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A study of the reactions between halamines and varieties of phosphorus species

Khabbass, Nabil Deeb A. H.

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A STUDY OF THE REACTIONS BETWEEN

HALAMINES AND VARIETIES OF PHOSPHORUS SPECIES

by

NABIL DEEB. A.H. KHABBASS,

B.Sc. Kuwait University

M.Sc. Dunelm Graduate Society

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of Durham

July 1981

To My Parents

with all the love in the world

ACKNOWLEDGEMENTS

PREFACE

The work described in this thesis is original, except in those portions where it is specifically stated to the contrary. It has not been submitted, either wholly, or in part, for a degree at this, or at any other university.

Nabil D. Khabbass

Abstract

In this work the oxidation of various low-valent phosphorus species with halomines and halogens has been studied. ^{31}P nuclear magnetic resonance spectroscopy has been used to follow the reactions, and the pairwise additivity rule has been tested to determine if it is possible to predict the chemical shifts of the new species prepared.

The reaction of Me_2NX (X = Cl or Br) with a number of phosphorus(III) species produced the phosphonium salt of the corresponding halide by simple amination at the phosphorus atom. This reaction occurred for $(Me_2N)_nPX_{(3-n)}$, (X = F, Cl, Br and n = 1, 2) except for Me_2NPF_2; for $Ph_nPR_{(3-n)}$ (R = Me, C_6H_{11}, Me_2N, and n = 0-3) except for $(Me_2N)_3P$; and for the species Me_2PCl, $MePCl_2$, $(C_6H_{11})_2PCl$ and Bu_3^nP.

The fluorine containing phosphorus species studied, where there was more than one fluorine on the phosphorus (PF_3 and Me_2NPF_2), gave more complex reactions which probably occurred due to rearrangement of the intially formed phosphorus(V) species. The overall stoichiometery of one such reaction was found to be:

$$2Me_2NPF_2 + 3Me_2NBr = [(Me_2N)_3PF]Br + (Me_2N)_2PF_3 + Br_2$$
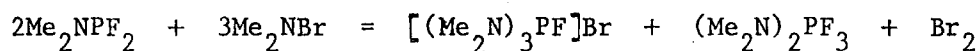
In the case of $(Me_2N)_3P$ halogenation was found to occur with formation of tetramethylhydrazene.

Reaction of dimethylchloramine and dimethyl bromamine with phosphorus(III) species containing the MeO group $((MeO)_nPX_{(3-n)}$, X = Cl or Ph and n = 1-3) may well have formed a phosphonium salt but the observed products were the halomethane and a phosphorus(V) species contain a P=O bond, e.g. $(MeO)_3P + Me_2NBr = Me_2NPO(OMe)_2 + MeBr$. In the case of the aryl and thioesters studied $((MeS)_3P$ and $(PhO)_3P)$ the intermediate species are observed.

The species studied which contained P-I and P-P bonds (PI_3, P_2I_4 and P_4) were all oxidised by the two halomines used with the eventual loss of all such bonds and the formation of the expected phosphonium salts.

In order to assist in the confirmation of the products of some of the above reactions, the halogenations of various phosphorus(III) species were studied. These were the reactions of iodine with $(Me_2N)_3P$ and Me_2NPBr_2, the reactions of chlorine with $(Me_2N)_2PPh$ and Me_2NPPh_2 and the reactions of bromine with the above four species and $(Me_2N)_2PBr$. In all these cases addition of one mole of halogen to one mole of the phosphorus(III) species occurred to produce the expected phosphonium salts.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The interest in the present work has arisen from studies done in this laboratory on the reactions of dimethylchloramine and phosphorus trichloride (1). The reaction in the presence of excess phosphorus trichloride was found to correspond to the equation:

$$4PCl_3 + 3Me_2NCl \longrightarrow 2Me_2NPCl_3^+ + PCl_6^- + Cl^- + Me_2NPCl_2$$

In this work the reaction mentioned above has been further studied and also the reactions of dimethylchloramine and dimethylbromamine with the other three phosphorus trihalides.

H.H. Sisler and his co-workers[24] had previously carried out several reactions between N-halamines and tricoordinate phosphorus compounds. They found that all these reactions were simple amination on the phosphorus atom except the reaction between dimethylchloramine and tris(dimethylamino) phosphine in which the phosphine was chlorinated. In order to extend Sisler's work and to throw some light on the phosphorus trichloride reactions mentioned above, a study of the reactions of dimethylhalamines with a variety of phosphorus III species was undertaken.

In the work of Patrova and Sokol'skii (2) dimethylchloramine had been reacted with a variety of phosphite esters and the expected phosphonium ions were not formed, but could have been produced as intermediates. This work has been extended to isolate the intermediate species and to rationalize the mechanisms.

In a parallel study to the oxidation of phosphorus III species by halamines, the reactions of halogens and hydrogen

chloride on these species and phosphonium salts was under-
taken, partly in order to help to confirm the assignments
of some of the ^{31}Pnmr shifts.   Chlorine was found to
oxidise and in some cases cleave the P-N bond.

The products formed in this work were studied by
analysis and a variety of physical technique, but the most
important technique used to follow the reactions was ^{31}Pnmr
spectroscopy.   Some of the compounds made in this study are
new and many of them have not had their ^{31}Pnmr chemical shift
reported.   Consequently an attempt was made to correlate
the chemical shift found with the structures of the various
species.

From the above discussion it would be helpful if the
various ways in which the halamines have been found to react
was categorised.   Consequently the reactions of halamines
are divided into the following sections:

1.   Aminating agents

2.   Halogenating agents

3.   Halaminating agents

4.   Decomposition

5.   Oxidising agents by the hydrogen atom abstraction.

1.2   Halamines as aminating agents

1.2.1   Amination on the phosphorus atom:

N-halamines react as aminating agents towards
several species of phosphorus III compounds.   Some typical
examples are given below:

When an arylphosphite is treated with R_2NCl

$$(R = CH_3, Cl, C_2H_5)$$
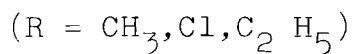
an addition compound is generated by simple amination on the phosphorus atom:

$$(C_6H_5O)_3P + R_2NCl \longrightarrow (C_6H_5O)_3PNR_2 \cdot Cl$$
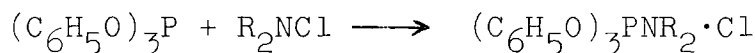
The ionic nature of $(C_6H_5O)_3PNMe_2 \cdot Cl$ has been confirmed by $^{31}Pnmr$ (1). When $(C_6H_5O)_3PNEt_2 \cdot Cl$ is heated vigorously EtCl is generated:

$$(C_6H_5O)_3PNEt_2 \cdot Cl \xrightarrow{\Delta} (C_6H_5O)_3P = NEt + EtCl$$
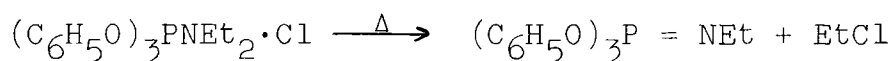
The expected phosphonium salts were not produced when an alkylphosphine was treated with N-halamines (2), but they may be produced as intermediates:

$$(EtO)_3P + Et_2NCl \longrightarrow (EtO)_2PONEt_2 + EtCl$$

$$(MeO)_3P + Me_2NCl \longrightarrow (MeO)_2PONMe_2 + MeCl$$
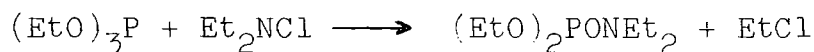
When alkylphosphines react with chloramine, phosphonium salts are produced in high yield which in some cases are difficult to isolate because of facile hydrolysis (3):

$$Me_3P + NH_2Cl \longrightarrow [Me_3PNH_2]^+ \cdot Cl^-$$

$$[Me_3PNH_2]^+ \cdot Cl^- + H_2O \longrightarrow OPMe_3 + NH_4Cl$$

$$[P(CH_2OH)_3] + (C_2H_5)_2NCl \longrightarrow [(CH_2OH)_3PN(C_2H_5)_2]^+ \cdot Cl^-$$
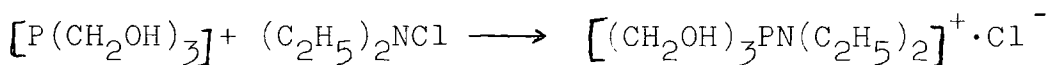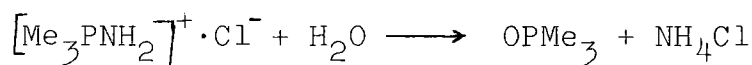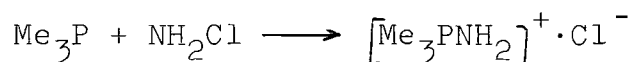
In previous work done in this laboratory by Khabbass (1) the reaction of dimethylchloramine and excess phosphorus trichloride has been studied and the stoichiometry of this reaction has been shown to be:

$$4PCl_3 + 3Me_2NCl \longrightarrow 2Me_2NPCl_3^+ + PCl_6^- + Cl^- + Me_2NPCl_2$$
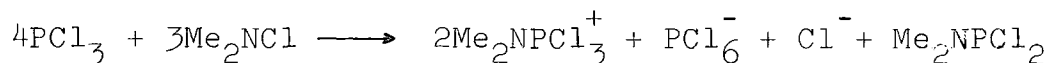
Although the above rather complex reaction occurs with PCl_3, with substituted phosphorus chlorine species simple amination occurs (1):

$$Me_2NPCl_2 + Me_2NCl \longrightarrow (Me_2N)_2PCl_2^+ \cdot Cl^-$$

$$(Me_2N)_2PCl + Me_2NCl \longrightarrow (Me_2N)_3PCl^+ \cdot Cl^-$$

$$PhPCl_2 + Me_2NCl \longrightarrow Me_2NPPhCl_2^+ \cdot Cl^-$$

$$Ph_2PCl + Me_2NCl \longrightarrow Me_2NPPh_2Cl^+ \cdot Cl^-$$

$$PhPNMe_2Cl + Me_2NCl \longrightarrow (Me_2N)_2PPhCl^+ \cdot Cl^-$$
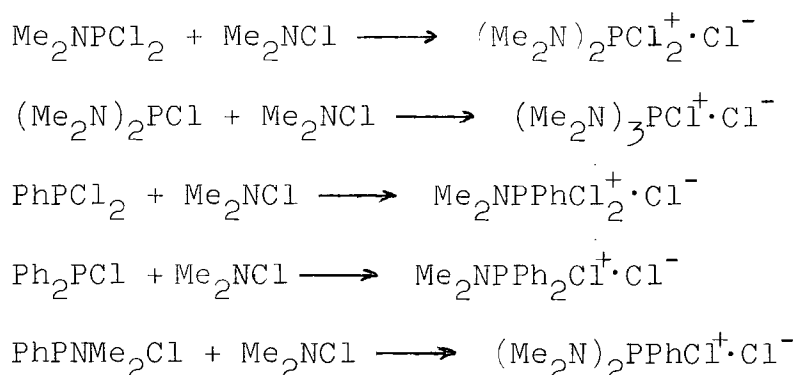
Dimethylchloramine behaves in a similar way and produces the corresponding phosphonium salts (4) when reacted with Me_2NPMe_2 and $(Me_2N)_2PMe$:

$$Me_2NPMe_2 + Me_2NCl \longrightarrow (Me_2N)_2PMe_2 \cdot Cl$$

$$(Me_2N)_2PMe + Me_2NCl \longrightarrow (Me_2N)_3PMe \cdot Cl$$
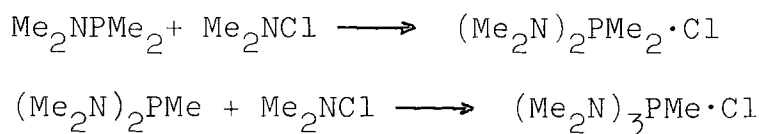
Simple amination occurs when chloramine reacts with an aminophosphine (5,6) or a hydrazinophosphine (7):

$$R_2NP(C_6H_5)_2 + NH_2Cl \longrightarrow R_2NPNH_2(C_6H_5)_2 \cdot Cl$$

$$Me_2N-NMeP(C_6H_5)_2 + NH_2Cl \longrightarrow \left[(C_6H_5)_2PNH_2 \cdot NMe-NMe_2^+ \right] Cl^-$$

$$(R = CH_3, C_2H_5 \text{ or } H)$$
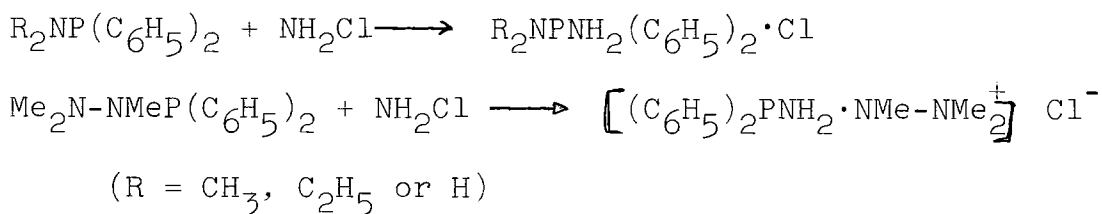
It was found that N,N-dihalogeno-S,S-dimethyl sulphur diimide with phosphine (8) as follows:
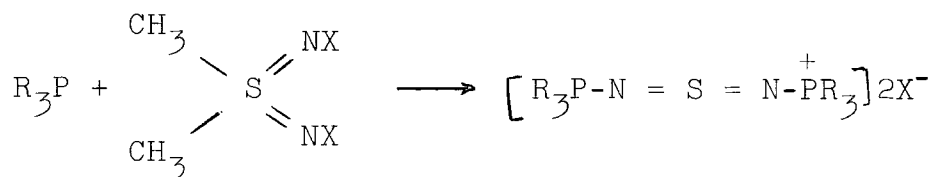
1.2.2 Amination at a nitrogen atom:

