^+. HPF_x^+ ions are also present in the mass spectra of $Me_2NP(F)$ compounds [144-5]. Crosbie has suggested that these rearrangements proceed by means of a four-membered ring intermediate,



$$\overset{+}{F_3P}-\ddot{N}-H \;(H-CH_2) \longrightarrow F_3PH^+ + H_2C=\ddot{N}H \qquad (10)$$

MASS SPECTRA OF ALKYLAMINOTETRAFLUOROPHOSPHORANES (Table 1.17 and Fig. 1.16).

Both $EtNHPF_4$ and Bu^tNHPF_4 in many ways show similar mass spectra to that obtained for $MeNHPF_4$. The major peak is due to PF_4^+; peaks due to $PNC_nH_m^+$ and PNH_m^+ fragments are in very low abundance, while those due to $C_nH_m^+$ are quite intense. Gradual changes in the nature of the spectra are however apparent. The abundance of PF_x^+ (x = 1-3) decreases with the increasing size of the alkyl group. The same trend is indicated for the abundance of the molecular ion. Both molecular ions can decompose by a route analogous to that given in equation (7). Peak heights suggest that $(EtNHPF_4)^{+\cdot}$ loses a methyl radical more easily than a hydrogen atom; this reflects both the greater stability of the methyl radical and the lower energy of the bond to be broken. For $(Bu^tNHPF_4)^{+\cdot}$, only one possible route to produce a C=N bond exists:-



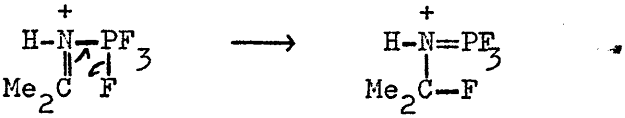
$$(H_3C)_2\underset{H_3C}{C}-\underset{H}{\overset{+}{\dot{N}}}-PF_4 \longrightarrow (H_3C)_2C=\underset{H}{\overset{+}{N}}-PF_4 + CH_3^{\bullet} \qquad (11)$$

The positive ion so formed is able to stabilize itself, through the electron-donating effect of the methyl groups, to a greater degree than is possible for $RNHPF_4$ (R =Me, Et). The greater stability of the daughter ion is reflected in the abundance of the molecular ion. No molecular ion is found for Bu^tNHPF_4, even when employing a reduced ionizing potential. This fragmentation pattern is the same as that observed for the parent amines, although a molecular ion was found in the mass spectrum of Bu^tNH_2 [39].

The increased abundance of $[M-CH_3]^+$ in $RNHPF_4$ (R = Et, Bu^t) is parallelled by a decreased abundance of $[M-F]^+$ as compared to that found for $MeNHPF_4$; only a very weak peak due to $Bu^tNHPF_3^+$ is, in fact, registered.

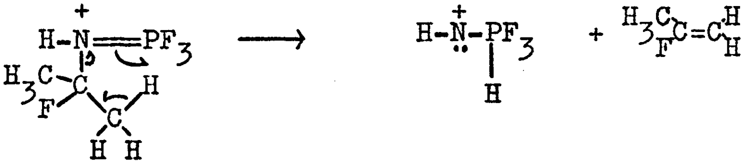
A major trend in these spectra is indicated by the increased importance of the fragment with m/e = 104, with the increasing molecular weight of the group attached to nitrogen. The relative heights of this peak and that at m/e = 85 indicate that the former does not arise from any POF_3 impurity in the sample (pure phosphoryl fluoride produces peaks at these two positions in approximately equal abundance). A mass measurement confirms that this peak in Bu^tNHPF_4 is due to $H_2NPF_3^+$. A metastable ion indicates that this ion is in fact derived from $[M-CH_3]^+$ by loss of a molecule of C_3H_5F which is assumed to possess the structure

Me(F)C=CH_2, since this involves no unnecessary hydrogen rearrangement processes. The elimination of C_3H_5F can best be visualized as a two stage process although a concerted mechanism is in fact more likely. In the first step a fluorine atom is transferred from the phosphorus atom to the carbon atom,



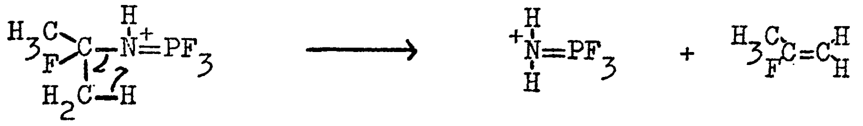
(12a)

Previous work has shown that extensive transfer of fluorine atoms from a carbon to a phosphorus atom take place in the mass spectra of perfluorophosphines (with the primary driving force for this process being attributed to the interaction of the p orbitals on fluorine with the unoccupied d orbitals on phosphorus [148]) but the opposite process does not appear to have been observed before. The almost identical values of the P-F and the C-F bond energies must surely also contribute to the ease of these rearrangement processes, since they will be entropy favoured and the re-organisation energies for these excited ions will be small. The ion so formed can then further rearrange via either a five-membered ring intermediate to transfer a hydrogen atom to the phosphorus atom,



(12b)

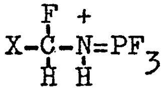
or via a four-membered ring intermediate to transfer the same hydrogen atom to the electron-deficient nitrogen atom,



(12c)

It is not possible to decide which mechanism operates although Crosbie has suggested that four-centred intermediates were favoured over five-centred intermediates in other rearrangement reactions involving aminophosphines [144]. The product formed by equation (12b) is likely to rearrange to $H_2\overset{+}{N}=PF_3$ because of the additional stability which the P=N bond endows upon this ion.

An analogous reaction with $RNHPF_4$ (R = Me, Et) can be visualized as taking place, although no metastable ions were observed for this process. The intermediate formed after fluorine rearrangement is

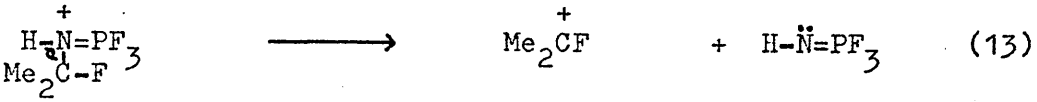


$$X\text{-}\overset{F}{\underset{H}{C}}\text{-}\overset{+}{\underset{H}{N}}=PF_3 \qquad (R = Me,\ X = H;\ R = Et,\ X = Me,\ H)$$

Cleavage of a C-H bond can take place either at the α- or β-carbon atom. Since only the latter method produces an alkene, which is much more stable than a carbene, C-H bond fission will be more favoured for $EtNHPF_4$ than $MeNHPF_4$, and so result in the much lower abundance of the peak at m/e = 104 found for $MeNHPF_4$ than for the other two fluorophosphoranes. Reactions involving the elimination of a molecule of ethylene frequently occur in the mass spectra of organic molecules [142] and are also prevalent in the mass spectrum of $(EtNH)_2PF_2H$.

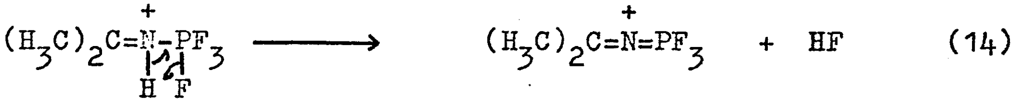
No ion corresponding to $C_3H_5F^+$ is observed in the mass spectrum of Bu^tNHPF_4, but an intense peak at m/e = 61 could be due to

$C_3H_6F^+$ formed by the break-down of the ion produced in equation (12a):-



$$\begin{matrix}\mathrm{H-\overset{+}{N}=PF_3}\\ \mathrm{Me_2C-F}\end{matrix} \longrightarrow \mathrm{Me_2\overset{+}{C}F} + \mathrm{H-\ddot{N}=PF_3} \qquad (13)$$

Ions containing P=N bonds are again found to be stable. The peak at m/e = 116 in the mass spectrum of $EtNHPF_4$ is attributed to $H_2C=\overset{+}{N}=PF_3$. This ion cannot be obtained from Bu^tNHPF_4 but a metastable ion shows that a similar type of ion is derived from $[M-CH_3]^+$ by loss of HF,



$$\mathrm{(H_3C)_2C=\overset{+}{N}-PF_3}\ (\mathrm{H},\ \mathrm{F}) \longrightarrow \mathrm{(H_3C)_2C=\overset{+}{N}=PF_3} + \mathrm{HF} \qquad (14)$$

There are also weak peaks at half integral masses corresponding to doubly charged ions containing the $N=PF_3$ unit in both the mass spectra of $EtNHPF_4$ and Bu^tNHPF_4; peaks of integral mass in the same vicinity also probably arise from doubly charged ions. There is evidence for the formation of $H_xCNPF_3^{++}$ (x = 1-3) from $EtNHPF_4$, and $C_2H_3NPF_3^{++}$ and $H_xC_3NPF_3^{++}$ (x = 5-7) from Bu^tNHPF_4.

Evidence for rearrangement products is also furnished by weak peaks at m/e = 118 and 137 in $EtNHPF_4$, which are attributed to $CH_4NPF_3^+$ and $CH_4NPF_4^+$ respectively. Mass measurements confirm that $CH_3NPF_4^+$, $CH_4NPF_3^+$, and $CH_2NPF_3^+$ are all present in the mass spectrum of Bu^tNHPF_4. No metastable ions are obtained corresponding to the formation of these ions but their formulation suggests that a methyl group migrates to the electron-deficient nitrogen atom (rather than to the phosphorus atom).

MASS SPECTRA OF ALKYLAMINODIFLUOROPHOSPHINES (Fig. 1.17).

Ionization of tetrafluorophosphoranes was understood to involve the removal of an electron from the lone pair on nitrogen. However, removal of an electron from the lone pair on either the nitrogen or phosphorus atom is possible for alkylaminodifluorophosphines. While the ionization potential of a nitrogen atom is greater than that of a phosphorus atom, these values are appreciably changed on incorporating these atoms into a molecule. The ionization potentials of methylamine and phosphorus trifluoride are 9.41 eV [149] and 9.71 eV [150] respectively; these values are sufficiently close to make removal of an electron from an orbital on phosphorus or nitrogen almost equally probable.

Unfortunately a pure sample of $MeNHPF_2$ could not be obtained, so a direct comparison of its mass spectrum with that of $MeNHPF_4$ or Me_2NPF_2 [145] could not be performed. A strong peak due to the molecular ion and intense peaks corresponding to loss of a hydrogen or a fluorine atom or a methylamino group from the molecular ion are all observed, as for $MeNHPF_4$. There is a slightly greater abundance of the ions $PNCH_n^+$ and PNH_n^+, which is as expected since fewer fluorine atoms have to be lost before they are produced.

Mass spectra were, however, obtained for Bu^tNHPF_2 and Bu^nNHPF_2. No molecular ion is present in the mass spectrum of Bu^tNHPF_2 but a weak one is present in that of Bu^nNHPF_2. The most abundant

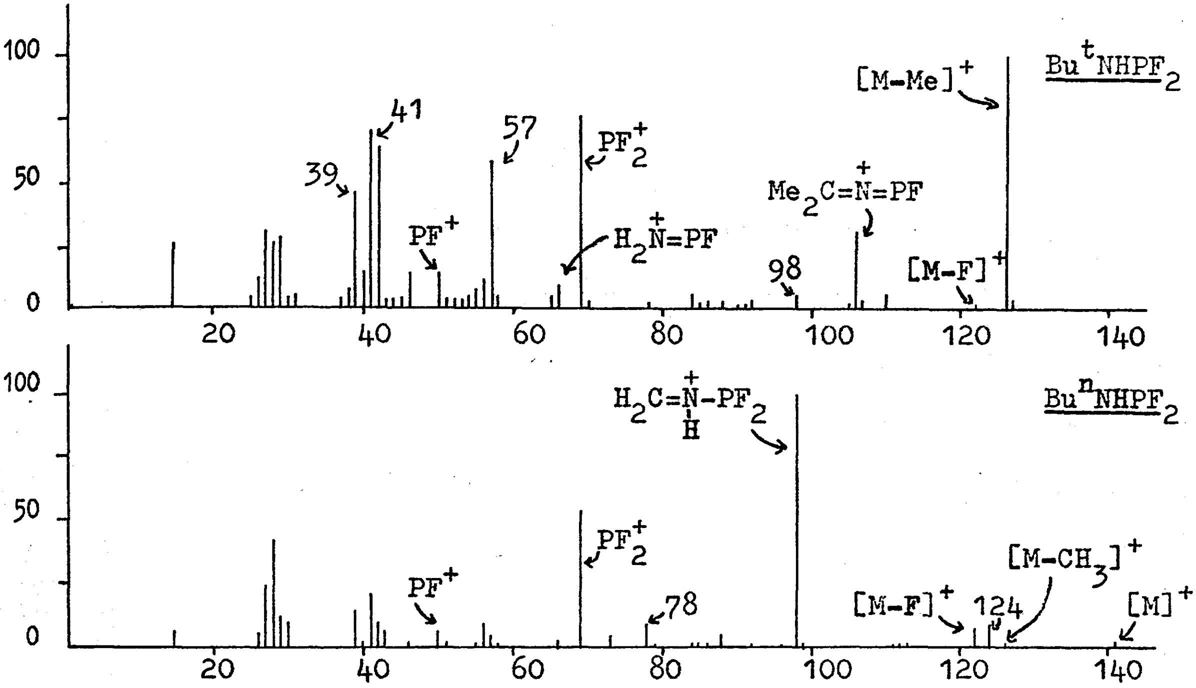
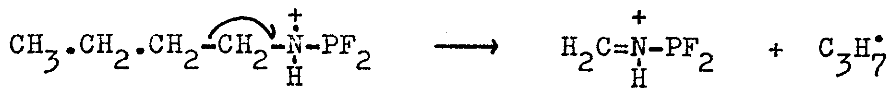


Fig. 1.17 Mass spectra of Bu^{t}NHPF$_2$ and Bu^{n}NHPF$_2$.

ions in the mass spectra of Bu^{t}NHPF$_2$ and Bu^{n}NHPF$_2$ are those corresponding to loss of $CH_3^{\bullet}$ and $C_3H_7^{\bullet}$ respectively, from the appropriate molecular ion. These are precisely the decomposition modes responsible for the most abundant ion in the mass spectra of the parent amines [39], i.e. the most favoured mode for stabilizing the positive charge on a nitrogen containing ion is the same as that employed for stabilizing the positive charge on an ion derived from an alkylaminophosphine. This then tends to suggest that the positive charge in aminophosphines is mainly localized on the nitrogen atom. While the molecular ion of Bu^{t}NHPF$_2$ loses a methyl radical in an analogous way to that previously considered for Bu^{t}NHPF$_4$ (see equation (11)), Bu^{n}NHPF$_2$ breaks up as follows:-



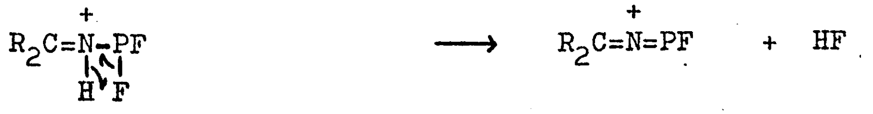
$$CH_3.CH_2.CH_2\text{-}CH_2\text{-}\overset{+\bullet}{\underset{H}{N}}\text{-}PF_2 \longrightarrow H_2C{=}\overset{+}{\underset{H}{N}}\text{-}PF_2 + C_3H_7^{\bullet} \qquad (15)$$

There is also evidence for alternative routes of fragmentation, as depicted in equations (1)-(6). While PF_4^+ carries the majority of the positive ion current for tetrafluorophosphoranes, PF_2^+ is not such an important charge carrier for difluorophosphines, presumably because four fluorine atoms are better than two in delocalizing the positive charge over the phosphorus containing cation. It appears that as (1) becomes a less popular fragmentation path the importance of (4) increases, for peaks at lower m/e values, which are derived from $C_nH_m^+$ or $C_nH_mN^+$, are more prominent in the spectra of difluorophosphines than in tetrafluorophosphoranes. Bu^tNHPF_2 shows a larger variety of low mass ions than does Bu^nNHPF_2, which is the same as was observed for the parent amines [39].

A metastable ion indicates that the $[M\text{-}CH_3]^+$ ion from Bu^tNHPF_2 can decompose with charge retention on the nitrogen atom,

$$(H_3C)_2C{=}\overset{+}{\underset{H}{N}}\text{-}PF_2 \longrightarrow (H_3C)_2C{=}\overset{+}{\underset{H}{N}}{\bullet} + PF_2^{\bullet} \qquad (16)$$

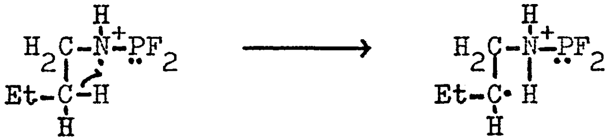
Note that this is usually considered to be an unfavourable fragmentation pattern: an even-electron species seldom fragments to form two radicals [141]. Another metastable ion shows that $[M\text{-}CH_3]^+$ can alternatively eliminate a molecule of HF (R = Me) (cf. equation 14),



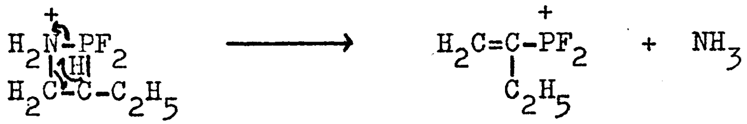
$$R_2C{=}\overset{+}{\underset{H}{N}}\text{-}\underset{F}{PF} \longrightarrow R_2C{=}\overset{+}{N}{=}PF + HF \qquad (17)$$

The ion $(H_3CNHPF_2)^+$ derived from Bu^nNHPF_2 can also eliminate a molecule of HF (equation(17), R = H).

A peak due to H_2NPF^+, corresponding to the $H_2NPF_3^+$ ion derived from tetrafluorophosphoranes, is only found in low abundance. The larger chain length of the alkyl group in Bu^nNHPF_2 leads to a greater opportunity for intramolecular rearrangement processes taking place than for the other amino derivatives of difluorophosphine. Rearrangements of secondary amines with hydrogen migration (often from the β-carbon atom) to nitrogen are common [39]. A metastable ion indicates that elimination of a molecule of ammonia from the molecular ion of Bu^nNHPF_2 can occur. This requires the migration of two hydrogen atoms; the initial step can be regarded as hydrogen migration from a β-carbon atom:-


(18a)

The radical so produced is then suggested to form a bond with the phosphorus atom and, after a further hydrogen atom has migrated from the β-carbon atom, then eliminate a molecule of ammonia:-


(18b)

It should be emphasized that this reaction scheme is only speculative. While hydrogen abstraction is less likely to take place from a terminal methyl group, since primary radicals are not as stable as secondary radicals, abstraction from the γ-carbon atom with a subsequent five-membered intermediate being formed seems just as probable. Deuteration studies are required to substantiate this mechanism. Without accurate mass measurement studies it is not possible to determine how prevalent other related rearrangement processes are; loss of methylamine in place of ammonia can readily be visualized. A peak at m/e = 51, corresponding to HPF^+, indicates that hydrogen migration to phosphorus also takes place (see equation (10)).

Rearrangement products are also suggested in the mass spectrum of Bu^tNHPF_2. The peak at m/e = 98 corresponds to an ion $CH_3NPF_2^+$, with a suggested structure $H_2C=\overset{+}{N}HPF_2$, but no metastable ion is present which would correspond to the formation of this ion and support this formulism.

MASS SPECTRUM OF BIS(t-BUTYLAMINO)FLUOROPHOSPHINE (Fig. 1.18).

On replacing one of the fluorine atoms in Bu^tNHPF_2 by another Bu^tNH group, the percentage of the positive charge carried by PF containing species is reduced. (Fig. 1.18 only shows the high mass region of the mass spectrum of $(Bu^tNH)_2PF$.) While $(Bu^tNH)_2PF$ only produces a small peak corresponding to PF^+ it does produce a fairly intense peak for the molecular ion, which can lose one but not two methyl groups. The former fragmentation is confirmed by a metastable ion.

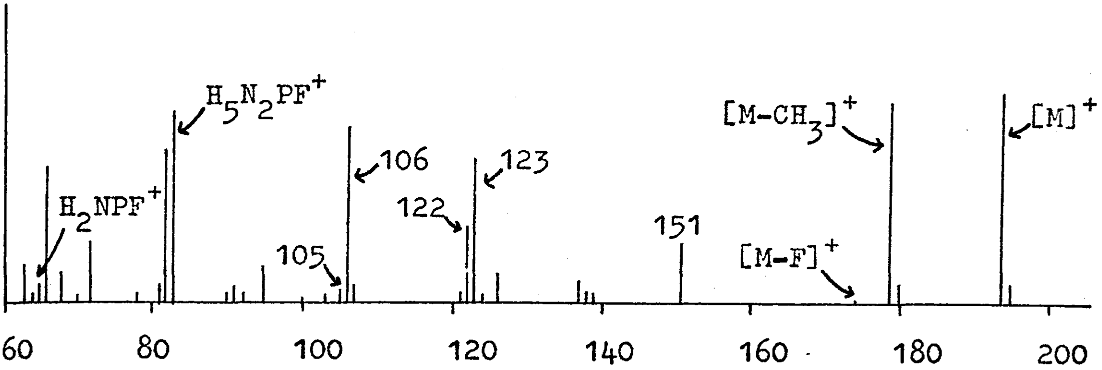
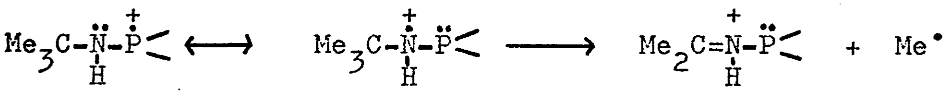


Fig. 1.18. Mass spectrum of $(Bu^tNH)_2PF$ (m/e > 60).

The appearance of an appreciable concentration of $[M]^+$ is surprising in view of the non-appearance of molecular ions for Bu^tNHPF_2 and Bu^tNHPF_4 and the very small peak for $(Bu^tNH)_2PF_3$. This can be rationalized by considering the process:-

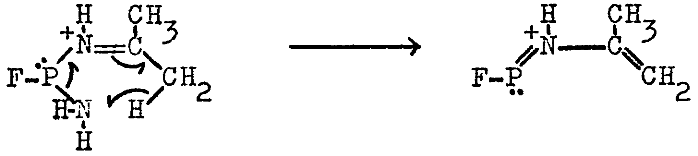


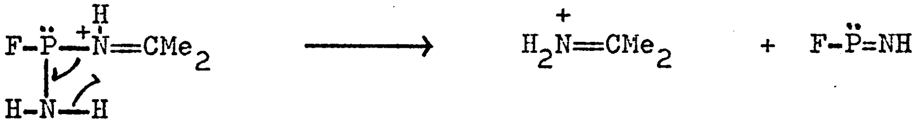
$$\mathrm{Me_3C}-\underset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{N}}}-\overset{+}{\mathrm{P}}< \longleftrightarrow \mathrm{Me_3C}-\underset{\mathrm{H}}{\overset{+}{\mathrm{N}}}-\overset{\cdot\cdot}{\mathrm{P}}< \longrightarrow \mathrm{Me_2C}=\underset{\mathrm{H}}{\overset{+}{\mathrm{N}}}-\overset{\cdot\cdot}{\mathrm{P}}< + \mathrm{Me}^{\bullet}$$

Ia Ib II

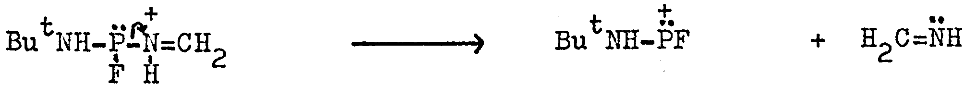
As the charge is localized on the nitrogen atom to a greater extent for II than for I, inductive effects will play a larger part in stabilizing the positive charge on I. Since alkylamino groups, but not a fluorine atom, will successfully delocalize the charge, the stability of $[M]^{+\bullet}$ will depend on the relative number of these two species in the molecule. Another means of stabilizing the molecule is to share the charge between the phosphorus and nitrogen atoms (as in the resonance hybrids, Ia and Ib); this method is available for fluorophosphines but not for fluorophosphoranes.

Extensive rearrangement processes take place in the mass spectrum of $(Bu^tNH)_2PF$. The fairly intense peak at m/e = 83, which is shown by an accurate mass measurement to arise from H_5NPF^+, is probably represented as $(H_2N)F\overset{H\,+}{P}=NH_2$ rather than $(H_2N)FP-\overset{+}{N}H_3$. Rearrangements are difficult to pin-point since hydrogen atoms can migrate between two alkylamino groups as well as to the phosphorus atom. In addition, it is not possible to unambiguously decide upon the empirical formula for a particular ion since (as was shown conclusively for Bu^nNHPF_2) rearrangement processes with P-C bond formation are possible. This makes a detailed analysis of the metastable transitions dubious in the absence of accurate mass measurements. However, two processes which are fairly unambiguous involve elimination of either NH_3 or HNPF from the ion with m/e = 123:-


(19)


(20)

Since the $[M-43]^+$ ion in Bu^tNHPF_2 is assumed to be due to $F_2P(H)\overset{+}{N}=CH_2$ the corresponding peak at m/e = 151 in $(Bu^tNH)_2PF$ is tentatively formulated as $F-P(NHBu^t)(H)\overset{+}{N}=CH_2$ which decomposes as follows (a metastable ion is obtained for this process):-

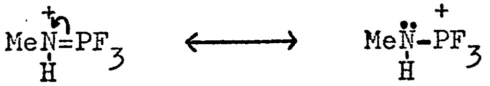

(21)

$$Bu^tNH-\underset{F}{\ddot{P}}-\underset{H}{\overset{+}{N}}=CH_2 \longrightarrow Bu^tNH-\overset{+}{\ddot{P}}F + H_2C=\ddot{N}H \quad (21)$$

The ion thus formed (m/e = 122) then loses a molecule of NH_3 as discussed for Bu^nNHPF_2. Loss of $H_2C{=}NMe$ is a common process in the mass spectra of dimethylamino derivatives of phosphorus [144].

MASS SPECTRA OF BIS(ALKYLAMINO)TRIFLUOROPHOSPHORANES AND BIS-(ALKYLAMINO)DIFLUOROPHOSPHORANES (Fig. 1.19).

$(MeNH)_2PF_3$ shows a fragmentation pattern very similar to that observed for both $MeNHPF_4$ and $(Me_2N)_2PF_3$ [146]. For both compounds the most abundant fragment is that obtained by loss of a methylamino group from the molecular ion. For $(MeNH)_2PF_3$ the fragment so formed (which also figures in the mass spectrum of $MeNHPF_4$) has additional means of stabilizing its charge over that available to PF_4^+, and this accounts for its even greater significance in the mass spectrum,



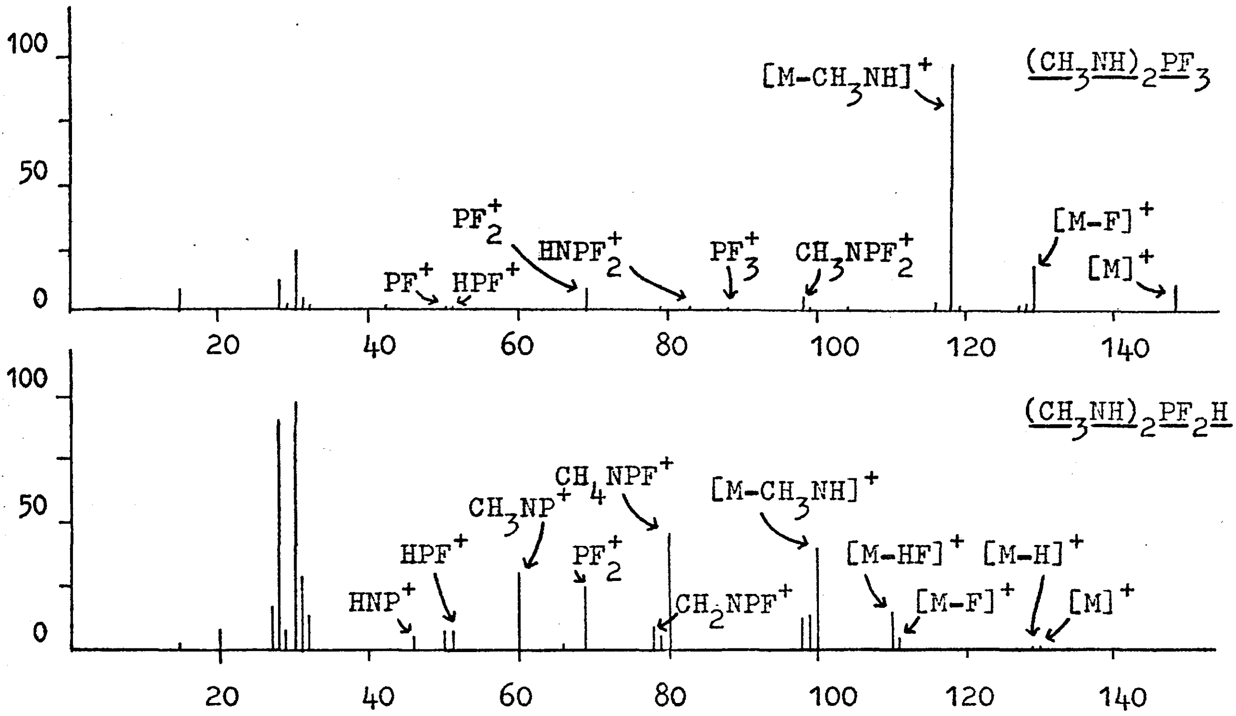
$$\mathrm{Me}\underset{\mathrm{H}}{\overset{+}{\mathrm{N}}}{=}\mathrm{PF_3} \longleftrightarrow \mathrm{Me}\underset{\mathrm{H}}{\overset{\cdot\cdot}{\mathrm{N}}}{-}\overset{+}{\mathrm{P}}\mathrm{F_3}$$

Ions closely related to the above have been isolated where chlorine rather than fluorine atoms were attached to the phosphorus atom [64]. There is no peak corresponding to $[M-H]^+$ in the mass spectrum of $(MeNH)_2PF_3$ but there is a large peak derived from $[M-F]^+$. Bis(ethylamino)trifluorophosphorane produces only a weak molecular ion but an intense peak for $(EtNHPF_3)^+$.

The $[M]^{+\cdot}$ and $[M-F]^+$ ions are the only species containing two nitrogen atoms which produce peaks of any significant intensity in the mass spectrum of $(MeNH)_2PF_3$. The spectrum of $(NH_2)_2PF_3$

did not even show these two ions [5]. All other ions can be considered as being formed by fragmentation of $MeNHPF_3^+$. Two metastable ions indicate that this ion is capable of losing a molecule of hydrogen (cf. equation (9)) or a molecule of hydrogen fluoride (cf. equation (14)). The abundance of PF_2^+ is larger than that of PF_3^+, which seems to be a general feature for trifluorophosphoranes. The peak due to HPF^+ has the same intensity as that due to PF^+; this is probably formed from $MeNHPF^+$ by the process depicted in equation (10).

Fig. 1.19 shows the mass spectrum of $(MeNH)_2PF_2H$; the peaks present show that a small quantity of $MeNHPF_2$ may be present as an impurity. However, there is no mass spectral evidence for PF_3, which was characterised in some i.r. spectra. There is only a small molecular ion present, while previous work has shown that HPF_4 [131], $MePF_3H$ [58] and Me_2PF_2H [135] produced no molecular ion. Amino groups have been reported to stabilize molecular ions [146]. The increased stability of $[M]^{+\bullet}$ can best be explained by examining how ionization takes place. For amino compounds an electron is assumed to be removed from the non-bonding electrons on the nitrogen atom while the electron which is removed from the other fluorophosphoranes is a bonding electron. An electron will preferentially be removed from one of the more diffuse bonding orbitals, and for fluorophosphoranes containing a P-H bond that orbital is likely to be the one which is concentrated between the phosphorus and the hydrogen atoms.



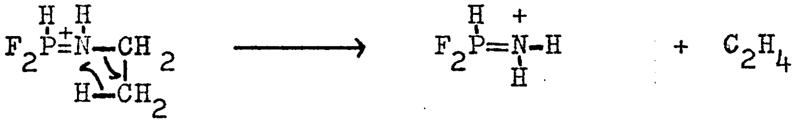
<u>Fig. 1.19</u> Mass spectra of $(MeNH)_2PF_3$ and $(MeNH)_2PF_2H$.

Phosphorus hydrogen bond energies are not high, and this further destabilizing influence will lead to the ready cleavage of a P-H bond.

The mass spectrum of $(MeNH)_2PF_2H$ shows that, as for $(MeNH)_2PF_3$, P-N bond cleavage is more readily achieved than P-F bond cleavage. However the ion formed in the former case, $(MeNHPF_2H)^+$, does not appear to possess quite the enhanced stability of $(MeNHPF_3)^+$ (which accounts for the larger number of ions appearing in the spectrum). $[M-H]^+$ may have been produced either by P-H bond fission or by removal of a hydrogen atom from the methyl group attached to nitrogen. Since no $[M-H]^+$ ion is found for $(MeNH)_2PF_3$ the former process seems more probable; this could easily be checked by observing the mass spectrum of $(MeND)_2PF_2D$.

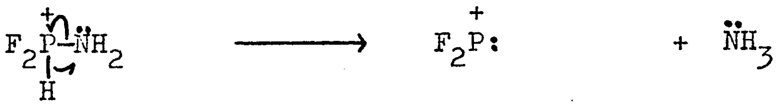
The peak due to $[M-HF]^+$ is larger than that due to $[M-F]^+$ for $(MeNH)_2PF_2H$. This is not observed for other RNHP(F) compounds, and may result from a certain degree of dehydrofluorination of $(MeNH)_2PF_2H$ to form $(MeNH)_2PF$. The formation of ions such as HNP^+, CH_3NP^+ and CH_4NP^+, which are not observed in the spectrum of $(MeNH)_2PF_3$, reflects the lower number of fluorine atoms in the parent fluorophosphorane.

The mass spectrum of $(EtNH)_2PF_2H$, like that of $(MeNH)_2PF_2H$, indicates a weak molecular ion which can lose H, F, HF and EtNH fragments as well as a methyl radical. Metastable peaks also indicate that the EtNH-P entity is capable of eliminating a molecule of ethylene:-



$$F_2\overset{H}{P}\overset{\pm}{=}\overset{H}{N}-\underset{H-CH_2}{CH_2} \longrightarrow F_2\overset{H}{P}=\underset{H}{\overset{+}{N}}-H + C_2H_4 \qquad (22)$$

The ion so formed then further eliminates a molecule of ammonia (as indicated by the presence of a metastable ion):-



$$F_2\underset{H}{\overset{+}{P}}-\ddot{N}H_2 \longrightarrow F_2\overset{+}{P}: + \ddot{N}H_3 \qquad (23)$$

Another metastable ion shows that the ion with m/e = 98, probably due to $F_2P-\underset{H}{\overset{+}{N}}=CH_2$, can also eliminate a molecule of HF (cf. equation (14)).

EXPERIMENTAL

Reagents were obtained from the sources indicated in Table 1.18. Phosphorus pentafluoride was purified by low temperature distillation (although its i.r. spectrum always showed traces of POF_3 to be present). Amines were distilled onto sodium wire. Acetonitrile and deuterioacetonitrile were dried with P_2O_5 and distilled onto molecular sieves.

In order to avoid excessive repetition Table 1.18 lists the i.r. and n.m.r. references for both the starting materials and those products identified by these techniques.

Practical techniques employed in the preparation and characterisation of compounds dealt with in this section are discussed in Appendix 1.

All analytical results are given in Table 1.19.