A review by Drago (9) listed reactions in which hydrazines can be synthesised by the reaction of chloramine

with amines as shown in the following equations:

$$NH_2Cl + 2NH_3 \longrightarrow NH_2 - NH_2 + NH_4Cl$$

$$NH_2Cl + 2RNH_2 \longrightarrow RNHNH_2 + RNH_3Cl$$

$$NH_2Cl + 2R_2NH \longrightarrow R_2NNH_2 + R_2NH_2Cl$$

$$NH_2Cl + R_3N \longrightarrow R_3NNH_2Cl$$
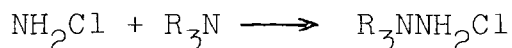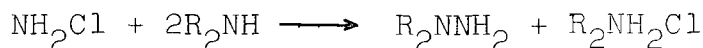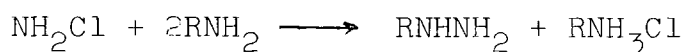
The reactions between formaldehyde in 2N sodium hydroxide and alkylamines with hypochlorite (10) produce diaziridines:
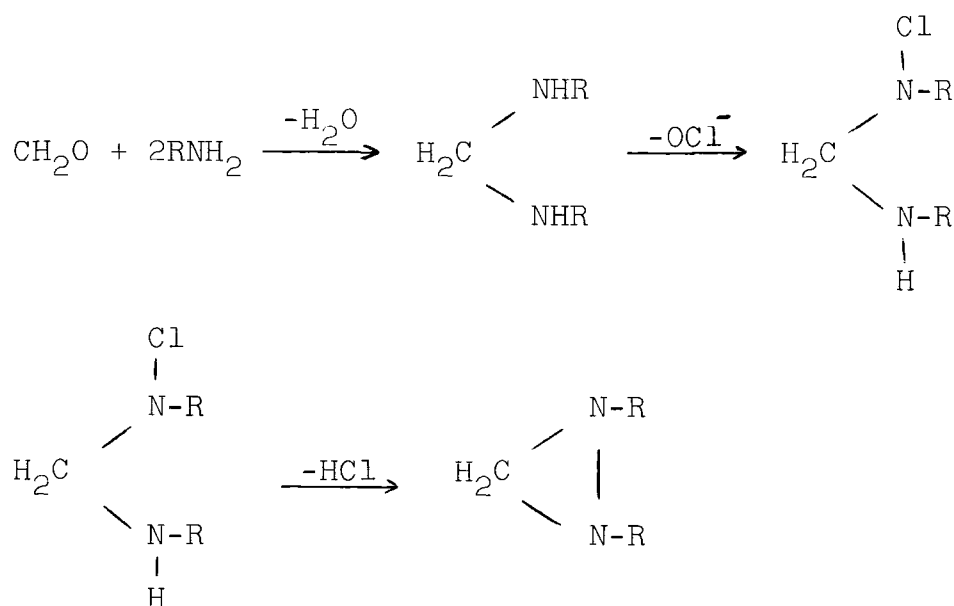
A gaseous mixture of ammonia and chloramine with 1.1-dialkylhydrazine (11) generated triazanium salt as shown by the following equation:

$$R_2NNH_2 + NH_2Cl \longrightarrow \left[H_2NNR_2NH_2\right]^+ \cdot Cl^-$$
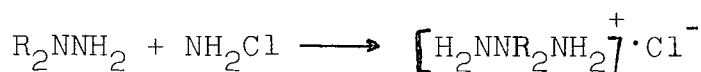
Chloramine reacts with α-pyridone in the presence of a base to form a hydrazine derivative (12) as shown in the following equation:
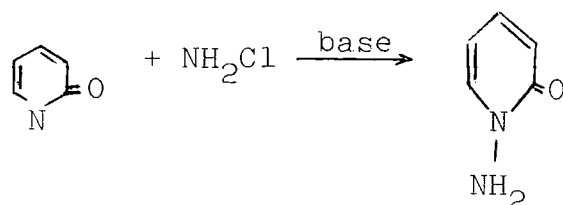
A mixture of formaldehyde oxime and chloramine generates diazomethane in a sequence of steps commencing with nucleophilic displacement taking place on the nitrogen of chloramine (13) as shown in the following:

$$R_2C = NOH + NH_2Cl \xrightarrow{-Cl^-} R_2C = \overset{+}{N}\overset{\overset{\displaystyle OH}{|}}{N}H_2$$

$$R_2C = \overset{+}{N}\overset{\overset{\displaystyle OH}{|}}{N}H_2 \xrightarrow[-H^+]{-H_2O} R_2C = N_2$$
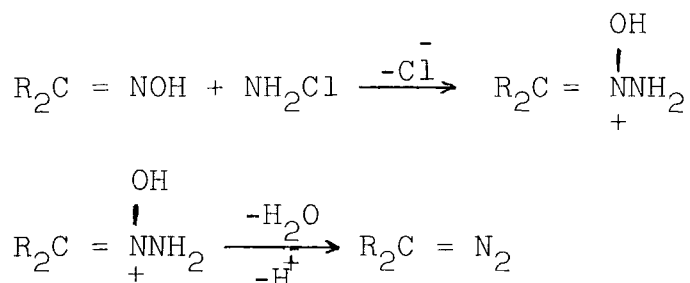
1.2.3 Amination at sulphur atoms:

It was shown that dialkylsulphonium amino chloride precipitated when dialkyl sulphides were treated with chloramine in ether solution (14):

$$R_2S + NH_2X \longrightarrow \left[R_2\overset{+}{S}NH_2\right]\cdot X^-$$
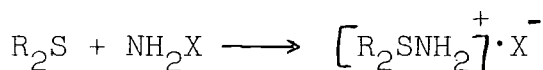
In alcoholic solvents sulphides react with chloramine (15) as follows:

$$2R_2S + 4NH_2Cl \longrightarrow 2\left[(R_2\overset{+}{S}NHN\overset{-}{H}]HCl + 2HCl\right.$$
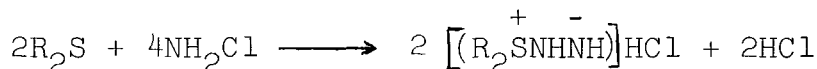
Nitrogen trichloride reacts with diphenyl sulphide to generate bis(diphenyl sulphide) nitride trichloride(16) as indicated in the following equation:

$$(C_6H_5)_2S + NCl_3 \longrightarrow \left[(C_6H_5)_2SNS(C_6H_5)_2\overset{+}{]}\cdot Cl_3\right.$$
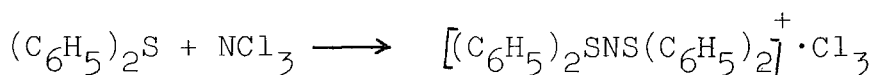
Bock and Kompa (17) generated various thiocynates according to the following general reaction:

$$RNCl_2 + 2NH_4SCN \longrightarrow RN(SCN)_2 + 2NH_4Cl$$
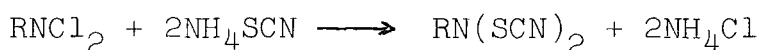
The reaction of N-halamines with sulphur compounds has not been extensively studied. The most common process appears to be nucleophilic substitution on the halamine nitrogen by

sulphur compounds; for example the reaction of N-monochloro derivatives of primary amines with metal mercaptides (18), which generate sulphinetriazine as a new ring compound (19):
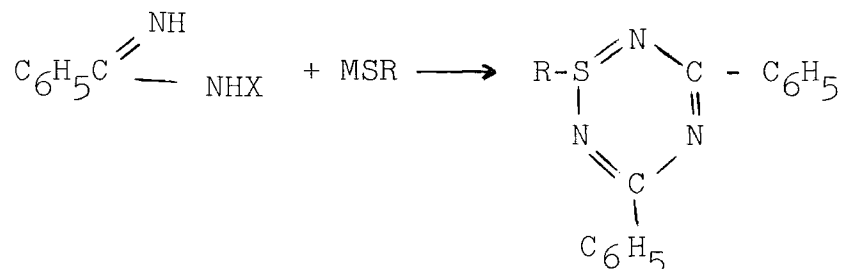
1.2.4 Amination on arsenic atoms:

Diphenylarsine and triphenylarsine react with chloramine to give aminoarsonium chlorides (20) as follows:

$$(C_6H_5)_3As + NH_2Cl \longrightarrow (C_6H_5)_3AsNH_2\ Cl$$
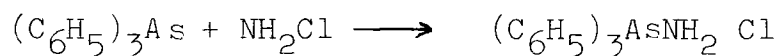
The fission of some arsenic-phenyl bonds with the production of chlorobenzene in the chloramination of phenylarsine was observed under some conditions (21).

1.2.5 Amination on antimony atoms:

Various substituted stibines combine with chloramine (20) to produce compounds of the type shown below:

$$R_3Sb + NH_2Cl \longrightarrow R_3Sb(NH_2)Cl$$
$$2R_3Sb(NH_2)Cl \longrightarrow [R_3SbCl]_2NH + NH_3$$
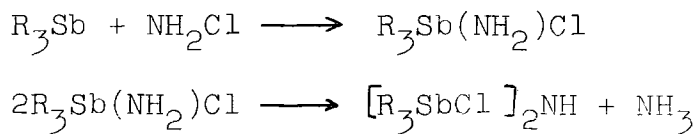
1.3 Halamines as halogenating agents

Nitrogen trichloride has been shown to be an important reagent for the preparation of vic-dichlorides in very high yield from certain types of olefins (22):

$$3RCH = CH_2 + 2NCl_3 \longrightarrow 3RCCHClCH_2Cl + N_2$$
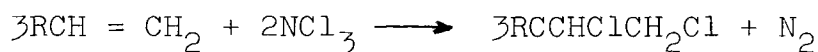
It was found that acetylenes undergo chlorination with nitrogen trichloride to give predominantly vic-dichloroalkenes.

Tris(dimethylamino)phosphine $(Me_2N)_3P$ was chlorinated by chloramine (24,1). Sisler and his co-workers proved the formation of $(Me_2N)_3PCl_2$ and suggested that the other product was tetramethylhydrazine as deduced from the stoichiometry of the reaction, however they did not isolate any of the hydrazine. The reaction was repeated in this laboratory under different circumstances and the formation of $(Me_2N)_3PCl_2$ was found. The formation of tetramethylhydrazine was confirmed by the gas phase infrared spectrum (1):

$$(Me_2N)_3P + 2Me_2NCl \longrightarrow (Me_2N)_3PCl^+ \cdot Cl^- + Me_2N-NMe_2$$
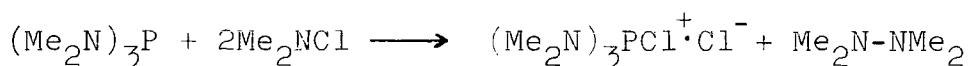
Phenylphosphine and diphenylphosphine did not give the expected phosphonium salts when they were treated with dimethylchloramine (24). This is due to the decomposition of the initially formed phosphonium salts as shown by the following equations:

$$Ph_2PH + (C_2H_5)_2NCl \longrightarrow Ph_2PHN(C_2H_5)_2 \cdot Cl$$

$$Ph_2PHN(C_2H_5)_2 \cdot Cl \longrightarrow Ph_2PN(C_2H_5)_2 + HCl$$

$$Ph_2PN(C_2H_5)_2 + HCl \longrightarrow Ph_2PCl + (C_2H_5)_2NH$$
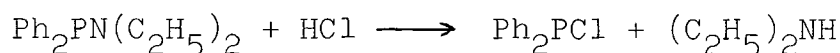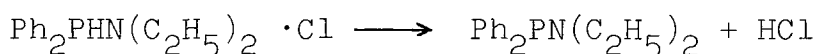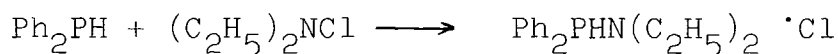
1.4 Halamines as halaminating agents

Nitrogen trichloride (25) oxidizes diphenylketene by halamination:

$$(C_6H_5)_2C = C = O + NCl_3 \longrightarrow (C_6H_5)_2\underset{Cl}{C} - \underset{NCl_2}{C} = O \longrightarrow$$

$$(C_6H_5)_2\underset{Cl}{C} - \underset{N}{C} = O \longrightarrow (C_6H_5)_2\underset{Cl}{C} - N = C = O$$
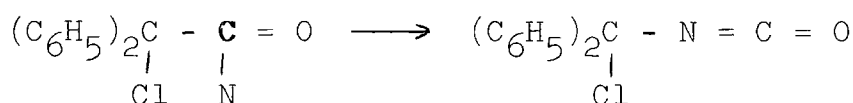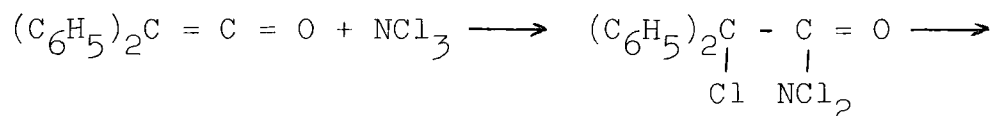
The reactions of aldehydes and ketones with chloramines represent an interesting study since the ald-chlorimines

are examples of the Shiff base reaction (26) as shown by
the following equation:

$$RCHO + NH_2Cl \longrightarrow R - \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} - NHCl$$
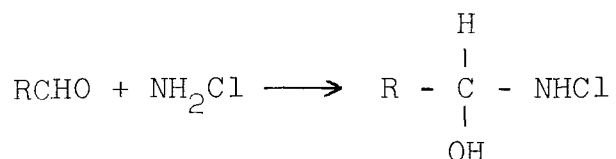
R.S. Neale found that allenes undergo 1,2-radical addition
with N-chlorodialkylamine in sulphuric acid-acetic acid
medium. Aminium radical attack results in nitrogen
becoming affixed to the least substituted carbon atom.
An example of this is the reaction between diethylchloramine
and allene producing 2-chloroallylamines (27,28) as indic-
ated below:

$$(C_2H_5)_2NCl + CH_2 = C = CH_2 \longrightarrow (C_2H_5)_2NCH_2\underset{\underset{Cl}{|}}{C} = CH_2$$
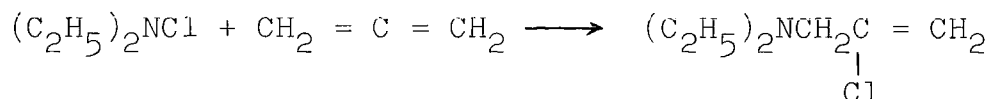
Phosphorus trichloride reacts with nitrogen trichloride in
the presence of a solvent to give pale greenish-yellow
crystals of P_3NCl_{12}(29) as shown by the following equation:

$$3PCl_3 + NCl_3 \longrightarrow [Cl_3P = N - PCl_3]^+ [PCl_6]^-$$
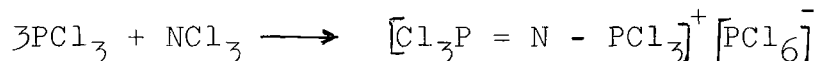
When phenyl dichlorophosphine was reacted with nitrogen
trichloride in chloroform, compound (1) was produced (in 20%
yield) with $C_6H_5PCl_4$(30)

$$PhPCl_2 + NCl_3 \longrightarrow [Ph - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{P}} = N - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{P}} - Ph]^+ \cdot Cl^- + PhPCl_4$$
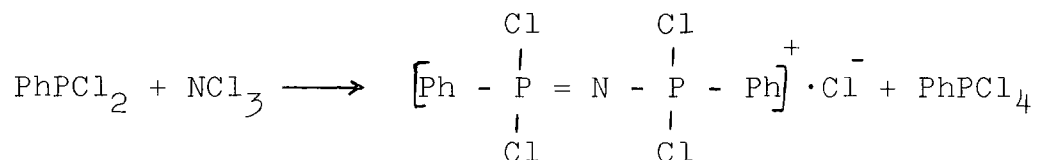
1.5 Decomposition reactions

Decomposition reaction can be classified into four
categories:

1.   Dehydrohalogenation;   2.   Disproportionation;

3.   Self halogenation;   4.   Photolysis.

1.5.1 Dehydrohalogenation:

It has been found that N-halamines with α-hydrogen atoms are susceptible to dehydrohalogenation by caesium fluoride in refluxing acetonitrile giving a nitrile, the yield was reported to be 90% (31). Typical examples are:

$$CH_3CH_2CH_2CH_2NCl_2 \xrightarrow{\text{CsF,CH}_3\text{CN}} CH_3CH_2CH_2C \equiv N \qquad (31)$$

$$(31)$$
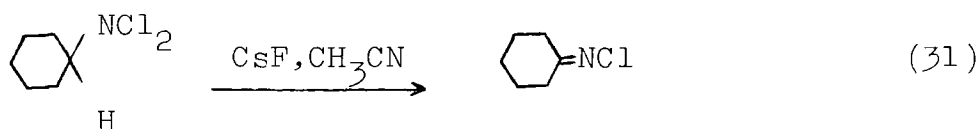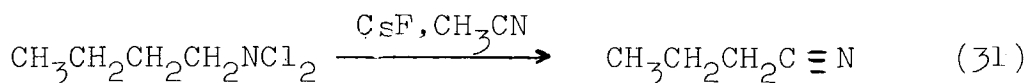
Nitriles are formed from ald-chlorimines as shown by the following equation by thermal decomposition or exposure to base:

$$CH_3CH_2CH_2CH = NCl \xrightarrow{-HCl} CH_3CH_2CH_2C \equiv N \qquad (32,33)$$
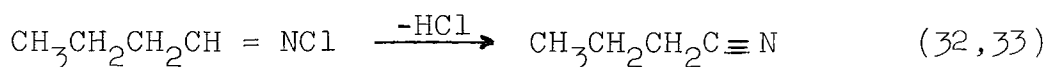
1.5.2 Disproportionation:

When N,N-dichlorotriphenylmethylamine was heated to $132^\circ C$ an explosion occurred and the characteristic crystals of benzophenone were obtained (34,35):

$$(C_6H_5)_3CNCl_2 \xrightarrow[\Delta]{-Cl_2} (C_6H_5)_3CN \quad (1)$$
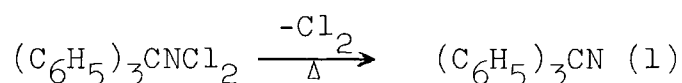
Compound (1) rearranged to produce the ketamine which hydrolysed to benzophenone:

$$(C_6H_5)_3CN \longrightarrow (C_6H_5)_2C = NC_6H_5$$
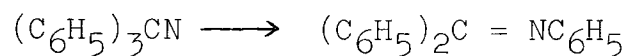
J. Jander and C. Lafrenz found that methylbromamine tended to be found in equilibrium with methyldibromamine and methylamine (36):

$$2CH_3NHBr \rightleftharpoons CH_3NBr_2 + CH_3NH_2$$
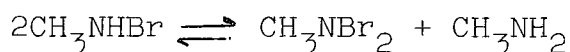
1.5.3 Self halogenation:

Due to the Hofman-Loeffer N-chloramine re-arrangement, the reaction pathway (suggested) indicated self chlorination (37) of the protonated N-chlorodibutylamine, in the presence of an aqueous solution of sulphuric acid

$$\overset{+}{Bu_2NHCl} + H_2O \xrightarrow{H_2SO_4} \overset{+}{BuNHCl} + H_3O + (C_4 \text{ fragment})$$

$$\overset{+}{BuNHCl} + \overset{+}{H} \rightleftharpoons \overset{+}{BuNH_2Cl}$$

$$\overset{+}{BuNHCl} + \overset{+}{BuNHCl_2} \longrightarrow BuNCl_2 + \overset{+}{Bu_2NH_2}$$
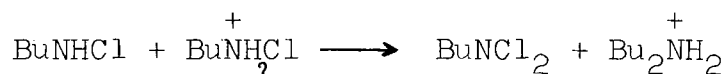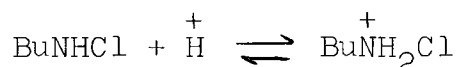
1.5.4 Photolysis:

The photochemistry of N-halamines has not been studied extensively and it has been concerned with simple molecules such as chloramine and nitrogen trichloride. The photolysis of chloramine at $-190^{\circ}C$ with ultraviolet light generated NH (38) which was proposed as an intermediate in the thermal decomposition of NH_2Cl at $500^{\circ}C$ in the presence of carbon monoxide in which hydrogen cyanate was produced. An extensive study of the photodecomposition of nitrogen trichloride in the presence of chlorine established that chlorine was acting as photosensitizer (39,40) and that the following chain mechanism was occurring:

$$Cl_2 + h\nu \longrightarrow 2Cl$$

$$NCl_3 + Cl \longrightarrow NCl_2 + Cl_2$$

$$NCl_3 + NCl_2 \longrightarrow N_2 + 2Cl_2 + Cl$$

$$X + Cl + NCl_3 \longrightarrow NCl_4 + X$$

$$2NCl_4 \longrightarrow N_2 + 4Cl_2$$
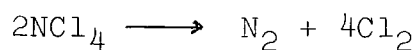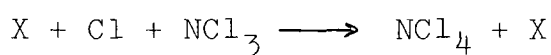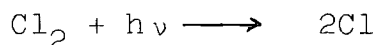
1.6 Halamines as oxidising agents by the abstraction of the hydrogen atom

The following equations show the reactions between NH_2Cl, Me_2NCl and arsines containing As-H bonds (41):

$$2AsH_3 + 3NH_2Cl \longrightarrow 2As + 3NH_4Cl$$

$$2AsH_3 + 3Me_2NCl \longrightarrow 2As + 3Me_2NH_2Cl$$

$$3MeAsH_2 + NH_2Cl \longrightarrow (MeAs)_3 + NH_4Cl$$

$$3MeAsH_2 + Me_2NCl \longrightarrow (MeAs)_3 + Me_2NH_2Cl$$

$$2Me_2AsH + NH_2Cl \longrightarrow Me_2As.AsMe_2 + NH_4Cl$$

$$2Me_2AsH + Me_2NCl \longrightarrow Me_2As.AsMe_2 + Me_2NH_2Cl$$
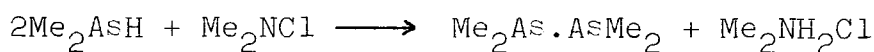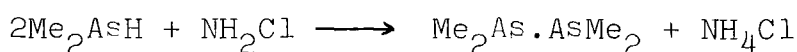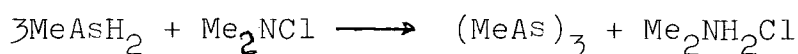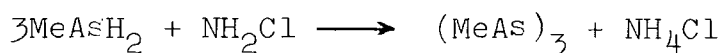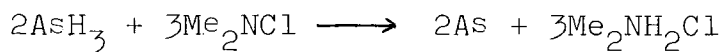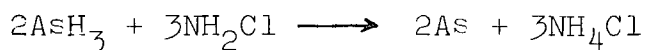
Similar results were obtained when phosphines containing P-H bond were reacted with R_2NCl (R = Me or H) (42) as shown by the following equations:

$$2PH_3 + 3Me_2NCl \longrightarrow 2P + 3Me_2NH_2Cl$$

Polymeric phosphorus hydrides were obtained when phenyl phosphines were treated with chloramine

$$4C_6H_5PH_2 + 4R_2NCl \longrightarrow (C_6H_5P)_4 + 4R_2NH_2Cl$$

$$2(C_6H_5)_2PH + R_2NCl \longrightarrow [(C_6H_5)_2P]_2 + R_2NH_2Cl$$
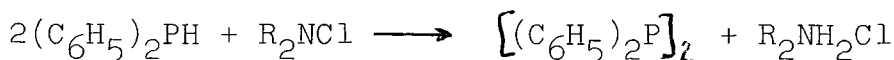
CHAPTER TWO

EXPERIMENTAL METHODS

2.1   Introduction

The study of the reactions of various phosphines with a variety of halamines required the use of a number of manipulative techniques.   The liquid halamines as well as some of the phosphines used in this study were very volatile substances.   The vacuum line allowed quantitative transference to be made under anhydrous conditions and it was also useful in the identification, removal and purification of the volatile substances formed in the reactions studied.   In this chapter the vacuum line, drybox, Pnmr equipment and associated apparatus will be described.   The methods employed to prepare and purify the reactants used in this study are also included.

2.2   The vacuum line

The vacuum line described previously (1) was used to perform some of the reactions in the present study, but in the latter part of this study a rather simpler version was used (figure 2.1) which had the advantage of being easily disconnected and cleaned.   This new vacuum line comprised of three sections:

1.   Pumping section (P)

2.   General working section (W)

3.   Fractionating section (F)

The pumping section contained a Jencons mercury diffusion pump backed by an Edwards two stage rotary oil pump.   The diffusion pump capacity was better than 30 litres per second at 10^{-3} to 10^{-5} mm/Hg.   This pump was heated electrically using a 320 watt wrap around heating element.   The critical backing pressure of 0.2 mm/Hg was easily obtained using the

two stage rotary oil pump. This provided a pumping speed of 22 litres per minute and optimum vacuum better than 10^{-3} mm/Hg. The diffusion pump was placed between the rotary oil pump and a cold trap and could be isolated from them by two taps (2a and 3a, figure 2.1). An air bleed via tap la was included and as a further precaution against suck-back of pump oil the device shown in figure 2.5 was introduced in the hose connection to the oil pump. The connections between the rotary pump and the diffusion pump and the rest of the line were as large as was convenient.

The general working section consisted of a row of three taps terminating in B14 sockets to facilitate the attachment of various pieces of apparatus such as an infrared gas cell. It was found more satisfactory to use B14 sockets rather than B14 cones as reactions were performed which often required the making and breaking of the connections of this part of the line, e.g. the reaction cell (figure 2.3), where the removal of the vacuum grease from the detached apparatus was made more convenient by having a cone and not a socket. This section was equipped with a Vacustat (a simple type of Mcleod guage which can measure pressure down to 10^{-5} mm/Hg).

The fractionating section was used for the purification of volatile chemical substances. This section comprised of three individually isolatable traps of a diameter making a close fit to the mouth of a "Thermos" dewar. Access to this section was via B14 sockets. Cold baths necessary for fractional condensation were made up using organic liquids of suitable melting points cooled to their freezing temperature using liquid nitrogen; or solid carbon dioxide mixed with a suitable solvent. The temperature of these baths are given in table 2.1.

Table 2.1

Low Temperature Baths

Solvent	Approximate Temperatures °C
Melting carbon tetrachloride	-23.0
Melting chlorobenzene	-45.0
Solid carbon dioxide with acetone	-83.0
Melting toluene	-96.0
Melting carbon disulphide	-112.5
Melting n-pentane	-131.0

The cold trap used in the pumping section was cooled in liquid nitrogen. The dewars used with the vacuum line were either standard wide-necked dewars or one litre "Thermos" flasks. The latter were predominantly for freezing very volatile, purified products to liquid nitrogen temperatures on the fraction train when such products could not be stored elsewhere (such as HCl and PF_3). Because the nitrogen evaporation rate was minimised by the narrow neck of the flask, complete loss of liquid nitrogen would take longer than 24 hours. These flasks were never used as containers for cold baths. The pressure inside the vacuum line was measured by a mercury manometer (figure 2.2a) which was of direct reading type. This U-shaped manometer was made from 10 mm bore tubing and it was fastened to a meter rule. The rule was fixed to a vertical wooden board. The manometer was initially set up by evacuating it as the mercury was added from a tap funnel in the top B14 socket. When the required amount of mercury had been added the funnel was replaced by a stopper. Air was blown into the manometer until the side reservoir was filled with mercury which trapped any traces of air or moisture in the reservoir.

When the manometer was under vacuum the level of
mercury was equal in both branches of the U-shaped tube; thus
pressure was measured by reading the difference in the
mercury levels.

A high tension coil (H.T. unit, type 1. Edwards High
Vacuum Ltd.) was used in the detection of any leak caused
by loose joints, pin holes in the glass, etc., by producing
a discharge colour inside the vacuum line.   Care was taken
in its use since it could have caused pin holes if used in
checking thin-walled containers such as molecular weight bulbs.

In most cases a saturated hydrocarbon grease 'M' obtained
from Apiezon Limited was used for joints which were parted
during manipulations.   Grade 'L' of this saturated hydro-
carbon grease was used for taps within the vacuum line, as
it proved more convenient, since when the ambient temperature
was low it remained more fluid than grade 'M' grease.   Grade
'W' Apiezon grease (or black Picene wax) was used for conn-
ections at the diffusion pump since this would withstand the
high temperature in this area.   For experiments involving
substances reactive towards the saturated hydrocarbon grease,
such as chlorine,Kel-F 90, a fully fluorinated grease was used.

2.3 Vessels associated with the vacuum line

2.3.1 The reaction vessel:

The reaction vessel (figure 2.2b) was formed
from a B24 cone and socket, the latter being connected to a
ground glass tap which terminated in a B14 cone by which the
cell could be attached to the vacuum line by means of a suit-
able 'L' shaped adaptor.   This vessel's advantage is that
with careful greasing materials can be weighed without coming

into contact with air. This reaction vessel was found to be better than using greaseless Rotaflo taps (figure 2.2c) when it was required to store materials at the freezer temperature ($-30^{\circ}C$) since the PTFE plug of the Rotaflo type stopcock was found to leak considerably at this temperature due to contraction.