Reaction between phosphorus pentafluoride and methylamine.- Excess phosphorus pentafluoride was condensed onto methylamine (5.9 mmoles), and the temperature increased to -78°. White solids were deposited in an exothermic reaction. When no more absorption of PF_5 was apparent the excess was pumped off; 3.2 mmoles of phosphorus pentafluoride had reacted (reaction ratio 1:1.8). The reaction mixture was warmed to room temperature and the volatile products pumped off. These were passed through a -86° trap to remove

Table 1.18

COMPOUND	SOURCE	I.R.	N.M.R.
PF_5	Matheson Co.	(a)	(b)
PF_3	PCl_3/SbF_3 (c)	(a)	(d)
POF_3	Ozark-Mahoning	(a)	(d)
HPF_6	Ozark-Mahoning		(d)
$PhPF_4$	$PhPCl_2/SbF_3$ (e)		(b)
$MeNH_2$ and $EtNH_2$	B.D.H.	(f,g)	(h)
Bu^nNH_2 and Bu^tNH_2	Koch-Light	(g)	(h)
Et_3N	Koch-Light	(i)	(h)
Me_3N	Matheson Co.	(f)	(h)
MeOH	B.D.H.	(f)	(h)
$(MeO)_3P$		(j)	(h)
$(MeO)_2PF$		(k)	(l)
$MeOPF_2$		(m)	(l)
$(POF_2)_2O$		(n)	
$(F_3PNMe)_2$	$PF_5/(Me_3Si)_2NMe$ (o)	(p)	(q)
$(PhF_2PNMe)_2$		(r)	(b,s)
SiF_4		(t)	(u)
Isopentane	B.D.H.	(v)	(h)
Me_2SO, MeCN and C_6H_6	B.D.H.		(h)
CD_3CN	C.I.B.A.		

Table 1.18 (cont.)

(a) [116].
(b) [3].
(c) H.S. Booth and C.F. Swinehart, J. Amer. Chem. Soc., 1932, 54, 4751.
(d) [1].
(e) R. Schmutzler, Inorg. Synth., 1967, 9, 64.
(f) [112].
(g) [126].
(h) [113].
(i) Sadtler Research Labs., Standard Grating Spectra.
(j) C.W. Heitsch and J.G. Verkade, Inorg. Chem., 1962, 1, 863.
(k) A.M. Noble, private communication.
(l) D.H. Brown, K.D. Crosbie, G.W. Fraser, and D.W.A. Sharp, J. Chem. Soc. (A), 1969, 872.
(m) G.I. Drozd, O.G. Strukov, E.P. Sergeeva, S.Z. Ivin, and S.S. Dubov, J. Gen. Chem. (U.S.S.R.), 1969, 39, 907.
(n) T.L. Charlton and R.G. Cavell, Inorg. Chem., 1970, 9, 379.
(o) [12].
(p) [45,46].
(q) [43].
(r) R. Schmutzler, D.M.S. Card A 0599, Butterworths, London.
(s) [42].
(t) F. Seel and R. Budenz, Chem. Ber., 1965, 98, 251.
(u) [104].
(v) R.S.Rasmussen, J. Chem. Phys., 1948, 16, 712.

Table 1.19

Compound	**Found:**					**Calculated:**				
	C%	H%	F%	N%	P%	C%	H%	F%	N%	P%
$(MeNH)_2PF_3$	16.3	5.3	38.3	18.9	21.0	16.2	5.4	38.5	18.9	20.9
$(EtNH)_2PF_3$	26.3	6.9	32.0	16.2	17.4	27.3	6.9	32.4	15.9	17.6
$(Bu^tNH)_2PF_3$	41.9	9.0	24.1	12.0	12.4	41.3	8.7	24.5	12.0	13.4
$2MeNH_2.PF_5$	12.8	5.4	50.7	14.7	16.4	12.8	5.4	50.5	14.9	16.5
$EtNH_2.PF_5$	14.0	4.1	55.2	8.4	17.8	14.0	4.1	55.6	8.2	18.2
$Bu^tNH_2.PF_5$	24.0	5.4	47.4	7.4	15.3	24.1	5.6	47.7	7.0	15.6
$MeNH_3^+\ PF_6^-$	6.8	3.4	64.3	8.0	16.7	6.7	3.4	64.6	7.9	17.4
$EtNH_3^+\ PF_6^-$	12.8	4.1	59.6	7.5	16.1	12.6	4.2	59.5	7.3	16.2
$Bu^tNH_3^+\ PF_6^-$	22.1	5.6	51.8	6.6	14.3	21.7	5.5	52.0	6.3	14.0
$EtNHPF_4$	16.0	4.1	50.0	9.3	20.3	15.9	4.0	50.3	9.3	20.5
Bu^tNHPF_4	26.8	5.4	42.3	7.9	17.3	26.8	5.6	42.4	7.8	17.3
Bu^nNHPF_2	33.9	6.9	26.9	9.8	21.8	34.1	7.1	26.9	9.9	22.0
Bu^tNHPF_2	34.2	7.3	26.8	10.1	21.9	34.1	7.1	26.9	9.9	22.0
$(Bu^tNH)_2PF$	49.3	10.4	10.0	14.3	15.9	49.4	10.3	9.8	14.4	16.0
$(Bu^nNH)_2PF_2H$	44.8	9.8	17.8	13.1	14.5	44.8	9.6	17.9	13.2	14.4

slight traces of the more volatile methylamine (identified by i.r.) and retain colourless BIS(METHYLAMINO)TRIFLUOROPHOSPHORANE [v.p. 9 mm. Hg at 25°; M found (mass spec.), 148; M calc., 148]. The solid products from this reaction were transferred in a dry box into a subliming apparatus, and then sublimed in vacuo at 60°; pure BIS(METHYLAMINE)-PHOSPHORUS PENTAFLUORIDE was collected on the cold finger and METHYLAMMONIUM HEXAFLUOROPHOSPHATE was retained in the bottom of the flask. The latter was heated to 140° to remove final traces of the adduct.

<u>Reaction between phosphorus pentafluoride and ethylamine</u>.- The procedure was similar to that for the methylamine reaction. Phosphorus pentafluoride reacted with ethylamine in the ratio 1:~1.5 to produce a rather mushy mixture of ETHYLAMINE-PHOSPHORUS PENTAFLUORIDE and ETHYLAMMONIUM HEXAFLUOROPHOSPHATE (separated by sublimation), and BIS(ETHYLAMINO)TRIFLUOROPHOSPHORANE [M found (mass spec.), 176; M calc.,176].

<u>Reaction between phosphorus pentafluoride and t-butylamine</u>.- The reaction between phosphorus pentafluoride (0.95 mmoles) and t-butylamine (1.24 mmoles) was carried out employing the same procedure as that used in the methylamine reaction. Since BIS(t-BUTYLAMINO)TRIFLUOROPHOSPHORANE [m.p. 31±2°] was found to be only slightly volatile the reaction products were pumped on for a considerable time to ensure its complete removal and thus avoid any contamination of the adduct which would result

when it was sublimed. Sublimation of the residue produced t-BUTYLAMINE-PHOSPHORUS PENTAFLUORIDE and t-BUTYLAMMONIUM HEXAFLUOROPHOSPHATE.

Thermal decomposition of bis(methylamine)-phosphorus pentafluoride adduct.- The adduct (0.120 g., 0.64 mmoles) was heated in an ampoule up to 140°, and the volatile products were removed as they were formed by condensing them in a -196° trap. The ampoule was re-weighed, and indicated that 0.013 g. volatile material had been formed. However, sublimation of some of the adduct out of the ampoule render these results non-quantitative. The volatile products were identified by i.r. as $MeNH_2$ and $(MeNH)_2PF_3$. The i.r. spectrum of the solid product showed undecomposed adduct along with methylammonium hexafluorophosphate.

Thermal decomposition of ethylamine-phosphorus pentafluoride adduct.- The above procedure was repeated. The adduct was observed first to melt and then decompose. As decomposition progressed a white solid was formed which was identified, on cooling, by its i.r. as ethylammonium hexafluorophosphate. The ETHYLAMINOTETRAFLUOROPHOSPHORANE [M found (vapour density), 152; M calc., 151] formed is just trapped by passage through a bath held at -100°.

Thermal decomposition of t-butylamine-phosphorus pentafluoride adduct.- t-BUTYLAMINOTETRAFLUOROPHOSPHORANE [M found (vapour density), 178; M calc., 179; v.p. 32 mm. Hg at 23°] and

$Bu^tNH_3^+ PF_6^-$ were prepared from the thermal decomposition of $Bu^tNH_2.PF_5$ by an analogous route to that employed above.

Reaction between alkylamine-phosphorus pentafluoride adducts and free amines.- These reactions were carried out by condensing excess amine onto the adduct and setting the system aside at a temperature below the boiling point of the amine for several hours. The mixture was then allowed to warm up and the volatile components distilled off. The identities of the volatile products are given below:-

$MeNH_2$ / $2.MeNH_2.PF_5$	—	$(MeNH)_2PF_3$ (i.r.).
$EtNH_2$ / $Bu^tNH_2.PF_5$	—	$(EtNH)_2PF_3$ (n.m.r.).
$MeNH_2$ / $EtNH_2.PF_5$	—	$(MeNH)_2PF_3$ and $(EtNH)_2PF_3$ (n.m.r.), ratio varies in different reactions.

Reaction between t-butylaminotetrafluorophosphorane and t-butylamine.- Excess Bu^tNH_2 reacted with Bu^tNHPF_4 to give $(Bu^tNH)_2PF_3$ along with excess starting material as volatile products and a mixture of $Bu^tNH_2.PF_5$ and a trace of $Bu^tNH_3^+ PF_6^-$ as solid products (all identified by i.r. and n.m.r. spectroscopy).

Reaction between hexafluorophosphoric acid and amines.- The appropriate amine was condensed onto an aqueous solution of hexafluorophosphoric acid. On warming up to room temperature and pumping off the volatiles, colourless salts were obtained.

Reaction between phosphorus pentafluoride and methylaminotetrafluorophosphorane.- Excess PF_5 and $MeNHPF_4$ were warmed up slowly in an ampoule from -78° to room temperature. A white solid was formed, and passage of the volatile products through a -95° bath trapped out $(F_3PNMe)_2$ from the excess of phosphorus pentafluoride. The solid decomposed on heating to 140° under vacuum; $MeNHPF_4$ and traces of SiF_4 and POF_3 were identified by i.r. as comprising the volatile material. The solid still remaining was not examined.

In the presence of Et_3N, the above reactants gave $(F_3PNMe)_2$ (i.r. identification) and a white solid, which was found to be stable up to 140° (at which temperature it was a liquid) and was presumably $Et_3NH^+ PF_6^-$.

Reaction between phosphorus pentafluoride and t-butylaminotetrafluorophosphorane.- t-Butylaminotetrafluorophosphorane did not react with phosphorus pentafluoride at room temperature. On heating the mixture for one hour at 40°, a small amount of solid was deposited. An ^{19}F n.m.r. of a solution of this product in acetonitrile indicated that this was a mixture of $Bu^tNH_2.PF_5$ and $Bu^tNH_3^+ PF_6^-$, but gave no evidence for $(F_3PNBu^t)_2$ which was reported to be a solid [16].

Reaction between phosphorus pentafluoride and bis(methylamino)-trifluorophosphorane.- The two reactants were condensed together at -196° and allowed to warm slowly up to room temperature. A white solid was deposited. The volatile products were pumped off the solid and fractionally distilled. Products identified by i.r.

(in approximate order of their volatility) were SiF_4, excess of PF_5, POF_3, traces of $(POF_2)_2O$, and $MeNHPF_4$. The solid was heated under vacuum and shown by i.r. to decompose to give a small quantity of $(F_3PNMe)_2$ and $MeNHPF_4$. A deuterioacetonitrile solution of the solid remaining gave a complex n.m.r. spectrum, which indicated the absence of any $2MeNH_2.PF_5$ or $MeNH_3^+ PF_6^-$. A doublet of doublets of triplets could be distinguished from the ^1H n.m.r. [δ_H^{**}, -2.9 ddt; J-values, 15.1, 5.5, 2.2 c/s], and there was a strong doublet in the ^{19}F n.m.r. [δ_F^{**}, +81; J(PF), 1031 c/s].

Reaction between phenyltetrafluorophosphorane and bis(methylamino)trifluorophosphorane.- Phenyltetrafluorophosphorane (0.753 g., 4.14 mmoles) was condensed with $(MeNH)_2PF_3$ (0.635 g., 4.28 mmoles), and the mixture left at 30° for two hours. The volatile products were then pumped off the solids formed. The former were then pumped on under vacuum, while they were held at -10°; at this temperature the slight excess of $(MeNH)_2PF_3$ could be removed. The product remaining was examined by n.m.r. (see Fig. 1.2 and Fig. 1.3) and was interpreted (on the basis of integration) as an approximately 1:2 mixture of $PhPF_3NMeH$ (see Table 1.20) and 2,2,4,4,4-PENTAFLUORO-1,3-DIMETHYL-2-PHENYL-1,3-DIAZA-2,4-DIPHOSPHACYCLOBUTANE. Analytical results obtained are in agreement with this. The values for $PhPF_3NMeH$, the mixture and $PhF(F_2PNMe)_2$ are given: C, 32.9, 36.0, 43.2%; H, 3.8, 3.8, 4.6%; F, 32.6, 31.1, 29.2%; N, 9.6, 7.8, 7.2%; P, 21.2, 17.2, 15.9%.

Table 1.20

Compound	δ_{CH_3}	δ_{Ph}	δ_F	J(PF)	J(PH)	J(FH)
Found [a]	-2.32** t	-7.6**	62.3**	~880 [f]	12.8	0.7 [h]
$(PhF_2PNMe)_2$ [b] [3,42]	-2.46* t	-7.7*	63.4	~900 [p]	12.5	

Compound	δ_{F_a}	$\delta_{F_{a'}}$	δ_{F_e}	$J(PF_a)$ [c]	$J(PF_{a'})$ [c]	$J(PF_e)$	$J(F_aF_e)$
Found	40*	51*	72*	776 [d]	813	970	56
$PhPF_3NHMe$ [e] [20]	39.7		71.8	770		953	52
$PhPF_3NHMe$ [18]	41	52	72	745	775	932	54

[a] Benzene or CD_3CN solution. [b] $CDCl_3$ solution. [c] Difference in $J(PF_a)$ and $J(PF_{a'})$ is very temperature dependent [20]. [d] Further coupling with amino-proton is discernible ($^3J(F_aH) = 13$ c/s). [e] Nonequivalence axial fluorine atoms not reported. [f] Obtained from ^{19}F n.m.r. [h] Obtained from ^1H n.m.r. spectrum. [p] Obtained from ^{31}P n.m.r. spectrum.

The solid formed was examined by sublimation at 70°. Diphenyldiazafluorodiphosphetidine was collected on the cold finger (confirmed by n.m.r.(Table 1.20) and i.r. spectra). The residue was shown by n.m.r. (acetonitrile solution) and i.r. spectroscopy to be composed of $MeNH_3^+$ PF_6^- and a small concentration of impurities containing N-methyl groups.

On repeating this reaction a small quantity of $(F_3PNMe)_2$ was found in the volatile fraction (i.r. and ^1H n.m.r. identification).

A solid giving an identical ^{19}F n.m.r. to $2MeNH_2.PF_5$ was also found to be present in small quantities in some samples of the sublimable product; the i.r. spectrum showed two intense peaks at 3317 and 3280 cm.$^{-1}$ (characteristic of 1:1 adducts) which suggests that $MeNH_2.PF_5$ might well have been present in the reaction product.

Reaction between phosphorus trifluoride and methylamine.- In a typical experiment PF_3 (0.899 g., 10.2 mmoles) and methylamine (0.961 g., 31 mmoles) were condensed together into an ampoule. The mixture was warmed up slowly and left for two hours at room temperature. The volatile products were pumped off to leave white solids, and a trace of the more volatile PF_3 (0.2 mmoles) was removed from the bulk of the material (0.735 g.) by passage through a -160° trap. The n.m.r. spectrum showed that this was predominantly BIS(METHYLAMINO)DIFLUOROPHOSPHORANE [M found (vapour density), 132; M calc., 131; v.p. 14 mm. Hg at 27°] with traces of $MeNHPF_2$, indicating an overall yield of about 55%. The majority of the $MeNHPF_2$ could be removed from the main product by repeated passage through a -60° bath, at which temperature $(MeNH)_2PF_2H$ was trapped out.

In order to obtain respectable yields of $MeNHPF_2$, methylamine was added to excess phosphorus trifluoride in the gas phase. The volatile products were pumped off and the excess of PF_3 was removed by distillation through a -160° trap.

Reaction between methylaminodifluorophosphine and methylamine.- Excess of methylamine (0.108 g., 3.48 mmoles) was condensed onto $MeNHPF_2$ (0.215 g., 2.17 mmoles) in an ampoule. The system was shaken up and, as it attained room temperature, the initially clear liquid deposited a white solid (in contrast to what would be expected for a simple addition reaction). The volatile materials were separated by fractional distillation and identified as $MeNH_2$ (0.050 g., 1.61 mmoles) (by i.r.) and 0.214 g. of a less volatile portion of almost pure $(MeNH)_2PF_2H$ (by n.m.r.), leaving 0.059 g. solids in the reaction vessel or precipitated in the traps; this indicates an overall yield of 75% for $(MeNH)_2PF_2H$, based on the expected 1:1 addition.

Reaction between phosphorus trifluoride and ethylamine.- ETHYLAMINODIFLUOROPHOSPHINE [M found (vapour density), 112; M calc., 113; v.p. 69 mm. Hg at 27°] and BIS(ETHYLAMINO)DIFLUOROPHOSPHORANE [M found (mass spec.), 158; M calc., 158; v.p. 2 mm. Hg at 25°] were isolated from the volatile reaction products, formed from the liquid phase reaction between PF_3 and $EtNH_2$.

Reaction between phosphorus trifluoride and n-butylamine.- The previously employed liquid phase technique was used to produce reasonable yields of BIS(n-BUTYLAMINO)DIFLUOROPHOSPHORANE, an involatile liquid moving with difficulty on the vacuum line. Owing to the low volatility of n-butylamine, a more convenient method for the preparation of Bu^nNHPF_2 than the gas phase reaction was employed. This involved shaking an isopentane solution of Bu^nNH_2 with excess of PF_3 in a closed ampoule. Fractional distillation through a -86° trap removed the more volatile components and left n-BUTYLAMINODIFLUOROPHOSPHINE [M found (vapour density), 141; M calc., 141; v.p. 12 mm. Hg at 25°].

Reaction between phosphorus trifluoride and t-butylamine.- t-Butylamine was shaken with excess phosphorus trifluoride in an ampoule to produce white solids and a mixture of volatile components. Separation on the vacuum line produced PF_3 (identified by i.r.), t-BUTYLAMINODIFLUOROPHOSPHINE [M found (vapour density), 141; M calc., 141; v.p. 38 mm. Hg at 25°] (which just passed a -40° trap) and a small amount of sublimable white solid, which was trapped at -40°. Yields of the latter were increased by shaking Bu^tNHPF_2 with excess amine in an ampoule held at 50°; the reaction was incomplete, but the product could be easily sublimed out of the reaction vessel to leave behind some involatile white solids. The volatile solid was freed from starting materials and identified as BIS(t-BUTYLAMINO)FLUOROPHOSPHINE [M found (mass spec.), 194.1351; M calc., 194.1348; m.p. 39 ± 3°].

Reaction between bis(methylamino)difluorophosphorane and amines.- A sample of $(MeNH)_2PF_2H$ slowly deposited white solids on being shaken with excess methylamine.

A mixture of $(MeNH)_2PF_2H$ and triethylamine was heated for three hours at 70°. Brown solids were precipitated. An i.r.

examination of the volatile products indicated that $(MeNH)_2PF_2H$, $MeNHPF_2$ and PF_3 were present but gave no evidence for a compound corresponding to $(MeNH)_2PF$.

Reaction between phosphorus trifluoride and methanol.- A 2:1 molar ratio of PF_3 and MeOH were condensed together. No reaction was indicated on warming the mixture up to room temperature. Addition of two parts of triethylamine to this mixture led to the precipitation of white solids at -70°. An i.r. and n.m.r. study of the volatile components showed that all the PF_3 had reacted and that no PH species were present; $(MeO)_3P$ and $(MeO)_2PF$ were identified along with excess triethylamine.

CHAPTER II

THE PREPARATION OF P-N(Me)-X BRIDGES

(X = P, S, Si).

INTRODUCTION

In Chapter I it was shown to be possible to form diazafluorodiphosphetidines from the reaction between bis(methylamino)trifluorophosphorane and phenyltetrafluorophosphorane or phosphorus pentafluoride. The general applicability of this type of reaction for the production of P-NMe-X bridges, where X = P, S and Si, has been tested. The results obtained both from these experiments and others, that have been aimed towards producing similar bridged systems, are presented in this chapter.

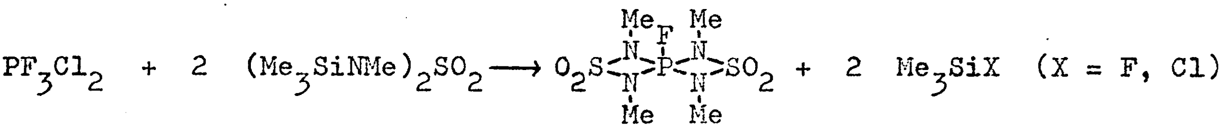
A method which has assumed considerable importance in the preparation of P-N bonds involves the cleavage of Si-N bonds with phosphorus-halides. Reactions in which cleavage of silicon-nitrogen bonds has been achieved by means of compounds from Groups IIIb - VIb have recently been reviewed [151]. The first application of this reaction to synthesize a phosphorus-fluoride derivative was that used to prepare dimethylaminotetrafluorophosphorane [12,152],

$$Me_3SiNMe_2 \quad + \quad PF_5 \longrightarrow Me_3SiF \quad + \quad Me_2NPF_4$$

With heptamethyldisilazane, phosphorus pentafluoride formed diazafluorodiphosphetidine [12,42,152],

$$2\ (Me_3Si)_2NMe \ + \ 2\ PF_5 \longrightarrow 4\ Me_3SiF \quad + \quad (F_3PNMe)_2$$

These reactions have been extended by employing other silicon-nitrogen compounds and derivatives of phosphorus pentafluoride as starting materials [3,42,152-4]. In this way it has proved possible to isolate a monofluorophosphorane [75]:-



$$PF_3Cl_2 + 2\ (Me_3SiNMe)_2SO_2 \longrightarrow O_2S{<}^{\overset{Me}{N}}_{\underset{Me}{N}}{>}\overset{F}{P}{<}^{\overset{Me}{N}}_{\underset{Me}{N}}{>}SO_2 + 2\ Me_3SiX \quad (X = F,\ Cl)$$

Few studies concerning analogous reactions with phosphorus(III)-fluorides have appeared in the literature. It has been reported that heptamethyldisilazane did not react with phosphorus trifluoride, but no reaction conditions were given [42]. However, all the fluorine atoms in PF_3 were replaced in the reaction with dimethylaminotrimethylstannane, Me_3SnNMe_2 [155].

(Thio)phosphoryl fluorides and fluorohalides have been reacted with hexamethyldisilazane to yield compounds with the general formula $Me_3SiNHP(X)F_{2-n}Cl_n$ (X = S, O; n = 0, 1) [156-7]. Similar reactions with heptamethyldisilazane were later found to take place [158].

Since all these reactions theoretically produce no solid by-products, this procedure for introducing a P-N bond into a molecule constitutes a much "cleaner" alternative to that given above. The exploitation of this method to produce phosphorus-fluorides containing a nitrogen-bridge relies only on the availability of compounds of the type $Me_3SiNRP(F)$.

An alternative method by which the desired bridged compounds can be produced involves the fluorination of the appropriate chloro-compounds where these are available. Good yields of Me_2NPF_2 have been obtained from the fluorination of Me_2NPCl_2; no evidence for the formation of fluorophosphorane by-products was reported [159]. A similar route has been used to prepare phosphoryl- and thiophosphoryl-fluorides [1,2] and has also been employed in the preparation of $(PF_2)_2NMe$ [117].

Many compounds are known in which two phosphorus atoms are linked by a nitrogen-bridge [65,160] but these phosphorus atoms were further linked to fluorine atoms in only a few instances. Fluorophosphazenes have been known for some time [1] and several (F)P-N=P(F) systems have recently been examined [2,161]. Compounds containing trico-ordinated nitrogen linking phosphorus-fluorine units are limited in number; these include diazafluorodiphosphetidines, $POF_2\text{-}NH\text{-}POCl_2$ [162], $(POF_2NH)_2$ [163], $(PXF_2)_2NMe$ ($X = S, O$) [164], and $(PF_2)_2NMe$ [117]. It should be noted that in none of these compounds does the nitrogen atom join two phosphorus nuclei in different oxidation states; the only compounds known to date which contain two fully fluorinated phosphorus atoms in different oxidation states are $P(O)F_2\text{-}O\text{-}PF_2$ and $P(S)F_2\text{-}S\text{-}PF_2$ [165-6], neither of which is very stable at room temperature. Recently the first examples of chloro-derivatives of phosphorus in two different oxidation states bridged by a N-methyl group have been prepared in these laboratories [167].

Very little work has been performed in elucidating the chemistry of these systems. In contrast to Me_2NPF_2, $(PF_2)_2NMe$ will not form a complex with BF_3 [117] but it has been found to co-ordinate to a transition metal through both phosphorus atoms [168]. While $(PF_2)_2NMe$ is cleaved by HCl at room temperature [117], $(PXF_2)_2NMe$ (X = S, O) required a much higher temperature for partial decomposition [164]. This enhanced stability was attributed to a reduction in the size of the d orbitals on phosphorus through electron withdrawal by the fluorine atoms; this makes them more suited to overlap with the p orbitals on nitrogen and hence enhances the (p-d)π-bonding in the PNP bridge, and at the same time reduces the basicity of the nitrogen atom. The compound $POF_2NHPOCl_2$ was reported to be only moderately stable to decomposition [162], presumably because of the lack of these stabilizing influences.

The reduced basicity of the nitrogen atom was also apparent in the preparation of $(PXF_2)_2NH$ (X = S, O); the product was formed in the presence of Me_3N, and an adduct $(PXF_2)_2NH.Me_3N$ was isolated [164]. In view of the formula given for a similar product obtained from $(P(CF_3)_2)_2NH$ and Me_3N by Burg [169] - as part of his contribution to the elucidation of the influence of perfluorocarbon groups on the chemistry of the phosphorus atom to which they are attached [170] - this is probably best regarded as a salt. Burg has provided further proof for the stabilizing influence of electronegative groups on P-N bonds, and his results suggested that this was due to even more enhanced π-bonding in these bonds than was proposed for the Si-N bonds in $(SiH_3)_3N$ [119, 169]. Nucleophilic attack can still take place at these phosphorus nuclei, for both $(PF_2)_2NMe$ [29] and $(P(CF_3)_2)_2NMe$ [169] were cleaved by $MeNH_2$.

RESULTS

REACTIONS BETWEEN RNH-P(F) AND PHOSPHORUS-HALIDES.

Since compounds containing the RNH-P(F) unit are stable with respect to self-condensation for fairly long periods it seems wisest, if one is attempting to prepare a P-NR-P derivative, to use the most reactive phosphorus-fluoride available. A combination of bond energy data [Appendix 2 presents data that is germane to all discussions in this chapter concerning bond energies] and previous chemical knowledge [1-3] suggest that phosphorus pentafluoride is the phosphorus-fluoride which is most prone to nucleophilic attack.

Reaction between phosphorus pentafluoride and methylaminodifluorophosphine.

The reaction between excess PF_5 and $MeNHPF_2$ takes place below room temperature to give a mixture of volatile products, consisting of PF_3, $(PF_2)_2NMe$, PF_2NMePF_4 and POF_3 (impurity in starting material), along with some solid products. The reaction is obviously complex and any mechanism proposed can only be of a tentative nature.

In view of the work published on the reaction between phosphorus pentafluoride and aminophosphines [171] it seems almost certain that the first stage in this reaction involves nucleophilic attack by $MeNHPF_2$ on PF_5 to form a 1:1 adduct (I). The mode of co-ordination is, however, uncertain. A P-P bond was believed to be present in $(Me_2N)_3P.PF_5$ [171]. The bulk of the evidence suggests that Me_2NPF_2 co-ordinates to transition metals through its phosphorus atom, with the decreased basicity of nitrogen and the increased co-ordinating power of phosphorus being a direct result of (p-d)π-bonding, which is promoted by the electronegative fluorine atoms [29]. While the crystal structure of the adduct of B_4H_8 and Me_2NPF_2 conclusively showed that a P-B bond was present [172] and the properties of $MeNHPF_2.BH_3$ were consistent with the same type of bonding [29,30], i.r. and n.m.r. evidence both favoured the presence of a N-B bond in $Me_2NPF_2.BF_3$ [26]. The reaction between Me_2NPF_2 and hydrogen halides likewise involved attack of the proton at the nitrogen atom [25]. It thus appears that the phosphorus atom will act as the donor atom only when there is a chance to form σ-bonds which are further stabilized through π-bonding.

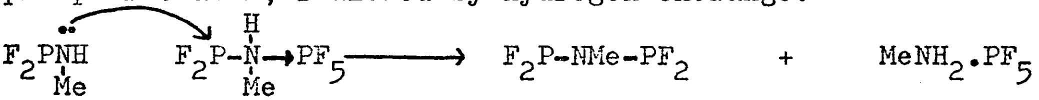
Both the similarity between the Lewis acid properties of BF_3 and PF_5 [1] and the nature of the products (especially PF_2NMePF_4 in which the PNP entity remains intact) are taken to suggest that bonding takes place through the nitrogen atom in I. The reaction is then assumed to proceed by means of further nucleophilic attack by another molecule of $MeNHPF_2$ on the amino-proton of I, which should be more acidic than it is in the unco-ordinated ligand as it is now coupled to two electron-withdrawing species, with displacement of a fluoride ion,

$$F_2P\overset{Me}{\underset{H}{N}}: \quad H-\overset{Me}{\underset{PF_2}{N}}\rightarrow PF_4-F$$

The overall reaction is written as:-

$$3\ MeNHPF_2 + PF_5 \longrightarrow PF_2NMePF_4 + 2\ MeNH_3^+F^- + PF_3$$

Since the nitrogen atom in I is now bonded to two phosphorus nuclei, the (p-d)π-bonding in the P(III)-N bond and the charge density on the P(III) atom are both likely to be less pronounced than in the free ligand. The formation of $(PF_2)_2NMe$ can then be envisaged as resulting from nucleophilic attack of $MeNHPF_2$ on this phosphorus atom, followed by hydrogen exchange:-



$$F_2P\underset{Me}{\ddot{N}}H \quad F_2P-\overset{H}{\underset{Me}{N}}\rightarrow PF_5 \longrightarrow F_2P-NMe-PF_2 + MeNH_2.PF_5$$

This interaction with phosphorus pentafluoride can thus be regarded as a means of promoting the disproportionation of $MeNHPF_2$:-

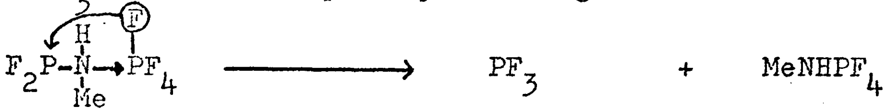
$$2\ MeNHPF_2 \rightleftharpoons (PF_2)_2NMe + MeNH_2$$

This process has previously been suggested to take place by Barlow et al. [29].

On heating the solid residue obtained from the above reaction $(PF_2)_2NMe$, PF_2NMePF_4 and $MeNHPF_4$ are produced. The latter compound would be expected to result from the thermal decomposition of the adduct $MeNH_2.PF_5$ produced above,

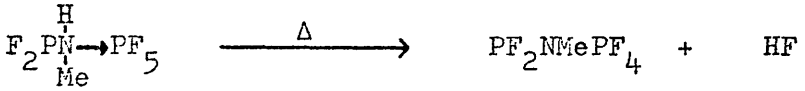
$$2\ MeNH_2.PF_5 \xrightarrow{\Delta} MeNHPF_4 + MeNH_3^+PF_6^-$$

but it could also be derived through exchange of substituents between the P(III) and P(V) nuclei in I (as has been proposed for the reaction between phosphorus pentafluoride and aminophosphines [171]), with the PF_3 formed subsequently reacting:-



$$F_2P-\overset{H}{\underset{Me}{N}}\rightarrow \overset{\textcircled{F}}{PF_4} \longrightarrow PF_3 + MeNHPF_4$$

Difluorophosphino(tetrafluorophosphoranyl)methylamine would also be expected to arise through thermal decomposition of I:-



$$F_2P\overset{H}{\underset{Me}{N}}\rightarrow PF_5 \xrightarrow{\Delta} PF_2NMePF_4 + HF$$

Reaction between phosphorus trifluoride and t-butylaminodifluorophosphine.

Phosphorus trifluoride and t-butylaminodifluorophosphine do not react at room temperature. This is not surprising in view of the results published for the reactions between aminophosphines and phosphorus trifluoride where high temperatures (which would have decomposed Bu^tNHPF_2) had to be employed before re-distribution of the ligand between the two phosphorus nuclei would take place [171]; these exchange reactions were presumably initiated through the reactants forming a weak 1:1 adduct. While the nitrogen atom in Bu^tNHPF_2 should be more basic than that in any of the other alkylaminodifluorophosphines studied, on account of the large inductive effect of the three methyl groups, the sheer bulk of the t-butyl group is likely to hinder the formation of 1:1 adducts.

Reaction between chlorodifluorophosphine and methylaminophosphoryl difluoride.

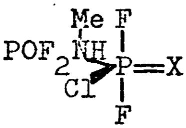
A reaction between methylaminophosphoryl difluoride and chlorophosphoryl difluoride was reported to take place only in the presence of a tertiary base [164]. In the present work a weak base (N,N-dimethylaniline) is also required to promote the reaction between PF_2Cl and $MeNHPOF_2$. (A weak base is employed in this reaction since there appears to be some evidence for interaction between stronger bases and PF_2Cl.)

$$MeNHPOF_2 \quad + \quad PF_2Cl \longrightarrow PF_2NMePOF_2 \quad + \quad HCl$$

There are no indications that a similar reaction will take place with PF_3 in place of PF_2Cl. The relative susceptibility of halodifluorophosphines to nucleophilic attack has not been well studied [1] A reaction between halodifluorophosphines, PF_2X, and hexafluoroacetone, which was postulated to proceed through nucleophilic attack on the phosphorus atom, has been reported for X = Br and I but not for X = Cl and F [173].

Molecular orbital calculations have indicated a significant degree of $(p-d)\pi$-bonding between the phosphorus and fluorine atoms in PF_3 [174], but the extent to which this changes on substituting a less electronegative halogen atom for a fluorine atom is unknown. There are thus two opposing processes which affect the total charge on phosphorus and hence its reactivity; electron withdrawal by electronegative substituents promotes nucleophilic attack while $(p-d)\pi$-bonding retards it.

While the inactivity of PF_3 may stem from its inability to form a suitable intermediate adduct, it is instructive to consider why the intermediate formed in the reaction between $MeNHPOF_2$ and either POF_2Cl or PF_2Cl, II, breaks down through cleavage of a P-Cl and not a P-F bond; this mode of decomposition appears to be fairly general [1]. II (which is probably formed through apical approach of the nucleophile and a subsequent pseudorotational step, so placing the fluorine atoms in axial positions) may be represented as:-



(X = O or :)

It is probable that a molecule of the tertiary base added, rather than the weakly basic $MeNHPOF_2$, will remove the amino-proton on II. The ease with which pseudorotation will take place, so placing the leaving group in the axial position, is highly critical for some reactions [59]. In II the fluorine atom is best placed for elimination but, for this particular molecule, barriers to pseudorotation are likely to be low and are unlikely to act as a constraint on the system. Bond energy values suggest that the cleavage of a P-Cl bond will be favoured over cleavage of a P-F bond, on account of the smaller activation energy required for this step.

The overall thermodynamics for this reaction, considered simply as either (a) rupture of a P-Cl bond and formation of H-Cl or (b) rupture of a P-F bond and formation of H-F, favour the former reaction mode to the extent of ~9 kcal./mole. The inclusion of a base necessitates the examination of the enthalpy for the process:-

$$\begin{tikzcd}
\text{H-X (g)} + R_3\text{N (l)} \arrow[r] \arrow[d, "1"'] & R_3\text{NH}^+ \text{X}^- \text{(s)} \\
\text{H, X} \quad R_3\text{N (g)} \arrow[r, "2"] & \text{X}^-, \text{H}^+, R_3\text{N (g)} \arrow[u, "3"']
\end{tikzcd}$$

The first two steps favour X = Cl to the extent of 36 kcal./mole; it seems unlikely that the difference in lattice energies of the salts that can be formed in step 3 will exceed this quantity [175]. Both kinetic and thermodynamic approaches are thus shown to favour the formation of the phosphorus product containing the maximum number of P-F bonds.