2.3.2 Ampoule breakers:

For the opening of 16mm diameter heavy walled pyrex reaction ampoules, an ampoule breaker (figure 2.3) was used. This was used by initially deeply scoring the sealed end of the ampoule, and coating the 6mm O.D. diameter neck of the ampoule with Apiezon-W wax. Whilst the wax was still soft. the open end of the ampoule breaker was slid on to the ampoule so that the scored end was close to the heavy eccentric lever of the ampoule breaker. Visual inspection usually revealed if the seal was adequate since the wax "wetted" the inside of the breaker tube. The complete breaker and ampoule was then fixed to the vacuum line *via* its Bl4 cone and the breaker evacuated. The ampoule was usually frozen in liquid nitrogen before opening and the tip of the ampoule cracked off by carefully turning the eccentric lever thus bringing the arm in an arc across the tip of the ampoule as is shown in figure 2.3.

2.3.3 The "Rotaflo" Storage Ampoule:

This tube (figure 2.2c) was used to store volatile substances where boiling point is less than room temperature (such as Me_2NH) and it was used as a container for reactants of high vapour pressure at room temperature (such as BCl_3). Such ampoules were never kept in the freezer and if cooling was necessary they were cooled by a cold bath to avoid leakage

due to the contraction of the "PTFE" plug in the Rotaflo
stopcock.   A good seal was obtained when both the "PTFE"
glass contact areas appeared "wetted".   It was important
to ensure that no dust particles or pieces of fibre adhered
to the valve seat or the valve stem otherwise this would cause
leakage.

2.4   The drybox

The drybox was of standard design of approximately 30
litres capacity and is shown along with the associated humidity
control equipment in figure 2.4.   The glove box was manu-
factured in the Science Site central workshops at Durham from
an original drawing from Warwick University from $\frac{1}{8}$-inch mild
steel; all joints were welded.   A tubular spanner was welded
into the base to take an infrared disk press.   The box was
kept even when not in use, under a positive pressure of
nitrogen, so that the gloves were inflated.   The nitrogen
used for the make-up of the box atmosphere was de-oxygenated
in the department, provided from the central liquid nitrogen
storage tank and rated at less than 6 p.p.m. and 10 p.p.m. O_2 and
H_2O.   The rate of nitrogen flow was controlled by a needle
valve.   The nitrogen was dried by passing through a drying
tower containing phosphorus pentoxide, before entering the
box.   The glove box itself was kept dry with dishes of
phosphorus pentoxide placed in strategic positions around
the box floor.   The efficiency of this method of desiccation
was noted from the spectra of extremely moisture sensitive
compounds.   Entry to and exit from the box for large objects
was *via* the main port 'A' which was purged with nitrogen for
between 30 and 45 minutes depending upon the items being taken
into the box, before opening the inside port.   For small

items, such as ^{31}Pnmr tubes, the quick entry and exit port 'Q' was used.   The box was connected to a water pump 'W' *via* a cold trap 'C'.   This helped in carrying out the filtration of moisture sensitive compounds inside the dry box and in pumping off solvent under vacuum.   The box was also fitted with an electrical connection *via* a 13 amp socket in the side wall.   All non-welded joints, for instance the large plastic window, were sealed with Silicoset silicone rubber.   Before initial use the box was purged with nitrogen for at least two weeks.

2.5   The phosphorus n.m.r. spectrometer

The ^{31}Pnmr spectra were recorded on a pulse spectrometer built around a Perkin Elmer R10 thermostatted permanent magnet.   The necessary electronics were built in the Chemistry Department by Dr. A. Royston.   Signals from the nmr probe were digitized and accumulated by a Varian 620/L computer which was controlled from the keyboard of a visual display unit (shown on page 36).   Apart from performing a Fourier transform on the nmr signal, and plotting it on the R/O chart recorder, the computer also controlled the pulse programmer.   This unit switched the transmitter on and off and organised all the required timing necessary for signal accumulation.   Many of these spectrometer functions are controlled by the computer and spectra obtained by it can be manipulated and measured from the keyboard.   All ^{31}P chemical shifts were reported with respect to 85% aqueous phosphoric acid (as 0.0 p.p.m. shift) with the upfield direction taken as positive.   It was found that the phosphorus nmr spectrometer error is $\pm$ 1.4 p.p.m.

Phosphorus n.m.r. tubes of 8mm diameter were used filled with phosphorus compound, (or their solutions) to about 2cm depth. The modified phosphorus nmr tube (shown in figure 2.5) is made of 8mm diameter tube terminating with a B14 cone. This cone was fitted to a B14 socket and cone tap by which it could be attached to the vacuum line. When nmr tubes were used for sealed tube reactions, when highly volatile substances were handled (such as liquid hydrogen chloride) the tubes were made of silica with a constriction below the B14 cone, so that the tubes could be easily sealed after the volatile materials had been condensed into them.

2.6 Vibrational spectra

The infrared spectra of solids were recorded on a Perkin-Elmer 577 instrument as nujol mulls between KBr plates. The infrared spectra of liquids were obtained as a thin film. Gas phase spectra were obtained using a 10cm cell with KBr windows, which were fixed to the ground glass ends by means of Apiezon 'W' wax (figure 2.5).

2.7 Analyses

C, H and N were determined by micro combustion with a Perkin-Elmer 240 instrument. The reliability of the machine was found to be variable. Phosphorus and halogen analyses were carried out by R. Coult. For phosphorus and chlorine a weighed sample was decomposed by fusing in a nickel parr bomb. The residue was acidified with concentrated nitric acid and made up to $100cm^3$ with distilled water. For phosphorus a suitable aliquot was treated with ammonium molybdate/ammonium vanadate reagent and the absorbance measured at 420nm using a Unicam SP500 spectrophotometer. Chlorine was determined by potentiometric titration against N/100 silver nitrate solution using Ag/AgCl electrodes in an acetone medium.

Bromine was determined iodometrically following a Schoniger oxygen flask combustion.

2.8 Solvents

Generally solvents of the best commercially available grade were used.   Chlorocarbons were dried over 4A mesh molecular sieve and stored under nitrogen.   Hydrocarbon solvents were dried over sodium wire and then stored under nitrogen over freshly activated molecular sieve.   Carbon disulphide was distilled from phosphorus pentoxide and stored over molecular sieve before use.

2.9 Preparation of halamines

2.9.1 Dimethylchloramine:

This substance has been prepared in the past by a variety of methods (43,44). In this work the method modified from that of Hoffman (45) was used in which di-methylammonium chloride was reacted with sodium chlorate (I):

$$(CH_3)_2NH_2^+ + ClO^- \longrightarrow (CH_3)_2NCl + H_2O$$
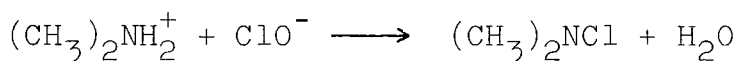
It was found to be an improvement if a very strong solution of sodium chlorate (1) was prepared just before the chlorination of the ammonium salt, and if the latter was added to the chlorate (I) solution in the solid phase in small portions.

Sodium chlorate (I) was prepared by the chlorination of a solution of sodium hydroxide as follows:

Sodium hydroxide (109g 2.7 moles) was dissolved in 150cm^3 water in a wide-mouthed 3 litre conical flask.   After cooling to room temperature, 625g of ice was added and chlorine passed in rapidly from a cylinder, with shaking until all but little of the ice remained unmelted by the heat of the reaction.

To this solution was added   dimethylammonium chloride
(82g. 1.0 mol) in small portions.   The flask was well shaken
during the addition and cooled externally in an ice-water
bath.   The dimethylchloramine separated as a pale yellow
upper layer and was quickly separated by using a separating
funnel.   The crude dimethylchloramine was kept in the freezer,
mixed with calcium chloride as drying agent at first and then
with phosphorus pentoxide.   Temperature control during the
addition of the ammonium salt was found to be very important,
since any rise favoured the formation of dichloro-derivatives
and possibly highly explosive nitrogen trichloride.   Dimethyl-
chloramine was purified by fractional condensation on the
vacuum line, the mixture being distilled through four traps
cooled with the following slush baths, one at -23°C, two
baths at -83°C and one at -196°C.   The majority of the pro-
duct was collected at -83°C and was shown to be pure by its
gas phase infrared spectrum (figure 1).   The dimethylchlor-
amine was kept in a reaction vessel (figure 2.2b) in the
freezer at -30°C, because of its decomposition at room temper-
ature.   Small pure samples of dimethylchloramine were pre-
pared by reacting n-chlorosuccinimide with dimethylamine (46):

$$\begin{array}{c} H_2C - C \\ | \\ H_2C - C \end{array} NCl + Me_2NH \longrightarrow Me_2NCl + \begin{array}{c} H_2C - C \\ | \\ H_2C - C \end{array} NH$$
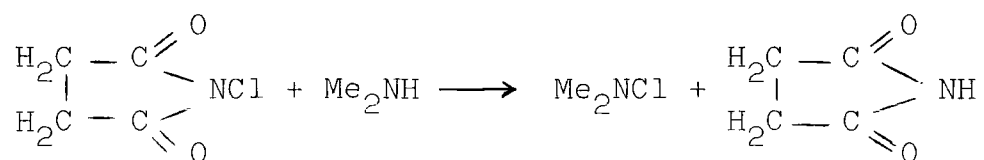
In a typical preparation of   dimethylchloramine, a sample
of dry dimethylamine was condensed into a calibrated cold
finger (figure 2.5) at -196°C, then the amine was degassed.
Dimethylamine was allowed to melt and its volume measured as
6.5 cm^3 (98.67 mmol).   This was transferred on to 19g
(142.38 mmol) of n-chlorosuccinimide in a 100 cm^3 flask
equipped with cone tap connection.   The flask was sealed

and kept at -30°C (the freezer temperature) for 24 hours, after which time the cell was returned to the vacuum line and the volatile material distilled out. The infrared spectrum showed the presence of dimethylchloramine only, (Fig.1.*P.89*)

2.9.2 Dimethylbromamine:

In a typical preparation 22g(123.66 mmol) of N-bromosuccinimide was weighed into a 100 cm^3 conical flask equipped with a cone tap connector. The flask was placed on the vacuum line and degassed. A sample of dimethylamine dried over sodium wire was condensed into a calibrated cold finger (figure 2.5) at -196°C, it was degassed and allowed to warm up gradually until it melted. The volume of this sample was measured as 6.1 cm^3 (92.16 mmol). This was then condensed onto the solid at -196°C. The flask was isolated from the vacuum line and held at -30°C (the freezer temperature) for 24 hours, the yellow colour of N-bromosuccinimide was observed to fade leaving a partially white residue. The product was distilled into a calibrated cold finger (figure 2.5) on the vacuum line resulting in the collection of 6.5 cm^3 of a bright brownish-yellow liquid, which was then distilled over as short a distance as possible into a rotaflo ampoule and kept at -196°C. The gas phase infrared spectrum of a sample of this product is shown in figure 2.

2.9.3 Methyldichloramine:

Methyldichloramine was prepared by a modification of the method of G.H. Coleman (47) in which methylammonium chloride was reacted with sodium chlorate (I):

$$MeNH_3Cl + 2NaOCl \longrightarrow MeNCl_2 + NaOH + H_2O + NaCl$$

The modifications were:

1. A very strong solution of sodium chlorate (I) was prepared just before the chlorination of the ammonium salt.

2. The ammonium salt was added in the solid phase and in small portions to the solution.

A solution of sodium chlorate (I) (2.2 mol) was prepared as described in 2.9.1. Then inside a three litre conical flask the solution was cooled internally by ice (650g) and externally by an ice-salt mixture. Solid methylammonium chloride (1 mol) was added to the sodium chlorate (I) solution in small portions with continuous stirring. After most of the solid had been added the colour of the solution changed to milkish white and the smell of methyldichloramine was noticeable. After the complete addition the contents of the flask were poured into a separating funnel when two layers were observed. The methyldichloramine layer was covered by an aqueous layer. The lower layer was separated and dried over calcium chloride. The gas phase infrared spectrum of the product is shown in figure 3 . The product was kept in a Rotaflo storage ampoule at $-196^{O}C$.

2.9.4 Methylchloramine:

Preparation of methylchloramine was attempted by reaction of methylammonium chloride with sodium chlorate (I) as described by G.H. Coleman (47).

$$MeNH_3Cl + NaOCl \longrightarrow MeNHCl + NaCl + H_2O$$
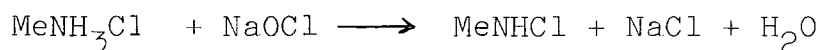
The gas phase infrared spectrum of the product showed the presence of methyldichloramine and methylamine. This disproportionation was found to occur too rapidly for the chloramine to be useful in the type of reactions studied in this work. This type of disproportionation has been studied by

J. Jander and C. Lafrenz (36)

$$2MeNHCl \rightleftarrows MeNCl_2 + MeNH_2$$
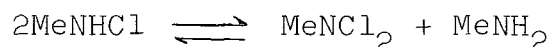
2.9.5 Dimethyliodamine:

The preparation of dimethyliodamine was attempted by reacting dimethylamine and iodine in aqueous solution in a similar manner to that used by J. Jander (48). Dimethylamine 4.02g (89.5 mmol) was mixed rapidly with a solution of 10.03g (39.5 mmol) iodine dissolved in an aqueous solution of potassium iodide at $0^{\circ}C$ inside a conical flask. A yellowish brown precipitate was formed, this was filtered on a glass sinter. The solid was washed three times with distilled water containing some dimethylamine at $0^{\circ}C$. The process of filtration was very slow and the colour of the solid changed to brown. The product was washed three times with methanol twice with diethyl ether and finally with pentane at $-35^{\circ}C$, the process of washing was also slow and that might be due to some frozen water blocking the pores of the glass sinter. The solid was dried under vacuum at $-35^{\circ}C$ and the colour of this solid changed to dark brown. Elemental analysis showed that the solid product was not dimethyliodamine and it implied the decomposition of the iodamine to compounds containing less iodine.

2.10 The preparation of phosphines

The preparations of dimethylaminodichlorophosphine and bis(dimethylamino)chlorophosphine were carried out by reacting phosphorus trichloride with dimethylamine(49,50) in different stoichiometric ratios as shown by the following equations:

$$PCl_3 + 2Me_2NH \longrightarrow Me_2NPCl_2 + Me_2NH_2Cl$$

$$PCl_3 + 4Me_2NH \longrightarrow (Me_2N)_2PCl + 2Me_2NH_2Cl$$
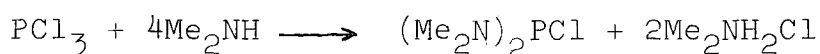
The procedures of the preparations were identical, so only the preparation of dimethylaminodichlorophosphine is discussed in detail:

Phosphorus trichloride 15.92g(162 mmol) was degassed, and dissolved in 50 cm^3 of dry degassed petroleum ether inside a three-necked round bottom flask which was kept under a dry atmosphere of nitrogen by a tap connected to the nitrogen line and fitted in one of the side necks. The central neck was equipped with a magnetic stirrer which kept the solution under continuous stirring. The third neck was equipped with a dropping funnel containing 16.5g(364 mmol) of dry degassed dimethylamine in 60 cm^3 of dry degassed petroleum ether. The flask was cooled to -6°C and the amine solution was added drop wise with continuous stirring. The formation of white solid was observed and when the addition of the amino solution was completed the reaction mixture was allowed to warm to room temperature whilst stirring for half an hour. The white solid (dimethylammoniumchloride) was separated by filtration (inside a dry box) and washed three times with petroleum ether. The filtrate was collected in a conical flask equipped with a tap and the solvent was pumped away through the vacuum line leaving a colourless liquid. The ^{31}Pnmr spectrum of this liquid showed one sharp peak at -165.1 p.p.m. due to the formation of Me$_2$NPCl$_2$(51). The ^{31}Pnmr spectrum of the product of the preparation of (Me$_2$N)$_2$PCl showed one sharp peak only at -158.9 p.p.m., close to the reported value of that compound (δ-158.7 p.p.m.) (51,52).

The results of elemental analysis are shown in the following tables:

Element	Calculated for Me_2NPCl_2	Found
C	16.45	16.32
H	4.11	4.29
N	9.60	9.86
P	21.25	21.20
Cl	48.59	48.41

Element	Calculated for $(Me_2N)_2PCl$	Found
C	31.08	31.25
H	7.77	7.81
N	18.13	18.39
P	20.07	20.01
Cl	22.95	22.74

The following table shows the other phosphines used in this work, the preparations of which are described in other chapters. The section number for their preparation is given in column three.

No.	Phosphine	Section No.	^{31}Pnmr/ppm found	^{31}Pnmr/ppm reported	References
1	$(Me_2N)_3P$	7.15	-122.5	-122.5	53
2	Me_2NPBr_2	4.7	-175.2	-	
3	$(Me_2N)_2PBr$	4.7	-170.9	-	
4	Me_2NPF_2	6.12	-143.5	-143.0	54
5	$(Me_2N)_2PF$	6.14	-151.9	-151.4	55
6	PI_3	5.12	-177.5	-178.0	56
7	$P(OMe)Cl_2$	3.11	-181.6	-181.0	57
8	$P(SMe)_3$	3.4	-124	-124.3	58
9	$PhP(C_6H_{11})_2$	8.4.2	-1.5	-2.5	59
10	$Ph_2P(C_6H_{11})$	3.4.3	3.2	4.4	59
11	Me_2NPPh_2	4.2	-64.3	-63.9	60
12	$Me_2N)_2PPh$	4.2	-99.8	-100.3	60

2.11 Other phosphorus compounds used

The following compounds were obtained from FluoroChem Ltd. and their purity was checked by ^{31}Pnmr spectroscopy. Methyl dichlorophosphine, dimethylchlorophosphine, bis(methyloxy) chlorophosphine, phenyl bis(methoxy)phosphine, diphenylmethoxy

phosphine, trimethylphosphine and dicyclohexylchlorophosphine. Tributylphosphine, triphenylphosphine, triphenylphosphite, hexamethyl phosphoramide, phosphorus trichloride and phosphorus tribromide were obtained from BDH Chemicals Ltd., and phenyldichlorophosphine and diphenylchlorophosphine from Alfa Division Lancaster Syntheses Ltd.

2.12 <u>Other chemicals</u>

2.12.1 Dimethylamine:

Dimethylamine was obtained in 250 cm^3 ampoule obtained from BDH Chemicals Ltd., which was cooled in a freezer at -30°C. The top of the ampoule was then cracked off and the liquid poured into a Rotaflo storage ampoule (figure 2.2c) containing sodium wire. The air was pumped off on the vacuum line while the amine was frozen at -196°C.

2.12.2 Hydrogen chloride:

The gas was obtained in cylinders from BOC Special Gases and introduced into a 10 litre bulb connected to the fractionation section of the vacuum line and purified by fractionation as described in 9.2.

2.12.3 Chlorine:

Chlorine was obtained in cylinders from BOC Special Gases.

2.12.4 Borontrichloride and borontribromide were obtained from Fisons, purified and kept in Rotaflo ampoule.

2.12.5 Other standard items of stock chemicals:

These chemicals were obtained from the usual sources. The petroleum ether used was the 30-40°C fraction and it was dried over sodium wire and transferred through the vacuum line into a storage Rotaflo ampoule.
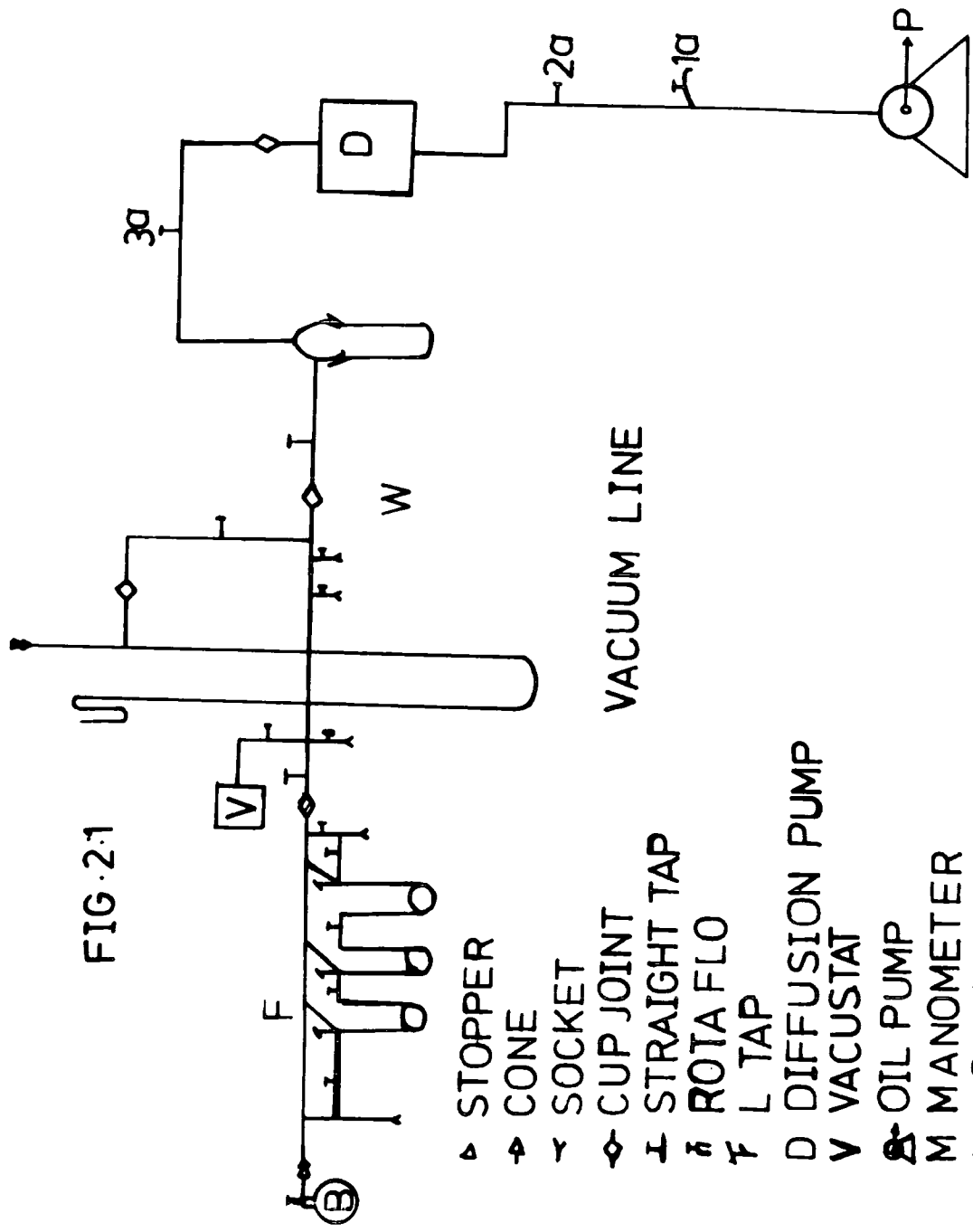
FIG.2.1

VACUUM LINE

△ STOPPER
♠ CONE
⊢ SOCKET
♢ CUP JOINT
⊥ STRAIGHT TAP
ⅱ ROTA FLO
⊤ L TAP
D DIFFUSION PUMP
V VACUSTAT
◔ OIL PUMP
M MANOMETER
B MOLECULER WEIGHT BULB

FIG·2·2

MANOMETER
FIG·2·2a

REACTION VESSEL
FIG·2·2b

STORAGE TUBE
FIG·2·2c

CONE
SOCKET
STOPPER
CUP JOINT
SCREW
RULE
TAP

FIG. 2·3

AMPOULE BREAKER
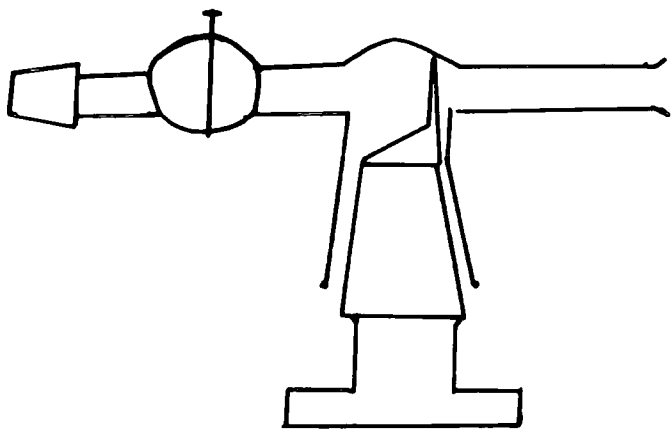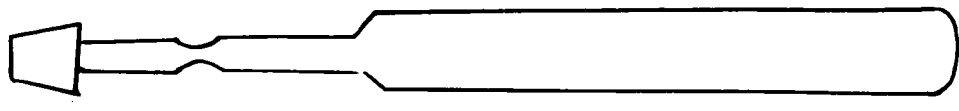
16MM
HEAVY WALL PYREX REACTION
AMPOULE
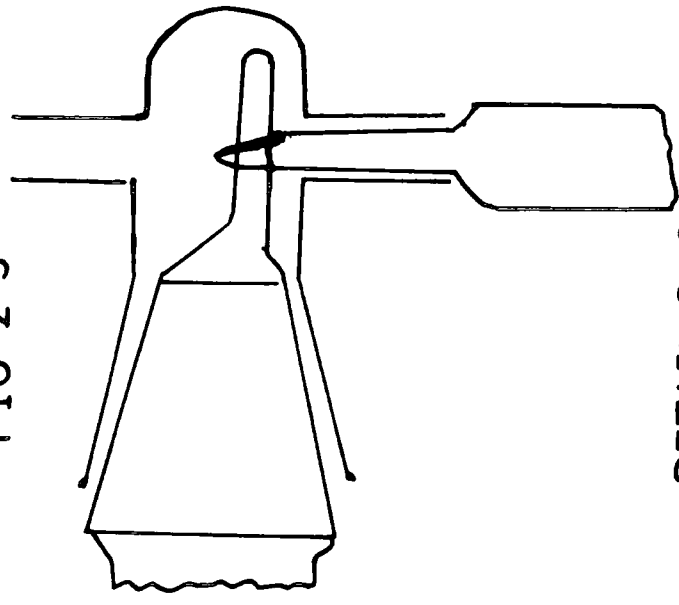
DETAIL SHOWING FITTING
OF 16MM AMPOULE PRIOR
TO OPENING