CLEAVAGE OF Si-N BONDS BY PHOSPHORUS-HALIDES.

The general principles involved in these reactions will first be illustrated by reference to the reaction of PF_5 with $Me_3SiNHMe$. The preparation of the compounds $Me_3SiNMeP(F)$ and their reactions with phosphorus-fluorides will then be discussed.

Reaction between phosphorus pentafluoride and methylaminotrimethylsilane.

Previous work has demonstrated that the reaction between PF_5 and Me_3SiNMe_2 proceeded by the formation of a 1:1 adduct which was stable at -78° [12]. The adduct rearranged when it was warmed up to room temperature,

$$Me_3SiNMe_2\ (l) + PF_5\ (g) \longrightarrow \text{1:1 adduct} \longrightarrow Me_3SiF\ (g) + Me_2NPF_4\ (l)$$

Since the difference between the Si-F and P-F bond energies is 34 kcal./mole and the values for the P-N and Si-N bond energies are almost identical, the re-distribution reaction is favoured from the thermodynamic point of view. If the reaction is set up so that the Me_3SiF is removed as soon as it is formed, then the reaction should go to completion. In principle then, since it will be impossible to compensate for so large an enthalpy difference, all reactions of this type will be expected to proceed with P-F bond cleavage.

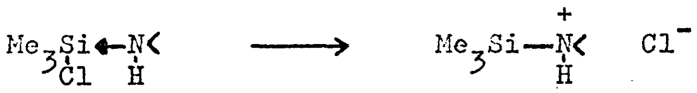
Since methylaminotetrafluorophosphorane could not be prepared in a similar manner to the other alkylaminotetrafluorophosphoranes, the reaction between PF_5 and $Me_3SiNHMe$ was studied. While Me_3SiF is liberated almost quantitatively after allowing the reaction mixture to warm up to room temperature, only a small quantity of $MeNHPF_4$ is isolated. On heating the solid material, however, more of the desired product is obtained. The $(F_3PNMe)_2$ which features as a by-product in this reaction is probably obtained from two sources: (a) from the heptamethyldisilazane impurity in the starting material and (b) from the methylaminotetrafluorophosphorane, either by its reaction with excess PF_5 or through its disproportionation (with the concurrent formation of $MeNH_3^+ PF_6^-$). It appears that this solid product must contain some form of loose adduct, $(PF_4NMeH \rightarrow PF_4NMeH)_n$, which dissociates on heating and whose formation is favoured by the reaction conditions. If the reaction were carried out in solution it is probable that the formation of such an adduct would not be favoured.

THE PREPARATION OF $Me_3SiNMeP(F)$.

Reaction between trimethylchlorosilane and methylaminodifluorophosphine.

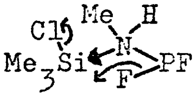
The most common way of establishing a bond between silicon and nitrogen is by the reaction of $\geq SiCl$ with a $>NH$ group [176-8]. The reaction between $Bu^tP(NH_2)_2$ and Me_3SiCl in the presence of Et_3N has recently been reported to yield $Bu^tP(NHSiMe_3)_2$ [179]. Accordingly the reaction between Me_3SiCl and $MeNHPF_2$ in the presence of a tertiary base was studied as a means of obtaining difluorophosphino(trimethylsilyl)methylamine, $Me_3SiNMePF_2$. With excess of Me_3SiCl required for a 1:1 ratio of reactants, none of the expected product is obtained and the only volatile product recovered is Me_3SiF.

It is generally accepted that reactions of the above type proceed through nucleophilic attack of nitrogen on silicon with subsequent cleavage of the Si-Cl bond to produce a substituted ammonium salt [178]:-



$$Me_3\underset{Cl}{Si}\leftarrow\underset{H}{N}< \longrightarrow Me_3Si-\overset{+}{\underset{H}{N}}< \quad Cl^-$$

This is then deprotonated by base. While the phosphorus atom in $MeNHPF_2$ could also act as a nucleophile it seems likely, on the basis of the evidence already cited, that the normal course of events is maintained and attack is through the nitrogen lone pair. Since $Me_3SiNMePF_2$, prepared by other routes, is found to be stable to heat [167] and is also stable in the presence of both Me_3SiCl and Et_3N, it is unlikely that the desired compound is ever in fact formed in the above reaction. The evidence, therefore, points to an alternative mode by which the intermediate can break down. One can visualize fluorine exchange taking place through a transition state involving a four-membered ring,



The driving force for such a reaction would be the high Si-F bond energy. The fate of the phosphorus entity is unknown as no volatile phosphorus-fluorides were isolated.

Reaction between trimethylchlorosilane and methylaminophosphoryl-difluoride (via its lithium derivative).

A second method used for the preparation of Si-N bonds, chiefly exploited by Scherer and his co-workers [180], involves reacting Me_3SiCl with the lithium salt of an aminosilane:-

$$Me_3SiCl + LiNRP< \longrightarrow Me_3SiNRP< + LiCl$$

An attempt was made to employ this route to prepare difluorophosphoryl(trimethylsilyl)methylamine, $Me_3SiNMePOF_2$. A white precipitate was formed in the low temperature reaction between n-butyl-lithium and methylaminophosphoryl difluoride. The solid was not isolated but Me_3SiCl was slowly added to the reaction mixture. The reaction set up was not designed to detect low boiling liquids, so it was not determined whether any Me_3SiCl or Me_3SiF was in fact present at the end of the reaction. The less volatile products were examined by n.m.r. and shown to contain a small quantity of unreacted starting material, but no signals corresponding to the presence of $Me_3SiNMePOF_2$, which has previously been characterised by n.m.r. having been prepared by another route [158], were seen.

The failure to observe any of the desired product is most likely to result from one of two causes:-

(i) An analogous reaction to that recorded above, where Me_3SiF was formed in preference to Me_3SiCl, is favoured.

(ii) The intermediate formed is not $MeN(Li)POF_2$. The reaction of $MeNHPOF_2$ with Bu^nLi could proceed with evolution of butane and the formation of LiF and $(MeNPOF)_n$:-

$$MeNHPOF_2 + Bu^nLi \longrightarrow 1/n\ (MeNPOF)_n + LiF + Bu^nH$$

The high lattice energy of lithium fluoride [175] and the known ability of some alkylaminophosphoryl difluorides to polymerise [181] both tend to favour this reaction. The reaction between Bu^nLi and $MeNHPOF_2$ has been repeated, and the butane evolved has been confirmed by its i.r. spectrum; The solid product is being further investigated [158].

Reaction between dichlorophosphino(trimethylsilyl)methylamine and sodium fluoride.

A further method of obtaining the desired $Me_3SiNMeP(F)$ simply involves fluorinating its chloro-derivative. The first preparation of $Me_3SiNMePF_2$ was achieved in low yield by the fluorination of $Me_3SiNMePCl_2$ with SbF_3 [167]. High yields have been recorded in some cases by using NaF instead of SbF_3 as the fluorinating agent in analogous reactions [159]. However, with a sulpholane slurry of NaF and $Me_3SiNMePCl_2$ the only volatile products recovered are PF_3 and Me_3SiF.

It is possible that $Me_3SiNMePCl_2$, which is known to be thermally unstable [167], decomposes to give products which include PCl_3 and Me_3SiCl; these compounds would then be fluorinated by NaF, and account for the above products. An alternative mechanism might however be operating. It has recently been found [158] that $Me_3SiNMePOF_2$ will react with CsF in an acetonitrile solution; one mode of attack was shown to involve Me_3SiF elimination and the production of a salt containing the $[F_2P(O)NMe]^-$ anion, which is stabilized by charge delocalisation over the oxygen and nitrogen atoms,

$$Me_3SiNMePOF_2 + CsF \longrightarrow Me_3SiF + Cs^+\left[\begin{smallmatrix}F\\F\end{smallmatrix}\!>\!P\!<\!\begin{smallmatrix}O\\NMe\end{smallmatrix}\right]^-$$

It is thus possible that nucleophilic attack by F^- on either silicon or phosphorus in $Me_3SiNMePF_2$ takes place to yield Me_3SiF and PF_3 respectively, with the unstable anionic species $(F_2PNMe)^-$ or $(Me_3SiNMe)^-$ once formed being removed by attacking the solvent.

Reaction between heptamethyldisilazane and phosphorus trifluoride or chlorodifluorophosphine.

The most successful method devised for preparing $Me_3SiNMePF_2$ is that in which cleavage of only one Si-N bond in $(Me_3Si)_2NMe$

is achieved through reacting the latter with a phosphorus halide. Schmutzler reported that $(Me_3Si)_2NMe$ and PF_3 did not react [42]. The system has been re-examined, and this result is confirmed in a room temperature reaction, but at higher temperatures it is possible to show that some interaction takes place; some Me_3SiF but no $Me_3SiNMePF_2$ is formed.

By employing PF_2Cl in place of PF_3 good yields of $Me_3SiNMePF_2$ are obtained if the reaction is carried out at ~90°. The temperature must not be allowed to become too high since this will promote the disproportionation of PF_2Cl. The reaction between PCl_3 and $(Me_3Si)_2NMe$ has been observed to take place at 0° [167], so it appears that replacement of chlorine for fluorine greatly enhances the ease of reaction.

An examination of the energies of the bonds broken and formed in the reaction of PF_2Cl with $(Me_3Si)_2NMe$ indicates that the reaction in which the P-F bond is cleaved is slightly favoured over that in which the P-Cl bond is cleaved, if the P-N bond energy is assumed to be the same for both possible products:-

$$\mathrm{PF_2Cl\ (g) + (Me_3Si)_2NMe\ (l)} \left\langle \begin{array}{l} \nearrow \mathrm{Me_3SiNMePF_2\ \ (l) + Me_3SiCl\ (g)}\ \Delta D = -20\ \mathrm{kcal./mole} \\ \searrow \mathrm{Me_3SiNMePFCl\ (l) + Me_3SiF\ \ (g)}\ \Delta D = -26\ \mathrm{kcal./mole} \end{array} \right.$$

However, $(p-d)\pi$-bonding effects are more likely to increase the P-N bond strength of the fully fluorinated aminophosphine and so slightly reduce this energy gap. Before determining why the reaction proceeds as it does the Lewis acidity of phosphorus-halides will be examined.

It is possible that the above reaction proceeds through the formation of a weak adduct between $(Me_3Si)_2NMe$ and the phosphorus-fluoride. It has recently proved possible to isolate similar adducts in the reaction between $(Me_3Si)_2NMe$ and boron-halides, BX_3 (X = F, Cl, Br) [182]; their stability with respect to trimethylhalosilane elimination was found to decrease in the order F > Cl > Br. It has been suggested that the ease of reaction between $(Me_3Si)_2NMe$ and fluorophosphoranes (where no alternative leaving groups were present) was a function of the Lewis acidity of the latter compounds [42]. This concept fits in well with the previously reported reactions between hexamethyldisilazane and (thio)phosphoryl-fluorohalides, where the temperatures required for the thiophosphoryl derivatives to react [157] were about 100° higher than those required for the phosphoryl derivatives [156]. The same difference in reactivity of phosphoryl and thiophosphoryl derivatives towards nucleophiles has previously been noted [183]. The reactivity of these systems depends on:-

(i) The electronegativity of the ligands which are attached to phosphorus. Oxygen and fluorine enhance the electrophilicity of the phosphorus atom to a greater extent than do sulphur and chlorine.

(ii) The extent to which $(p-d)\pi$-bonding is allowed to build up the charge on the phosphorus atom. This form of bonding is most pronounced in phosphorus-fluoride derivatives [184].

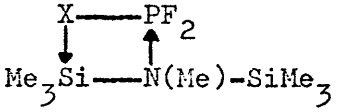
The difference in reactivity between PF_3, POF_3 and PSF_3 may be approached from another angle. Gillespie has shown that bond angles for a given series of compounds indicate the relative size of the electron pairs attached to the central atom; in his treatment, the two electron pairs of a double bond occupy a large double bond orbital [185]. The $F\hat{P}F$ bond angles in the series POF_3 (102.5° [1]), PSF_3 (100.3° [1]) and PF_3 (97.8° [186]) imply that the lone pair on PF_3 occupies a larger effective volume than either of the other bonding electron pairs which link phosphorus to either oxygen or sulphur, if the P-F bonds are assumed to remain unchanged in this series. If one regards the size of an electron pair as being a rough indication of how diffuse the electron cloud composing it is, i.e. how closely the latter is associated with the phosphorus nucleus, then one would expect that those central atoms which are closely associated to the electron pair would be less prone to nucleophilic attack. On this basis the predicted ease with which the phosphorus atom is attacked by a nucleophile (i.e. the Lewis acidity) decreases down the series:-

$$POF_3 \quad > \quad PSF_3 \quad > \quad PF_3$$

Suitable kinetic data are not available to test this hypothesis. However, if reaction temperatures are taken as a guide to the ease with which phosphorus-fluorides will react, then the kinetics of the above reaction between phosphorus-fluorides and disilazanes follow the expected trend - the difference in Lewis basicity between $(Me_3Si)_2NMe$ and $(Me_3Si)_2NH$ is ignored here.

If it is agreed that one of the factors influencing the rates of reaction between phosphorus-fluorides and silicon-nitrogen compounds is the Lewis acidity of the former, the question now remains: why does the P-Cl rather than the P-F bond in PF_2Cl break when a thermodynamic approach would tend to favour the latter fragmentation pathway? Reaction pathways depend on two factors, the thermodynamic and kinetic factors. It is presumably the latter which plays the dominant role in deciding what products are formed.

Once the initial adduct is formed there is a chance for additional interaction between a fluorine or a chlorine atom and silicon to form a four-membered intermediate,



$$\begin{array}{ccc} X & \text{——} & PF_2 \\ \downarrow & & \uparrow \\ Me_3Si & \text{——} & N(Me)\text{-}SiMe_3 \end{array} \qquad (X = F,\ Cl)$$

The ability of chlorine and fluorine atoms to form bridges in some transition metal and non-metal halides (e.g. SbF_5) reflects the stability of this type of interaction. It is not, however, clear which of the halide atoms in PF_2Cl will act as the best nucleophile towards silicon. Factors which are likely to influence the extent to which interaction takes place are (a) the polarizability of the halogen atom [187], (b) the acceptor properties of silicon, and (c) the degree to which d orbitals on silicon and chlorine can promote bonding. While it is not possible to provide any information as to the relative importance of these factors, results can be rationalized by assuming either that silicon preferentially bonds with chlorine or that the bonding with chlorine, but not with fluorine, sufficiently lowers the energy of the Si-N and P-Cl bonds to permit their fission. It seems likely that formation of Me_3SiF rather than Me_3SiCl will be favoured if the activation energy for the reaction can be sufficiently reduced by weakening the P-F bonds. High reaction temperatures are also likely to promote Me_3SiF formation. The four-centre intermediate has been introduced above to provide an additional means of stabilizing an intermediate where the reactants only possess low nucleo/electrophilic reactivity; the importance or indeed the existence of such an intermediate has yet to be ascertained.

To sum up, the reaction between disilazanes and phosphorus-halides appears to be kinetically controlled, with the most reactive systems being those which contain phosphorus-halides possessing high Lewis acidity and easily broken bonds.

THE REACTIONS OF $Me_3SiNMeP(F)$.

The evidence for (p-d)π-bonding in aminosilanes has been summarized [177], and tends to suggest that the basicity of the lone pair on nitrogen decreases on increasing the number of silicon atoms directly bonded to nitrogen. A slight increase of 3 kcal./mole in the Si-N bond energy in passing from a primary to a secondary silazane has tentatively been attributed to increased delocalisation in the Si-N-Si bridge [188]. Replacement of one of the trimethylsilyl groups in heptamethyldisilazane by a difluorophosphino group introduces a more electronegative substituent onto nitrogen, which is also capable of withdrawing electrons from the nitrogen atom by means of (p-d)π-bonding. It is thus expected that $Me_3SiNMePF_2$ will act as an even weaker Lewis base than $(Me_3Si)_2NMe$. The ^1H n.m.r. spectrum of a mixture of these two compounds shows that the resonance due to the N-methyl group shifts 0.1 p.p.m. to lower field on the replacement of the trimethylsilyl group - the direction which would be predicted on the basis of the above argument [177]. This lower basicity would lead one to expect that $Me_3SiNMePF_2$ will be less reactive than $(Me_3Si)_2NMe$ in its reactions with phosphorus-fluorides, assuming that attack still takes place through the nitrogen atom's lone pair.

Reaction between difluorophosphino(trimethylsilyl)methylamine and phosphorus pentafluoride.

Phosphorus pentafluoride reacts with $Me_3SiNMePF_2$ at room temperature to produce difluorophosphino(tetrafluorophosphoranyl)-methylamine in good yield,

$$Me_3SiNMePF_2 \quad + \quad PF_5 \quad \longrightarrow \quad Me_3SiF \quad + \quad PF_2NMePF_4$$

Attempts to effect a second substitution of a fluorine atom in the tetrafluorophosphoranyl group met with no success. Since PF_2NMePF_4 is a weaker Lewis acid than PF_5 a higher temperature is required before it will react with $Me_3SiNMePF_2$. However, PF_2NMePF_4

is found to be unstable to heat and it starts to decompose at a lower temperature than that required for a reaction to take place. Hence the volatile products isolated from this reaction are the same as those formed on decomposing a pure sample of PF_2NMePF_4. Both PF_3 and $(F_3PNMe)_2$ can be identified, which suggests that one decomposition mode is:-

$$2\ PF_2NMePF_4 \longrightarrow 2\ PF_3 + (F_3PNMe)_2$$

A more suitable system to study would be the reaction between $PhPF_4$ and $Me_3SiNMePF_2$; the expected product, $PhPF_3(NMePF_2)$, should possess interesting n.m.r. parameters (vide infra).

Reaction between difluorophosphino(trimethylsilyl)methylamine and phosphoryl fluoride.

There is no reaction between $Me_3SiNMePF_2$ and POF_3 at room temperature, although partial conversion to $PF_2NMePOF_2$ takes place at 60°. At higher temperatures (∼110°) only a small amount of the desired product is obtained along with a lot of viscous material, PF_3 and some $(POF_2)_2NMe$. Separate experiments indicate that both $Me_3SiNMePF_2$ [167] and $PF_2NMePOF_2$ are stable at these temperatures. Difluorophosphino(difluorophosphoryl)methylamine tends to decompose in the presence of excess POF_3; both PF_3 and a viscous liquid, giving an i.r. similar to that obtained from the reaction above, but no $(POF_2)_2NMe$ are produced. These products tend to suggest that the following disproportionation takes place:-

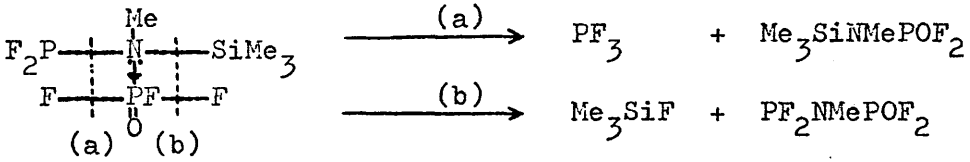
$$PF_2NMePOF_2 \longrightarrow 1/n\ [FP(O)NMe]_n + PF_3$$

The identity of the involatile component has not been established. There is, however, information that such products appear as by-products of unspecified molecular weight in the reaction between primary amines and phosphoryl fluoride [181].

Under the experimental conditions employed in the reaction between POF_3 and $Me_3SiNMePF_2$, it appears that another mode of decomposition is also operating:-

$$POF_3 + PF_2NMePOF_2 \longrightarrow (POF_2)_2NMe + PF_3$$

An alternative route by which the $(POF_2)_2NMe$ could have been formed involves the displacement of PF_3 from $Me_3SiNMePF_2$ to produce $Me_3SiNMePOF_2$, which then reacts with excess POF_3. The production of $Me_3SiNMePOF_2$ can best be rationalized by examining the intermediate adduct formed between $Me_3SiNMePF_2$ and POF_3, which can break down in two ways:-



Both fragmentations could involve a four-centre transition state. It should be noted that there is no evidence for a similar fragmentation, in which PF_3 is eliminated, taking place in the reaction between PF_5 and $Me_3SiNMePF_2$.

The reaction between POF_2Br and $Me_3SiNMePF_2$ was briefly examined as an alternative route to $PF_2NMePOF_2$. However, large quantities of involatile material, probably originating from the thermal break-down of POF_2Br [189], precluded further investigation of this system.

In the above reactions both PF_5 and POF_3 have been observed to react with $Me_3SiNMePF_2$. It would be expected from previous discussions that the reaction of $Me_3SiNMePF_2$ with PF_3 would require a higher temperature than that with POF_3. Although this reaction was not performed, that between PF_2Cl and $(Me_3Si)_2NMe$ was carried out using excess PF_2Cl, with no evidence for the formation of $(PF_2)_2NMe$ being obtained; bis(difluorophosphino)methylamine has previously been characterised by Nixon [117,190].

The general trend in the above reactivities is completely in agreement with the decreased Lewis basicity of $Me_3SiNMePF_2$ as compared to $(Me_3Si)_2NMe$ and the decreasing Lewis acidity down the series $PF_5 > POF_3 > PF_3$. The reactions also show that Si-N rather than P-N bond cleavage is favoured despite the near equivalence in the values of these bond energies. The differing reactivities of $(Me_3Si)_2NMe$ and $Me_3SiNMePF_2$ could alternatively be attributed to an increase in the Si-N bond strength on the replacement of a trimethylsilyl group in heptamethyldisilazane by a fluorophosphino group, which would increase the activation energy for these reactions with phosphorus-fluorides. In the absence of physical measurements to determine exact bond strengths and basicities it is not possible to distinguish which of these alternative factors dominates.

FLUORINATION OF CHLORO-DERIVATIVES CONTAINING THE P-NMe-P BRIDGE.

Fluorination of $PCl_2NMePOCl_2$ was attempted by using a slurry of NaF in sulpholane; low yields of $PF_2NMePOF_2$ are obtained along with a trace of POF_3 and large quantities of PF_3. This is in contrast to the large yields that were reported for the fluorination of $(PCl_2)_2NMe$ [117]. These results may be rationalized by supposing that the fluoride ion, acting as a nucleophile, is capable of eliminating both Cl^- and $(POF_2NMe)^-$ from the parent molecule. The latter reaction is represented as:-

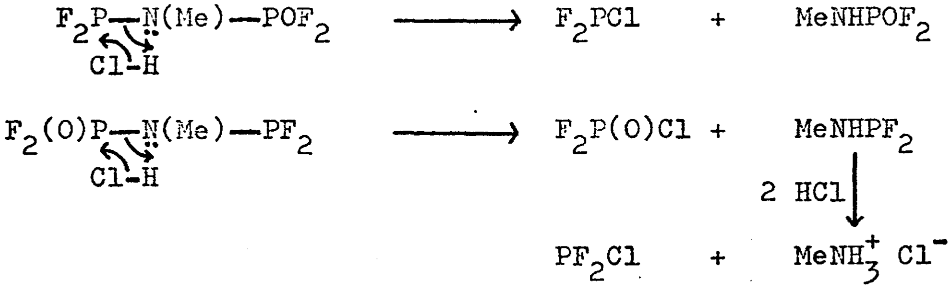
$$F^- \quad F_2P\text{-}NMe\text{-}POF_2 \longrightarrow PF_3 + (POF_2NMe)^-$$

The stability of the $(POF_2NMe)^-$ anion [158] as compared to the $(F_2PNMe)^-$ anion favours preferential nucleophilic attack at the P(III) atom and accounts for the very low yield of POF_3. Attack by F^- on $(PF_2)_2O$ similarly gave POF_3 and $(PO_2F_2)^-$ [191].

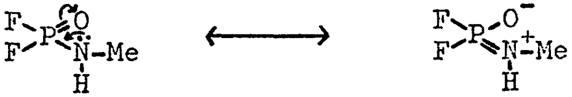
PROPERTIES OF DIFLUOROPHOSPHINO(DIFLUOROPHOSPHORYL)METHYLAMINE AND DIFLUOROPHOSPHINO(TETRAFLUOROPHOSPHORANYL)METHYLAMINE.

Some of the chemical properties of $PF_2NMePOF_2$ and PF_2NMePF_4 have already been dealt with in the main text. The cleavage of $PF_2NMePOF_2$ with HCl was studied in order to see how the results would compare with analogous cleavage reactions performed on $(PF_2)_2NMe$ and $(POF_2)_2NMe$. An approximately 1:1 ratio of HCl and $PF_2NMePOF_2$ react together at room temperature. An investigation of the volatile products shows that all the HCl is absorbed and that excess $PF_2NMePOF_2$ is recovered along with PF_3, PCl_3, POF_3, POF_2Cl, and $MeNHPOF_2$. The temperature required for the reaction is a lot lower than that required to cleave $(POF_2)_2NMe$ [164]. Hydrogen chloride cleaved $(PF_2)_2NMe$ at room temperature to give a mixture of PF_2Cl, PF_3 and PCl_3, with the last two compounds being derived from the disproportionation of PF_2Cl [117].

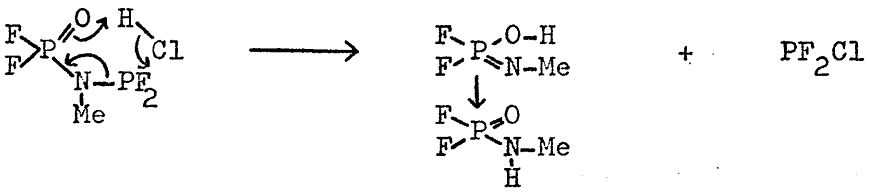
Protonation at the nitrogen atom does not appear to be significantly hindered by replacing one of the difluorophosphino groups in $(PF_2)_2NMe$ by a difluorophosphoryl group. The relative quantities of product formed indicate that nucleophilic attack at the PF_2 centre is slightly favoured to that at the POF_2 centre,



No $MeNHPF_2$ is isolated; this is presumably due to the enhanced basicity of the nitrogen atom which is immediately protonated, and leads to P-N bond cleavage. The less basic character of the nitrogen atom in $MeNHPOF_2$ is best viewed in terms of a valence bond description,



An alternative mechanism for bond cleavage could originate from the protonation of an oxygen atom:-



However, this is unlikely to assume much significance since, if it did, a similar reaction temperature would be expected for cleavage of both $PF_2NMePOF_2$ and $(POF_2)_2NMe$ by HCl, which is not in accordance with experimental results.

Further reactions of PF_2NMePF_4 and $PF_2NMePOF_2$ with a whole variety of reagents (nucleophiles, transition metals etc.) are called for, in order to elucidate the differing roles played by the two phosphorus centres. The above synthetic methods can be extended to prepare a wide range of nitrogen bridged compounds linking together not only different groups containing phosphorus but also a wide range of other non-metal ligands. The preparation of compounds containing -NH- bridges would be particularly interesting since, by a simple extension of the above techniques, compounds containing three different phosphorus ligands connected to the same nitrogen atom could be prepared.

N.M.R. SPECTRA OF $PF_2NMePOF_2$ AND PF_2NMePF_4.

Both $PF_2NMePOF_2$ and PF_2NMePF_4 give complicated n.m.r. spectra, but these are readily interpreted by a first order analysis. The fluorine spectra are most useful in characterising these compounds; their line diagrams are given in Fig. 2.1 together with those for

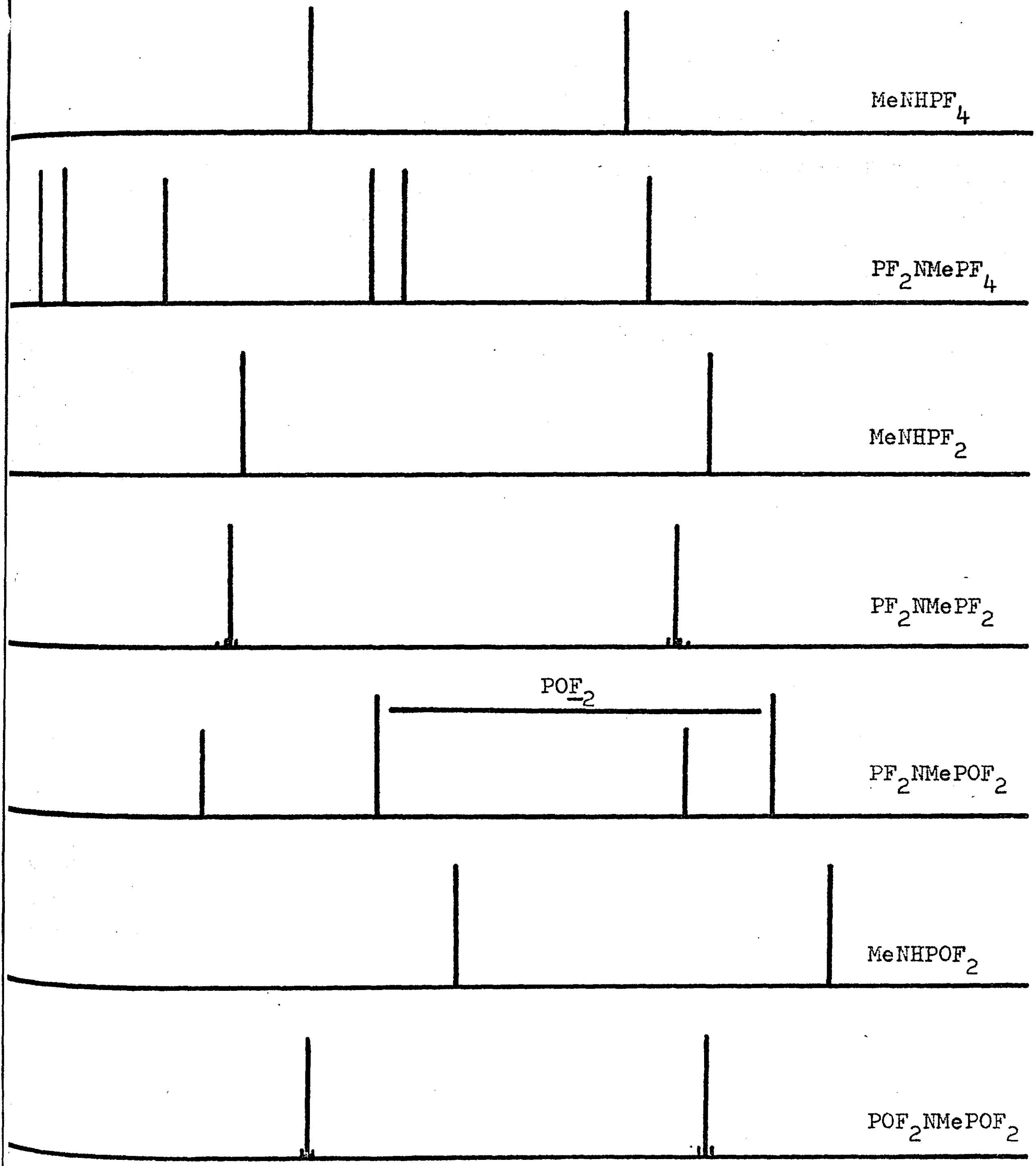


Fig. 2.1 ^{19}F n.m.r. spectra MeNHP(F) and (F)P-NMe-P(F)

$MeNHPF_2$, $MeNHPOF_2$ (vide infra), $MeNHPF_4$ (at +70°), $(POF_2)_2NMe$, and and $(PF_2)_2NMe$ [190]. The latter two compounds possess magnetically non-equivalent phosphorus and fluorine nuclei, which lead to extra lines over those expected on the basis of a first order analysis in the ^{19}F n.m.r. spectrum; to date, no full analysis for $(POF_2)_2NMe$ has been reported. In each case the ^{19}F chemical shift is to slightly lower field and the value of $^1J(PF)$ is slightly larger for the nitrogen-bridged compound than in the corresponding parent methylamino-derivative.

The peaks due to the $P\underline{F}_4$ in PF_2NMePF_4 indicate that pseudorotational processes render the fluorine atoms equivalent at room temperature. On lowering the temperature to -80° (at which temperature the compound starts to solidify) a slight broadening of the signals but no macroscopic change in the appearance of the spectrum is noted. The markedly lower barrier to pseudorotation present in this compound as compared to $MeNHPF_4$ is surely a consequence of the lack of hydrogen-bonding in the former compound.