A THE MAIN PORT
C COLD TRAP
W WATER

B BUBBLER
N NEEDLE VALVE
O QUICK ENTRY PORT
→ DIRECTION OF FLOW
⊥ TAP
D DRYING TOWER
ROTA FLOW

FIG·24
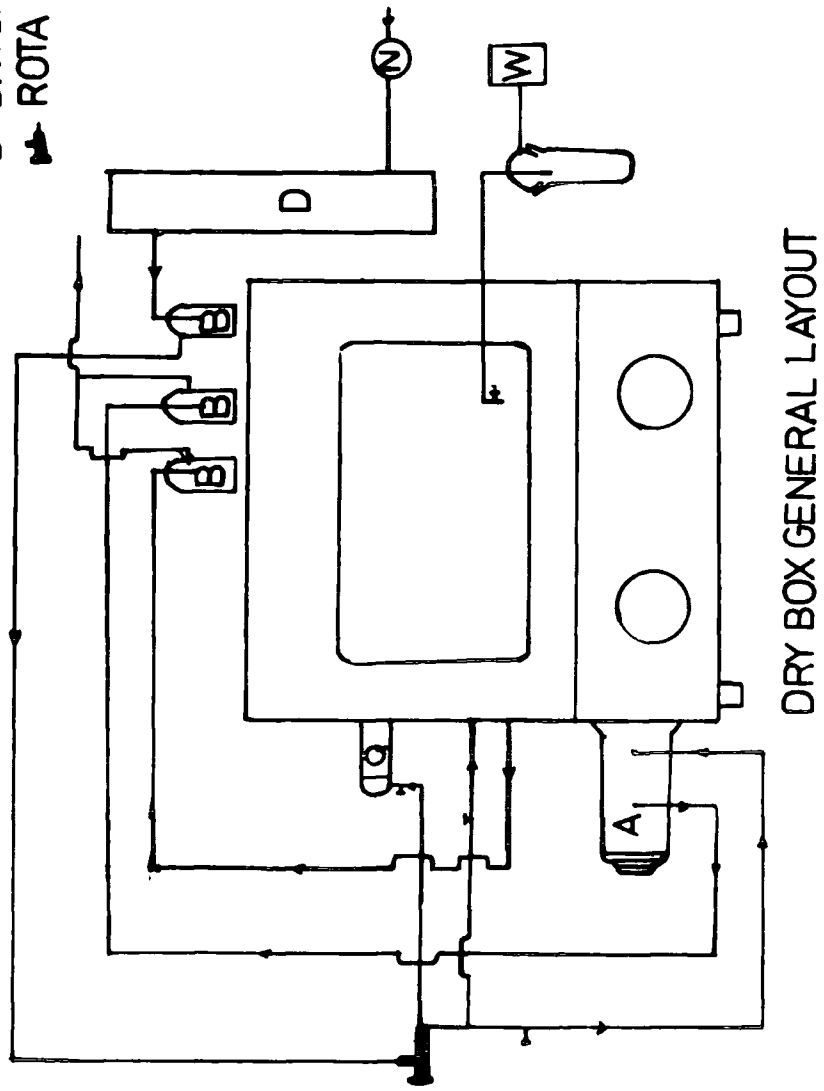
DRY BOX GENERAL LAYOUT

SIDE VIEW

FIG. 2.5

INFRARED GAS CELL

DEVICE AGANST
SUCK-BACK

I INTERNAL B14 SOCKET

B B14 STOPPER EXPANDED SO
THAT IT WILL FLOAT ON OIL

MODIFIED NMR TUBE

NMR TUBE

CALIBRATED
COLDFINGER
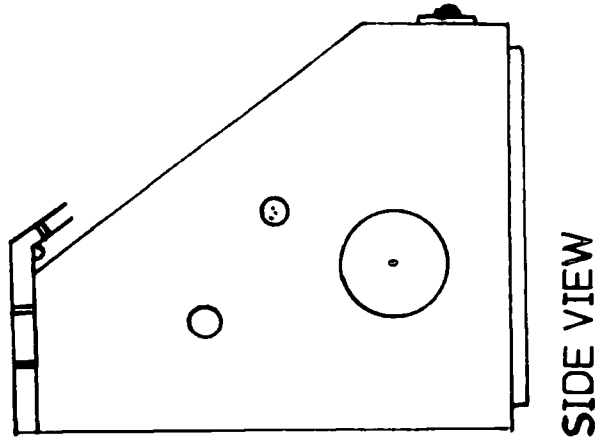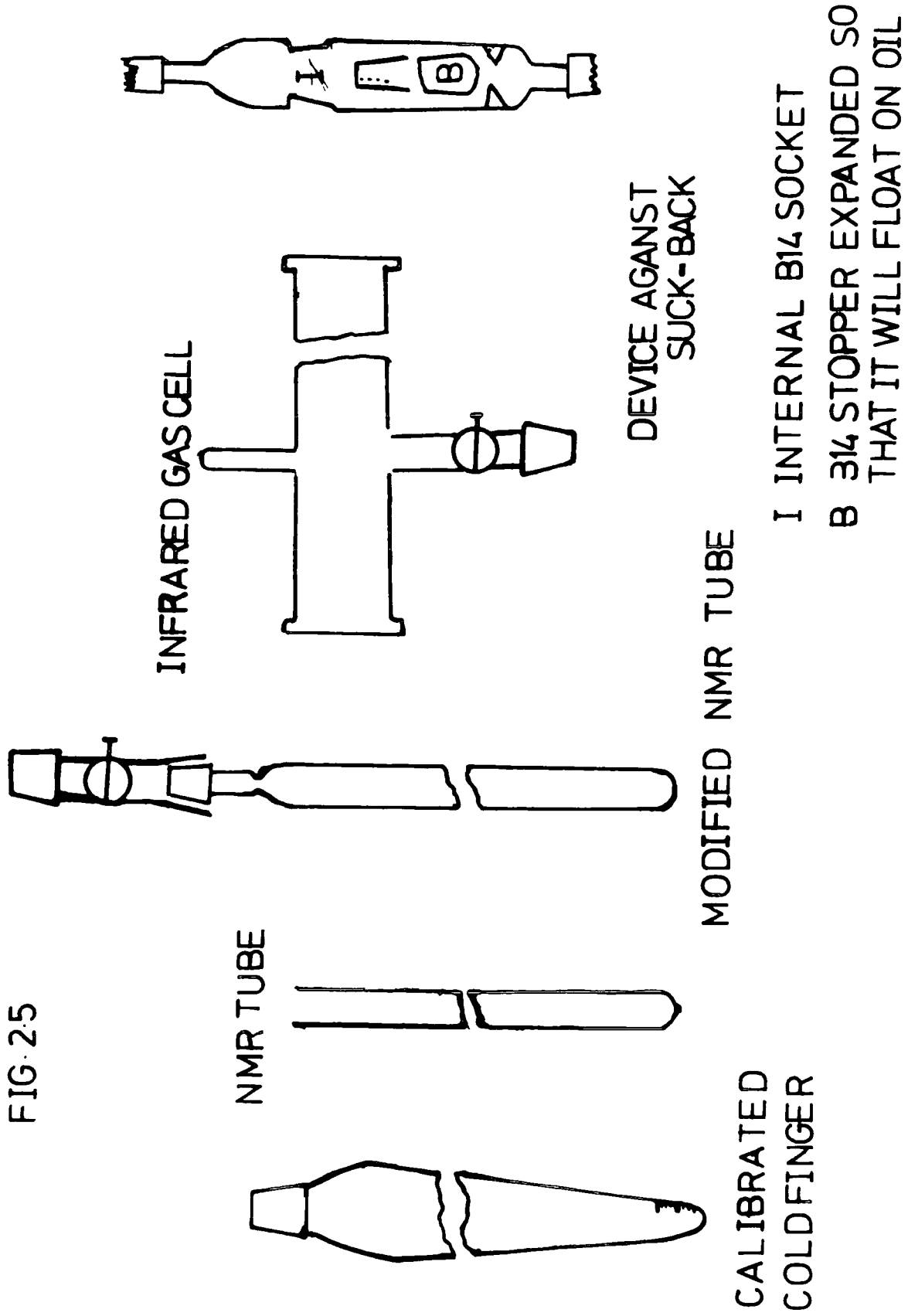
CHAPTER THREE

THE REACTIONS OF HALAMINES WITH

A VARIETY OF PHOSPHITES

3.1 Introduction

Very few studies of the reactions between phosphorus acid esters and N-halamines have been reported. Petrova and Sokol'skii reacted Et_2NCl with some phosphorus acid esters (phosphites) (2).

$$Et_2NCl + (MeO)_3P \longrightarrow (MeO)_3P\text{-}NEt_2{}^+ \cdot Cl^- \longrightarrow (MeO)_2PONEt_2 + MeCl$$
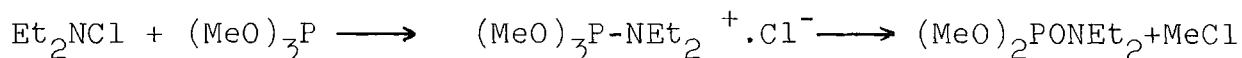
They assumed that an addition compound was formed first, then the chloride ion attacked one of the carbon atoms of the methoxy groups, in an S_N2 reaction to produce MeCl and $(MeO)_2PONEt_2$. In this reaction the addition product and the alkyl halide were not isolated. The intermediate product was isolated in reactions of R_2NCl with $(PhO)_3P$ in ether solution with cooling (2 ,1) and the ionic nature of the product was confirmed by its [31]Pnmr (1).

$$R_2NCl + (PhO)_3P \longrightarrow (PhO)_3PNR_2Cl$$

$$(R = CH_3 \text{ or } C_2H_5)$$
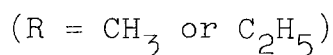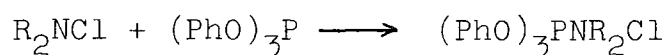
In a parallel reaction to those described above Petrov and Sokol'skii reacted trimethylphosphite with ethylhypochlorite (2). The products of this reaction were ethyldimethyl phosphite and methyl chloride. They suggested that the products of this reaction were formed by way of the phosphonium salt:

$$C_2H_5OCl + (CH_3O)_3P \longrightarrow (CH_3O)_3POC_2H_5{}^+ \cdot Cl^- \longrightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}OC_2H_5$$
$$+ CH_3Cl$$
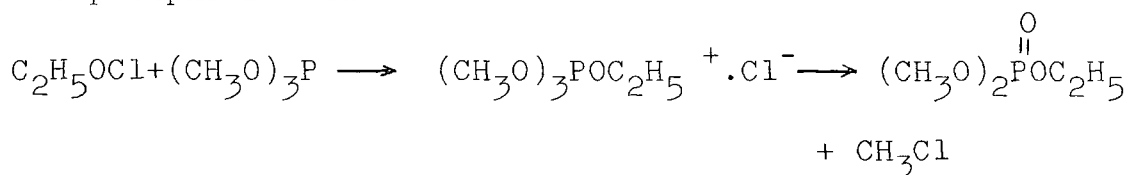
The same team of workers reacted triphenyl phosphite with ethyl hypochlorite (2) and they found that the phosphite was oxidised to phosphate, with the production of ethyl chloride. These workers suggested that the final products were formed from an addition product, where the chloride ion attacked the carbon atom of the ethoxy group by an S_N2 reaction:

$$C_2H_5OCl+(PhO)_3P \longrightarrow (PhO)_3P\text{-}O\text{-}C_2H_5 {}^+.Cl^- \longrightarrow (PhO)_3PO+C_2H_5Cl$$
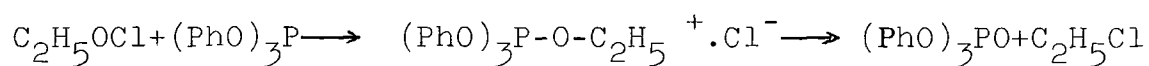
Trialkyl phosphites have been reacted with sulphenyl halides (61,62).

$$(C_2H_5O)_3P+CH_3SCl \longrightarrow (C_2H_5O)_3P\text{-}SCH_3 {}^+.Cl^- \longrightarrow (C_2H_5O)_2POSCH_3$$
$$+ C_2H_5Cl$$
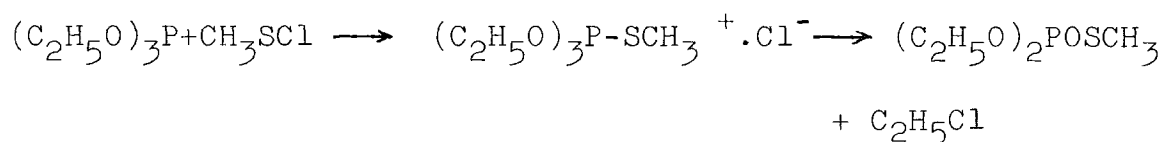
Petrov, Sokol'skii and their co-worker (61) reacted triphenyl phosphite with ethane sulphenyl chloride, the reaction produced good yield of O,O,O-tri-phenyl phosphorothioate. This is a rare example of cleavage of a carbon-sulphur bond in reactions of this type:

$$(PhO)_3P+C_2H_5SCl \longrightarrow (PhO)_3PSC_2H_5 {}^+.Cl^- \longrightarrow (PhO)_3PS + C_2H_5Cl$$
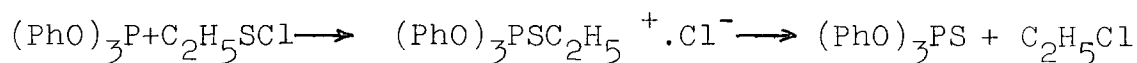
The intermediate compounds of these reactions were not isolated. From the above reactions it is clear that the susceptibility of carbon atoms bonded through an electronegative atom to phosphorus decreases in the order OCH_3, OC_2H_5, SCH_3, SC_2H_5, OC_6H_5.

The present work has been directed to expand the research in this field and to rationalise the mechanism of this type of reaction.

3.2 The reaction between triphenyl phosphite and dimethyl bromamine

A sample of triphenyl phosphite (3.7 mmol) was dissolved in $4cm^3$ of dry, degassed petroleum ether inside a reaction vessel (figure 2.2b). A dry, degassed dimethyl bromamine (4.3 mmol) was condensed onto the phosphite solution at $-196^\circ C$. The vessel was kept at $-46^\circ C$ for five hours with occasional shaking, then it was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of petroleum ether and dimethyl bromamine. These were pumped away through the vacuum line leaving a creamish-white solid as a product. This was washed three times with petroleum ether inside the dry box and it was dried under vacuum. The ^{31}Pnmr spectrum of this solid showed one broad peak at 18.1 p.p.m., this chemical shift is very close to that of $(PhO)_3PNMe_2^+.Cl^-$ (1) prepared by reacting Me_2NCl with $(PhO)_3P$. The infrared spectrum of the product is shown in figure 4 and the elemental analyses data are listed in Table 3.1.

Table 3.1

Element	Calculated for $(PhO)_3PNMe_2Br$	Found
C	55.31	54.79
H	4.84	5.02
N	3.23	3.51
P	7.14	7.10
Br	18.41	18.27

The previous results indicate that simple amination occurred in the phosphorus atom:

$$(PhO)_3P + Me_2NBr \longrightarrow (PhO)_3PNMe_2^+.Br^-$$
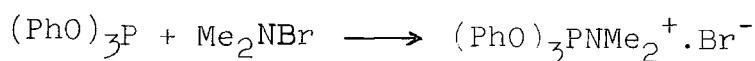
3.3 The reaction between trimethyl phosphite and dimethyl bromamine

A sample of trimethyl phosphite (4.1 mmol) was dissolved in $3cm^3$ of dry, degassed petroleum ether inside a modified nmr tube (figure 2.5). Dry, degassed dimethyl bromamine (5.3 mmol) was condensed onto the phosphite solution at $-196^{\circ}C$. The tube was kept at $-46^{\circ}C$ for five hours with occasional shaking and then it was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of methyl bromide, petroleum ether and dimethyl bromamine. These were pumped away through the vacuum line, leaving a colourless liquid. The $^{31}Pnmr$ spectrum of this liquid showed one sharp peak at -8.5 p.p.m., this chemical shift is very close to the chemical shift of $(MeO)_2PONMe_2$ which was prepared by reacting dimethyl chloramine and trimethyl phosphite (1). The infrared spectrum of the liquid is very similar to that of $(MeO)_2PONMe_2$, the elemental analysis results are listed in Table 3.2.

Table 3.2

Element	Calculated for $(MeO)_2PONMe_2$	Found
C	31.37	30.79
H	7.84	8.03
N	9.15	9.31
P	20.26	20.17

These results indicated that the overall reaction was:

$$(MeO)_3P + Me_2NBr \longrightarrow (MeO)_2PONMe_2 + MeBr$$
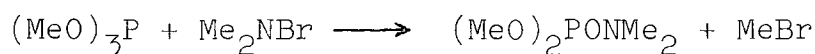
The products of this reaction might have been produced through an unstable phosphonium salt $((MeO)_3PNMe_2.Cl)$.

3.4 The preparation of tris(thiomethoxy) phosphine

This was prepared by reacting yellow phosphorus 3.1g (0.1 mmol) with dimethyl sulphide 14.1g (0.15 mmol) (63) The purity of the product was checked by ^{31}Pnmr spectroscopy which showed one sharp peak only at -124 p.p.m. due to the formation of tris(thiomethoxy)phosphine (58).

The elemental analyses are listed in Table 3.3.

Table 3.3

Element	Calculated for	Found
C	20.93	19.69
H	5.23	5.77
S	55.83	55.40
P	18.02	18.16

3.5 The reaction between dimethylchloramine and tris(thiomethoxy) phosphine

Tris(thiomethoxy)phosphine (6.98 mmol) was dissolved in 3cm^3 of dry, degassed dichloromethane inside a reaction vessel (figure 2.2b) and 8.8 mmol of dimethylchloramine was condensed into it. The vessel was held at -45°C for eight hours. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dichloromethane and dimethyl chloramine which were pumped away leaving a white solid. A sample of this solid was placed inside a modified Pnmr tube

(figure 2.5) and it was noticed that the solid substance started to look wet. The ^{31}Pnmr spectrum of the sample showed one sharp peak only due to a liquid phosphorus compound at -98.4 p.p.m. and it was noticed that the solid had liquefied at the spectrometer probe temperature 35°C. The tube was connected to the vacuum line and the gas phase infrared spectrum showed the presence of methylchloride only and a colourless liquid remained inside the tube. The infrared spectrum of the liquid is shown in figure 5 and the elemental analysis data are listed in table 3.4.

Table 3.4

Element	Calculated for $(MeS)_2PSNMe_2$	Found
C	23.88	23.69
H	5.97	6.35
N	6.97	7.30
P	15.42	15.62
S	47.76	47.41

These results indicate that the overall reaction was as follows:

$$(MeS)_3P + Me_2NCl \longrightarrow Me_2NPS(SMe)_2 + MeCl$$
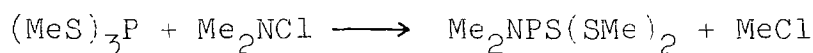
With, perhaps, intermediate formation of the ionic species $(MeS)_3PNMe_2^+ Cl^-$.

3.6 The reaction between dimethylbromamine and tris(thiomethoxy)phosphine

A sample of dry degassed dimethylbromamine (4.9 mmol) was condensed into 2.9 mmol of tris(thiomethoxy)phosphine dissolved in $4cm^3$ of dry degassed petroleum ether inside a

reaction vessel (figure 2.2). The vessel was kept at -46.5°C for eight hours when the tube was allowed to warm to room temperature. the infrared spectrum of the most volatile fraction showed a mixture of petroleum ether and dimethylbromamine. The volatile substances were pumped away leaving a yellowish-white solid inside the tube. A sample of the solid product was transferred into a modified Pnmr tube (figure 2.5) in the drybox. The ^{31}Pnmr spectrum showed one sharp peak at -98.4 p.p.m. and it was noticed that the solid had melted to a colourless liquid.

The tube was attached to the vacuum line and the gas phase infrared spectrum showed the presence of bromomethane only, this was pumped away leaving the colourless liquid inside the tube. The infrared spectrum of this liquid was identical to the infrared spectrum of $(MeS)_2PSNMe_2$ (figure 5) obtained from the corresponding dimethylchloramine reaction (3.5). The elemental analyses are shown in table 3.5.

Table 3.5

Element	Calculated for $(MeS)_2PSNMe_2$	Found
C	23.88	22.46
H	5.97	7.01
N	6.97	6.88
P	15.42	15.56
S	47.76	47.91

Then the overall reaction was as follows:

$$(MeS)_3P + Me_2NBr \longrightarrow (MeS)_2PSNMe_2 + MeBr$$

With the likely formation of $(MeS)_3PNMe_2^+ \cdot Br^-$ as an intermediate.

3.7 The reaction between dimethylchloramine and bis(methoxy)phenyl phosphine

A sample of bis(methoxy)phenyl phosphine (4.7 mmol) was dissolved in 2 cm^3 of dry degassed petroleum ether inside a modified Pnmr tube (figure 2.5). A dry degassed sample (5.65 mmol) of dimethylchloramine was transferred by the vacuum line and condensed on to this solution at -196°C. The tube was held at -46.5°C for eight hours and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethylchloramine, petroleum ether and methyl-chloride. These were pumped away leaving a colourless liquid which showed one sharp peak in the ^{31}Pnmr spectrum at -24.2 p.p.m. (figure 33). The infrared spectrum of the liquid product is shown in figure 6 and the elemental analyses are shown in table 3.6.

Table 3.6

Element	Calculated for (MeO)POPhNMe$_2$	Found
C	54.23	73.70
H	7.04	7.53
N	7.04	7.21
P	15.58	15.47

These results indicate that the overall reaction was as follows:

$$Me_2NCl + (MeO)_2PPh \longrightarrow (MeO)POPhNMe_2 + MeCl$$
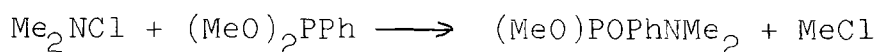
3.8 The reaction between dimethylbromamine and bis(methoxy)phenyl phosphine

This reaction was carried out using the same technique

described above (3.7),   except that the tube was kept
at -30°C (the freezer temperature) for eight hours.   The
amount of the reactants were 3.7 mmol of methoxy phenyl phos-
phine and 4.3 mmol of dimethyl bromamine.   The tube was
allowed to warm to room temperature and the gas phase infra-
red spectrum of the most volatile fraction showed a mixture
of methylbromide, petroleum ether and dimethylbromamine.
These were pumped away leaving a colourless liquid giving
one sharp peak at -24.1 p.p.m. in its ^{31}Pnmr spectrum.   This
chemical shift was close to the chemical shift found for
(MeO)POPhNMe$_2$ which was prepared by reacting dimethyl-
chloramine with bis(methoxy)phenyl phosphine (3.7).
The infrared spectra for the two liquids were also very
similar.   These results indicate that the overall reaction
was:

$$Me_2NBr + (MeO)_2PPh \longrightarrow (MeO)POPhNMe_2 + MeBr$$
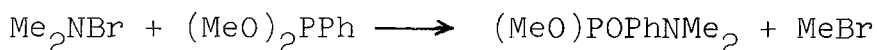
3.9   The reaction between methoxydiphenyl phosphine and dimethyl chloramine

A sample of methoxydiphenyl phosphine (5.56 mmol)
was dissolved in 4cm^3 of dry degassed petroleum ether
inside a reaction vessel (figure 2.2b).   On to this solution
8.8 mmol of dimethyl chloramine was condensed at -196°C.
After the reactant had been kept at -46.5°C for seven hours,
a brownish orange solid formed.   The cell was allowed to
warm to room temperature and the gas phase infrared spectrum
of the most volatile fraction showed a mixture of methyl
chloride, dimethyl chloramine and petroleum ether.   These
were pumped away through the vacuum line leaving a brownish
orange solid.   The ^{31}Pnmr spectrum of this solid dissolved
in dichloromethane showed one sharp peak at -29.1 p.p.m.,

this chemical shift corresponds to the known chemical shift of Ph_2PONMe_2 (δ -29.6 p.p.m.(64). The infrared spectrum of this product showed the formation of a phosphorus oxygen double bond, by its characteristic band at 1260 cm^{-1} (Fig.7). The elemental analyses results are listed in table 3.7.

Table 3.7

Element	Calculated for Ph_2PONMe_2	Found
C	68.57	67.93
H	6.53	7.20
N	5.71	6.15
P	12.65	13.01

These results indicate that the reaction was as follows:

$$(MeO)PPh_2 + Me_2NCl \longrightarrow Ph_2PONMe_2 + MeCl$$
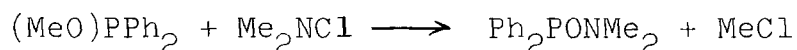
3.10 The reaction between methoxydiphenyl phosphine and dimethyl bromamine

A sample of methoxy diphenyl phosphine (3.7 mmol) dissolved in 4 cm^3 of dry degassed petroleum ether, was reacted with 5.6 mmol of dry degassed dimethyl bromamine in a reaction vessel at -22.2°C for seven hours. The infra red spectrum of the most volatile fraction showed a mixture of methyl bromide, dimethyl bromamine and petroleum ether. These were pumped away leaving a brownish orange solid. The ^{31}Pnmr spectrum of the solid product dissolved in dichloromethane showed one sharp peak only at -29.1 p.p.m., this chemical shift is identical to the chemical shift of Ph_2PONMe_2 which was prepared by reacting $(MeO)PPh_2$ with dimethylchloramine(3.9). The infrared spectrum of

this compound corresponds very closely to the infrared
spectrum of Ph_2PONMe_2 (figure 7   ).   The elemental analyses
results are listed in table 3.8.

Table 3.8

Element	Calculated for Ph_2PONMe_2	Found
C	68.57	67.38
H	6.53	6.71
N	5.71	5.53
P	12.65	12.72

These results indicate that this reaction can be represented
by the following equation:

$$(MeO)PPh_2 + Me\ NBr \longrightarrow Ph_2PONMe_2 + MeBr$$
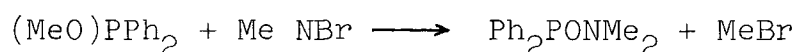
3.11 The preparation of bis(methoxy)chloro phosphine

This was prepared by reacting tri(methoxy)phosphine
15g (121 mmol) with phosphorus trichloride 33.24g (242 mmol)
(65).   The purity of the product was checked by [31]Pnmr
spectroscopy, which showed one sharp peak only at -196.0
p.p.m. due to the formation of bis(methoxy)chloro phosphine.
The elemental analyses data are shown in table 3.9.

Table 3.9

Element	Calculated for $(MeO)_2PCl$	Found
C	18.68	18.95
H	4.67	5.01
P	24.13	24.07
Cl	27.60	27.26

3.12 The reaction between bis(methoxy)chloro phosphine and dimethyl chloramine

A dry degassed sample of dimethyl chloramine (7.5 mmol) was transferred by the vacuum line and condensed on to 5.6 mmol of bis(methoxy)chloro phosphine dissolved in 3 cm^3 of dry degassed dichloromethane inside a modified Pnmr tube (figure 2.5) at -196°C. The tube was kept at -45°C for eight hours. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dichloromethane, dimethylchloramine and methyl chloride. On pumping the volatile materials away a colourless liquid was left, which had a ^{31}Pnmr spectrum (figure 34) showing the presence of one sharp peak only at -19.3 p.p.m. This chemical shift corresponded to the chemical shift of (MeO)PONMe$_2$Cl which has a tetrahedral structure. The infrared spectrum of this liquid is shown in figure 8. The elemental analyses are listed in Table 3.10 and agreed with the molecular formula (MeO)PClNMe$_2$.

Table 3.10

Element	Calculated for (MeO)PClNMe$_2$	Found
C	22.86	21.94
H	5.72	6.07
N	8.89	9.11
P	19.69	19.54
Cl	22.52	22.21

These results indicate that the above reaction could be represented by the following:

$$(MeO)_2PCl + Me_2NCl \longrightarrow (MeO)POClNMe_2 + MeCl$$
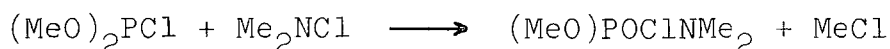
3.13 The reaction between bis(methoxy)chloro phosphine and dimethylbromamine

This reaction was carried out by applying the same technique employed in 3.12. The amount of the reactants were 5.8 mmol of dimethyl bromamine and 5.1 mmol of

bis(methoxy)chloro phosphine.   After the reaction the gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethylbromamine, dichloromethane (used as a solvent) and methyl bromide.   These were pumped away leaving a colourless liquid, the ^{31}Pnmr spectrum of which showed one sharp peak only at -19.1   p.p.m.   This chemical shift is very close to that of $(MeO)POClNMe_2$ prepared as described in section 3.12.   The infrared spectrum of this liquid is identical to that of $(MeO)POClNMe_2$ (figure 8).   The elemental analyses results are shown in table 3.11.

Element	Calculated for $(MeO)POClNMe_2$	Found
C	22.86	22.07
H	5.72	5.53
N	8.89	8.49
P	19.69	20.11
Cl	22.52	21.94

These results indicate that the above reaction was

$$(MeO)_2PCl + Me_2NBr \longrightarrow (MeO)POClNMe_2 + MeBr$$
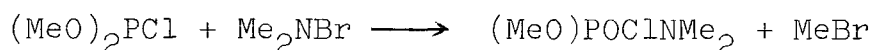
3.14 The reaction between methoxydichloro phosphine and dimethyl chloramine

Methoxydichloro phosphine (6.7 mmol) was degassed and dissolved in 4 cm^3 of dry degassed petroleum ether, inside a modified Pnmr tube (figure 2.5).   Dimethylchloramine (8.5 mmol) was degassed and condensed onto the phosphine solution at -196°C.   The tube was kept at -30°C (the freezer temperature) for eighteen hours and then allowed to warm to room temperature.   The gas phase infrared spectrum of the

most volatile fraction showed a mixture of methylchloride, petroleum ether, and dimethylchloramine. These were pumped away through the vacuum line leaving a colourless liquid. The ^{31}Pnmr spectrum of this liquid showed one sharp peak only at -19.7 p.p.m. (figure 35). The infrared spectrum is shown in figure 9, and the elemental analyses are listed in table 3.12.