The full analysis for the ^1H and ^{19}F n.m.r. spectra of PF_2NMePF_4 and $PF_2NMePOF_2$ is given in Table 2.1. One half of the $P\underline{F}_2$ resonance in $PF_2NMePOF_2$ is reproduced in Fig. 2.2, together with a line diagram for the theoretical spectrum calculated using the parameters of Table 2.1. A theoretical line diagram is also reproduced for one half of the ^{19}F resonance of the PF_2 group in PF_2NMePF_4 (Fig. 2.3). The surprisingly simple $PO\underline{F}_2$

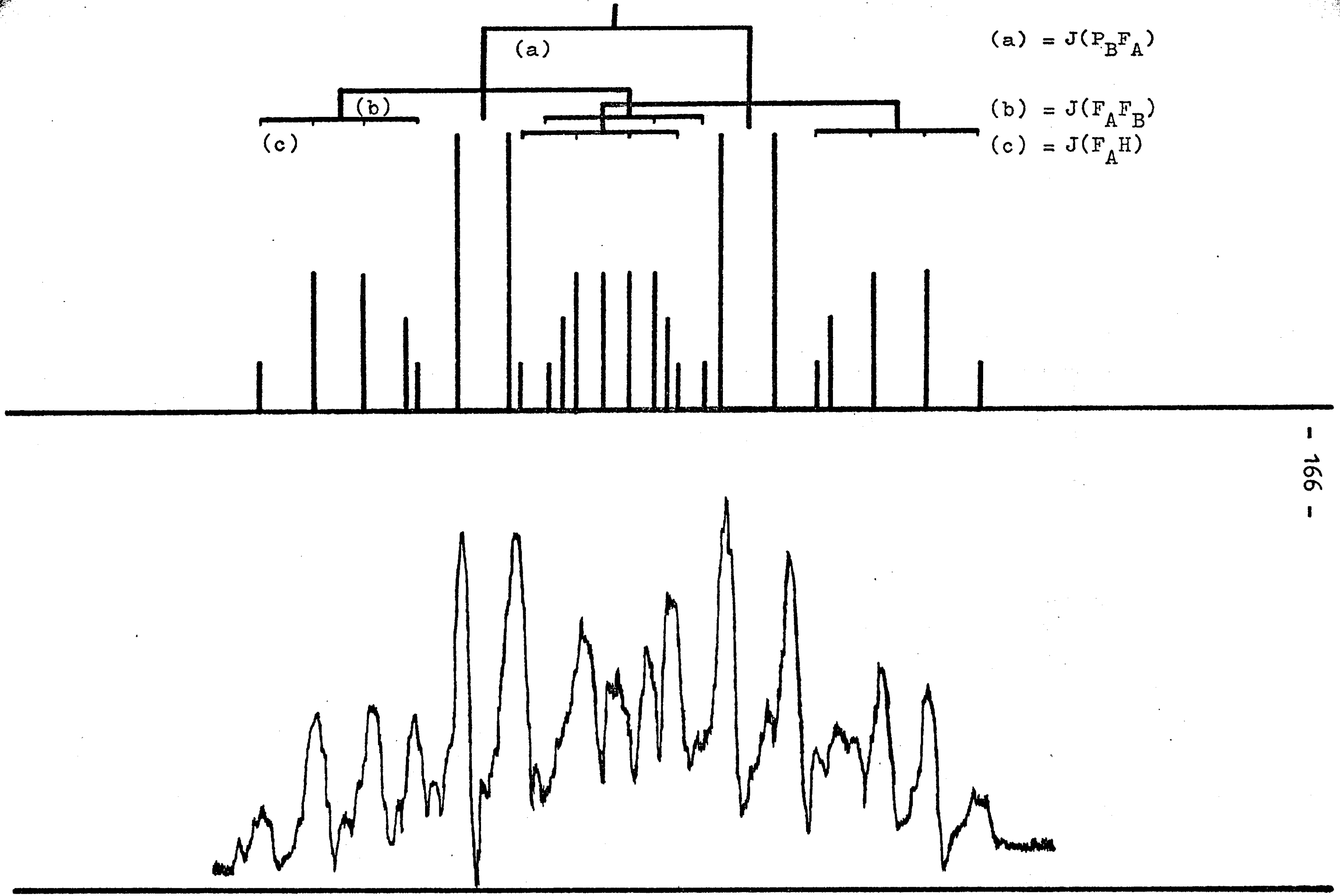
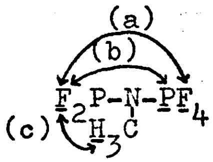


Fig. 2.2 One half of $P\underline{F}_2$ resonance in ^{19}F n.m.r. of $P\underline{F}_2NMePOF_2$ (theoretical & observed)

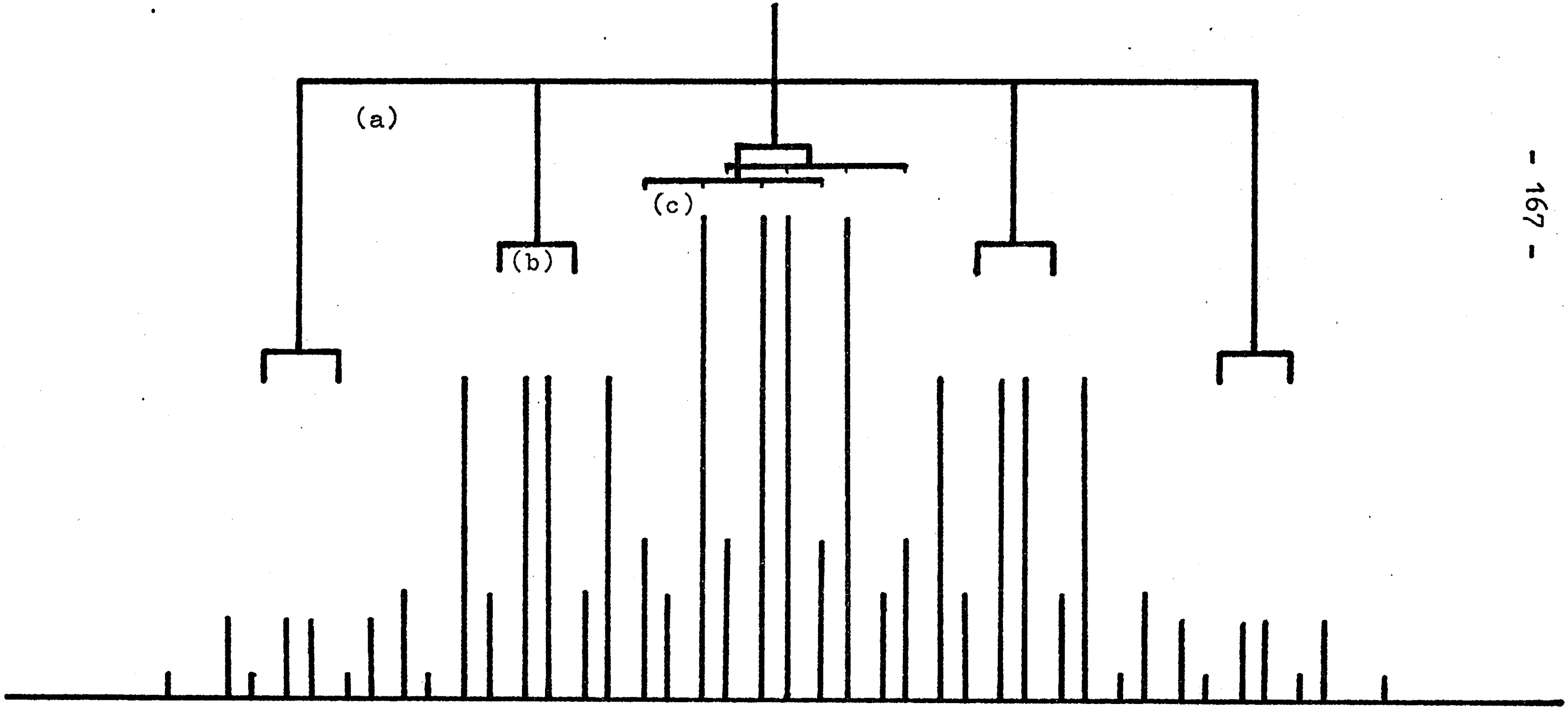


$\underline{F}_2P\text{-}N(\underline{H}_3C)\text{-}\underline{P}\underline{F}_4$

(a) = $J(F_AF_B)$

(b) = $J(P_BF_A)$

(c) = $J(F_BH)$



<u>Fig. 2.3</u> One half of $P\underline{F}_2$ resonance in ^{19}F n.m.r. of $P\underline{F}_2NMePF_4$ (theoretical)

Table 2.1

Compound[a]	δ_{F_A}	δ_{F_B}	δ_{P_A}	δ_{P_B}	$J(P_AP_B)$
PF_2NMePF_4**	70 dpdq	61 ddtq	-139	+46	<40
$PF_2NMePOF_2$**	71 ddtq	78 dt	-135	+12	83
PF_2NMePF_2	75[b,c]		-142[b]		433[c], 437[b]

Compound[a]	$J(P_AF_A)$	$J(P_BF_B)$	$J(P_BF_A)$	$J(P_AF_B)$	$J(F_AF_B)$
PF_2NMePF_4	1280[f]	896[f]	3.7[f]	87.0[f]	9.8
$PF_2NMePOF_2$	1272[f]	1039[f]	8.2[f]	<1[f]	4.5
PF_2NMePF_2	1264[b,c,d]		42.2[c], 47[b,d]		11.7, 1.7[b] 19.9, 3.0[c]

Compound[a]	$J(F_AH)$	$J(F_BH)$	δ_{Me}	$J(P_AH)$	$J(P_BH)$
PF_2NMePF_4	2.7[f]	2.0[f]	-2.9 dz	2.2	15.2
$PF_2NMePOF_2$	1.7[f,h]	0.5[h]	-2.9 ddtt	1.7	12.0
PF_2NMePF_2	1.6[b], 1.5[c]		-2.7[b]	2.0[b]	

[a] 'A' represents PF_2 and 'B' represents POF_2 or PF_4; A = B, for $(PF_2)_2NMe$.
[b] [190]. [c] [193]. [d] These values are of opposite sign [190]. [f] Obtained from ^{19}F n.m.r. spectrum. [h] Obtained from ^{1}H n.m.r. spectrum.

resonance for $PF_2NMePOF_2$ results from the very low values of $^3J(PF)$ and $^4J(FH)$ and the somewhat lower resolution usually obtainable for ^{19}F as compared to ^1H spectra (line width ≈ 1 c/s); the value of $^4J(FH)$ can be evaluated from the high resolution ^1H n.m.r. spectrum (see Fig. 2.4). Multiple line overlap for the methyl resonance in PF_2NMePF_4 leads to two sets of ill-resolved octets. The very poor resolution which can be achieved in the ^{31}P spectra (stationary tubes were used) ensures that only splitting of peaks arising from coupling constants having values greater than about 30 c/s can be detected. The values of δ_P depend on the co-ordination number of phosphorus, as reported in previous work [192], but changes in both δ_P and δ_F for the PF_2 group are minimal. However, the values of $^2J(PP)$ and $J(P_AF_B)$ change significantly for these compounds; changes in the signs of the coupling constants seem quite probable. The value of $^2J(PP)$ in $(PF_2)_2NR$ was reported both to be uncommonly large and to depend extensively on the nature of R [190]; the authors also reported that variations in $^2J(PP)$ were not well understood and were difficult to rationalize in terms of any one parameter. A later variable temperature n.m.r. study [193] showed that this parameter was the only one that was significantly temperature dependent.

Interesting correlations are obtained by studying variations in some of the n.m.r. parameters resulting from changing the nature of X in $PF_2NMe\text{-}X$ (X = PF_4, POF_2, PF_2, $SiMe_3$, Me, and H)

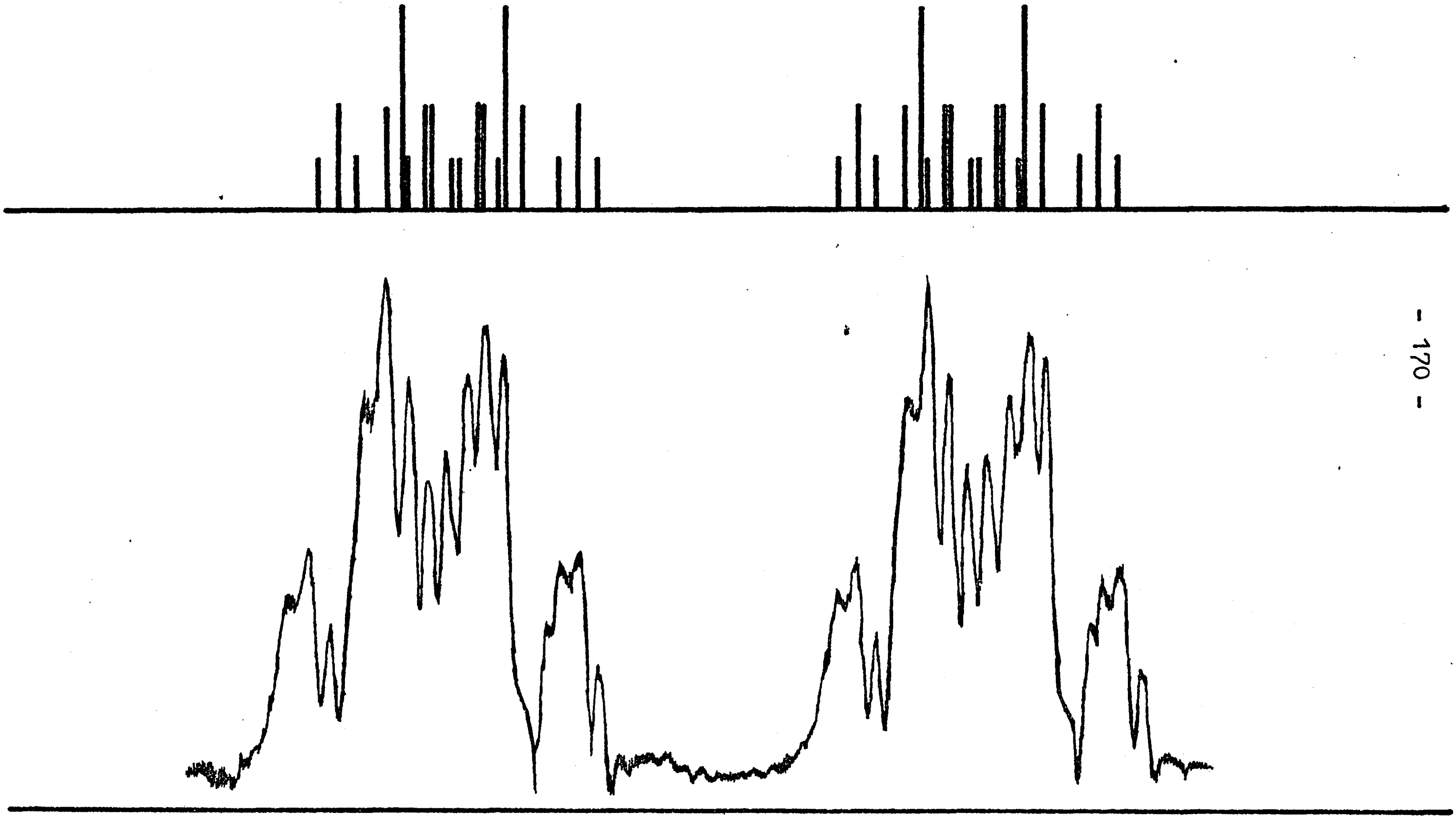


Fig. 2.4 Methyl resonance in ^{1}H n.m.r. of $\mathrm{PF_2N\underline{Me}POF_2}$ (theoretical and observed)

Table 2.2

Compound[a]	δ_H	$^3J(PH)$	δ_F	$^1J(PF)$	$^4J(HF)$	δ_P
$(POF_2)_2NMe$[b]	-3.3					
PF_2NMePF_4[b]	-2.9	~2.2	70	1280	2.7	-139
$PF_2NMePOF_2$[b]	-2.9	1.7	71	1272	1.7	-135
$(PF_2)_2NMe$[b]	-2.7	3.2	75	1264[c]	1.6	-142[c]
$Me_3SiNMePF_2$[b]	-2.6	5.8	69	1218	1.9	
Me_2NPF_2[b]	-2.6	9.0	65	1197	3.7	-145[d]
$MeNHPF_2$[b]	-2.6	10.4	71	1193	2.0	-141[e]
$(Me_3Si)_2NMe$[b]	-2.5					

[a] Values only for P(III). [b] This work. [c] From complete analysis [190]. [d] ^{31}P n.m.r. from [25]. [e] ^{31}P n.m.r. from [29].

(see Table 2.2). Attempts to interpret δ_H values in detail are fruitless because of the number of different effects which contribute to chemical shifts; however, when discussing homologous series of compounds, observed trends can often be interpreted on the basis of inductive effects [194]. The increasing magnitude of δ_H is roughly in line with what one observes experimentally to be the increasing electron-withdrawing power of X; increases in both the (p-d)π-bonding character of the P-N bond and the electron-withdrawing ability of the groups attached to the N-methyl group are expected to raise the magnitude of δ_H. While correlations between δ_H and J(PH) over a wide range of compounds are not generally applicable [195], there is found to be a fairly regular increase in the value of ^{3}J(PH) on going down the Table which parallels the decreasing value of ^{1}J(PF). The latter's dependence on electron-withdrawing effects follows the normal trends [194].

N.m.r. spectra of mixtures of $PF_2NMePOF_2$ and $MeNHPOF_2$.

In both its preparation and its cleavage reaction with HCl, $PF_2NMePOF_2$ is present with $MeNHPOF_2$. Despite the appreciably lower volatility of the latter compound this mixture is difficult to separate. The n.m.r. spectra of this mixture of compounds is revealing and will now be discussed:-

(i) ^{31}P n.m.r.

$\underline{P}F_2$ resonance - occurs as a doublet (P-P coupling) shifted down field to -171 p.p.m..

$\underline{P}OF_2$ resonance - for both $MeNHPOF_2$ and $PF_2NMePOF_2$ these are essentially unaltered (but the low resolution will only reveal large effects).

(ii) ^{19}F n.m.r.

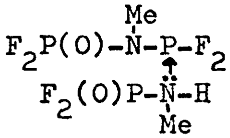
$P\underline{F}_2$ resonance - is not present.

$PO\underline{F}_2$ resonance - unshifted for both $PF_2NMePOF_2$ and $MeNHPOF_2$. That for $PF_2NMePOF_2$ shows short-range ^{1}J(PF) coupling and is further split into a doublet (J = 2.8 c/s). That for $MeNHPOF_2$ is of slightly lower resolution than is observed for the neat compound.

(iii) ^1H n.m.r.

The difference between the chemical shifts for the N-methyl resonance of $MeNHPOF_2$ and $PF_2NMePOF_2$ is slightly concentration dependent. In $PF_2NMePOF_2$, coupling of the methyl group with both phosphorus atoms is maintained but no coupling with the fluorine atoms of the fluorophosphino group is evident. In $MeNHPOF_2$, coupling is observed between the methyl group and both the phosphorus atom and the amino-proton; long-range coupling with fluorine is not well resolved. The amino-proton produces a broad peak at δ ≈ -5.0.

These results indicate that $PF_2NMePOF_2$ interacts with $MeNHPOF_2$ in such a manner that the fluorine atoms on the difluorophosphino group but not those on the difluorophosphoryl group are exchanging on the n.m.r. time scale. Since both P-F and P-N-H coupling are maintained in $MeNHPOF_2$, exchange cannot involve fission of any bonds in this compound. The most probable solution to this problem then is that a weak adduct is formed in which the fluorine atoms on the difluorophosphino group are capable of interacting with the amino-proton in such a manner that the P-F but not the N-H bonds are broken,



$$\begin{array}{l} F_2P(O)-\overset{\overset{Me}{|}}{N}-\underset{\uparrow}{P}-F_2 \\ \quad F_2(O)P-\underset{\underset{Me}{|}}{\overset{\cdot\cdot}{N}}-H \end{array}$$

The considerable shift of $\delta_{\underline{P}F_2}$ to lower field on forming a complex is in agreement with an increase of charge at the P(III) nucleus [196]. The coupling of 2.8 c/s obtained in the ^{19}F n.m.r. of $PF_2NMePO\underline{F}_2$ is presumably due to long-range coupling with the phosphorus atom in the PF_2 group, which is not observed in the n.m.r. of the neat liquid. The extent of this coupling is likely to be susceptible to a small change in the $P\hat{N}P$ bond angle.

The above effect is interesting since it indicates that the PF_2 centre in $PF_2NMePOF_2$ is more prone to form an adduct with this weak base than is the POF_2 centre. This suggests that adducts with stronger bases, such as trimethylamine, could be isolated. An infra-red study of solutions of this mixture in various solvents would merit investigation to determine the magnitude of changes in frequency which are associated with the NH and PF_2 modes in these compounds.

INFRA-RED SPECTRA OF $PF_2NMePOF_2$ AND PF_2NMePF_4 (Table 2.3).

Fig. 2.5 reproduces the i.r. spectra of $PF_2NMePOF_2$ and PF_2NMePF_4 together with those reported for $(PF_2)_2NMe$ [117] and $(POF_2)_2NMe$ [164]; the latter spectrum includes one printing error (the peak cited to be at 1185 $cm.^{-1}$ is in fact present at 1085 $cm.^{-1}$) and some assignments which are thought to be incorrect.

One feature of all four spectra is a noticeably lower intensity for the peaks due to the methyl stretching modes than has been observed for these modes in methylamino- and dimethylamino-derivatives of phosphorus-fluorides. The methyl bending modes

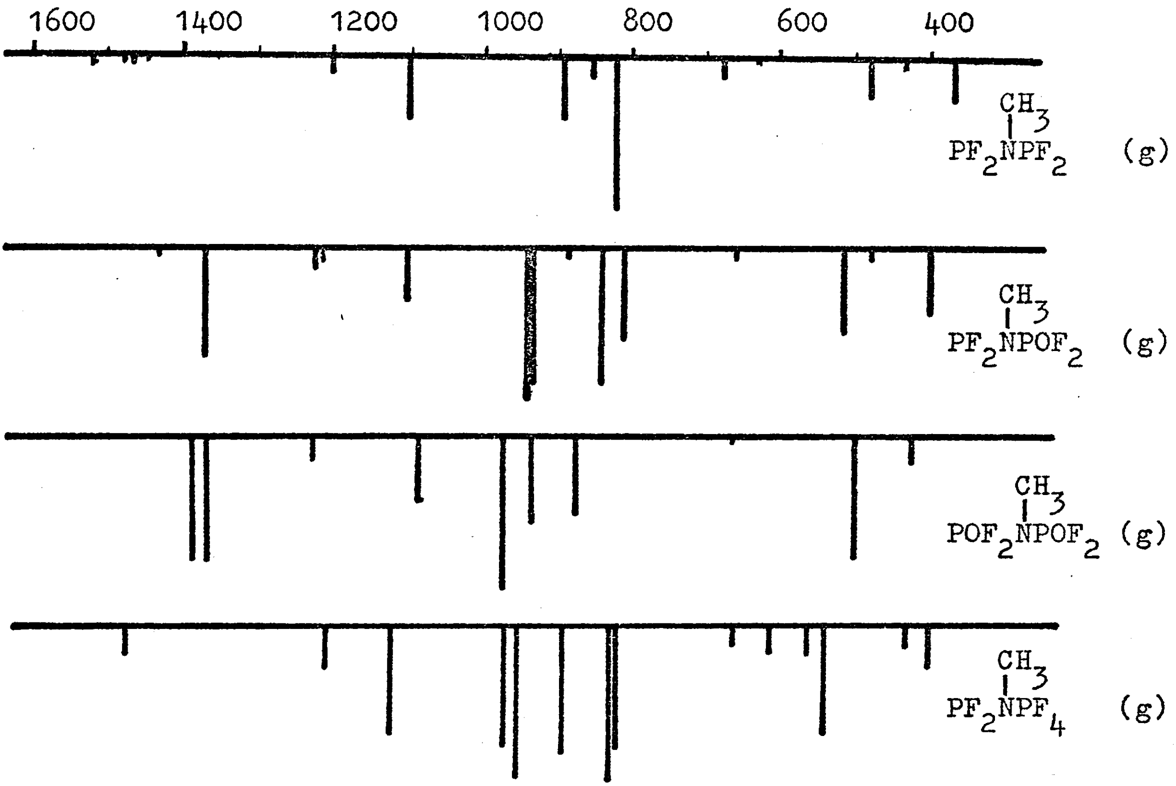


Fig. 2.5 I.r spectra of PF_2NMeX ($X = PF_2$, POF_2, PF_4) and $(POF_2)_2NMe$ 400-1600 cm.$^{-1}$.

also produce very weak peaks except in the spectrum of PF_2NMePF_4. Two other bands in these spectra can be associated with the N-methyl group; these are the bands at ~1100 cm.$^{-1}$ and a less intense band at ~1200 cm.$^{-1}$. The value of ν_{CN} decreases along the series $MeNHPF_4$ (1171 cm.$^{-1}$), $MeNHPOF_2$ (1130 cm.$^{-1}$) and $MeNHPF_2$ (1095 cm.$^{-1}$). The first peak is then assigned to the CN stretching mode while the second one is assigned to a methyl rocking mode. The CN stretching mode occurs at a slightly lower frequency in

$(PF_2)_2NCH_3$	$PF_2NCH_3POF_2$	$PF_2NCH_3PF_4$	$(POF_2)_2NCH_3$	Assignments
	2970 w 2910 vw 2842 vw	3035 vw 2988 w 2925 vw,sh 2862 vw		ν_{CH}
	1436	1477		δ_{CH}
	1370		1387 1368	$\nu_{P=O}$
1195	1226 1215 sh	1208	1229	ρ_{CH_3}
1100	1096 br	1121	1085	ν_{CN}
		973		$\nu_{as.PF_2(e)}$
	937		975 935 ? 877	$\nu_{PF_2(O)}$
890	927 sh	954	975 or 935	$\nu_{as.PNP}$
		888		$\nu_{sym.PF_2(e)}$ & $\nu_{as.\ PF_2(a)}$
	888 vw			Comb.
829 R 824 Q 819	840 R 837 Q 832 P 811	838 R 833 Q 828 P 817		ν_{PF_2}
677	664	663	663	$\nu_{sym.PNP}$
		613		$\nu_{sym.PF_2(a)}$
	517 R 514 Q 508 P 480 400	570 538 429 399		δ_{PNP} & δ_{PF}

Table 2.3 I.r spectra of PF_2NMeX (X = PF_2, POF_2, PF_4) and $(POF_2)_2NMe$.

dialkylamino-derivatives of phosphorus-fluorides (vide supra). The same modes presumably are responsible for peaks in these two regions in the i.r. spectra of $(PCl_2)_2NMe$ (1092, 1169 cm.$^{-1}$ [117]), $PCl_2NMePOCl_2$ (1073, 1186 cm.$^{-1}$ [167]), and $(POCl_2)_2NMe$ (1040, 1205 cm.$^{-1}$ [167]) as well as those of $Me_3SiNMePF_2$ (1085, 1195 cm.$^{-1}$) and $(Me_3Si)_2NMe$ (1065, 1186 cm.$^{-1}$ [197]). Charlton et al. have assigned the band at 1229 cm.$^{-1}$ in $(POF_2)_2NMe$ to ν_{CN} [165]; in view of the results reported here, their assignment is considered to be incorrect.

The stretching modes for the PF_2 group are clearly assigned to two bands in the spectra of PF_2NMeX ($X = PF_2$, POF_2, PF_4). In $(PF_2)_2NMe$ these bands overlap, but it is possible to distinguish the R and Q branches of the band at the higher frequency.

There is as yet insufficient data to give unambiguous assignments to stretching modes associated with the PNP skeleton. The values reported for $\nu_{as.PNP}$ diverge greatly, and values from 1085 cm.$^{-1}$ in $(POF_2)_2NMe$ [164] to 840 cm.$^{-1}$ have been quoted for this mode [120]. A recent study by Keat [167] has shown that this mode can be assigned to a strong band in the 828 - 912 cm.$^{-1}$ range for a variety of phosphorus-chlorides. The frequency decreased in the order:-

$(POCl_2)_2NMe$ (912 cm.$^{-1}$) $>$ $PCl_2NMePOCl_2$ (875 cm.$^{-1}$) $>$ $(PCl_2)_2NMe$ (828 cm.$^{-1}$)

These values lie close to those obtained for $(P(CF_3)_2)_2NMe$ (869 cm.$^{-1}$ [169]) and $(P(CF_3)Cl)_2NMe$ (853 cm.$^{-1}$ [119]). This mode is unambiguously assigned to the band at 890 cm.$^{-1}$ for $(PF_2)_2NMe$, which agrees with the original assignment [117]. A satisfactory assignment for the PF modes in the other molecules is obtained by assuming that the above order for the values of $\nu_{as.PNP}$ will hold for the corresponding fluorinated compounds. In $PF_2NMePOF_2$ there are two bands in the region above 900 cm.$^{-1}$ which can be assigned to this mode; these are at 927 and 937 cm.$^{-1}$. If the former band is assigned to this mode, then the latter band can be assigned to the PF_2 stretching modes of the difluorophosphoryl group. This then ensures that the latter modes occur at frequencies at least as high as those reported for the corresponding modes in $MeNHPOF_2$ (vide infra). An increase in frequency is also observed for the PF_2 stretching modes on substituting a difluorophosphino group for the amino-proton in $MeNHPF_2$.

The band at 888 cm.$^{-1}$ in PF_2NMePF_4 is regarded as arising from the same two modes, $\nu_{sym.PF_2(e)}$ and $\nu_{as.PF_2(a)}$, as were considered to contribute to the band at 867 cm.$^{-1}$ in the spectrum of $MeNHPF_4$. The band at 973 cm.$^{-1}$ is then assigned to the asymmetric PF_2(e) stretching mode (cf. 958 cm.$^{-1}$ for $MeNHPF_4$) which leaves the band at 954 cm.$^{-1}$ to be assigned to $\nu_{as.PNP}$. As these three modes all increase in value on replacing the amino-proton in $MeNHPF_4$ by a difluorophosphino group, the band at 613 cm.$^{-1}$ in PF_2NMePF_4 is assigned to $\nu_{sym.PF_2(a)}$. The symmetric PNP stretching mode, which also lies in this region, is much less affected by changes in the nature of the substituents on the phosphorus atom.

No attempt has been made to assign the PF deformation modes which lie in the 400 - 600 cm.$^{-1}$ region. Assignments for $PF_2NMePOF_2$ and PF_2NMePF_4 with some relevant assignments for $(PF_2)_2NMe$ [117] and re-assignments for $(POF_2)_2NMe$ are given in Table 2.3.

MASS SPECTRA OF $PF_2NMePOF_2$ AND $(PF_2)_2NMe$ (Tables 2.4 - 2.6).

The mass spectra of $(PF_2)_2NMe$, which has not been reported previously, and $PF_2NMePOF_2$ are reproduced in Fig. 2.6. The mass spectrum of PF_2NMePF_4 is mainly that of its volatile hydrolysis products, PF_3, POF_3 and $PF_2NMePOF_2$ (vide infra). The mass spectrum of $(POF_2)_2NMe$ has been published [164].

While $(PF_2)_2NMe$ shows a strong molecular ion and a weak peak corresponding to $[M-H]^+$, the intensities of these two ions in the mass spectrum of $PF_2NMePOF_2$ are reversed. For $\overset{O}{\overset{\|}{P}}F_2NMePOF_2$, the molecular ion was reported to be extremely weak but that due to $[M-H]^+$ much more intense. These two ions are of comparable importance for Me_2NPF_2 and Me_2NPOF_2 [144]. It has previously been noted that rearrangements and fission of bonds away from the charge bearing atom are more likely to be observed where no low energy fragmentation modes are available. A metastable ion and a large peak at m/e = 152 do indeed show that $[(PF_2)_2NMe]^+$

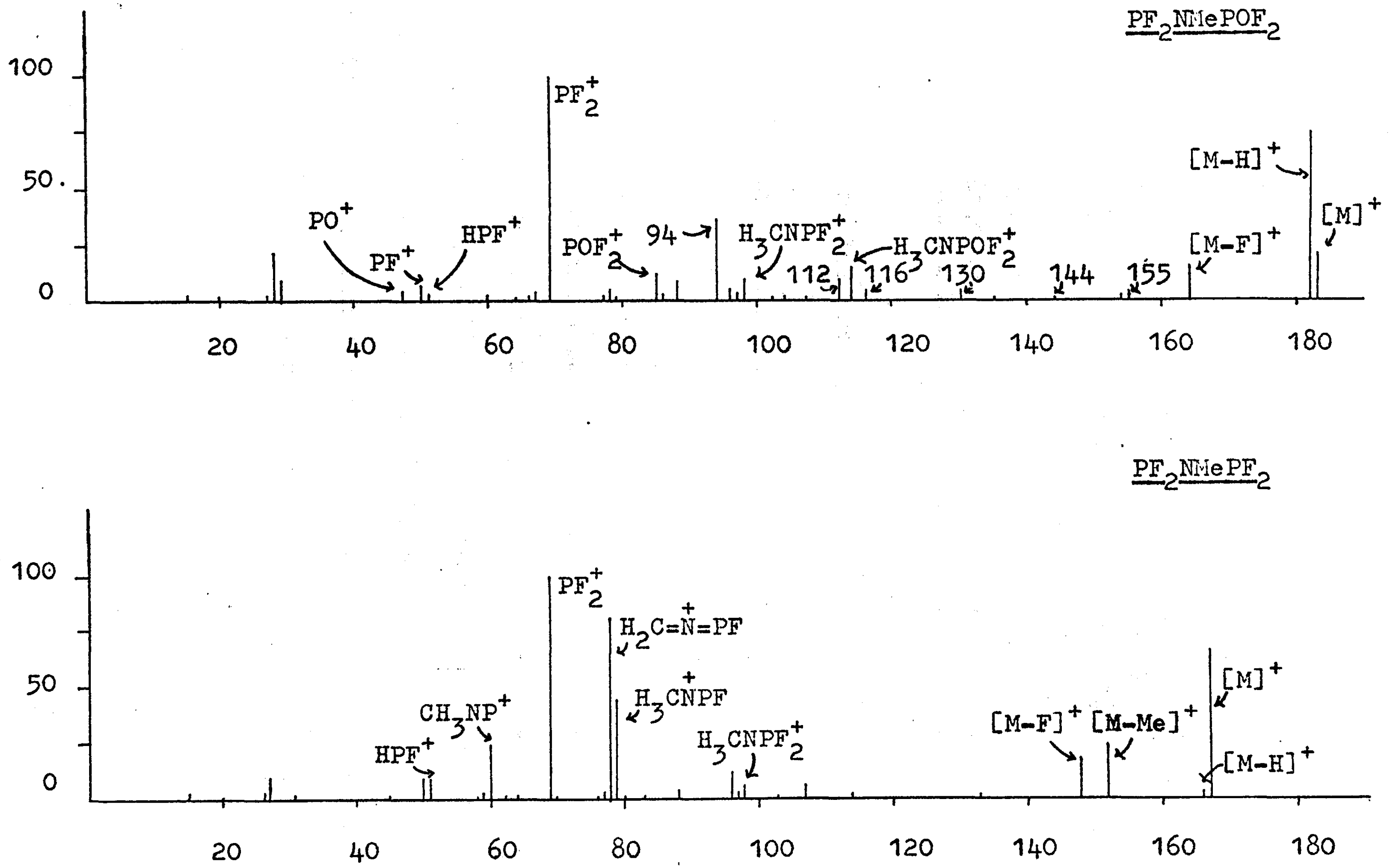
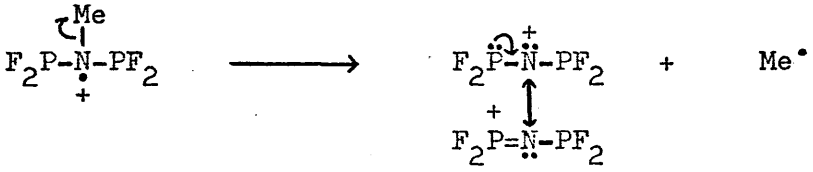


Fig. 2.6 Mass spectra of $(PF_2)_2NMe$ and $PF_2NMePOF_2$.

Table 2.4 Mass measurements of ions obtained from $PF_2NMePOF_2$.

Mass found	Mass calc.	Ion
168.9471	168.9470	$HNP_2OF_4^+$
154.9438	154.9439	$HP_2OF_4^+$
134.9371	134.9376	$P_2OF_3^+$
115.9875	115.9877	$CH_2NPF_3^+$
113.9925	113.9920	$CH_3NPOF_2^+$
93.9858	93.9858	CH_2NPOF^+
61.9473	61.9475	P_2^+

readily loses a methyl group,



while the corresponding process is not observed for those bridged compounds which contain a phosphoryl group. The large peak due to $(PF_2)_2N^{+\bullet}$ is surprising in view of the observed reluctance for dimethylamino- [144-5] as well as methylamino-derivatives of phosphorus to lose a methyl group. It seems that the possibility of stabilizing this ion through partial localization of the positive charge on two phosphorus atoms leads to this anomaly; this is in agreement with the n.m.r. results, that have already been presented,which indicate that a positive charge is more likely to be accommodated on a difluorophosphino group than on a difluorophosphoryl group.

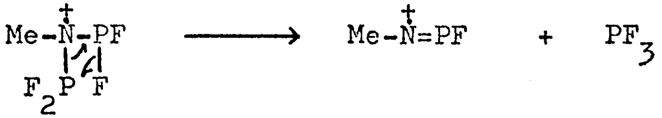
A metastable ion shows that $[(PF_2)_2NMe]^+$ can fragment through

Table 2.5 Metastable transitions obtained for PF_2NMeX ($X = PF_2$, POF_2).

m_1	Transition	m_2	m^* calc.	m^* found
	$PF_2NMePOF_2$			
183	$CH_3NP_2OF_4^+ \longrightarrow CH_2NP_2OF_4^+ + H$	182	181.0	181.0
182	$CH_2NP_2OF_4^+ \longrightarrow HP_2OF_4^{+\ \Delta} + HCN$	155	131.3	131.2
164	$CH_3NP_2OF_3^+ \longrightarrow CH_2NP_2OF_2^+ + HF$	144	126.4	126.5
164	$CH_3NP_2OF_3^+ \longrightarrow NP_2OF_2^+ + CH_3F$	130	103.1	103.0
164	$CH_3NP_2OF_3^+ \longrightarrow CHNPOF_2^+ + H_2PF$	112	76.5	76.5
182	$CH_2NP_2OF_4^+ \longrightarrow CH_2NPF_3^{+\ \Delta} + POF$	116	73.9	74.0
183	$CH_3NP_2OF_4^+ \longrightarrow CH_3NPOF_2^{+\ \Delta} + PF_2$	114	71.0	71.0
183	$CH_3NP_2OF_4^+ \longrightarrow CH_3NPF_2^+ + POF_2$	98	52.5	52.5
182	$CH_2NP_2OF_4^+ \longrightarrow CH_2NPOF^{+\ \Delta} + PF_3$	94	48.6	48.6
182	$CH_2NP_2OF_4^+ \longrightarrow PF_2^+ + CH_2NPOF_2$	69	26.2	26.2
	PF_2NMePF_2			
167	$CH_3NP_2F_4^+ \longrightarrow NP_2F_4^+ + CH_3$	152	138.3	138.3
167	$CH_3NP_2F_4^+ \longrightarrow CH_3NPF^+ + PF_3$	79	37.4	37.4
148	$CH_3NP_2F_3^+ \longrightarrow CH_3NP^+ + PF_3$	60	24.4	24.4

$^{\Delta}$ Confirmed by mass measurement (Table 2.4).

elimination of a molecule of PF_3,



The ion $(P_2F_3NMe)^+$, which is produced from $(PF_2)_2NMe$, is also shown, by the presence of a metastable ion, to be capable of

Table 2.6 Mass spectra of PF_2NMeX (X = PF_2, POF_2) (m/e value, relative abundance, ion - respectively).

$(PF_2)_2NMe$:

168, 1, $^{13}CH_3NP_2F_4^+$; 167, 65, $CH_3NP_2F_4^+$; 166, 4, $CH_2NP_2F_4^+$; 152, 24, $NP_2F_4^+$; 148, 17, $CH_3NP_2F_3^+$; 133, 2, $NP_2F_3^+$; 114, 1, $NP_2F_2^+$; 107, 7, PF_4^+; 98, 7, $CH_3NPF_2^+$; 97, 3, $CH_2NPF_2^+$; 96, 11, $CHNPF_2^+$; 88, 3, PF_3^+; 83, 1, NPF_2^+; 79, 45, CH_3NPF^+; 78, 81, CH_2NPF^+; 77, 2, $CHNPF^+$; 69, 100, PF_2^+; 62, 1, P_2^+; 60, 23, CH_3NP^+; 59, 3, CH_2NP^+; 58, 1, $CHNP^+$; 51, 13, HPF^+; 50, 14, PF^+; 45, 1, NP^+; 31, 2, P^+; 28, 15, CH_2N^+; 27, 5, CHN^+; 20, 1, HF^+; 15, 3, CH_3^+.

$PF_2NMePOF_2$:

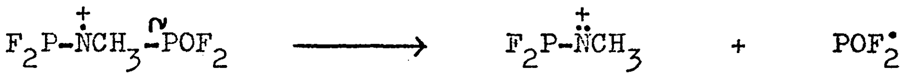
183, 21, $CH_3NP_2OF_4^+$; 182, 74, $CH_2NP_2OF_4^+$; 169, tr, $HNP_2OF_4^{+\Delta}$; 168, tr, $NP_2OF_4^+$; 166, tr, $CH_2NP_2F_4^+$; 164, 14, $CH_3NP_2OF_3^+$; 155, 3, $HP_2OF_4^{+\Delta}$; 154, 2, $P_2OF_4^+$; 135, 1, $P_2OF_3^{+\Delta}$; 130, 4, $NP_2OF_2^+$; 116, 4, $CH_2NPF_3^{+\Delta}$; 114, 15, $CH_3NPOF_2^{+\Delta}$; 112, 10, $CHNPOF_2^+$; 107, 1, PF_4^+; 104, 1, POF_3^+; 102, 1, NPF_3^+; 98, 9, $CH_3NPF_2^+$; 97, 3, $CH_2NPF_2^+$; 96, 4, $CHNPF_2^+$; 94, 35, $CH_2NPOF^{+\Delta}$; 88, 8, PF_3^+; 86, 2, $HPOF_2^+$; 85, 11, POF_2^+; 79, 1, CH_3NPF^+; 78, 4, CH_2NPF^+; 77, 2, $CHNPF^+$; 69, 100, PF_2^+; 67, 3, $HPOF^+$; 66, 2, POF^+; 62, tr, $P_2^{+\Delta}$; 64, 1, NPF^+; 60, 1, CH_3NP^+; 51, 3, HPF^+; 50, 6, PF^+; 47, 4, PO^+; 31, tr, P^+; 29, 9, CH_3N^+; 28, 21, CH_2N^+; 27, 1, CHN^+; 20, 2, HF^+; 15, 3, CH_3^+.

$^{\Delta}$Confirmed by mass measurement (Table 2.4).

---

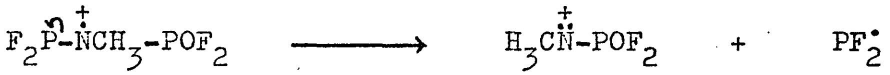
eliminating a molecule of PF_3.

There are four possible modes by which $(PF_2NMePOF_2)^+$ can fragment through simple P-N bond cleavage; the two which involve no shift of charge from the nitrogen atom are detected by metastable ions. The charge can be carried by the P(III) portion,



$$F_2P\text{-}\overset{+}{\dot{N}}CH_3\text{-}POF_2 \longrightarrow F_2P\text{-}\overset{+}{\ddot{N}}CH_3 + POF_2^{\bullet}$$

or by the P(V) portion,



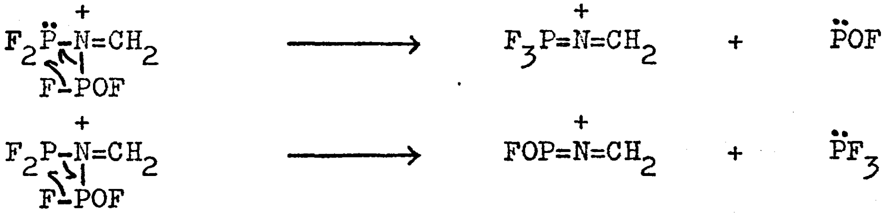
$$F_2P\text{-}\overset{+}{\dot{N}}CH_3\text{-}POF_2 \longrightarrow H_3C\overset{+}{\ddot{N}}\text{-}POF_2 + PF_2^{\bullet}$$

The other two fragmentation modes, which require a shift of charge onto either of the phosphorus atoms to produce POF_2^+ or PF_2^+, are not detected by metastable ions.

Metastable ions indicate that the $[M\text{-}H]^+$ ion for $PF_2NMePOF_2$ could decompose through straight P-N bond cleavage with charge transfer to the phosphorus atom,

$$F_2\ddot{P}\text{-}\underset{CH_2}{\overset{+}{N}}\text{-}POF_2 \longrightarrow F_2\overset{+}{\ddot{P}} + \underset{CH_2}{\ddot{N}}\text{-}POF_2$$

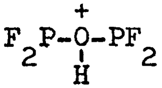
or through fluorine atom migration with charge retention on the nitrogen atom,



$$F_2\ddot{P}\text{-}\underset{F\text{-}POF}{\overset{+}{N}}=CH_2 \longrightarrow F_3P=\overset{+}{N}=CH_2 + \ddot{P}OF$$

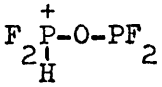
$$F_2P\text{-}\underset{F\text{-}POF}{\overset{+}{N}}=CH_2 \longrightarrow FOP=\overset{+}{N}=CH_2 + \ddot{P}F_3$$

The ion formed in the last rearrangement also figures prominently in the mass spectrum of $MeNHPOF_2$ (vide infra). The $[M\text{-}H]^+$ ion can also eliminate a molecule of HCN. This is similar to the reported elimination of CH_2N from $[(POF_2)_2NMe]^+$ [164]. Three possible structures are suggested for the $HP_2OF_4^+$ ion which is produced,



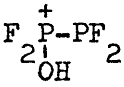
$$F_2P\text{-}\underset{H}{\overset{+}{O}}\text{-}PF_2$$

(I)



$$F_2\underset{H}{\overset{+}{P}}\text{-}O\text{-}PF_2$$

(II)

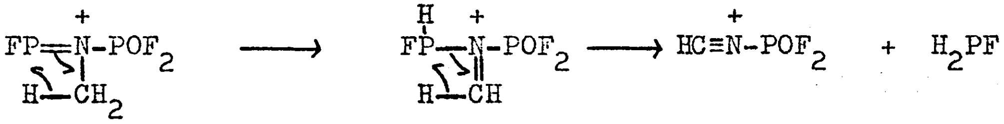


$$F_2\underset{OH}{\overset{+}{P}}\text{-}PF_2$$

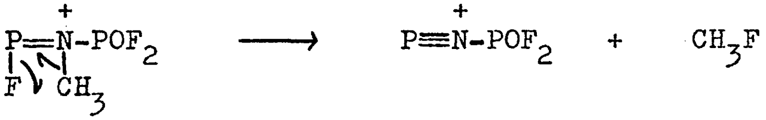
(III)

Structure III might appear to be unstable on the basis of the non-formation of $F_2P-P(O)F_2$, which rearranges to $F_2P-O-P(O)F_2$ [165], but a mass measurement of the ion with m/e = 62 shows that $(P-P)^+$ is present in the spectrum. However, other more important fragments containing the P_2O group without an associated hydrogen atom are also present, which favour structures I and II. Small quantities of rearrangement products are detected in the mass spectra of both $(PF_2)_2NMe$ and $PF_2NMePOF_2$.

Fairly large peaks corresponding to the loss of one, but not two, fluorine atoms from $[(PYF_2)_2NMe]^+$ (Y = O, lone pair) are observed. It is possible to lose a fluorine atom from either phosphorus atom in $(PF_2NMePOF_2)^+$; three modes of decomposition for the ion so formed are indicated by metastable ions. That which involves loss of H_2PF (a molecule which has not yet been isolated) suggests that the ion predominantly exists as $(PFNMePOF_2)^+$,



Loss of methyl fluoride is also observed:-



Loss of HF, which can proceed by cleavage of a P-F bond belonging to either a PF_2 or a POF_2 group, is shown not to be particularly favoured since there is only a small peak at m/e = 144. It should be noted that HF elimination is usually assumed to implicate the cleavage of an N-H rather than a C-H bond in the mass spectra of methylamino-derivatives of phosphorus-fluorides.

THE ATTEMPTED PREPARATION OF $PF_2NMeSOF$.

Reaction between methylaminodifluorophosphine and thionyl fluoride or sulphur dioxide.

Previous work has indicated [198] that thionyl fluoride will react with a secondary amine to form N,N-dialkylfluorosulphinamide, R_2NSOF:-

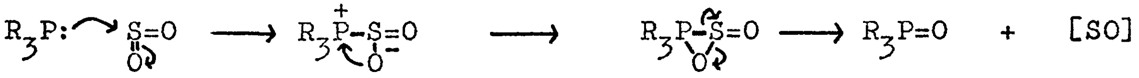
$$SOF_2 \quad + \quad 2 \quad R_2NH \longrightarrow R_2NSOF \quad + \quad R_2NH_2^+ \; F^-$$

It was anticipated that SOF_2 would react with $MeNHPF_2$ to produce $PF_2NMeSOF$ by an analogous route. However, the volatile products are identified as a mixture of methylaminothiophosphoryl difluoride, $MeNHPSF_2$, and thionylmethylamine, MeNSO, which is contaminated by small quantities of methylaminophosphoryl difluoride, $MeNHPOF_2$, phosphorus trifluoride and sulphur dioxide. The low volatility of $MeNHPOF_2$ compared to $MeNHPSF_2$ parallels the difference in the boiling points observed for $RPOF_2$ and $RPSF_2$; this difference was attributed to a larger degree of association in the phosphoryl derivatives [199].

In order to determine if the reaction proceeds through the interaction of $MeNHPF_2$ with the SO_2 which has been formed by the hydrolysis of SOF_2, these two compounds were reacted together. The volatile products do indeed contain MeNSO and $MeNHPSF_2$, but accompanied by an increased yield of PF_3 and $MeNHPOF_2$. It thus appears that both SO_2 and SOF_2 are capable of oxidising $MeNHPF_2$

to the P(V) state.

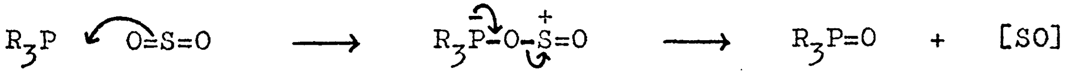
Previous work has shown that mixtures of SO_2 and PF_3 are stable at room temperature, but that oxidation to POF_3 proceeds at 450°[200]. It has also been reported that P(III) compounds react with SO_2 to form the appropriate thio-derivatives [201-2]. Also noteworthy is the use of potassium fluorosulphinate, KSO_2F, to both fluorinate and oxidize chlorophosphines [199]. Since the ease of attack by SO_2 parallels the inductive effects of the ligands attached to phosphorus, it was originally proposed that the initial step involved nucleophilic attack by the phosphorus atom on SO_2 with subsequent nucleophilic attack by the oxygen atom on the phosphonium ion so produced [201]:-



$$R_3P: \; \underset{O}{\underset{\|}{S}}=O \longrightarrow R_3\overset{+}{P}-\underset{O^-}{\underset{|}{S}}=O \longrightarrow R_3P-\underset{O}{S}=O \longrightarrow R_3P=O + [SO]$$

$$[SO] \longrightarrow \tfrac{1}{2}\,S + \tfrac{1}{2}\,SO_2$$

However, sulphur dioxide is also capable of converting thiophosphoryl to phosphoryl-derivatives. The method put forward to explain this reaction, in which the oxygen atom on SO_2 acts as a nucleophile towards phosphorus, can also be applied to reactions in which P(III) is oxidized to P(V) [202]:-

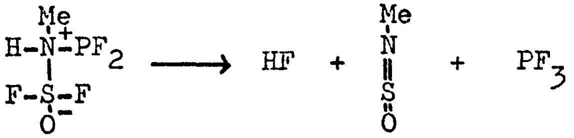


$$R_3P \; O=S=O \longrightarrow R_3\overset{-}{P}-O-\overset{+}{S}=O \longrightarrow R_3P=O + [SO]$$

The thio-derivatives are then formed by direct attack of the sulphur so produced on the P(III) compounds [202].

The electron-withdrawing substituents attached to phosphorus would tend to favour a reaction proceeding by the second of these alternative mechanisms in compounds containing P-F bonds. While it seems unlikely that the thio-derivative is formed through oxidation of P(III) by sulphur, since high temperatures were required to convert Me_2NPF_2 to Me_2NPSF_2 by this route [203], a lower reaction temperature would probably be required for "nascent" sulphur. This step could also be initiated through direct attack of [SO] on the phosphorus atom. Both an investigation into the factors which affect the yields of the various products and further experiments, to determine whether SO_2 will react with either $MeNHPSF_2$ or $MeNHPOF_2$, are required before further comment can be made on the veracity of this reaction mechanism. The same precautions hold about specifying a particular mechanism for the reaction of SOF_2 with $MeNHPF_2$; $[SF_2]$ rather than [SO] may be formed here. The low yield of $MeNHPOF_2$ obtained is a noted feature of this reaction.

Phosphorus trifluoride and MeNSO figure as by-products in the reaction of $MeNHPF_2$ with both SOF_2 and SO_2. Their appearance can be rationalized by assuming that the nitrogen atom constitutes a third potential nucleophile in this system. In the reaction of $MeNHPF_2$ with SOF_2, the intermediate compound can eliminate both HF and PF_3:-



$$\begin{array}{c} Me \\ H\text{-}\overset{+}{N}\text{-}PF_2 \\ | \\ F\text{-}S\text{-}F \\ O^{-} \end{array} \longrightarrow HF + \begin{array}{c} Me \\ N \\ \| \\ S \\ O \end{array} + PF_3$$

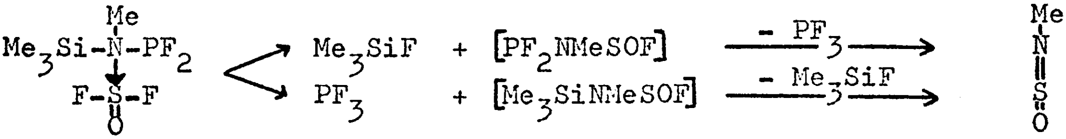
It appears that, under the conditions employed, $PF_2NMeSOF$ is unstable with respect to elimination of PF_3. The possibility that the MeNSO also plays a role in the oxidation of P(III) cannot be overlooked.

Reaction between difluorophosphino(trimethylsilyl)methylamine and thionyl fluoride.

An alternative method used for the formation of S-N bonds exploits the easy cleavage of Si-N bonds by S-F bonds [133]:-

$$SOF_2 + Me_3SiNMe_2 \longrightarrow Me_2NSOF + Me_3SiF$$

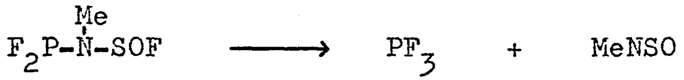
Difluorophosphino(trimethylsilyl)methylamine and thionyl fluoride react only slowly at 100°. The volatile material recovered contains, in addition to excess starting material, a mixture of PF_3 , Me_3SiF, MeNSO and a trace of $PF_2NMePOF_2$. The high temperature used in this reaction is in agreement with the low Lewis acidity of SOF_2. The reaction products can be rationalized by assuming that the intermediate can break down via two possible routes:-



Attempts to prepare $Me_3SiNMeSOF$ fron the reaction between SOF_2 and $(Me_3Si)_2NMe$ only yielded MeNSO [204], so both pathways seem to be equally favoured.

The small amount of $PF_2NMePOF_2$ which is identified could have come from several sources. One route to this compound would involve oxidation of $Me_3SiNMePF_2$ to $Me_3SiNMePOF_2$ by SOF_2, with the compound so formed subsequently attacking a molecule of PF_3 and eliminating a molecule of Me_3SiF.

An alternative synthesis of $PF_2NMeSOF$, involving (a) a low temperature reaction between $Me_3SiNMePCl_2$ and $SOCl_2$ and (b) fluorination of the $PCl_2NMeSOCl$ so produced, could be attempted to determine whether the above instability observed for this compound is inherent or simply a function of the reaction conditions employed in its attempted synthesis. The stability of $PF_2NMeSOF$ with respect to PF_3 elimination is likely to be low because of the large difference between the energy of a P-F and a S-F bond,



$$F_2P\text{-}\overset{Me}{N}\text{-}SOF \longrightarrow PF_3 + MeNSO$$

A similar instability has been reported for the related compound $POF_2\text{-}N{=}SF_2$ [71]:-

$$F_2(O)P\text{-}N{=}SF_2 \longrightarrow POF_3 + N{\equiv}SF$$

Owing to the smaller difference between the energy of a P-Cl and a S-Cl bond, compounds containing chlorine rather than fluorine attached to the phosphorus atom are likely to be stable.

PROPERTIES OF METHYLAMINOPHOSPHORYL DIFLUORIDE AND METHYLAMINOTHIOPHOSPHORYL DIFLUORIDE.

The existence of alkylaminothiophosphoryl and alkylaminophosphoryl difluorides has been established for some time [1]. Both $MeNHPOF_2$ and $MeNHPSF_2$ have been prepared in good yield by fluorination of the corresponding chlorides, by using a slurry of NaF in sulpholane [205]. However, their n.m.r., i.r. and mass spectra have not previously been published and are, therefore, presented here.

N.M.R. SPECTRA OF $MeNHPOF_2$ AND $MeNHPSF_2$.

The n.m.r. parameters for $MeNHPOF_2$ and $MeNHPSF_2$, given in Table 2.7, closely resemble those of Me_2NPOF_2 [206] and Me_2NPSF_2 [207] respectively.

I.R. SPECTRA OF $MeNHPOF_2$ AND $MeNHPSF_2$ (Table 2.8).

The assignments of the bands in the spectrum of $MeNHPSF_2$ are made predominantly on the basis of the complete i.r. analysis reported by Nyquist et al. for $MeNHPSCl_2$ [124]. The shape of the band due to ν_{NH} resembles that which has previously been ascribed to the existence of more than one rotational isomer (see Chapter 1 and [122]). Although there was only one band observed for ν_{NH} in a dilute solution of $MeNHPSCl_2$ there were

Table 2.7

Compound	δ_F^{**}	δ_P^{*}	$\delta_{CH_3}^{**}$	δ_{NH}^{**}
CH_3NHPOF_2	79	+3	-2.7 ddt	-5.3 br
CH_3NHPSF_2	52	-67	-2.8 ddt	-4.5 br

Compound	$J(PCH_3)$	J(HH)	$J(H_3CF)$	J(HNF)
CH_3NHPOF_2	13.9	5.6	0.9	3.3
CH_3NHPSF_2	14.4	5.8	1.3	3.0

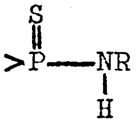
MeNHPOF$_2$		Assignments
gas	liquid	
3478 vw		ν_{NH}
3261 s	3270 s,br	
2959 mw	2958 mw	ν_{CH}
2918 w	2915 w	
2846 mw	2845 mw	
	1485 mw;sh	δ_{CH_3}
1453 m	1445 m,sh	
1436 m	1430 m	δ_{NH}
1325 vs	1314 vs	$\nu_{P=O}$
1146 m		ρ_{CH_3}
1130 m,sh	1122 s,br	$\nu_{as.PNC}$
1075 vw		?
935 s	934 vs	$\nu_{as.PF_2}$
915 vs	900 vs	$\nu_{sym.PF_2}$
		$\nu_{sym.PNC}$
	821 w	?
802 vw	805 w	
534 w	525 w	τ_{NH}
459 m	463 m	δ_{PF_2}

MeNHPSF$_2$	Assignments
gas	
3479 m	ν_{NH}
3443 m,sh	
2960 w	ν_{CH}
2920 w	
2844 vw,sh	
1390 m	δ_{NH}
1112 s	$\nu_{as.PNC}$
922 vs	$\nu_{as.PF_2}$
878 vs	$\nu_{sym.PF_2}$
	$\nu_{sym.PNC}$
699 m	$\nu_{P=S}$
652 vw	
462 w	w_{PF_2}
414 m	δ_{PF_2}

<u>Table 2.8</u> (All frequencies in cm.$^{-1}$) I.r. spectra of MeNHPYF$_2$ (Y = S, O).

two bands, a strong one at 734 cm.$^{-1}$ and a weak one at 694 cm.$^{-1}$, which were assigned to $\nu_{P=S}$ for the two different isomers. The two bands at 699 cm.$^{-1}$ (m) and 652 cm.$^{-1}$ (vw) are, therefore, similarly assigned. Previous work would tend to suggest that the isomer in which the P=S and N-H bonds are cis to each other, I, produces the peak at higher frequency for the ν_{NH} mode; in the other isomer, II, these two groups are trans to each other [122]:-

$>\overset{\overset{S}{\|}}{P}-\overset{\overset{H}{|}}{N}R$ (I)



$>\overset{\overset{S}{\|}}{P}-\underset{\underset{H}{|}}{N}R$ (II)

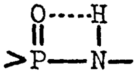
Splitting of other bands was not observed [124].

In $MeNHPSCl_2$, two strong bands are assigned to the asymmetric and symmetric PNC stretching modes, more usually referred to as ν_{CN} and ν_{PN} respectively, at 1099 and 839 $cm.^{-1}$. A band due to the former mode is observed at 1112 $cm.^{-1}$ in $MeNHPSF_2$, while there are two bands present in the region where the latter mode is expected to be present. The i.r. spectrum of Me_2NPSF_2 showed three intense bands in this region; those at 902 and 850 $cm.^{-1}$ were unanimously assigned to the two PF_2 stretching modes [207-8], while that at 782 $cm.^{-1}$ was either assigned to ν_{PN} [208] or $\nu_{P=S}$ [207]. In view of the lower assignment for $\nu_{P=S}$ made here, the former alternative seems to be the correct one; a band at 625 $cm.^{-1}$ was assigned to $\nu_{P=S}$ in this work [208]. It looks as though the two bands at 922 and 878 $cm.^{-1}$ in $MeNHPSF_2$ are best assigned to the two PF_2 stretching modes, although one of these bands is probably also associated with $\nu_{sym.PNC}$.

The i.r. spectrum for NH_2PSF_2 has been reported to show one band at 875 $cm.^{-1}$, assigned to ν_{PF_2}, and another at 1000 $cm.^{-1}$, assigned to ν_{PN} [209] while that for $Me_3SiNHPSF_2$ showed two peaks at 902 and 859 $cm.^{-1}$, which were assigned to the two PF_2 stretching modes, and one at 1016 $cm.^{-1}$, assigned to the asymmetric SiNP stretching mode ("ν_{PN}") [157]. On the basis of a Raman and i.r. study, the symmetric and asymmetric PF_2 stretching modes in PSF_2Cl were assigned to bands at 939 and 913 cm.$^{-1}$ respectively [210]. The symmetric mode was also assigned to a peak (940 cm.$^{-1}$) occurring at a higher frequency than the asymmetric mode (913 cm.$^{-1}$) in $MeOPSF_2$ on the basis of cursory depolarization studies; these bands were not significantly shifted in the deuterated analogue [211]. Since this is the opposite order to that generally accepted for symmetric and asymmetric stretching modes an unambiguous assignment cannot be made for these modes in $MeNHPSF_2$.

The two bands at 462 and 414 cm.$^{-1}$ are assigned to the PF_2 wagging and deformation modes respectively, since almost identical values were reported for these modes in $MeOPSF_2$ [211].

The intense narrow band at 3261 cm.$^{-1}$ in the gas phase spectrum of $MeNHPOF_2$ is attributed to ν_{NH}, which is a considerably lower value for this mode than has been given for other MeNHP(F) compounds studied. Nyquist has compared the value of ν_{NH} for $MeNHPOCl_2$ with that observed for $MeNHPSCl_2$ [122] and proposed that intramolecular hydrogen bonding of the type



takes place with the exclusive production in the former compound of one rotational isomer. The liquid phase spectrum of $MeNHPOF_2$ shows a very broad band at 3270 cm.$^{-1}$, which suggests that intramolecular hydrogen-bonding is as effective in this particular compound as is intermolecular hydrogen-bonding. The very weak peak at 3478 cm.$^{-1}$ in the gas phase spectrum is ascribed to the non-hydrogen-bonded isomer. A higher value for δ_{NH} in $MeNHPOF_2$ than in $MeNHPSF_2$ is also in agreement with Nyquist's results [122].

Studies show that the value of $\nu_{P=O}$ depends on the electronegativity of the substituents attached to phosphorus but that this correlation breaks down where there are alkylamino groups present [120]; this is due to the tendency for intramolecular hydrogen-bonding to lower the value of $\nu_{P=O}$. Hence the band due to $\nu_{P=O}$ is at 1325 cm.$^{-1}$ in $MeNHPOF_2$ and at 1365 cm.$^{-1}$ in Me_2NPOF_2 [206]. Due to the similar i.r. spectra of $MeNHPSF_2$ and Me_2NPSF_2 [208] and almost similar spectra of $MeNHPOF_2$ and Me_2NPOF_2 [206] in the 380 - 600 cm.$^{-1}$ range, the extra band at 534 cm.$^{-1}$ in the spectrum of $MeNHPOF_2$ is assigned to γ_{NH} (displacement of the hydrogen atom perpendicular to the plane of the molecule). The value of γ_{NH} is highly dependent on the degree of intramolecular hydrogen-bonding which is present in a molecule; the mode was observed in the same region for $MeNHPOCl_2$ [212] as for $MeNHPOF_2$ but at a considerably lower frequency for $MeNHPSCl_2$ [124].

The same precautions have to be taken over the assignments of the PF_2 stretching modes in $MeNHPOF_2$ as were taken for $MeNHPSF_2$. There is disagreement between the value of $\nu_{sym.PF_2}$ assigned here for $MeNHPOF_2$ and that reported for Me_2NPOF_2 (708 cm.$^{-1}$) [206], which is at a much lower value than would be expected. The peak at 708 cm.$^{-1}$ in Me_2NPOF_2 is then re-assigned to ν_{PN} and the complex band at 890 cm.$^{-1}$ is assigned to both the symmetric and asymmetric PF_2 stretching modes. The intense band at 850 cm.$^{-1}$ in the spectrum of $MeNHPOCl_2$ [167] is most reasonably assigned to $\nu_{sym.PNC}$. The spectrum of $Me_3SiNHPOF_2$ showed bands which were assigned to $\nu_{sym.PF_2}$ (845 cm.$^{-1}$), $\nu_{as.PF_2}$ (901 cm.$^{-1}$) and $\nu_{as.SiNP}$ (1040 cm.$^{-1}$, "ν_{PN}") [156].

INFRA-RED CORRELATIONS FOR Me_2N-P AND MeNH-P.

Previous work has shown that compounds containing the Me_2N-P group are characterised by absorption bands in the 1300, 1180, 1065 and 975 cm.$^{-1}$ regions as well as by a band due to ν_{PN}, whose position was much less rigorously defined, in the 750 cm.$^{-1}$ region [121,208,213]. The characteristic bands due to the MeNH-P group are fewer and are spread over a wider frequency range. In this work bands due to ν_{NH} and $\nu_{as.PNC}$ have been found in the 3200 - 3500 cm.$^{-1}$ and 1020 - 1180 cm.$^{-1}$ ranges respectively and a band at 1390 - 1450 cm.$^{-1}$ has been assigned to δ_{NH}. Despite the presence of strong bands due to $\nu_{sym.PNC}$ in chloro-derivatives, it has seldom proved possible to unambiguously assign this mode in their fluoro analogues. It is, however, clear that this mode occurs at a considerably higher frequency than that due to ν_{PN} in Me_2N-P derivatives, a conclusion that has been hinted at by Chittenden et al. [121] but later disputed by Corbridge [120]. Some values for "ν_{PN}" are presented in Table 2.9 which have been observed for Me_2N-P, MeNH-P and $(MeNH)_2P$ derivatives.

Table 2.9 "ν_{PN}" (all frequencies in cm.$^{-1}$).

Me$_2$N-P derivatives (690 - 782 cm.$^{-1}$):

Me_2NPCl_2, 690 [213]; Me_2NPF_4, 703 [12]; Me_2NPF_2, 704 [27]; Me_2NPOF_2, 708^a [206]; Me_2NPOCl_2, 723 [213]; Me_2NPSCl_2, 762 [214]; Me_2NPSF_2, 782 [208].

MeNH-P and (MeNH)$_2$P derivatives (782 - 958 cm.$^{-1}$):

$MeNHP(CF_3)_2$, 782 or 809 [118]; $CD_3NHPSCl_2$, 785 [124]; $MeNHPSCl_2$, 839 [124]; $MeNHPOCl_2$, 850 [167]; $MeNHPCl(CF_3)$, 853 [119]; $MeNHPSF_2$, 878 or 922; $(MeNH)_3PF_2$, 905: $MeNHPOF_2$, 915 or 935; $(MeNH)_2PCF_3$, 931 [119]; $(MeNH)_2PF_2H$, 944; $MeNHPF_4$, 958.

[a] Re-assignment (previous value was 842 cm.$^{-1}$).

MASS SPECTRA OF $MeNHPOF_2$ AND $MeNHPSF_2$ (Fig. 2.7 and Tables 2.10 - 2.12).

Several important differences are apparent between the mass spectra of $MeNHPOF_2$ and $MeNHPSF_2$. Some of these are duplicated in the mass spectra of Me_2NPOF_2 [144,206] and Me_2NPSF_2 [207], with which they shall be compared. While intense peaks due to PF_2^+ and PXF_2^+ (X = S, O) are present in all four spectra, a larger proportion of the positive ion current is carried by phosphorus containing ions in the thiophosphoryl- than the phosphoryl-derivatives, probably because the less electronegative sulphur atom is more capable of stabilizing a positive charge on the phosphorus containing species.

All four molecules exhibit large molecular ions but, while

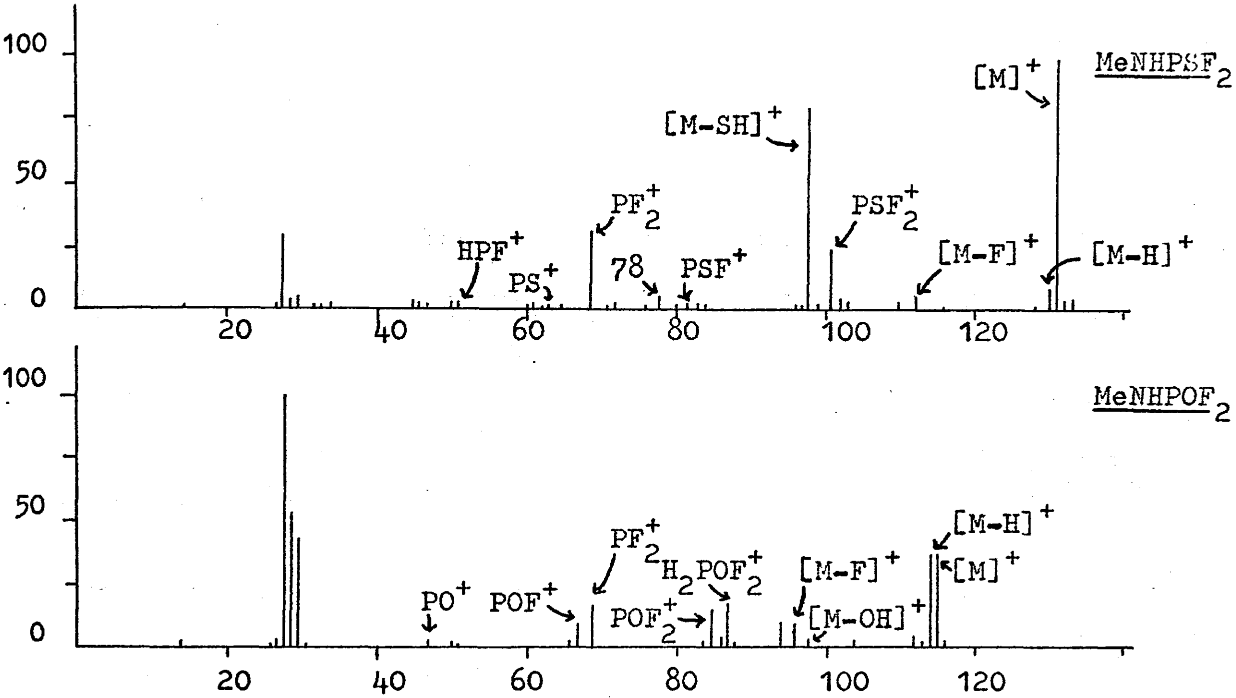


Fig. 2.7 Mass spectra of $MeNHPOF_2$ and $MeNHPSF_2$.

those derived from the phosphoryl derivatives readily lose a hydrogen atom (from the methyl group, as discussed in Chapter 1) to give a large peak due to $[M-H]^+$, those obtained from the thiophosphoryl derivatives preferentially lose a $HS^\bullet$ fragment; a metastable ion is observed for the latter process in $MeNHPSF_2$. Weak peaks are also obtained in the mass spectra corresponding to loss of $H^\bullet$ from thiophosphoryl-derivatives and $OH^\bullet$ from phosphoryl derivatives. The identity of both $[M-OH]^+$ in the mass spectra of Me_2NPOF_2 [144] and $MeNHPOF_2$ has been confirmed by mass measurements. The different behaviour observed for these two types of compound may be explained by noting the difference between

Table 2.10 Mass measurements of ions obtained from $MeNHPXF_2$ (X = S, O).

$MeNHPOF_2$:-

Mass		
Found	Calc.	Ion
97.9974	97.9971	$CH_3NPF_2^+$
93.9854	93.9858	CH_2NPOF^+
86.9809	86.9811	$H_2POF_2^+$
84.9656	84.9655	POF_2^+
66.9753	66.9749	$HPOF^+$

$MeNHPSF_2$:-

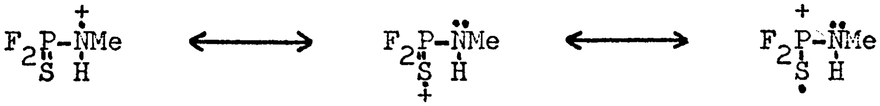
Mass		
Found	Calc.	Ion
111.9788	111.9786	CH_4NPSF^+
97.9971	97.9971	$CH_3NPF_2^+$
82.9535	82.9521	$HPSF^+$
70.9868	70.9862	$H_2PF_2^+$
64.9834	64.9831	$HNPF^+$
62.0052	62.0064	CH_4NS^+
60.9987	60.9986	CH_3NS^+
60.0012	60.0003	CH_3NP^+
59.9913	59.9908	CH_2NS^+
50.9798	50.9799	HPF^+
46.9957	46.9955	CH_3S^+
46.9832	46.9830	HNS^+
45.9854	45.9847	HNP^+
45.9753	45.9751	NS^+
33.9876	33.9877	H_2S^+

the P=O and P=S bond energies. However, an alternative explanation can be given for this difference, based on the lower ionization potential found for sulphur than for the corresponding oxygen containing compounds [149]. Ionization of PSF_3 (I.P. = 11.1 eV) was postulated to proceed through loss of an electron from an orbital on either the phosphorus or sulphur atom [143]. Similarly an electron can be lost from either of these two atoms or a nitrogen atom in compounds containing the NP(S) unit. It then seems probable that the molecular ion of $MeNHPSF_2$ can be regarded as:-

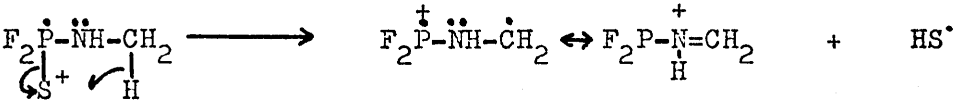
Table 2.11 Metastable transitions obtained for $MeNHPOF_2$ and $MeNHPSF_2$.

$\underline{m}_1$	Transition				$\underline{m}_2$	$\underline{m}^*$ calc.	$\underline{m}^*$ found	
	$MeNHPOF_2$							
114	$CH_3NPOF_2^+$	$\longrightarrow$	$CH_2NPOF^{+\ \Delta}$	+ HF	94	77.5	77.6	
114	$CH_3NPOF_2^+$	$\longrightarrow$	$H_2POF_2^{+\ \Delta}$	+ HCN	87	66.4	66.5	
115	$CH_4NPOF_2^+$	$\longrightarrow$	$HPOF_2^+$	+ CH_3N	86	64.3	64.5	vw
112	or $CHNPOF_2^+$	$\longrightarrow$	$POF_2^{+\ \Delta}$	+ HCN	85	64.5		
87	$H_2POF_2^{+\ \Delta}$	$\longrightarrow$	PF_2^+	+ H_2O	69	54.7	54.7	
87	$H_2POF_2^{+\ \Delta}$	$\longrightarrow$	$HPOF^{+\ \Delta}$	+ HF	67	51.6	51.6	
	$MeNHPSF_2$							
130	$CH_3NPSF_2^+$	$\longrightarrow$	CH_2NPSF^+	+ HF	110	93.1	93.0	vw
131	$CH_4NPSF_2^+$	$\longrightarrow$	$CH_3NPF_2^{+\ \Delta}$	+ HS	98	73.3	73.3	
98	$CH_3NPF_2^{+\ \Delta}$	$\longrightarrow$	CH_2NPF^+	+ HF	78	62.1	62.1	

$^\Delta$ Confirmed by mass measurement (Table 2.10).


$$F_2\underset{\overset{\shortparallel}{S}}{P}-\underset{H}{\overset{\overset{+}{\bullet}}{N}}Me \longleftrightarrow F_2\underset{\underset{+}{\overset{\shortparallel}{\dot{S}}}}{P}-\underset{H}{\overset{\bullet\bullet}{N}}Me \longleftrightarrow F_2\underset{\underset{\bullet}{S}}{\overset{+}{P}}-\underset{H}{\overset{\bullet\bullet}{N}}Me$$

Migration of a hydrogen atom to the electron-deficient sulphur atom can then take place:-


$$F_2\underset{S^+}{\dot{P}}-\ddot{N}H-\underset{H}{C}H_2 \longrightarrow F_2\overset{+}{\dot{P}}-\ddot{N}H-\dot{C}H_2 \leftrightarrow F_2P-\underset{H}{\overset{+}{N}}=CH_2 \quad + \quad HS^\bullet$$

Evidence that the hydrogen atom is lost from the alkyl group has been obtained from a study on $HS^\bullet$ elimination in a series of

Table 2.12 Mass spectra of $MeNHPOF_2$ and $MeNHPSF_2$ (m/e value, relative abundance, ion - respectively).

$MeNHPOF_2$:

116, 2, $^{13}CH_4NPOF_2^+$; 115, 37, $CH_4NPOF_2^+$; 114, 39, $CH_3NPOF_2^+$; 113, 1, $CH_2NPOF_2^+$; 112, 4, $CHNPOF_2^+$; 104, 2, POF_3^+: 98, 2, $CH_3NPF_2^{+\Delta}$; 96, 9, CH_4NPOF^+; 94, 10, $CH_2NPOF^{+\Delta}$; 88, tr, PF_3^+; 87, 19, $H_2POF_2^{+\Delta}$; 86, 4, $HPOF_2^+$; 85, 17, $POF_2^{+\Delta}$; 84, 1, $HNPF_2^+$; 69, 19, PF_2^+; 67, 9, $HPOF^{+\Delta}$; 66, 4, POF^+; 51, 1, HPF^+; 50, 3, PF^+; 47, 5, PO^+; 31, 1, P^+; 30, 37, CH_4N^+; 29, 50, CH_3N^+; 28, 100, CH_2N^+; 27, 5, CHN^+; 26, tr, CN^+; 20, 2, HF^+; 18, 1, H_2O^+; 15, 3, CH_3^+ and HN^+.

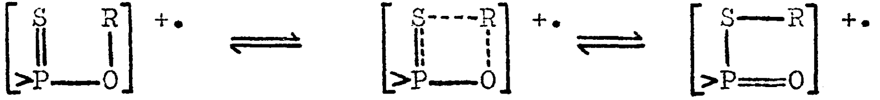
$MeNHPSF_2$:

133, 5, $CH_4NP^{34}SF_2^+$; 132, 3, $^{13}CH_4NPSF_2^+$; 131, 100, $CH_4NPSF_2^+$; 130, 8, $CH_3NPSF_2^+$; 128, 2, $CHNPSF_2^+$; 112, 6, $CH_4NPSF^{+\Delta}$; 110, 4, CH_2NPSF^+; 103, 4, $H_2PSF_2^+$, $P^{34}SF_2^+$; 102, 5, $HPSF_2^+$; 101, 26, PSF_2^+; 99, 3, $CH_4NPF_2^+$; 98, 82, $CH_3NPF_2^{+\Delta}$; 96, 2, $CHNPF_2^+$; 83, 2, $HPSF^+$; 82, 2, PSF^+; 80, 3, CH_4NPF^+; 78, 5, CH_2NPF^+; 76, 1, $CNPF^+$; 71, 1, $H_2PF_2^{+\Delta}$; 69, 31, PF_2^+; 65, 1, $HNPF^{+\Delta}$; 63, 2, PS^+; 62, 1, $CH_4NS^{+\Delta}$; 61, 1, $CH_3NS^{+\Delta}$; 60, 2, $CH_2NS^{+\Delta}$, $CH_3NP^{+\Delta}$(tr); 51, 1, $HPF^{+\Delta}$(not SF^+); 50, 2, PF^+; 47, 2, $HNS^{+\Delta}$, $CH_3S^{+\Delta}$ (tr); 46, 3, $NS^{+\Delta}$, $HNP^{+\Delta}$ (1:1); 45, 3, NP^+; 34, 1, $H_2S^{+\Delta}$; 32, 1, S^+; 30, 7, CH_4N^+; 29, 5, CH_3N^+; 28, 30, CH_2N^+; 27, 1, CHN^+; 15, 1, CH_3^+ and HN^+.

$^{\Delta}$ Confirmed by mass measurement (Table 2.10).

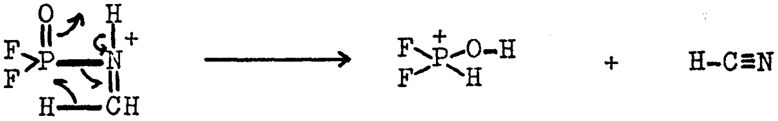
phosphoramidothioates, $>P(S)NR_2$ (R = H, Alkyl); it was also noted that loss of $HS^{\bullet}$ was promoted by electronegative substituents on phosphorus [215]. Elimination of HF from the $CH_3NPF_2^+$ ion formed (which has been shown in Chapter 1 to involve cleavage of the N-H bond) further confirms this mechanism for $HS^{\bullet}$ elimination.

Previous work has shown that transfer of an alkyl group to a sulphur atom is possible in the mass spectrometer, with the ions so formed decomposing to give an RS^+ fragment [216],

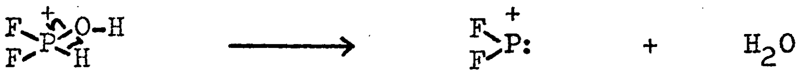


Mass measurements of the small concentration of ions in the regions with m/e = 60 - 62, 44 - 47 indicate that only a trace of an RS^+ fragment is present (R = Me). A more common type of rearrangement process is however indicated, for ions in these two regions possessing the general formula CH_nSN^+ (n = 2 - 4), which presumably contain a S-N bond, and H_nNS^+ (n = 0, 1) are found to predominate over ions containing P-N bonds. Mass spectral evidence is obtained for the presence of CH_3NP^+ and HNP^+ but not for ions containing a P-C bond.

A metastable ion indicates that the prominent peak due to $H_2POF_2^+$ in the mass spectrum of $MeNHPOF_2$ is derived from $CH_3NPOF_2^+$. Since an ion with the same formula (but probably with a different structure, $F_2P(O)\text{-}NCH_3^+$) at m/e = 114 but no ion at m/e = 87 were present in the mass spectrum of Me_2NPOF_2, it appears that the formation of $H_2POF_2^+$ requires that one of the two migrating hydrogen atoms is an amino-proton,

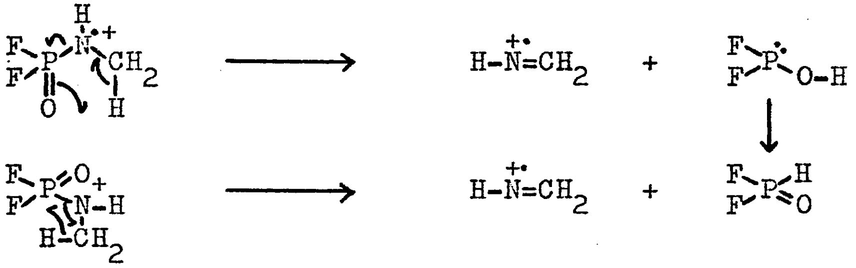


The ion formed can further decompose to eliminate a molecule of water,



or a molecule of HF,

A large broad metastable ion at m/e ≈ 7 (m/e calc. = 7.3) might correspond to a rearrangement process analogous to that reported for Me_2NPOF_2, with hydrogen migration to either oxygen or phosphorus:-



The ions and radicals formed are formulated as containing a P=O bond on account of the known preference for phosphorus to adopt a pentavalent structure [55].

EXPERIMENTAL

Practical techniques employed in the preparation and characterisation of compounds dealt with in this section are discussed in Appendix 1.

Tables 1.18 and 2.13 list the i.r. and n.m.r. references for both the starting materials and those products identified by these techniques.

Reaction between phosphorus pentafluoride and methylaminodifluorophosphine.- Excess PF_5 and $MeNHPF_2$ (0.51 g., 5.2 mmoles) were allowed to warm up slowly from -196°. After leaving at room temperature for a short time, the mixture was held at -90° and the majority of the excess PF_5 together with some POF_3 and PF_3 (i.r. identification) were pumped off, to reveal that less than 5.2 mmoles of PF_5 had reacted. A white solid (0.33 g.) was left on pumping off the remaining volatile material; i.r. spectroscopic examination of the latter revealed a mixture of products which was separated by fractional distillation; they were (in approximately decreasing order of volatility) PF_3, PF_5, POF_3, $(PF_2)_2NMe$, PF_2NMePF_4, and traces of an unidentified material. The solid residue was heated up to 100° and the volatile components trapped out at -196°. Further fractional distillation showed that this was a mixture of POF_3, $(PF_2)_2NMe$, PF_2NMePF_4 and $MeNHPF_4$ (in

Table 2.13

COMPOUND	SOURCE	I.R.	N.M.R.
Me_3SiF		(a)	^1H (b), ^{19}F (c)
Me_3SiCl	Midland Silicones	(a)	(b)
$Me_3SiNHMe$	$Me_3SiCl/MeNH_2$ (d,e)	(f)	
$(Me_3Si)_2NMe$	$Me_3SiCl/MeNH_2$ (e,g)	(h)	
$(Me_3Si)_2O$		(i)	(b)
$Me_3SiNMePCl_2$	$(Me_3Si)_2NMe/PCl_3$ (j)		(j)
$Me_3SiNMePF_2$	See text	(j)	(j)
$Me_3SiNMePOF_2$			(k)
PCl_3	Hopkin & Williams	(l)	(m)
PF_2Cl	Me_2NPF_2/HCl (n)	(l)	(m)
POF_2Cl	Me_2NPOF_2/HCl (o)	(p)	(m)
POF_2Br	Me_2NPOF_2/HBr (o)	(q)	(m)
Me_2NPF_2	PF_3/Me_2NH (n)	(r)	(n)
$MeNHPOCl_2$	$POCl_3/MeNH_3^+ Cl^-$ (s)		
$MeNHPOF_2$	$MeNHPOCl_2/NaF$ (t)		
$PCl_2NMePOCl_2$	$Me_3SiNMePCl_2/POCl_3$ (j)		
$(POF_2)_2NMe$		(u)	(v)
$(PF_2)_2NMe$	$(PCl_2)_2NMe/SbF_3$ (w)	(w)	(w,x)
Bu^nLi/n-hexane	Alpha Inorganics, Inc.		
NaF, SbF_3	B.D.H.		
Sulpholane	B.D.H.		
N,N-Dimethylaniline	B.D.H.		

Table 2.13 (cont.)

COMPOUND	SOURCE	I.R.	N.M.R.
SOF_2	$SOCl_2$/NaF/MeCN (y)	(z)	(aa)
MeNSO		(ab)	(ac)
SO_2	B.D.H.	(z)	
HCl, HBr	Matheson Co.	(z)	

(a) H. Bürger, Spectrochim. Acta, 1968, 24A, 2015. (b) H. Schmidbaur, J. Amer. Chem. Soc., 1963, 85, 2336. (c) [104]. (d) R.O. Sauer and R.H. Hasek, J. Amer. Chem. Soc., 1946, 68, 241. (e) These were found to be most easily prepared by gas phase reactions, thus eliminating the need of a solvent. (f) H. Bürger and U. Goetze, Monatsh., 1968, 99, 155. (g) R.C. Osthoff and S.W. Kantor, Inorg. Synth., 1957, 5, 55. (h) [197]. (i) H. Bürger, Organometallic Chem. Rev. (A), 1968, 3, 425. (j) [167]. (k) [158]. (l) A. Müller, E. Niecke, B. Krebs, and O. Glemser, Z. Naturforsch., 1968, 23b, 588. (m) A. Müller, E. Niecke and B. Krebs, Mol. Phys., 1968, 14, 591. (n) [25]. (o) [206]. (p) A. Müller, O. Glemser and E. Niecke, Z. anorg. Chem., 1966, 347, 275. (q) A. Müller, E. Niecke and O. Glemser, Z. anorg. Chem., 1967, 350, 246. (r) [27]. (s) A. Michaelis, Annalen, 1903, 326, 149. (t) [205]. (u) [164]. (v) L. Stobbs, private communication. (w) [117]. (x) [190]. (y) C.W. Tullock and D.D. Coffman, J. Org. Chem., 1960, 25, 2016. (z) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York and London, 1963. (aa) J.K. Ruff in "Preparative Inorganic Reactions", Interscience, 1966, vol. 3, p. 35. (ab) W.K. Glass and A.D.E. Pullin, Trans. Faraday Soc., 1961, 57, 546. (ac) [204].

approximately decreasing order of volatility).

Reaction between phosphorus trifluoride and t-butylaminodifluorophosphine.- A mixture of PF_3 and Bu^tNHPF_2 was shaken for one week. A small amount of solid was formed. Since no new volatile components were identified by n.m.r. or i.r. spectroscopy, it is thought that the solid was formed in the removal of final traces of Bu^tNH_2 from Bu^tNHPF_2.

Reaction between chlorodifluorophosphine and methylaminophosphoryl difluoride.- $MeNHPOF_2$ (7.35 g., 63.5 mmoles) and PF_2Cl (7.078 g., 67.8 mmoles) were condensed together with an isopentane solution of N,N-dimethylaniline (7.088 g., 61.5 mmoles) into a reaction vessel, and the mixture was shaken since the liquid separated into two layers. The N,N-dimethylaniline hydrochloride came out of solution when the volatile material was pumped off under vacuum. The fraction passing -60° was examined by i.r. spectroscopy and found to contain, in addition to isopentane, a considerable quantity of PF_3. A mixture of $MeNHPOF_2$ and $PF_2NMePOF_2$ could be separated from the less volatile compounds (unidentified) by passage through a 0° trap. While pure $MeNHPOF_2$ only passed a -23° trap with difficulty and pure $PF_2NMePOF_2$ was only partially stopped at -44°, complete recovery of $PF_2NMePOF_2$ was a lengthy process. Finally a pure sample of DIFLUOROPHOSPHINO(DIFLUOROPHOSPHORYL)METHYLAMINE [Found: M, 186 (vapour density), 183 (mass spec.); C, 6.7; H, 1.8; F, 41.7; N, 7.5; O, 8.6; P, 33.7%.

Calc.: M,183; C, 6.6; H, 1.6; F, 41.5; N, 7.7; P, 33.9%. V.p. 24 mm. Hg at 25°] was recovered.

A sample contained in an n.m.r. tube was heated at 100° for six hours, and found to remain intact.

Reaction between phosphorus pentafluoride and methylaminotrimethylsilane.- Methylaminotrimethylsilane (1.349 g., 13.1 mmoles), which was difficult to prepare pure and contained traces of $(Me_3Si)_2NMe$ and $(Me_3Si)_2O$, was condensed with excess of PF_5 into an ampoule. The mixture was then allowed to warm slowly up to room temperature. A reaction was indicated by the formation of white solids. The ampoule was then placed in a -100° bath and the excess of PF_5 was then pumped off; re-weighing the ampoule indicated that 1.333 g. (10.6 mmoles) of PF_5 had been absorbed. The remaining volatile components were fractionated through a -100° bath; Me_3SiF (1.136 g., 12.4 mmoles) collected in the -196° trap and 0.096 g. of a mixture of $MeNHPF_4$, $(Me_3Si)_2O$ and $(F_3PNMe)_2$ was collected in the -100° bath (all compounds identified by i.r.). The solid remaining (1.375 g.) was heated up to 140°, and the volatile material removed by pumping on the system under vacuum. 1.044 g. of a volatile liquid was shown by i.r. to consist mainly of $MeNHPF_4$ contaminated with traces of $(Me_3Si)_2O$, Me_3SiF and $(F_3PNMe)_2$. The solid residue was identified by both n.m.r. and i.r. to be $MeNH_3^+ PF_6^-$. Final purification was achieved by fractional distillation through a series of traps held at -60° ($(F_3PNMe)_2$ and

$(Me_3Si)_2O$), -95° ($MeNHPF_4$) and -196° (Me_3SiF) to produce an approximately 60% total yield of METHYLAMINOTETRAFLUOROPHOSPHORANE [Found: M, 141 (vapour density), 137 (mass spec.); C, 9.0; H, 3.1: F, 55.8; N, 10.4; P, 22.0%. Calc.: M, 137; C, 8.8; H, 2.9; F, 55.6; N, 10.2; P, 22.6%. V.p. 133mm. Hg at 20°].

Reaction between trimethylchlorosilane and methylaminodifluorophosphine.- Methylaminodifluorophosphine (1.44g., 14.4 mmoles), trimethylchlorosilane (3.078 g., 28.5 mmoles) and trimethylamine (1.268 g., 21.4 mmoles) were condensed together into an ampoule and warmed up to room temperature. The mixture was shaken to complete the reaction. A white solid was formed. Besides recovering excess of Me_3SiCl and traces of Me_3N, an i.r. and n.m.r. analysis showed that the main products were Me_3SiF with traces of $(Me_3Si)_2O$ (an impurity in the Me_3SiCl) and Me_2NPF_2 (an impurity in the $MeNHPF_2$). There was no evidence for any formation of $Me_3SiNMePF_2$. Similar products resulted when Et_3N was used in place of Me_3N.

Reaction between trimethylchlorosilane and methylaminophosphoryl difluoride (via its lithium derivative).- A solution of $MeNHPOF_2$ (7.48 g., 65 mmoles) dissolved in 70 mls. of ether was stirred in a round bottomed flask kept at -78° under an atmosphere of nitrogen. An equimolar solution of n-butyl-lithium dissolved in n-hexane was slowly added, and a white precipitate was immediately formed. Trimethylchlorosilane (65 mmoles) dissolved in ether was slowly added to the stirred mixture maintained at -78°. The mixture was slowly warmed up to room temperature, and kept at this temperature for an hour. The white solid was filtered off and the resulting solution reduced on a rotary evaporator. Only a small quantity of residual liquid was obtained, and identified by n.m.r. to be unreacted $MeNHPOF_2$. No $Me_3SiNMePOF_2$ was observed.

Reaction between dichlorophosphino(trimethylsilyl)methylamine and sodium fluoride.- $Me_3SiNMePCl_2$, excess of NaF and sulpholane were heated at 40° for two hours. The only volatile products obtained were PF_3 and Me_3SiF (identified by i.r.).

Reaction between heptamethyldisilazane and phosphorus trifluoride.- These compounds did not react at room temperature, so they were heated up to 100° for three hours in a closed vessel. After removal of PF_3 and examination of the volatile products, no $Me_3SiNMePF_2$ was observed. In some reactions Me_3SiF was identified by its i.r. spectrum.

Reaction between heptamethyldisilazane and chlorodifluorophosphine.- PF_2Cl (2.19 g., 21 mmoles) and $(Me_3Si)_2NMe$ (2.76 g., 15.5 mmoles) were condensed together into an ampoule and slowly warmed up to 90° and then left overnight. The products were purified by fractional distillation and identified by i.r. spectroscopy. Difluorophosphino(trimethylsilyl)methylamine (2.19 g., indicating an 85% yield) passed a -23° bath but was trapped out at -45°, thus removing $(Me_3Si)_2O$ (trapped at -65°), Me_3SiF (trapped at -126°), excess of PF_2Cl (trapped at -160°), and traces of PF_3 (trapped at -196°). Slight decomposition occurred if the reaction mixture was heated beyond 90°. The n.m.r. spectrum of $Me_3SiNMePF_2$ had the following parameters: δ^*_F, 69; $\delta^*_{C\underline{H}_3Si}$, -0.1; $\delta^*_{C\underline{H}_3N}$, -2.6; J(PF), 1218; J($H_3CNP$), 5.8; J($H_3CNF$), 1.9; J($H_3CSiP$), 2.3. The i.r. spectrum is as follows (cm.$^{-1}$): 2960 s, 2905 m, 2825 w, ν_{CH}; 1410 vw, δ_{CH_3}; 1260 s, $\delta_{sym.SiMe_3}$; 1195 m, ρ_{MeN}; 1085 vs, ν_{CN}; 910 vs, $\nu_{as.PNC}$; 840 vs, $\rho_{as.SiMe_3}$; 805 vs, $\nu_{as.PF_2}$; 765 vs, $\nu_{sym.PF_2}$; 685 w, $\nu_{as.SiC_3}$; 655 w, $\nu_{sym.SiC_3}$; 600 m, $\nu_{sym.SiNP}$; 485 vw, δ_{PF_2}. (See [217] for assignments of Me_3Si skeleton).

Reaction between difluorophosphino(trimethylsilyl)methylamine and phosphorus pentafluoride.- $Me_3SiNMePF_2$ (0.585 g., 3.4 mmoles) and PF_5 (0.45 g., 4.2 mmoles) were condensed together into a reaction vessel at -196° and allowed to warm slowly up to room temperature. The volatile components were removed to leave a very small amount of solid product. Excess of PF_5 and Me_3SiF were both removed by passing the mixture through a trap held at -90° to leave a volatile liquid, DIFLUOROPHOSPHINO(TETRAFLUOROPHOSPHORANYL)METHYLAMINE [Found: M, 206 (vapour density; average of three readings); C, 5.8; H, 1.5, F, 55.6; N, 6.8; P, 30.3%. Calc.: M, 205; C,5.7; H, 1.6; F, 55.3; N, 6.6; P, 29.9%.].

When moist air was admitted to a sample of PF_2NMePF_4 in an i.r. gas cell, instantaneous production of PF_3 and POF_3 was recorded. The mass spectrum also suggests that hydrolysis has taken place, since large peaks attributed to POF_3 and PF_3 are recorded; in addition there is a major peak at m/e = 183 corresponding to the molecular ion of $PF_2NMePOF_2$, and indicating that this species may constitute the first formed hydrolysis product. The stability of PF_2NMePF_4 was studied by heating the pure liquid in an n.m.r. tube. After heating for four hours at 50°, slight solid deposition and formation of a small quantity of PF_3 were noted. On increasing the temperature to 80°, PF_3 formation took place at a faster rate, but in addition a doublet of peaks appeared in the ^{19}F n.m.r. spectrum due to the formation of $(F_3PNMe)_2$ (confirmed by i.r.). Decomposition appeared to be catalysed by traces of impurities.

Reaction between difluorophosphino(trimethylsilyl)methylamine and difluorophosphino(tetrafluorophosphoranyl)methylamine.- Approximately equimolar quantities of PF_2NMePF_4 and $Me_3SiNMePF_2$ were condensed together into an n.m.r. tube. No reaction was observed at room temperature, but on raising the temperature to 50° solid deposition was noted. New peaks were observed in the n.m.r. arising from the formation of PF_3, $(F_3PNMe)_2$ and Me_3SiF in addition to very small traces of unidentified compounds. These observations were confirmed by breaking open the n.m.r. tube under vacuum and examining the i.r. spectra of the volatile products.

Reaction between difluorophosphino(trimethylsilyl)methylamine and phosphoryl fluoride.- $Me_3SiNMePF_2$ and excess of POF_3 did not react in a closed vessel at room temperature. The temperature was slowly raised to 60° and the system kept at this temperature for several hours. Fractionation of the products gave some PF_3 (trapped at -196°), unreacted POF_3 and Me_3SiF (trapped at -160°), and a mixture of $PF_2NMePOF_2$ and $Me_3SiNMePF_2$ retained in the -45° trap. On performing the reaction at 110°, an examination of the volatile material showed that, in addition to the formation of PF_3 and Me_3SiF, a less volatile liquid had been formed. The n.m.r. spectrum of the latter indicated traces of $PF_2NMePOF_2$ along with the bulk component, $(POF_2)_2NMe$ [δ^{**}_{Me}, -3.2 tp; δ^{**}_{F}, 75 d; J(PH), 11.0; J(FH), 1.3; J(PF), ~1060]. A viscous oil was left in the reaction vessel; its i.r. spectrum included the following very broad bands (cm.$^{-1}$): ~3200 w, ν_{NH} or ν_{OH}; 2980 m, 2830 w, ν_{CH}; 1470 m, δ_{CH}; 1300 s, $\nu_{P=O}$ or $\nu_{P=N}$; 1070, ν_{CN}; 880 s, ν_{PF}.

Reaction between difluorophosphino(difluorophosphoryl)-methylamine and phosphoryl fluoride.- $PF_2NMePOF_2$ was heated in a closed vessel with excess of POF_3 for two days. Only slight decomposition occurred. A trace of PF_3 was identified by its i.r. spectrum, on fractionating the reaction mixture through a -160° trap. No other products other than starting materials could be identified. In another run at 100° for eight hours using a slightly less pure sample of $PF_2NMePOF_2$, in addition to PF_3, a small quantity of involatile liquid was formed. The i.r. spectrum of the latter included the following very broad bands (cm.$^{-1}$):

~3280 w, ν_{NH} or ν_{OH}; 2980 m, 2840 w, ν_{CH}; 1450 w, δ_{CH}; 1330 s, $\nu_{P=O}$ and/or $\nu_{P=N}$; 1210 ms; 1080 ms, ν_{CN}; 1020 ms; 800 s, ν_{PF}.

Reaction between bromophosphoryl difluoride and difluorophosphino(trimethylsilyl)methylamine.- A 1:1 mixture of POF_2Br and $Me_3SiNMePF_2$ was found to give a large quantity of involatile products at 60° along with some $PF_2NMePOF_2$; the latter reaction was not studied further.

Reaction between dichlorophosphino(dichlorophosphoryl)-methylamine and sodium fluoride.- $PCl_2NMePOCl_2$ was heated at 80° in a closed vessel with a slurry of excess of NaF in sulpholane. The mixture was cooled down and the volatile components were fractionated and identified by i.r. spectroscopy. Large quantities of PF_3 and a very small trace of POF_3 could be separated from $PF_2NMePOF_2$, which was formed in low yield.

Reaction between difluorophosphino(difluorophosphoryl)methylamine and hydrogen chloride.- $PF_2NMePOF_2$ (0.899 g., 4.91 mmoles) was condensed together with HCl (0.174 g., 4.76 mmoles) and allowed to warm up to room temperature. The volatile products were pumped off the solid product (0.088 g.) and separated by fractional distillation. PF_3 (0.257 g., 2.92 mmoles) passed a -126° trap and a mixture of POF_2Cl and POF_3 (0.108 g., shown by n.m.r. to be in the approximate ratio 3:5, i.e. 0.34 mmoles and 0.65 mmoles respectively) passed a -65° trap to leave a mixture of $MeNHPOF_2$, PCl_3 and unreacted $PF_2NMePOF_2$ (0.611 g., shown by n.m.r. to include traces of other PF containing species). Neither PF_2Cl nor $MeNHPF_2$ were identified by i.r. spectroscopy.

Reaction between methylaminodifluorophosphine and thionyl fluoride.- $MeNHPF_2$ (1.739 g., 17.6 mmoles) was condensed with SOF_2 (0.786 g., 9.2 mmoles) in an ampoule and allowed to warm up slowly to room temperature. The volatile products were small quantities of PF_3 and SO_2 together with larger quantities of MeNSO (all i.r. identified), which all passed a -75° trap, and a mixture of METHYLAMINOTHIOPHOSPHORYL DIFLUORIDE (majority) and METHYLAMINOPHOSPHORYL DIFLUORIDE along with traces of MeNSO (δ_H^*, -3.5), which were all identified by n.m.r.. The $MeNHPSF_2$ can be separated from $MeNHPOF_2$ by trapping the latter in a -23° bath. 0.689 g. of solid were recovered.

In the presence of excess of SOF_2, less $MeNHPOF_2$ and more PF_3 were produced and a pale yellow solid was recovered.

Reaction between methylaminodifluorophosphine and sulphur dioxide.- $MeNHPF_2$ (0.349 g., 3.53 mmoles) was condensed with excess of SO_2 and allowed to warm up to room temperature. The reaction being complete, the volatile components were removed. PF_3 (0.025 g., 0.28 mmoles) was separated from the excess of SO_2 (recovery showed that 0.026 g., 0.41 mmoles, had reacted; this is probably low since it was contaminated with traces of MeNSO) and a less volatile liquid (0.175 g.), shown by its n.m.r. spectrum to be an approximately 1:1 mixture of $MeNHPOF_2$ and $MeNHPSF_2$.

0.167 g. of a viscous liquid remained, which probably contained some trapped $MeNHPOF_2$ (liquid film i.r.).

Reaction between difluorophosphino(trimethylsilyl)methylamine and thionyl fluoride.- $Me_3SiNMePF_2$ (0.616 g., 3.6 mmoles) and SOF_2 (1.024 g., 11.9 mmoles) were heated in a closed vessel for 24 hours at 100°. After the volatile material had been pumped off 0.047 g. of a viscous yellow liquid was left. The volatile material was fractionated to give the following compounds (all identified by i.r.): PF_3 (passed -160°), SOF_2 (passed -126°), Me_3SiF (passed -86°), MeNSO (passed -65°), and a mixture of compounds which were trapped at -65°. The majority of the SOF_2 was recovered. The pressure exerted by the partially purified compounds in the same part of the vacuum line gave a rough measure of the quantity of the more volatile gases: $PF_3 \approx MeNSO < Me_3SiF$. The ^1H n.m.r. spectrum of the less volatile compounds showed that the following products had been formed, in decreasing order of abundance: unreacted $Me_3SiNMePF_2$, MeNSO, $(Me_3Si)_2O$ (an impurity in the starting compound), and a trace of $PF_2NMePOF_2$.

The same products were also identified when $Me_3SiNMePF_2$ was heated with excess of SOF_2 at 130° for five days.

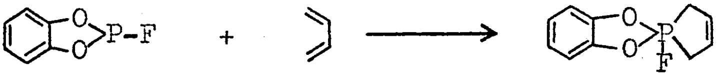
CHAPTER III

THE REACTIONS BETWEEN ALKENES AND COMPOUNDS CONTAINING P-X BONDS

(X = H, F, Cl, Br).

INTRODUCTION

Phosphorus-fluorides which contain P-C bonds are usually prepared by fluorinating the corresponding phosphorus-chloride derivative [1]. Few other reactions with the aim of forming the C-P(F) unit have been studied. Cleavage of the Sn-C bond in Me_4Sn by PF_5 gave $MePF_4$ [218], and syntheses of phenylphosphonitrilic fluoride trimers have been effected by both organolithium and Friedel-Crafts reactions [219]. The direct addition of dienes to P(III) derivatives can sometimes be accomplished [220]:-



Some success in producing P-C bonds has been achieved by directly reacting an alkene with a P-H or a P-Hal bond [221-2]. This chapter will be concerned with the extension of this technique to prepare compounds containing the C-P(F) unit.

RESULTS

The reactions between alkenes and P-F bonds.

Since the object of the reactions studied in this chapter is to add an olefin across a P-X bond (where X = H or a halogen, not including fluorine), the reactivity of P-F bonds was briefly studied to ascertain whether or not they were likely to play a part in these reactions.

No evidence is obtained for the addition of PF_3, PSF_3 or PF_5 to $H_2C{=}CH_2$, $F_2C{=}CF{-}CF_3$ or $F_3C{-}C{\equiv}C{-}CF_3$ under the influence of heat or U.V. light. The very small quantities of product that are isolated are believed to originate from the break-down of the alkene itself. The photolysis of PSF_3 and C_2H_4 gives a very small amount of $EtPSF_2$ and Et_2S. It is not certain by which route the $EtPSF_2$ is obtained, but the Et_2S is believed to originate from some H_2S impurity in the PSF_3 starting material; ethylene has previously been shown to add across both the S-H bonds in H_2S [221]. The liquid isolated from the thermal reaction between PF_3 and C_3F_6 in the presence of CsF has an i.r. spectrum which shows no appreciable absorption in the PF stretching region; the mass spectrum indicates that this product is mainly composed of the dimer and a smaller amount of the trimer of C_3F_6. The products from the reaction between CsF and C_3F_6 consisted of a mixture of isomers of the dimer [223], while the main product reported for the photochemical decomposition of C_3F_6 was the trimer, which was formed along with traces of the tetramer and pentamer of C_3F_6 [224].

Results thus indicate that the addition of P-F to olefins does not take place. An article appeared which showed that the CsF catalysed addition of SF_4 across C_3F_6 took place at 150° [225]. The difference in reactivity of phosphorus- and sulphur-fluorides has as a primary source the larger bond energy of the P-F bond.

The reactions between alkenes and P-H bonds.

Since all phosphorus-fluorides containing a P-H bond tend to be thermally unstable, hydrothiophosphoryl difluoride, which only decomposed to give small amounts of PF_3 and PSF_3 together with some solid products over a period of several months [226], was employed in these addition reactions. Self-irradiation of $HPSF_2$ tends to hasten its decomposition, but not to a marked degree; a small amount of non-condensable gas, assumed to be hydrogen, is formed along with the expected volatile decomposition products.

Photolysis of a 1:1 mixture of $HPSF_2$ and C_2H_4 gives mainly ethylphosphonothioic difluoride, $EtPSF_2$, along with smaller amounts of hydrogen, ethane and n-butylphosphonothioic difluoride and some unidentified involatile liquid probably containing higher telomers, $H(C_2H_4)_nPSF_2$ $(n > 2)$, and polymerised ethylene. The main product resulting from the photolysis of a 1:1 mixture of

$HPSF_2$ and C_3H_6 is n-propylphosphonothioic difluoride. The involatile liquid remaining was not identified but is also presumably composed of a mixture of telomers, $H(C_3H_6)_nPSF_2$ ($n \geq 2$).

Some phosphonothioic difluorides have been characterised before [1], but no previous reports of n-propyl- or n-butyl-phosphonothioic difluoride are known to exist. Ethylphosphonothioic difluoride was first prepared by the fluorination of $EtPSCl_2$, and it has been prepared more recently by Roesky through the interaction of HF and EtP(S)FSH [209]; Roesky has also reported the i.r. and n.m.r. spectra of this compound.

These compounds are most conveniently characterised by their n.m.r. spectra (Table 3.1) but these are not always straightforward, since the similar chemical shifts of the methylene and methyl groups produce second order effects which are most apparent in the ^1H n.m.r. spectra. The methyl resonance for all three phosphonothioic difluorides appears as a triplet, due to coupling with the protons of the neighbouring methylene group (with further coupling to phosphorus being clearly visible for the ethyl derivative), which is distorted so that the low field band is less intense than that at high field. While the ^{19}F n.m.r. indicates that the fluorine atoms in $EtPSF_2$ are further coupled to both methylene and methyl protons of the ethyl group, this coupling is not clearly visible in the methyl resonance obtained in the ^1H n.m.r. spectrum. The methylene protons in $EtPSF_2$

Table 3.1

Compound	δ_F	J(PF)	δ_{CH_3}	δ_{CH_2}
MePSF$_2$ [209]	41.7	1148	-2.30	
EtPSF$_2$ [209]	50.1	1165	-1.29	-2.3
EtPSF$_2$	50.0** dtq	1171	-1.27**	-2.4 comp.
Pr^{n}PSF$_2$	48.5** dt^a	1172	-1.23*	-1.4 - -2.8 v comp.
Bu^{n}PSF$_2$	47.4** dt^a	1172	-1.1*	-1.3 - -2.8 v comp.

Compound	^{2}J(PH)	^{3}J(PH)	^{3}J(HF)	^{4}J(HF)	J(H$_2$CCH$_3$)
MePSF$_2$	16.5		6.5		
EtPSF$_2$	b	25	5	b	7.5
EtPSF$_2$	c	25.0	4.7^f	0.5^f	7.7
Pr^{n}PSF$_2$	d	d	4.9^f		6.5
Bu^{n}PSF$_2$	d	d	5.0^f		6.1

[a] Further fine structure is apparent. [b] Not given. [c] See text.
[d] Not possible to determine. [f] Obtained from ^{19}F n.m.r. spectrum.

produce a complicated resonance with many more lines being observed than would be expected for a first order analysis. This results in the inability to define the value of ^{2}J(PH). If this were required it could easily be obtained either from a high resolution ^{31}P n.m.r. study or by decoupling the two sets of protons by irradiating the methyl resonance; previous work [104] would lead one to expect that the magnitude of ^{3}J(PH) is about equal that of $^2J(PH)$. The methylene groups in both Pr^nPSF_2 and Bu^nPSF_2 produce complex overlapping resonances to high field of the methyl resonance. Integration of the bands in the ^1H n.m.r. of Pr^nPSF_2 shows that the ratio CH_2:CH_3 is 4:3, and thus rules out the alternative formulation, Pr^iPSF_2, for this compound. The ^{19}F n.m.r. spectrum shows only one set of resonances, which indicates that Pr^iPSF_2, if it is formed at all, is present in very low yield.

^{19}F n.m.r. results show that there is a large difference in the chemical shift between $MePSF_2$ and $EtPSF_2$ but that that between $EtPSF_2$ and other homologues is small. A marginal increase in the value of J(PF) is apparent as the molecular weight of the compound increases. Muetterties et al. [72] have also noted that the value of δ_F for R_xPF_{5-x} $(x = 1 - 3)$ increased along the series

$$\mathrm{Me} \quad < \quad \mathrm{Bu^n} \quad < \quad \mathrm{Et}$$

while J(PF) increased in the fluorophosphoranes with the increasing molecular weight of the alkyl group. Both an impurity in the sample of Bu^nPSF_2 and a deuteriochloroform solution of the involatile liquid formed in the reaction between $HPSF_2$ and C_2H_4 give resonances in their ^{19}F n.m.r. spectra at chemical shifts which are to low field of that due to Bu^nPSF_2, thus falling in the expected region for $H(C_2H_4)_nPSF_2$ $(n > 2)$. The ^1H n.m.r. spectrum of the $CDCl_3$ solution gives a complex set of peaks in the position characteristic of methylene protons.

Gas	Liquid	Assignments	Comments
2966 w	2995 w	ν_{CH}	
2962 w	2954 w		
2933 vw	2924 w		
2903 vw	2893 vw		
1465 w	1460 m	$\delta_{as.CH_3}$	
1414 w	1405 w	δ_{CH_2}	
	1387 vw	$\delta_{sym.CH_3}$	
1275 w	1275 w	w_{CH_2}	These two bands are characteristic of Et-P [231].
1249 w	1234 w	CH_2 twist	
1042 m sh	1040 m	ν_{CC}	Two bands also observed in this region for Et_3PS and $EtPSCl_2$.
1022 m PQR	1021 m	ν_{CC}	
984 w.	982 vw	ρ_{CH_3}	
896 vs	885 vs br	$\nu_{as.PF_2}$	Same precautions for assignments as given in Chapter 2.
878 vs		$\nu_{sym.PF_2}$	
807 s PQR	803 s	ν_{PC}	Two bands in both regions for $EtPSCl_2$ (777, 748; 675, 647 cm.$^{-1}$) suggest that rotational isomers are present.
790 ms sh	782 s	ν_{PC}	
642 vw PQR	642 w	$\nu_{P=S}$	
614 vw	612 w	$\nu_{P=S}$, ?ρ_{CH_2}	
433 w	430 m	w_{PF_2}	

Table 3.2 I.r. spectra of $EtPSF_2$ (all frequencies in cm.$^{-1}$).

The i.r. spectrum obtained for $EtPSF_2$ (Table 3.2) agrees well with that previously reported for a liquid phase sample of this compound by Roesky [209]. By comparing the spectra of RPF_2 and $RPSF_2$, Schmutzler has assigned $\nu_{P=S}$ for alkylphosphonothioic difluorides to a band in the 650 - 700 cm.$^{-1}$ region, but he admitted that these assignments were only tentative [199]. More success has been achieved in assigning the PF stretching modes for $RPSF_2$ which were allocated to two strong bands generally found close together in the 840 - 920 cm.$^{-1}$ region.

Since bands in the $\nu_{P=S}$ region are of low intensity, no assignment can definitely be made for this mode in the spectra of $RPSF_2$ (R = Et, Pr^n, Bu^n); the intense band at ~800 cm.$^{-1}$ is near the upper limit for $\nu_{P=S}$, and is better assigned to another mode. Identification of $\nu_{P=S}$ in PSX_3 is difficult due to both the variable intensity of the band it produces and the tendency of this mode to couple with other vibrations of the PX_3 skeleton [120,227]. The assignments of the bands in the i.r. spectrum of $EtPSF_2$ are made on the basis of the partial assignments for the i.r. spectrum of $EtPSCl_2$ (which it much resembles in the 1000 cm.$^{-1}$- 3000 cm.$^{-1}$ region) [214], and the complete analyses made for $MeOPSF_2$ [211], Et_3PS [228], $MePSCl_2$ [229] and $MePOF_2$ [230].

While little work has been published concerning the mass spectra of alkyl derivatives of phosphorus-fluorides, the mass spectra of alkylphosphines and alkyldiphosphines have received more attention [142,232]. It was indicated that the main form of break-down for ethyl derivatives was, through the elimination of a molecule of ethylene, to produce a P-H bond. It was noted that $(Bu^n_2P)_2$ tended to eliminate both $Bu^{n\cdot}$ radicals and butene. Hydrocarbon fragments did not figure prominently in these mass spectra [232].

The mass spectra of $RPSF_2$ (R = Et, Pr^n, Bu^n) (Tables 3.3 - 3.5, Fig. 3.1) all show abundant molecular ions. Peaks due to

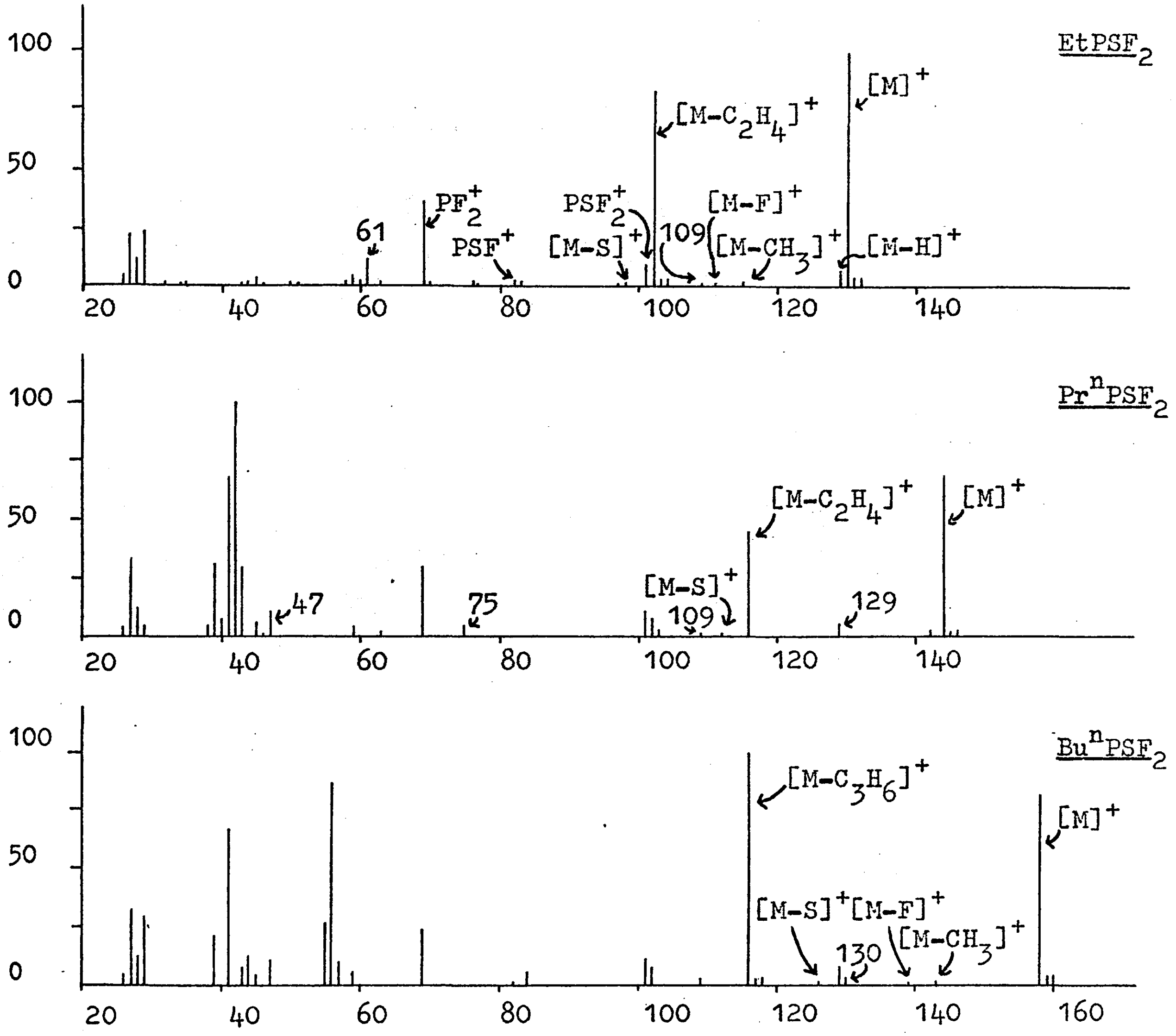


Fig. 3.1 Mass spectra of $RPSF_2$ ($R = Et, Pr^n, Bu^n$).

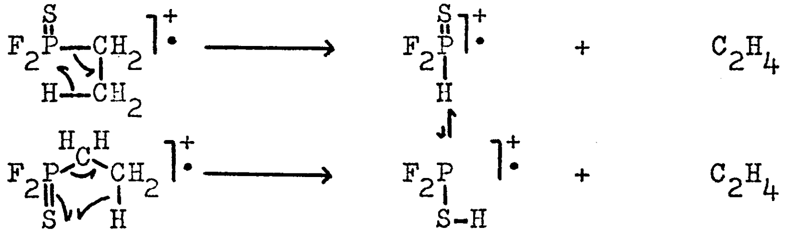
$PS_nF_m^+$ ($n = 0, 1; m = 0 - 2$) are only prominent for PF_2^+ and PSF_2^+. For ethylphosphonothioic difluoride, there is a large peak corresponding to the elimination of ethylene from the molecular ion, but less intense ones due to the elimination of F$^\bullet$, Me$^\bullet$ or Et$^\bullet$ radicals. (It is interesting to note that the former mode is

Table 3.3 Mass measurements of ions obtained from $EtPSF_2$.

Mass found	Mass calc.	Ion
108.9677	108.9677	$C_2H_3PSF^+$
101.9514	101.9505	$HPSF_2^+$
82.9512	82.9521	$HPSF^+$
81.9433	81.9442	PSF^+
76.9956	76.9956	$C_2H_3PF^+$
69.9774	69.9784	HPF_2^+
63.0068	63.0070	$C_2H_5{}^{34}S^+$ *
62.9793	62.9800	$CHPF^+$ **
62.9704	62.9705	CSF^+ **
62.9453	62.9458	PS^+ *
61.0115	61.0112	$C_2H_5S^+$

* About equal intensities. ** Very low intensity

the reverse process by which the parent compound was initially prepared.) Although elimination can proceed with hydrogen migration to phosphorus or sulphur, both the ground-state stabilities and the work published on the mass spectra of dialkylphosphinic acids, R'_2PO_2H, [233] would tend to favour the former process (1a),



(1a)

(1b)

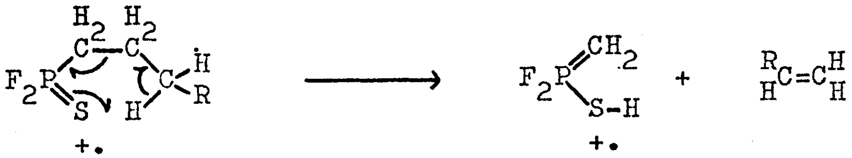
A metastable ion indicates that $(Pr^nPSF_2)^{+\cdot}$ can also eliminate a molecule of ethylene. This is visualized as proceeding with S-H bond formation, since similar processes have been envisaged

Table 3.4 Metastable transitions obtained for $RPSF_2$ ($R = Et, Pr^n$).

m_1	Transition				m_2	m^* calc.	m^* found
		$EtPSF_2$					
129	$C_2H_4PSF_2^+$	$\longrightarrow$	$C_2H_3PSF^{+\,\Delta}$	+ HF	109	92.1	92.1
102	$HPSF_2^{+\,\Delta}$	$\longrightarrow$	PF_2^+	+ HS	69	46.7	46.7
29	$C_2H_5^+$	$\longrightarrow$	$C_2H_3^+$	+ H_2	27	25.1	25.1
28	$C_2H_4^+$	$\longrightarrow$	$C_2H_2^+$	+ H_2	26	24.1	24.1
		Pr^nPSF_2					
144	$C_3H_7PSF_2^+$	$\longrightarrow$	$CH_3PSF_2^+$	+ C_2H_4	116	93.4	93.4
129	$C_2H_4PSF_2^+$	$\longrightarrow$	$C_2H_3PSF^+$	+ HF	109	92.1	92.1
43	$C_3H_7^+$	$\longrightarrow$	$C_3H_5^+$	+ H_2	41	39.1	39.1
41	$C_3H_5^+$	$\longrightarrow$	$C_3H_3^+$	+ H_2	39	37.1	37.1
39	$C_3H_3^+$	$\longrightarrow$	C_3H^+	+ H_2	37	35.1	35.1
75	$C_3H_7S^+$	$\longrightarrow$	CH_3S^+	+ C_2H_4	47	29.5	29.5 w
29	$C_2H_5^+$	$\longrightarrow$	$C_2H_3^+$	+ H_2	27	25.2	25.1
28	$C_2H_4^+$	$\longrightarrow$	$C_2H_2^+$	+ H_2	26	24.2	24.1
116	or { $CH_3PSF_2^+$	$\longrightarrow$	CH_3S^+	+ PF_2	47	19.0	19.1
41	$C_3H_5^+$	$\longrightarrow$	$C_2H_4^+$	+ CH	28	19.1	

$^{\Delta}$ Confirmed by mass measurement (Table 3.3).

in the break-down of some dialkyl alkylphosphonates, $R'PO(OR'')_2$, [234]; for R = H:-



(2a)

Table 3.5 Mass spectra of $RPSF_2$ (R = Et, Pr^n, Bu^n) (m/e value, relative abundance, ion - respectively).

$EtPSF_2$:

132, 4, $C_2H_5P^{34}SF_2^+$; 131, 3, $^{13}CCH_5PSF_2^+$; 130, 100, $C_2H_5PSF_2^+$; 129, 7, $C_2H_4PSF_2^+$; 115, 1, $CH_2PSF_2^+$; 111, 2, $C_2H_5PSF^+$; 109, 2, $C_2H_3PSF^{+\Delta}$; 104, 3, $HP^{34}SF_2^+$; 103, 3, $H_2PSF_2^+$, $P^{34}SF_2^+$; 102, 83, $HPSF_2^{+\Delta}$; 101, 9, PSF_2^+; 98, 2, $C_2H_5PF_2^+$; 97, 1, $C_2H_4PF_2^+$; 83, 2, $HPSF^{+\Delta}$; 82, 2, $PSF^{+\Delta}$; 77, 1, $C_2H_3PF^{+\Delta}$; 76, 2, $C_2H_2PF^+$; 70, tr, $HPF_2^{+\Delta}$; 69, 37, PF_2^+; 63, 2, $PS^{+\Delta}$, $C_2H_5{}^{34}S^{+\Delta}$, $CHPF^{+\Delta}$ (tr), $CSF^{+\Delta}$ (tr); 61, 12, $C_2H_5S^{+\Delta}$ (not $C_2H_6P^+$); 60, 1, $C_2H_4S^+$, $C_2H_5P^+$; 59, 4, $C_2H_3S^+$, $C_2H_4P^+$; 58, 2, $C_2H_2S^+$, $C_2H_3P^+$; 57, 1, C_2HS^+, $C_2H_2P^+$; 51, 1, HPF^+; 50, 2, PF^+; 46, 1, CH_2S^+, CH_3P^+; 45, 4, CHS^+, CH_2P^+; 44, 2, CHP^+; 43, 2, CP^+; 34, 1, $^{34}S^+$, H_2S^+; 32, 1, S^+; 29, 25, $C_2H_5^+$; 28, 11, $C_2H_4^+$; 27, 25, $C_2H_3^+$; 26, 4, $C_2H_2^+$; 20, 1, HF^+; 15, 1, CH_3^+.

Pr^nPSF_2 (Most prominent peaks with m/e > 44, only):

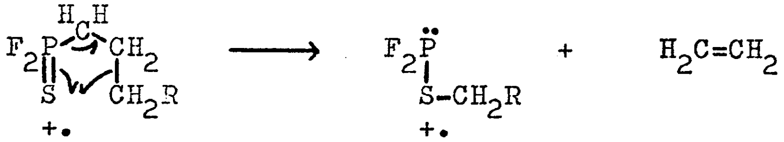
144, 67, $C_3H_7PSF_2^+$; 142, 3, $C_3H_5PSF_2^+$; 129, 6, $C_2H_4PSF_2^+$; 116, 44, $CH_3PSF_2^+$; 109, 2, $C_2H_3PSF^+$; 103, 3, $H_2PSF_2^+$, $P^{34}SF_2^+$, $C_3H_4PS^+$; 102, 7, $HPSF_2^+$; 101, 11, PSF_2^+; 75, 4, $C_3H_7S^+$; 69, 31, PF_2^+; 63, 2, PS^+; 59, 4, $C_2H_3S^+$, $C_2H_4P^+$; 47, 11, CH_3S^+; 46, 3, CH_2S^+, CH_3P^+; 45, 7, CHS^+, CH_2P^+.

Bu^nPSF_2 (Most prominent peaks with m/e > 50, only):

158, 80, $C_4H_9PSF_2^+$; 143, 2, $C_3H_6PSF_2^+$; 139, 1, $C_4H_9PSF^+$; 130, 3, $C_2H_5PSF_2^+$; 129, 8, $C_2H_4PSF_2^+$; 116, 100, $CH_3PSF_2^+$; 109, 3, $C_2H_3PSF^+$; 102, 9, $HPSF_2^+$; 101, 11, PSF_2^+; 84, 5, $CH_3PF_2^+$; 69, 24, PF_2^+; 59, 6, $C_2H_3S^+$, $C_2H_4P^+$; 57, 10, $C_4H_9^+$; 56, 87, $C_4H_8^+$; 55, 27, $C_4H_7^+$.

$^{\Delta}$ Confirmed by mass measurement (Table 3.3).

There is an alternative method available for this fragmentation mode which involves P-C bond cleavage and the formation of a trivalent phosphorus derivative:-

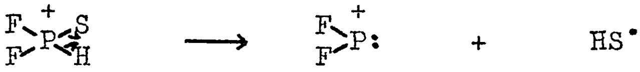


(2b)

If this mechanism is the favoured one, then elimination of $H_2C=CH_2$ rather than $RHC=CH_2$ (R = Me) from the molecular ion of Bu^nPSF_2 would be anticipated. The base peak in the mass spectrum of Bu^nPSF_2 in fact corresponds to elimination of propene from the molecular ion (no metastable ion is present to substantiate this fragmentation mechanism) and the peak at m/e = 130, due to the loss of ethylene from $[M]^+$ is of low intensity (this peak might in fact be largely derived from some $EtPSF_2$ impurity in the sample). The mechanism could be confirmed by preparing $D(C_3H_6)PSF_2$, since the former mode would lead to $RHC=CH_2$ elimination (R = D) and the latter mode C_2H_4 elimination.

There are no significant peaks in the mass spectra of $RPSF_2$ (R = Et, Pr^n, Bu^n) corresponding to the loss of $HS^\bullet$ from the molecular ion, which was shown (vide supra) to constitute a major break-down path for $MeNHPSF_2$. Both $EtPSF_2$ and $MeNHPSF_2$ produce intermediate ions $F_2(S)\overset{+\bullet}{P}-X-\overset{\bullet}{C}H_2$ (X = CH_2, NH). However, while it is possible to stabilize this ion by localizing the positive charge on X if X = NH, this cannot be achieved for X = CH_2. One might then expect that $HS^\bullet$ loss from the molecular ion for which

X = O would once again figure prominently in the compound's mass spectrum; the published spectrum of $MeOPSF_2$ bears this out [235]. A metastable ion does, however, show that $HPSF_2^{+}$, formed by the break-down of $EtPSF_2$, is able to lose $HS^{\cdot}$. This was also presumably an important route to PF_2^{+} in the mass spectrum of $HPSF_2$, although no metastable ion was observed for this transition [226],

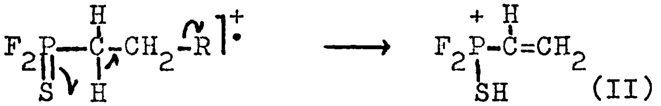


(3)

Metastable ions indicate that $C_2H_4PSF_2^{+}$, formed in the mass spectra of both $EtPSF_2$ and Pr^nPSF_2, can lose a molecule of HF. Both the parent and daughter ions also figure prominently in the mass spectrum of Bu^nPSF_2, which suggests that all three parent ions are formed by the same route, and would rule out a mechanism involving simple cleavage of an α-hydrogen atom to produce $C_2H_4PSF_2^{+}$ from $C_2H_5PSF_2^{+}$. This could be achieved through the straight cleavage of a bond attached to the β-carbon atom in the molecular ion,

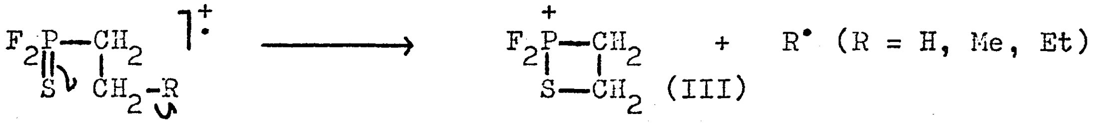
$$F_2(S)P\text{-}CH_2CH_2\text{-}R]^{+\cdot} \longrightarrow \underset{(I)}{F_2(S)P\text{-}CH_2\dot{C}H_2]^{+\cdot}} + R^{\cdot}\ (H,\ Me,\ Et) \qquad (4a)$$

or through cleavage of a bond attached to the β-carbon atom and accompanying migration of an α-hydrogen atom,



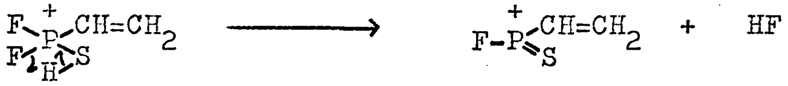
$$F_2P(S)\text{—}CH_2\text{-}CH_2\text{-}R]^{+\cdot} \longrightarrow \underset{(II)}{F_2\overset{+}{P}(SH)\text{-}CH{=}CH_2} + R^{\cdot}\ (H,\ Me,\ Et) \qquad (4b)$$

The latter process, which has been proposed to occur in the fragmentation of di-n-butyl-phosphinic acid [233], seems much more likely on account of the production of a less stable diradical, I, by route (4a). The production of a cyclic intermediate, III, cannot be ruled out,



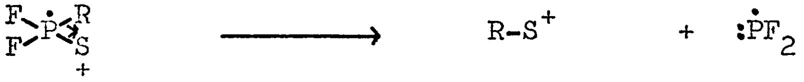
(4c)

II would probably eliminate a molecule of HF by breaking an S-H rather than a C-H bond,



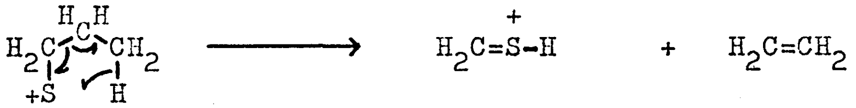
(5)

While migration of a hydrogen atom to sulphur almost certainly takes place in some of the above reactions, there is also some evidence for the similar migration of alkyl groups to sulphur. A mass measurement confirms that the prominent peak at m/e = 61 for $EtPSF_2$ is due to $C_2H_5S^+$. This is probably formed by the following process:-



(6)

Bond forming processes between sulphur atoms and species other than hydrogen have previously been reported [215]. A weak peak in the mass spectrum of Pr^nPSF_2 is thought to be a metastable ion corresponding to the loss of ethylene from the ion with m/e = 75:-



(7)

Mechanism for addition of $HPSF_2$ to alkenes.

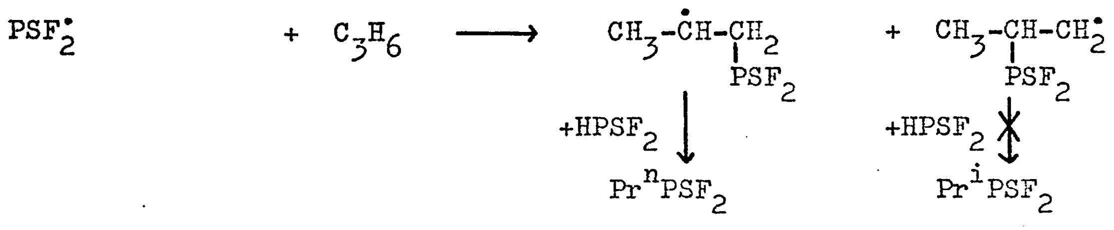
The U.V. photolysed addition of PH_3 to alkenes has previously been suggested to involve free radical formation, with the initiation process involving the attack of the phosphino radical formed on the alkene [236]. The same processes can be used to explain how the products isolated from the reaction between $HPSF_2$ and ethylene (as well as the other alkenes) are derived:-

$$\begin{array}{llcll}
HPSF_2 & & \xrightarrow{h\nu} & PSF_2^\bullet & + \; H^\bullet \\
PSF_2^\bullet & + \; C_2H_4 & \longrightarrow & PSF_2C_2H_4^\bullet & \\
PSF_2C_2H_4^\bullet & + \; HPSF_2 & \longrightarrow & \underline{EtPSF_2} & + \; PSF_2^\bullet \\
H^\bullet & + \; C_2H_4 & \longrightarrow & C_2H_5^\bullet & \\
C_2H_5^\bullet & + \; HPSF_2 & \longrightarrow & \underline{C_2H_6} & + \; PSF_2^\bullet \\
H^\bullet & + \; HPSF_2 & \longrightarrow & \underline{H_2} & + \; PSF_2^\bullet \\
PSF_2C_2H_4^\bullet & + \; nC_2H_4 & \longrightarrow & PSF_2(C_2H_4)_nC_2H_4^\bullet & \\
PSF_2(C_2H_4)_{n+1}^\bullet & + \; HPSF_2 & \longrightarrow & \underline{H(C_2H_4)_{n+1}PSF_2} & + \; PSF_2^\bullet
\end{array}$$

There is no evidence for the formation of $F_2(S)P\text{-}C_2H_4\text{-}P(S)F_2$ (analogous to the compound $H_2P\text{-}C_2F_4\text{-}PH_2$ formed from PH_3 and C_2F_4 [236]); i.e.

$$PSF_2C_2H_4^\bullet \; + \; PSF_2^\bullet \; \not\longrightarrow \; F_2(S)P\text{-}C_2H_4\text{-}P(S)F_2$$

$PSF_2^\bullet$ can add to propylene to produce two possible products:-



$$PSF_2^\bullet + C_3H_6 \longrightarrow \underset{\substack{\big\downarrow +HPSF_2 \\ Pr^nPSF_2}}{CH_3\text{-}\overset{\bullet}{C}H\text{-}\underset{PSF_2}{CH_2}} \; + \; \underset{\substack{\not\big\downarrow +HPSF_2 \\ Pr^iPSF_2}}{CH_3\text{-}\underset{PSF_2}{CH}\text{-}CH_2^\bullet}$$

The exclusive formation of Pr^nPSF_2 is in complete harmony with the recently reported photolytic reaction between dimethyl- and bis(trifluoromethyl)-phosphines and alkenes, which proceeded to give the product which was in accord with a free radical mechanism in which the phosphino radical attacked the olefin to give the most stable intermediate radical [237].

oOo

The addition of $HPSF_2$ to alkenes is illustrated to be a viable route to some alkylphosphonothioic difluorides. This method can obviously be extended to include the use of other known phosphorus-fluoride derivatives containing a P-H bond (e.g. $HPOF_2$, HPF_2 and HPF_4), and would probably also prove to be of greater use in the synthesis of perfluoro derivatives of phosphorus-fluorides. In a preliminary study, the photolysis of $HPSF_2$ with both C_2F_4 and C_3F_6 was briefly examined. Isolation of a pure product is hampered by the concurrent formation of volatile compounds produced by the photolysis of the perfluoroalkene. The reaction with C_3F_6 proceeds at a much slower rate than that with C_2F_4; the same difference in rates was observed in the corresponding reactions between these alkenes and PH_3 [236]. Both the ^1H and ^{19}F n.m.r. spectra show that the products formed include phosphorus derivatives containing partially fluorinated alkyl groups, but these were not further characterised.

A more interesting application of this reaction would involve the use of alkenes of the type CF_2=CF-PF_4 [238] and alkenes which are already co-ordinated to transition metals.

The reactions between alkenes and P-Cl or P-Br bonds.

While no evidence is obtained for the addition of the P-Cl bond in POF_2Cl to ethylene, the addition of the P-Br bond in POF_2Br to ethylene does take place to produce 2-bromoethylphosphonic difluoride, $BrC_2H_4POF_2$, along with 1,2-dibromoethane, ethylphosphonic difluoride and traces of ethane, 1,4-dibromobutane and ethyl phosphorodifluoridate, $EtOPOF_2$.

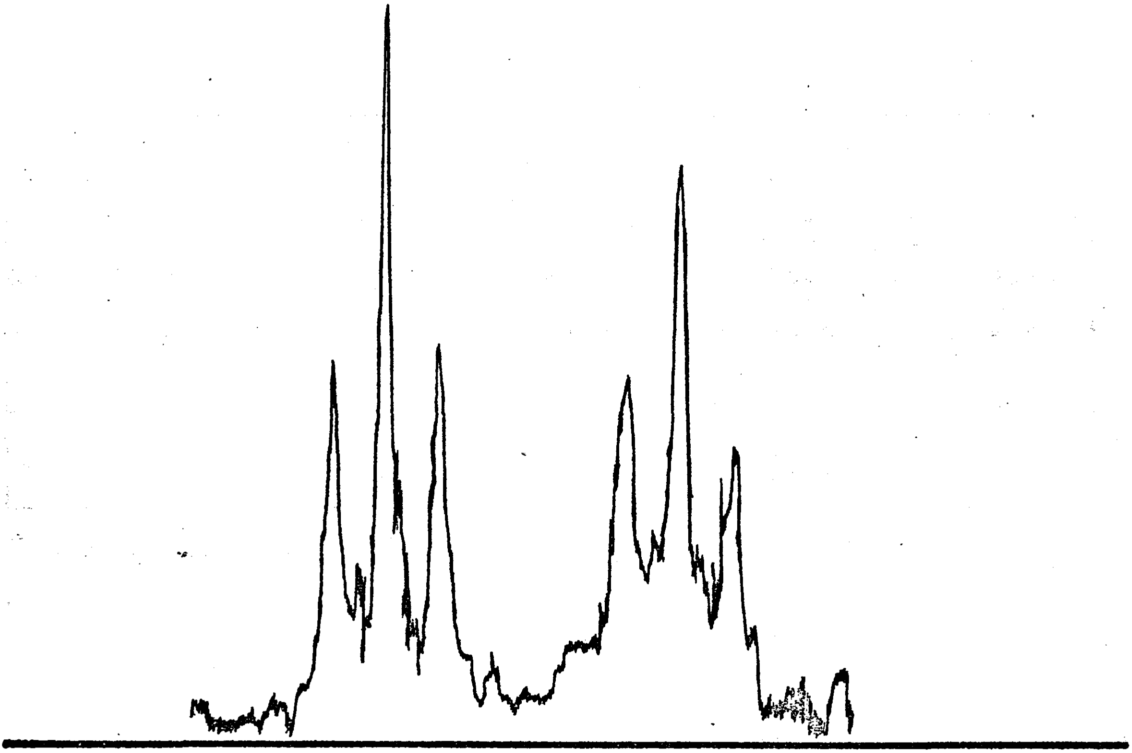
2-Bromoethylphosphonic difluoride is best characterised by means of its n.m.r. spectrum (Tables 3.6 and 3.7). The close proximity of the values of δ_{CH_α} and δ_{CH_β} produces a ^1H n.m.r. spectrum which, under high resolution, shows that each line is further split due to second order effects. In order to reduce the latter tendency, a n.m.r. spectrum was recorded on a 100 MHz machine. Fig. 3.2 reproduces the P-methylene resonance both when coupled to the CH_2Br group and when the latter coupling is removed by irradiating at the Br-methylene frequency. Second order effects render the evaluation of $J(FH_\beta)$ from the ^1H n.m.r. spectrum difficult, but this parameter is readily deduced from the ^{19}F n.m.r. spectrum. Table 3.7 lists the n.m.r. parameters for some closely related 2-chloroethyl derivatives of phosphorus [239]. While δ_{CH_β} is larger than δ_{CH_α}, the order expected in view of the electronegativity differences between the halogen and phosphorus atoms, the relative magnitudes of $J(PH_\alpha)$ and $J(PH_\beta)$ are more variable.

<u>Table 3.6</u> Products from photolysis of C_2H_4 and POF_2Br.

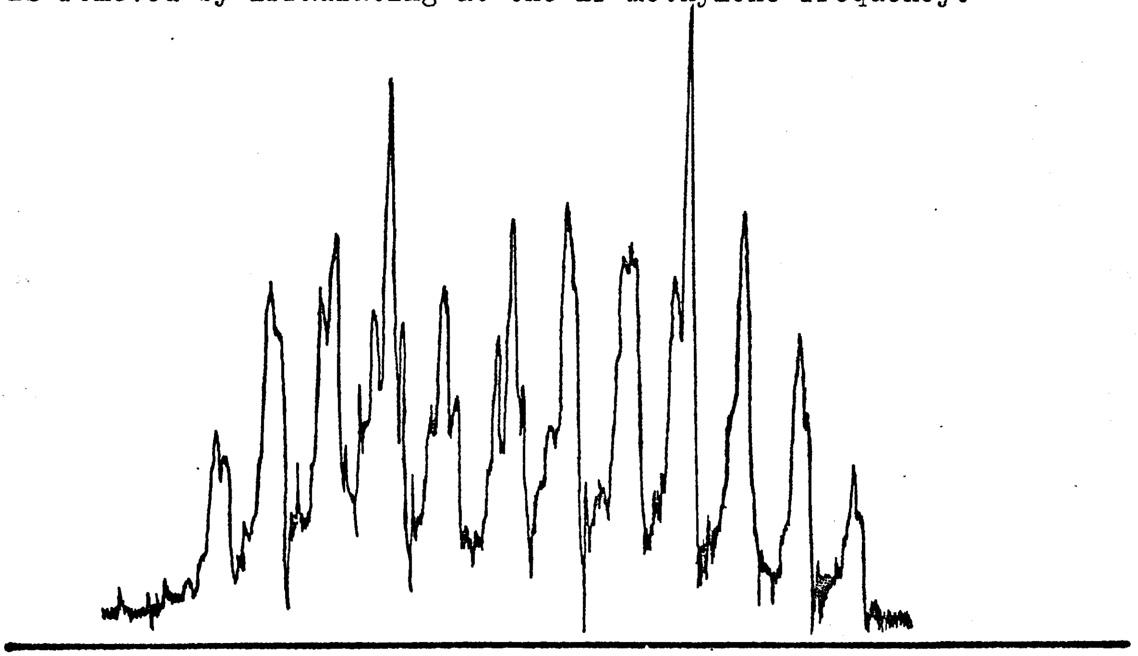
Compound		δ_F	$J(PF)$	δ_{CH_α}	δ_{CH_β}	$J(PH_\alpha)$
$EtPOF_2$	[240]	67 - 68.5	1120 - 1140			
	[104]					23.6
	found	68**	1128	-2.1**	-1.27**	a
$EtOPOF_2$	[240]	85 - 85.7	1009 - 1014			
	[191]	85.6	1012	-4.2	-1.13	10
	found	83**	997			
$BrCH_2CH_2POF_2$	found	64** dtt	1135	-2.73**	-3.59**	19.6^b
$BrCH_2CH_2Br$	[113]			-3.62 - -3.78		
	found			-3.63		

Compound		$J(PH_\beta)$	$J(FH_\alpha)$	$J(FH_\beta)$	$J(HH)$
$EtPOF_2$	[104]	23.6			
	found	24.0	4.2^f		7.5
$BrCH_2CH_2POF_2$	found	15.0^b	2.9^f , $3.6^{h,b}$	0.4^f	7.6

[a] Not measured. [b] Found from decoupling on 100 MHz machine. [f] Obtained from ^{19}F n.m.r..spectrum. [h] Obtained from ^1H n.m.r. spectrum.



<u>Fig 3.2</u> P-Methylene resonance in $BrCH_2CH_2POF_2$ in which H-H coupling is removed by irradiating at the Br-methylene frequency.



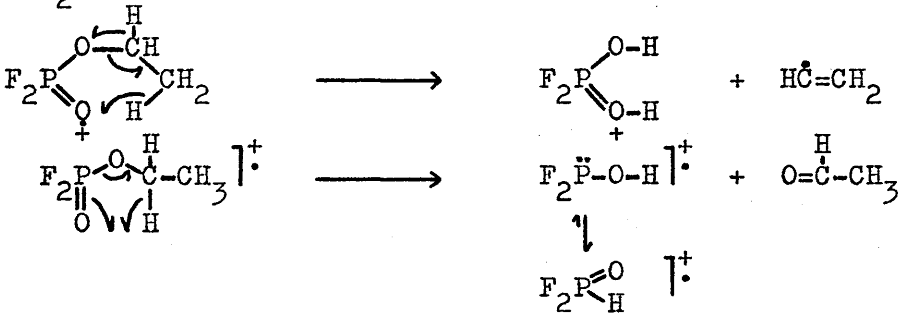
<u>Fig 3.2</u> P-Methylene resonance in $BrCH_2CH_2POF_2$ run on 100 MHz n.m.r. machine.

Table 3.7

Compound	δ_{CH_α}	δ_{CH_β}	$J(PH_\alpha)$	$J(PH_\beta)$
$ClCH_2CH_2POCl_2$ [a]	-3.12	-3.90	15.1	19.4
$ClCH_2CH_2PSCl_2$ [a]	-3.30	-3.92	13.5	13.5
$ClCH_2CH_2PCl_2$ [a]	-2.78	-3.83	17.0	8.5
$BrCH_2CH_2POF_2$ [b]	-2.73	-3.59	19.6	15.0
$HCH_2CH_2POF_2$ [b]	-2.1	-1.27	23.6	23.6

[a] See [239]. [b] See Table 3.6.

The ^{19}F n.m.r. spectrum of $EtPOF_2$ agrees with that previously published [240]. The appearance of the ^1H n.m.r. spectrum is similar to that observed for $EtPSF_2$, in that distortions are caused by second order effects. Ethyl phosphorodifluoridate is chiefly characterised by comparison of its ^{19}F n.m.r. parameters with those previously published [191,240]; due to the more intense signals of other species, its ^1H spectrum could not be detected. A mass spectrum of a sample slightly more volatile than one giving a mass spectrum predominantly showing evidence for $EtPOF_2$ (b.p. $EtPOF_2$, 91° [1]; b.p. $EtOPOF_2$, 80 - 89° [1]) indicates major peaks which are assigned to PO^+, POF^+, $HPOF_2^+$, $PO_2F_2^+$ and $H_2PO_2F_2^+$ (in addition to those arising from $EtPOF_2$). While there is no peak at m/e = 130, corresponding to $[M]^+$, these peaks are believed to be derived from $EtOPOF_2$. A weak peak at m/e = 111 may be derived from $[M-F]^+$. The mass spectrum of triethyl phosphate, $(EtO)_3PO$, has been studied [241], and rearrangement ions were found to predominate. Metastable ions showed that prominent peaks resulted from the loss of $C_2H_3^{\bullet}$ and C_2H_4O from $[(EtO)_3PO]^+$. In the present work, the same processes for $EtOPOF_2$ would produce $H_2PO_2F_2^+$ and $HPOF_2^+$ respectively:-



(8)

(9)

The mass spectrum of diethyl phosphorochloridate, $(EtO)_2POCl$, also showed a metastable ion corresponding to loss of $C_2H_3^{\bullet}$ from its molecular ion; the ions $[M]^+$ and $[M-Cl]^+$ were only present in very low abundance [242].

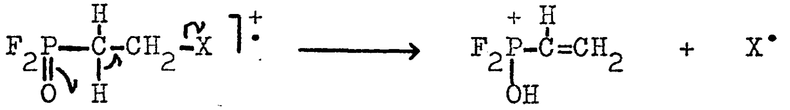
The P=O and two PF_2 stretching modes have previously been assigned to very strong peaks present in a liquid film sample of $EtPOF_2$ at 1328, 930 and 916 cm.$^{-1}$ respectively [199]. In this work, a gaseous sample of $EtPOF_2$ gave strong peaks in these two regions at 1355 and 895 (complex) cm.$^{-1}$ respectively. A similar increase in $\nu_{P=O}$ on going from the liquid to the gaseous phase is also noted for $BrCH_2CH_2POF_2$ (see experimental section). The peak at 566 cm.$^{-1}$ is the only one that lies in the expected range for ν_{C-Br} [127,243]. The complete analysis of the i.r. spectrum of

$BrCH_2CH_2POF_2$ is likely to prove difficult, since that for $ClCH_2CH_2POCl_2$ indicated that at least three conformers were present [244].

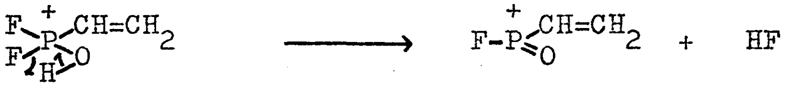
The isotope abundance of bromine (^{79}Br, 50.5%; ^{81}Br, 49.5%) acts as a distinctive tag for ions containing this atom. The intense peaks at m/e = 192, 194 in the mass spectrum of $BrCH_2CH_2POF_2$, therefore, conclusively confirm the existence of the molecular ion. The only other bromine containing ions present are $C_2H_3Br^+$ and $C_2H_4Br^+$. The intense peaks at m/e = 135, 137 and weak ones at m/e = 214, 216, and 218 due to $C_4H_8Br^+$ and $C_4H_8Br_2^+$ respectively are thought to be derived from $C_4H_8Br_2$; the mass spectrum for 1,4-dibromobutane has been published [245], and the former ion constituted the base peak for this compound.

The mass spectrum of $EtPOF_2$, which does not appear to have been published previously, and $BrCH_2CH_2POF_2$ are very similar. While weak peaks due to PO^+ and POF^+ are observed, more intense peaks are found for PF_2^+, POF_2^+, $HPOF^+$, $HPOF_2^+$, and $H_2POF_2^+$. The prevalence of these ions containing hydrogen atoms indicates the importance of pathways which involve the elimination of alkenes in the break-down of phosphonic difluorides. Neither spectrum shows any tendency to produce $[M-F]^+$, $[M-CH_3]^+$ or $[M-O]^+$.

Metastable ions are observed for loss of $H^\bullet$ from $EtPOF_2$, which only possesses a weak molecular ion in contrast to that found in the mass spectrum of $BrC_2H_4POF_2$, (m* found, 112.0; m* calc., 112.1) and for loss of $Br^\bullet$ from $BrC_2H_4POF_2$ (m* found, ~66 (this is very broad); m* calc., 65.8 and 66.5). Both the daughter ions produced constitute the base peaks of the respective spectra, and are assumed to be formed in the same manner (cf. equation 4b):-


(X = H, Br)

The only other metastable ion registered for either compound (high pressures were not used to produce these mass spectra, and other metastable ions might well be present) is that involving HF elimination from the ion with m/e = 113 for $BrC_2H_4POF_2$ (m* found, 76.6; m* calc., 76.5) (cf. equation 5):-



A similar fragmentation pattern is not favoured for the same ion produced from $EtPOF_2$. The only other phosphorus containing ion of any significance is $CH_3POF_2^+$, presumably with the structure $F_2(H\overset{+}{O})P{=}CH_2$, which is present in both spectra.

Mechanism for addition of POF_2Br to ethylene.

Few straight photolysis reactions aimed at directly adding a phosphorus-halide to an alkene have been attempted in the absence of oxygen [221]. Only one of the P-Br bonds in PBr_3 added across a C=C bond when subjected to the influence of U.V. light or an increased temperature; both processes were assumed to be initiated by the fission of a P-Br bond to produce two radicals [246].

Presumably the initial step in the reaction of POF_2Br with ethylene also involves the production of two radicals:-

$$F_2(O)P\text{-}X \xrightarrow{h\nu} F_2(O)P^{\bullet} + X^{\bullet}$$

It appears that, under the reaction conditions employed, this step is favoured where X = Br but not where X = Cl or F. The different reactivity of the phosphorus-halides probably has as its source the different values of the P-X bond energy; for PX_3, the bond energies decrease in the order:-

$$P\text{-}F\ (117) > P\text{-}Cl\ (76) > P\text{-}Br\ (62)$$

Depending on their reactivity, either the bromine atom or the difluorophosphoryl radical produced can then react with a molecule of ethylene. In the reaction between unsymmetrical alkenes and PBr_3, the product distribution was taken as evidence for the greater reactivity of the halogen atom [246]. The reactions between SF_5Cl and olefins , which have been the subject of more critical research [247], likewise indicate the greater reactivity of the halogen atom. In the present work the reaction of C_2H_4 with both $POF_2^{\bullet}$ and $Br^{\bullet}$ ultimately gives the same product, so it is not possible to draw any conclusion about the activity of the difluorophosphoryl radical.

Bromophosphoryl difluoride has previously been photolysed in the presence of mercury [166] to give difluorophosphoryl-μ-oxo-difluorophosphine:-

$$Hg + 2\ POF_2Br \xrightarrow{h\nu} F_2\ddot{P}\text{-}O\text{-}P(O)F_2 + HgBr_2$$

The product can be regarded as resulting from the combination of

$F_2\ddot{P}{-}O^\bullet$ and $^\bullet P(O)F_2$. Since no evidence is found for a trivalent phosphorus derivative, $BrC_2H_4OPF_2$, in the present work, the latter radical can be regarded as the more stable species.

Both 1,2-dibromoethane and 1,4-dibromobutane are probably derived by means of the following processes:-

$$Br^\bullet + C_2H_4 \longrightarrow BrC_2H_4^\bullet \xrightarrow{C_2H_4} Br(C_2H_4)_2^\bullet$$

$$Br(C_2H_4)_n^\bullet + POF_2Br \longrightarrow Br(C_2H_4)_nBr \quad (n = 1,\ 2) \quad + \quad POF_2^\bullet$$

Telomers, $Br(C_2H_4)_nPOF_2$, presumably constitute part of the involatile product which was not characterised.

The origin of both $EtPOF_2$ and $EtOPOF_2$ is uncertain. Difluorophosphoryl-μ-oxo-difluorophosphine would be expected to be a probable by-product in this reaction (with C_2H_4 playing the same role as did mercury in the original reaction) but was not found among the products. This compound is, however, found to be extremely sensitive to traces of water, and has been shown to decompose by way of both $HPOF_2$ and $HOPOF_2$ [166]. Addition of these compounds to ethylene would produce $EtPOF_2$ and $EtOPOF_2$ respectively.

oOo

In order to correctly identify the small amounts of products formed in these photolysis reactions, extensive use should be made of gas phase chromatography to separate the products and mass spectrometric techniques to characterise the individual components.

EXPERIMENTAL

Practical techniques employed in the preparation and characterisation of compounds dealt with in this section are discussed in Appendix 1.

Tables 1.18, 2.13 and 3.8 list the i.r., n.m.r. and mass spectra references for both the starting materials and those products identified by these techniques.

Reactions between phosphorus-fluorides and alkenes.- These are listed below:-

Reactants	Conditions	Period	Results
PF_5, C_2H_4 (1:1)	120°, bomb	8 hours	No reaction.
PF_5, C_3F_6, CsF	150°, pyrex	3 days	No reaction.
PF_5, C_4F_6 (1:1)	120°, bomb	12 hours	No reaction.
PF_5, C_4F_6, CsF	170°, bomb	1 week	No reaction.
PF_3, C_3F_6, CsF	150°, bomb	1 week	Dimer + traces. trimer (i.r. + m.s.).
PF_3, C_3F_6 (~1 atmos.)	hν, quartz	3 days	Trace brown oil.
PSF_3, C_2H_4 (~1 atmos.; 1:1)	hν, quartz	8 hours	Traces $EtPSF_2$ (i.r. + m.s.) + Et_2S (m.s.).

Self-photolysis of alkenes.- The following reactions were undertaken to establish the extent to which side products were

Table 3.8

COMPOUND	SOURCE	I.R.	N.M.R.	M.S.
$HPSF_2$	Me_2NPSF_2/HI (a)	(a)	(a)	(a)
$HPOF_2$		(a)	(a)	(a)
C_2H_4	Matheson Co. C.P. (b)	(c)		
C_3H_6	Matheson Co. C.P. (b)	(c)		
$F_3C-CF=CF_2$	Pierce Chemical Co.	(d)		
$F_3C-C\equiv C-CF_3$	Peninsular Chemresearch	(e)		
$(C_3F_6)_2$		(f)	(f)	
$(C_3F_6)_3$		(g)		
$H-C\equiv C-H$		(c)		
C_2H_6		(c)		
PSF_3	$PSCl_3$/NaF/Sulpholane (h)	(i)	(j)	(k)
Et_2S		(l)	(m)	(n)
$EtPSF_2$		(o)	(o)	
$EtPOF_2$		(p)	(q,r)	
$EtOPOF_2$			(r,s)	
$C_2H_4Br_2$		(t)	(m)	(u)
$C_4H_8Br_2$		(t)		(u)
CsF	Ozark-Mahoning			
$CDCl_3$	C.I.B.A.			

(a) [226]. (b) See "Matheson Gas Data Book" for stated purity. (c) [112]. (d) J.R. Nielsen, H.H. Claassen and D.C. Smith, J. Chem. Phys., 1952, 20, 1916. (e) R.N. Haszeldine, J. Chem. Soc., likely to be formed:-

Alkene	Period	Results
C_2H_4	16 hours	A small quantity of yellow liquid (i.r. showed peaks in ν_{CH} and δ_{CH} regions), H_2, C_2H_2 (i.r.) and a very small amount of a less volatile portion were formed. Hg ($^3P_1$) irradiation has previously been shown to give H_2, C_2H_2 and butylene [248].
C_3H_6	3 days	A small amount of product other than C_3H_6 but no polymeric material were formed. The former was identified as C_2H_2 together with hydrocarbons containing C=C bonds (i.r.). Hg ($^3P_1$) irradiation gave allene, C_2H_2, 1,5-hexadiene and liquid polymers [248].

Self-photolysis of $HPSF_2$.- After irradiating a gaseous sample of $HPSF_2$ for two days in a quartz vessel, a small amount of

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1952, 2504. (f) [223]. (g) [224]. (h) C.W. Tullock and D.D. Coffman, J. Org. Chem., 1960, 25, 2016. (i) [210]. (j) A. Müller, E. Niecke and B. Krebs, Mol. Phys., 1968, 14, 591. (k) [143]. (l) G. Blyholder and D.O. Bowen, J. Phys. Chem., 1962, 66, 1288. (m) [113]. (n) E.J. Levy and W.A. Stahl, Analyt. Chem., 1961, 33, 707. (o) [209]. (p) [199]. (q) [104]. (r) [240]. (s) [191]. (t) [243]. (u) [245].

involatile liquid and some yellowish solid products were recovered along with some non-condensable gas. Fractionation of the volatile material indicated that the bulk of the material was unchanged $HPSF_2$ which was contaminated with a small quantity of SiF_4, PSF_3 and PF_3 together with a trace of POF_3 and $HPOF_2$ (both are impurities in the starting material), which were all identified by their i.r. spectra.

Photolysis of hydrophosphoryl difluoride and ethylene.- A vapour phase mixture of $HPSF_2$ (0.388 g., 3.81 mmoles) and C_2H_4 (0.480 g., 17.1 mmoles) was irradiated in a quartz reaction vessel for two days. On opening up the tube, a small amount of non-condensable gas was found. Fractional distillation of the volatile components produced excess ethylene (0.377 g., 13.5 mmoles) and a mixture of volatile components, shown by i.r. to be free from $HPSF_2$; 0.053 g. of an involatile liquid was left in the reaction vessel (and was later examined by n.m.r.). The less volatile components were identified as ethylphosphonothioic difluoride [M found (vapour density), 130; M calc., 130], which passed through a -60° trap, and the less volatile n-BUTYLPHOSPHONOTHIOIC DIFLUORIDE [Found: C, 30.2; H, 5.5; F, 24.1; P, 19.5; S, 20.2%; M (mass spec.), 158. Calc.: C, 30.4; H, 5.7; F, 24.1; P, 19.6; S, 20.2%; M, 158. V.p. 5.2 mm. Hg at 25°], which passed a -30° trap.

Photolysis of a 1:1 mixture of $HPSF_2$ and C_2H_4 over a five hour period removed the majority of the ethylene but left a considerable amount of unreacted $HPSF_2$. In addition to $EtPSF_2$ and Bu^nPSF_2, infra-red spectroscopy was used to identify traces of PF_3, SiF_4, PSF_3 and POF_3 along with some C_2H_6. The quantity of C_2H_6 recovered was considerably greater than would be expected if it were derived solely from an impurity originating in the ethylene.

Photolysis of mixtures of $HPSF_2$ and C_2H_4 in pyrex reaction vessels produced no reaction.

The main peaks in the i.r. spectrum of Bu^nPSF_2 (g) are as follows (cm.$^{-1}$): 2975 m, 2945 m sh, 2882 w, 1469 w, 1410 vw, 1360 vw, 1228 vw, 1096 vw, 1054 w, 919 vs, 884 s, 835 m, 814 w, 770 w, 679 vw, 648 w, 434 w.

Thermal reaction between hydrophosphoryl difluoride and ethylene.- A 1:3 mixture of $HPSF_2$ and C_2H_4 was heated for ten hours at 80° in a pyrex vessel. A small amount of white solid was formed, but the majority of the starting material was recovered. A trace of $EtPSF_2$ was identified by its i.r. spectrum.

Photolysis of hydrophosphoryl difluoride and propylene.- A 1:1 gas phase mixture of C_3H_6 and $HPSF_2$ was irradiated for 30 hours in a quartz reaction vessel. After removing the volatile materials, a small amount of involatile liquid and some solid were left in the vessel. The volatile material was fractionated to give C_3H_6 and traces of PSF_3 and PF_3 (passed a -126° trap) together with unreacted $HPSF_2$ and a trace of POF_3 (passed -86°

trap) and a fraction which passed a -44° bath but was trapped in a -64° bath. The latter was identified as n-PROPYLPHOSPHONOTHIOIC DIFLUORIDE [Found: M (mass spec.), 144; C, 24.9; H, 4.3; F, 26.2; P, 21.3; S, 22.1%. Calc.: M, 144, C, 25.0; H, 4.9; F, 26.4; P, 21.5; S, 22.2%. V.p. 23mm. Hg at 25°]. The main peaks in the i.r. spectrum of $Pr^{n}PSF_2$ (g) are as follows ($cm.^{-1}$):- 2980 m; 2946 w; 2921 vw; 2891 w; 1469 vw; 1410 vw; 1353 vw; 1244 vw; 1084 w; 1044 w; 907 vs; 883 s; 839 m; 813 m; 768 w; 682 vw; 650 vw; 446 w.

Photolysis of chlorophosphoryl difluoride and ethylene.- An equimolar mixture of C_2H_4 and POF_2Cl (total pressure ~2 atmospheres) was irradiated for nine days in a quartz vessel. A thin brownish yellow film, but no liquid, was formed on the inside of the reaction vessel. On opening the latter, a small amount of non-condensable gas was recovered. All the volatile components passed a -45° trap, and i.r. spectroscopy indicated trace amounts of acetylene and phosphoryl fluoride to be present along with the original starting material.

Photolysis of bromophosphoryl difluoride and ethylene.- A gaseous mixture, composed of equimolar quantities of C_2H_4 and POF_2Br (total pressure 82 cm. Hg), was irradiated for one week in a quartz reaction vessel. On opening the latter, no non-condensable gas was recovered. The volatile fractions were removed to leave a quantity of involatile liquid in the bottom of the vessel. The former were then separated by fractional distillation. The more volatile components (passing a -86° trap) were identified by i.r. as POF_2Br and a trace of C_2H_6. The majority of the remaining material passed a 0° bath but was trapped at -23°; it was characterised as 2-BROMOETHYLPHOSPHONIC DIFLUORIDE contaminated with 1,2-dibromoethane (i.r. and mass spec.) and 1,4-dibromobutane (mass spec.). The small amount of material that passed was examined by n.m.r.; peaks corresponding to $C_2H_4Br_2$, $EtPOF_2$ and $EtOPOF_2$ were identified. The n.m.r. tube was broken open under vacuum and the compounds examined by i.r. and mass spectroscopy; these were identified as $C_2H_4Br_2$ (trapped at -45°), $EtPOF_2$ and a trace of $C_2H_4Br_2$ (trapped at -65°), and $EtOPOF_2$ and $EtPOF_2$ (passed -65° bath).

The most prominent peaks in the i.r. spectrum of $BrC_2H_4POF_2$ (1) are as follows ($cm.^{-1}$): 3030 vw; 2963 w; 2922 w; 1442 w; 1395 w; 1334 vs (1360 in gas phase; $\nu_{P=O}$); 1293 s; 1269 s; 1177 w; 1111 w; 1020 m; 905 vs br and 888 vs (ν_{PF_2}); 768 w; 710 w; 566 w (ν_{CBr}); 499 m; 486 s; 426 m; 408 m.

APPENDIX 1.

Apparatus and methods commonly used for the manipulation of air sensitive compounds were used throughout [249]. The majority of the work was performed in a pyrex vacuum line. Gas phase reactions were carried out in a system similar to that employed for the preparation of fluorophosphoranes [131], except that the greased stopcocks were replaced by teflon stopcocks and the two bulbs were connected by a single stopcock; this ensured that gases with pressures in excess of one atmosphere could be handled. Liquid phase reactions were invariably carried out in a pyrex ampoule fitted with a high pressure teflon stopcock. Involatile liquids and solids were handled in a dry box. Molecular weights were determined by the vapour density method.

Ultra-violet photolysis reactions were carried out using a Hanovia U.V. lamp employing a 100 watt medium pressure arc tube. The range over which this emitted ultra-violet light is given below:-

Wavelength (mμ)	Energy (kcal./mole)	% Light emitted
1367.3 - 404.5	20.9 - 70.7	47.1
404.5	70.7	7.5
366.0	78.1	16.4
313.0	91.3	9.2
296.7	96.3	3.3
265.2	107.9	2.6
253.7	112.5	2.2

Wavelength limits [248] show that pyrex does not transmit light efficiently below about 350 mμ while silica remains fairly transparent down to ~200 mμ.

Elemental analyses were performed by Bernhardt or Beller.

N.m.r. spectra, both at room and other temperatures, were recorded on a Perkin-Elmer R. 10 spectrometer operating at 60 MHz for ^{1}H, 56.4 MHz for ^{19}F and 24.3 MHz for ^{31}P n.m.r. spectra. The nuclear magnetic double resonance spectrum was recorded on a Varian Associates 100 MHz HA 100 spectrometer. References employed throughout were trichlorofluoromethane for fluorine spectra, tetramethylsilane for proton spectra, and 85% phosphoric acid (always external) for phosphorus spectra. Due to the lack of a standard reference for fluorine spectra, literature values have been amended, where necessary, to give the chemical shift with respect to CCl_3F. The following conversion factors were employed (all chemical shifts quoted in p.p.m.) [104]:-

$$\begin{aligned}\delta_F\ (CCl_3F) &= \delta_F\ (CF_3COOH) + 77.5\\ &= \delta_F\ (C_6H_5CF_3) + 63.8\\ &= \delta_F\ (F_2) - 430\end{aligned}$$

The following abbreviations have been used in the text: *, external standard; **, internal standard; n.o., not observed; n.r., not resolvable; br, broad; comp., complex; s, singlet; d, doublet; t, triplet; q, quartet; p, quintet; x, sextet; y, septet; z, octet.

Infra-red spectra of gases were recorded in 5 or 10 cm.

gas cells fitted with KBr windows. Solid spectra were taken as nujol or fluorolube mulls using KBr or CsI plates. All spectra were recorded on Perkin-Elmer 225, 237 or 457 spectrophotometers. The following abbreviations have been used in the text: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very; sym., symmetric; as., asymmetric; δ, angle deformation; ρ, rocking; w, wag; ν, stretch.

Mass spectra were recorded at 70 eV using an A.E.I. M.S. 12 or an A.E.I. M.S. 9 spectrometer; mass measurements were performed on the latter machine. Conventions used in depicting fragmentation processes are those used by Budzikiewicz et al. [142].

APPENDIX 2.

Bond energy data.

Compound	Bond Energy (kcal./mole)		Bond	Reference
PF_3	117		P-F	[250]
PCl_3	76		P-Cl	[250]
PBr_3	62		P-Br	[250]
PH_3	77		P-H	[250]
PF_5	109		P-F	[251]
PCl_5	83	av. = 63	$P-Cl_e$	[250]
	34		$P-Cl_a$	[250]
POF_3	130		P=O	[250]
$POCl_3$	128		P=O	[250]
$(Et_2N)_3P$	67	av. = 75	P-N	[250]
$(Me_2N)_3P$	70		P-N	[250]
$(PhNH)_2P(O)Me$	82		P-N	[250]
$Ph_3P=NEt$	125		P=N	[188]
$Me_3P=NEt$	99		P=N	[188]
BF_3	154		B-F	[175]
CF_4	117		C-F	[175]
SF_6	79		S-F	[175]
SiF_4	143		Si-F	[175]
F_2	38		F-F	[175]
HF	136		H-F	[175]
HCl	103		H-Cl	[175]
$SiCl_4$	96		Si-Cl	[175]
SCl_2	65		S-Cl	[175]
$(Me_3Si)_2NH$	77		Si-N	[188]
Me_3SiNEt_2	74		Si-N	[188]
$(Me_2SiNH)_4$	82		Si-N	[188]
Organic	73		C-N	[175]
Organic	99		C-H	[175]
Organic	83		C-C	[175]

Compound	Bond Energy (kcal./mole)		Bond	Reference
NH_3	103	av. = 94	N-H	[252]
$MeNH_2$	92		N-H	[252]
Me_2NH	86		N-H	[252]

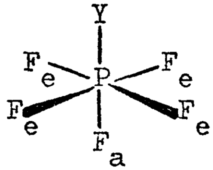
Ionization Potentials [149], Electron Affinities [149] and Electronegativities [110].

Atom	I.P. (eV)	E.A. (eV)	x
Fluorine	17.418	3.58	3.98
Chlorine	13.01	3.76	3.16
Oxygen	13.614		3.44
Sulphur	10.357		2.58
Nitrogen	14.53		3.04
Phosphorus	10.484		2.19
Carbon	11.256		2.55
Hydrogen	13.595		2.20

APPENDIX 3.

Analysis of AB_4X spin system.

Both alkylamine-phosphorus pentafluoride adducts, $RNH_2.PF_5$, and alkylpentafluorophosphate anions, $(RPF_5)^-$, are examples of compounds containing phosphorus co-ordinated to two different kinds of fluorine atoms, for the axial fluorine atom, F_a, opposite the substituted entity is both stereochemically and magnetically distinct from the remaining four equatorial fluorine atoms, F_e.

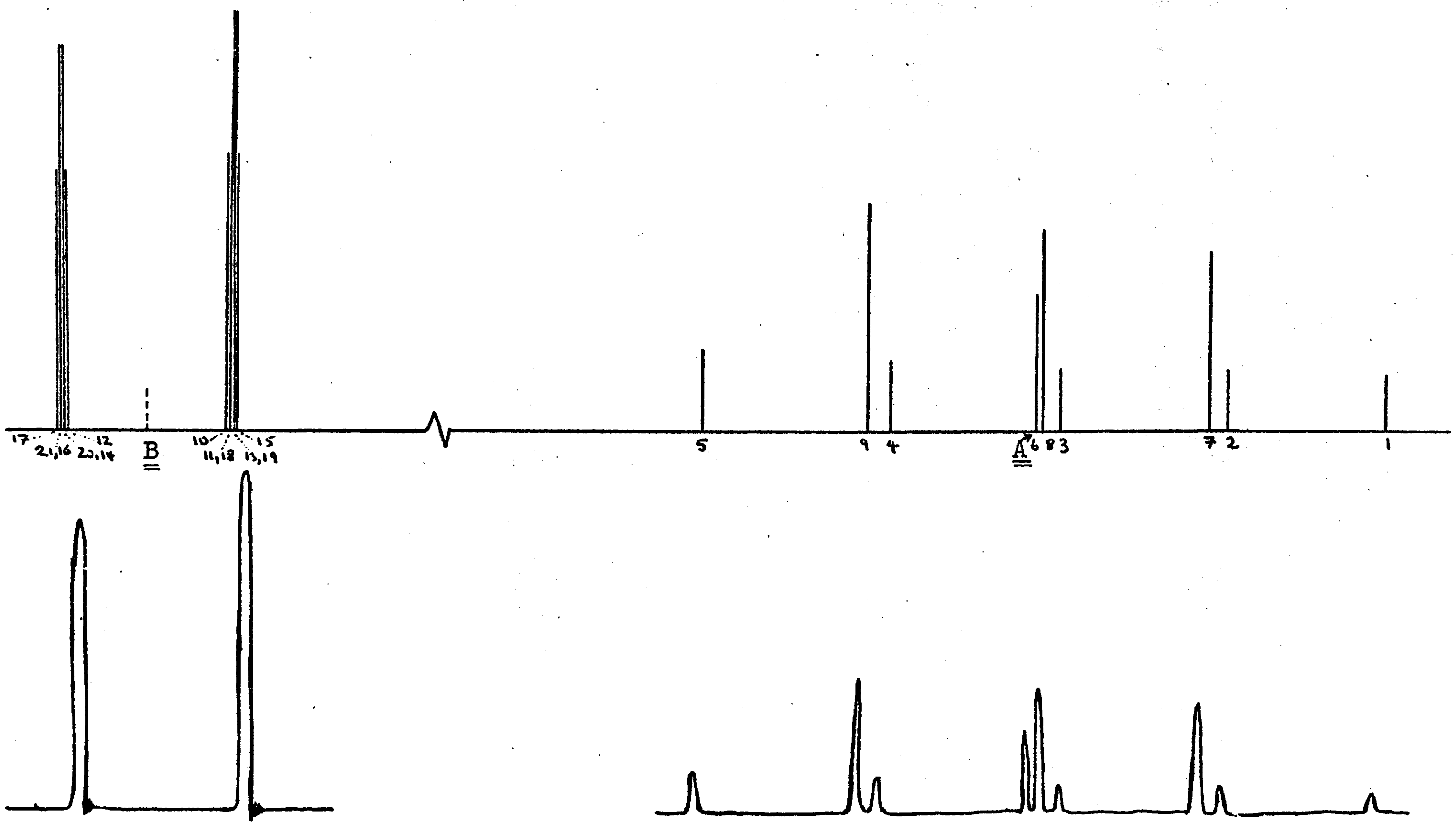


The appearance of the ^{19}F n.m.r. spectrum for the related groups, SF_5 [111,253] and TeF_5 [144], is characteristic of the AB_4 spin system and depends only on the coupling constant, J, and the chemical shift difference, $\nu_o\delta$ (in c/s), between the F_a and F_e atoms. When $J/\nu_o\delta$ is small, the spectrum approaches that of the first order AX_4 system. At intermediate values, the number of lines increases and the spectrum becomes more complex, while the spectrum once again becomes simpler for large values of $J/\nu_o\delta$. The analysis given by Emsley et al. [104] for the AB_4 system showed that there are eighteen spin wave functions giving rise to a maximum of twenty-five lines, comprising nine lines due to F_a, twelve lines due to F_e and four combination lines (which are always weak). Using their notation, line number 6 is at the unshifted resonance of the A nucleus (which is taken as the origin), while the lines 11 and 12, 13 and 14, 15 and 16, and 19 and 20 are symmetrically placed about the resonance position of the B nuclei. (For numbering system used, see the accompanying figure.) If the experimentally obtained spectrum is compared with several theoretical spectra obtained for different $J/\nu_o\delta$ values, it is possible to assign appropriate line numbers to each band, locate the resonance positions of both sets of fluorine nuclei, and hence determine a value for $\nu_o\delta$. If E_i denotes the position of the i^{th} line from the origin, then the coupling constant is given by several equations of the type:-

$$5\ J = E_5 + E_{17} - (E_1 + E_{10})$$

Note that the analysis does not reveal the absolute sign of J. For more accurate values of J and $\nu_o\delta$, the services of a computer are required.

Replacement of sulphur or tellurium by phosphorus produces a six spin system, AB_4X (where X is phosphorus), which results in perturbations of the resonance frequencies of the five fluorine atoms. It has been shown [253] that in simple cases, such as that concerning pentafluorosulphur fluorosulphate, SF_5OSO_2F, this led to a first order splitting of each line in the AB_4 spectrum. However, the ^{19}F spectrum of the phenylpentafluorophosphate anion resembles that of two AB_4 systems which possess slightly different values for $J/\nu_o\delta$ [254]. While the full



Theoretical spectrum calculated for $J/\nu_o\delta = 0.05$ and observed spectrum for an acetonitrile solution of $2MeNH_2.PF_5$ ($J/\nu_o\delta$ calc. = 0.06).

analysis given by the authors is desirable, the simple analysis outlined above on each component AB_4 system can be shown to give satisfactory values for J and $\nu_o\delta$. The significance of this greater accuracy is somewhat dubious in view of the fact that $\nu_o\delta$ is both concentration and solvent dependent.

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