Table 3.12

Element	Calculated for Me_2NPOCl_2	Found
C	14.82	14.65
H	3.71	4.01
N	8.65	8.80
P	19.15	19.39
Cl	43.79	42.44

These results indicate that this reaction was:

$$(MeO)PCl_2 + Me_2NCl \longrightarrow Me_2NPOCl_2 + MeCl$$
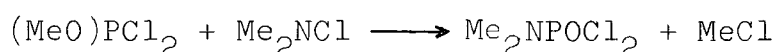
3.15 The reaction between methoxydichloro phosphine and dimethyl bromamine

A degassed sample of methoxy dichloro phosphine (5.3 mmol) was condensed onto 4 cm^3 of dry degassed petroleum ether, inside a modified Pnmr tube (figure 2.5). A dry degassed sample of dimethyl bromamine (7.1 mmol) was condensed onto the phosphine solution at -196°C. The tube was kept at -30°C for nine hours and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of methyl bromide,

petroleum ether and dimethyl bromamine. These were pumped away leaving a colourless liquid the ^{31}Pnmr spectrum of which showed one sharp peak only at -19.3 p.p.m. The chemical shift corresponded (within experimental error) to that of Me_2NPOCl_2 (prepared by reacting dimethyl chloramine with methoxy dichloro phosphine as described in Section 3.14). The infrared spectrum of this compound was very similar to that of Me_2NPOCl_2 (figure 9). Elemental analyses are shown in Table 3.13.

Table 3.13

Element	Calculated for Me_2NPOCl_2	Found
C	14.82	14.61
H	3.71	3.95
N	8.65	8.89
P	19.15	19.11
Cl	43.79	42.96

These results suggest that the reaction which occurred was:

$$(MeO)PCl_2 + Me_2NBr \longrightarrow Me_2NPOCl_2 + MeBr$$
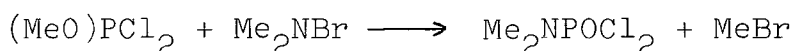
3.16 Results and Discussion

It was found that $(MeO)_{3-n}PY_n$ (n = 0,1,2 and Y = Cl or Ph) reacted with Me_2NX (X = Cl or Br) to produce MeX and $(MeO)_{2-n}POY_nNMe_2$. When Me_2NX was reacted with tris-thio-methoxy phosphine, the products were $(MeS)_2PSNMe_2$ and MeX. When tris-phenoxy- phosphine was reacted with Me_2NBr the product was $(PhO)_3P.NMe_2^+.Br^-$. This product might have been

formed by an S_N2 attack by the phosphorus atom on the nitrogen of the halamine. It seems likely that the reaction of Me_2NX and the aliphatic phosphorus acid esters passes through two steps; the first is an S_N2 attack by the phosphorus atom on the nitrogen atom of the halamine. This would produce an intermediate phosphonium salt and in a second step the halide ion would attack a methyl group in an S_N2 reaction (producing MeX and P = O compounds):

$$PhP(OMe)_2 + Me_2NCl \longrightarrow \underset{\overset{|}{NMe_2}}{\overset{\overset{OMe}{|}}{Ph-P}}-O-\underset{\overset{|}{H}}{\overset{\overset{H}{|}}{C}}-H \cdot Cl^- \longrightarrow \underset{\overset{|}{NMe_2}}{\overset{\overset{OMe}{|}}{Ph-P}}=O + MeCl$$
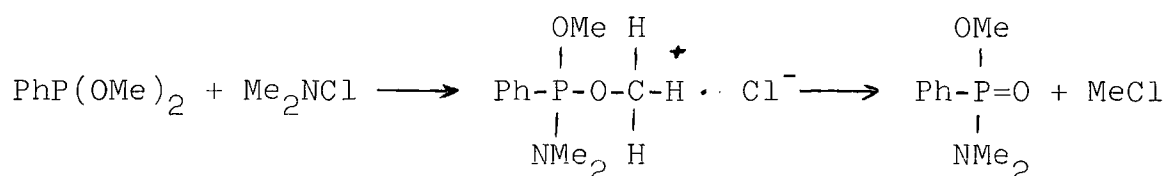
It was very difficult to detect the formation of the intermediate compounds in many cases, but the intermediate species were isolated when Me_2NX was reacted with $(MeS)_3P$. The intermediate compound was probably $(MeS)_3PNMe_2^+ - X^-$ which was isolated as a solid. It decomposed slowly at room temperature ($18^\circ C$) and was transformed completely to $(MeS)_2$ $PNMe_2$ and MeX at $35^\circ C$ in a few seconds. The reaction between Me_2NBr and $(PhO)_3P$ produced $(PhO)_3PNMe_2^+ \cdot X^-$ which is stable at room temperature and its ionic character was indicated by its $^{31}Pnmr$ spectrum which showed a peak in the region expected for tetracoordinate phosphonium ion (1). The stability of this phosphonium ion is attributed to the fact that the chlorine anion cannot easily attack the bond between the benzene ring and oxygen atom. The phenyl derivatives are known to be unreactive towards nucleophilic reactions (67).

From this work it is possible to conclude that $(MeO)_3P$ and $(MeS)_3P$ behaved in a similar manner towards Me_2NX. This is due to the fact that both oxygen and sulphur are strongly electronegative atoms, consequently the electronic cloud of the σ-bond will be shifted towards these atoms producing a partial positive charge on the carbon atom. Thus the carbon atom will be susceptible to a nucleophilic attack by the halide ion. The rate of the S_N2 attack by the halide ion is related to the extent of the susceptibility of the carbon atom and since the oxygen atom is more electronegative than the sulphur atom, the partial positive charge produced on the carbon atom linked to oxygen will be greater than that generated on the carbon atom linked to sulphur. Thus the rate of S_N2 reaction will be slower and thus it was possible to observe the intermediate phosphonium salt when $(MeS)_3P$ was reacted with Me_2NX. To support this concept it is possible to describe the reaction of triethylphosphite and sulphenylchloride (61,62)

$$(C_2H_5O)_3P + CH_3SCl \longrightarrow (C_2H_5O)_3P-SCH_3^+ \cdot Cl^- \longrightarrow C_2H_5Cl + (C_2H_5O)POSCH_3$$
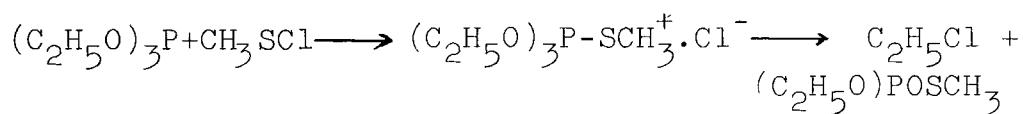
The alkyl halide formed was ethyl chloride instead of methyl chloride, since cleavage of a carbon-oxygen bond by a nucleophile is easier than cleavage of a carbon-sulphur bond (68).

CHAPTER FOUR

THE HALOGENATION OF A VARIETY

OF P-N PHOSPHINES

4.1 Introduction

The simplest halogenating agents are halogen molecules, which react vigorously with many phosphines to produce phosphorus (V) compounds (69) e.g.:

$$Ph_3P + Cl_2 \longrightarrow Ph_3PCl_2$$

The interhalogens also react and ICl can act as a chlorinating agent for example phenyldichloro phosphine reduces iodine monochloride to iodine (70):

$$PhPCl_2 + 2ICl \longrightarrow PhPCl_4 + I_2$$
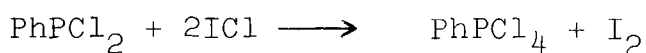
In the studies on phosphorus trifluoride, the final product of oxidation by chlorine, bromine (with the presence of HCl) and iodine monochloride was found to be dichlorotrifluorophosphorane (71):

$$PF_3 + Cl_2 \longrightarrow PF_3Cl_2$$

$$PF_3 + Br_2 + 2HCl \longrightarrow PF_3Cl_2 + 2HBr$$

$$PF_3 + 2ICl \longrightarrow PF_3Cl_2 + I_2$$
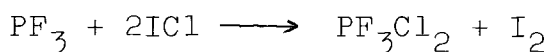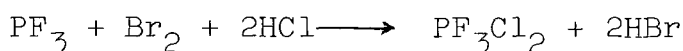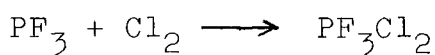
Dichlorotrifluorophosphorane slowly becomes ionic in nature:

$$2PF_3Cl_2 \longrightarrow PCl_4^+ \cdot PF_6^-$$
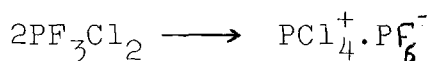
Although halogens oxidise phosphorus (III) compounds to phosphorus (V) compounds it has been reported that careful halogenation can convert primary (72) and secondary phosphines (73) to halophosphines:

$$C_4H_9PH_2 + 2Br_2 \xrightarrow{10^o} C_4H_9PBr_2 + 2HBr$$

$$(C_4H_9)_2PH + Br_2 \longrightarrow (C_4H_9)_2PBr + HBr$$
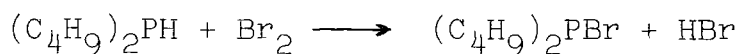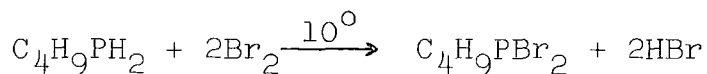
Another study was directed towards the halogenations of some phosphites (74):

$$(C_2H_5O)_3P + Cl_2 \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}Cl + C_2H_5Cl$$

$$(PhO)_2P-O-C_6H_{11} + I_2 \longrightarrow (PhO)_2\overset{O}{\overset{\|}{P}}-I + H_{11}C_6-I$$
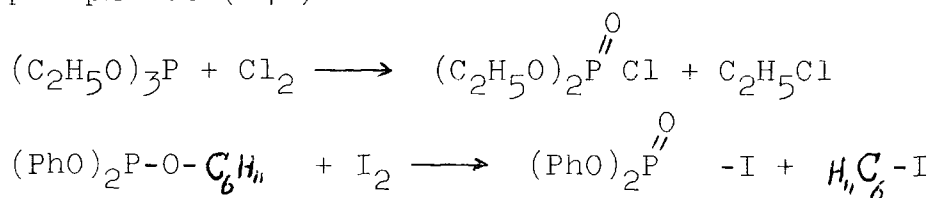
Gorbatenko and Feshchenko reacted tris(dialkylamino)phosphine with iodine (75):
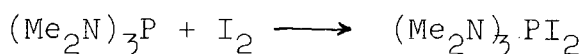
$$(Me_2N)_3P + I_2 \longrightarrow (Me_2N)_3PI_2$$

In the presence of excess iodine $(Me_2N)_3PI_2$ was produced. The ^{31}Pnmr chemical shift of these products were not reported. The same workers reacted bis(dialkylamino)iodophosphine with an equimolecular amount of iodine (75); and they found that disproportionation of the initial product occurred:

$$2(Me_2N)_2PI + 2I_2 \longrightarrow 2(Me_2N)_2PI_3 \longrightarrow (Me_2N)_3PI_4 + Me_2NPI_2$$
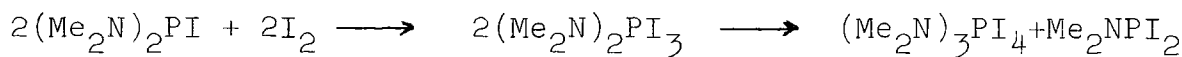
A similar set of reactions occurs when the dimethylamino group is replaced by phenoxy (76):

$$(PhO)_2PX + X_2 \longrightarrow (PhO)_2PX_3$$

$$2(PhO)_2PX_3 \longrightarrow (PhO)_3PX_2 + PhOPX_4$$

$$2(PhO)_3P + X_2 \longrightarrow (PhO)_4PX + (PhO)_2PX$$

$$(PhO)_2PX_3 + (PhO)_4PX \qquad 2(PhO)_3PX_2$$

$$(X = Cl, Br, I)$$
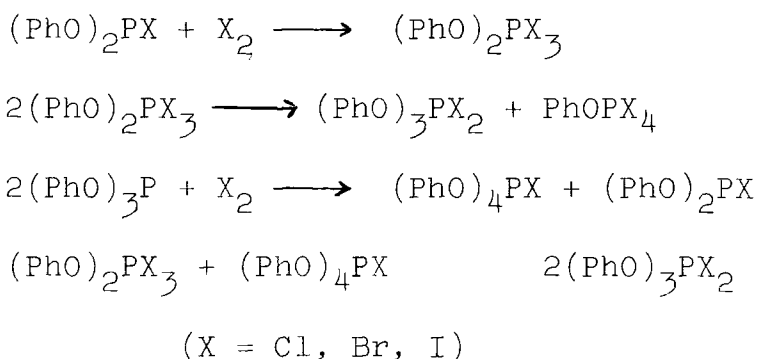
with iodine at temperatures greater than room temperature (77):

$$(PhO)_4PI + (PhO)_2PI + I_2 \longrightarrow (PhO)_3PI^+ \cdot I_3^- + (PhO)_3P$$
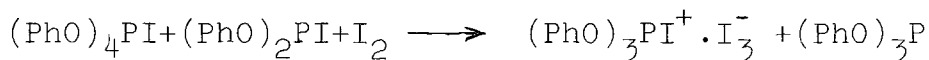
In previous work carried out in this laboratory, dimethylamino dichlorophosphine was chlorinated in a vigorous reaction (1):

$$3Me_2NPCl_2 + 4Cl_2 \longrightarrow (Me_2NPCl_3)_2Cl \cdot PCl_6 + Me_2NCl$$
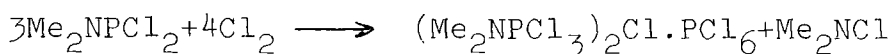
To expand the work in this field a variety of substituted dimethyl-aminophosphines have been halogenated.

4.2 The preparation of dimethylaminodiphenyl phosphine (I) and bis(dimethylamino)phenyl phosphine (II)

The compounds I and II were prepared by reacting dimethyl-amine with the corresponding phenyl phosphine (78):

$$Ph_2PCl + 2Me_2NH \longrightarrow (Me_2N)PPh_2 + Me_2NH_2Cl$$

$$PhPCl_2 + 4Me_2NH \longrightarrow (Me_2N)_2PPh + 2Me_2NH_2Cl$$
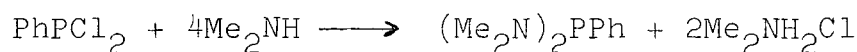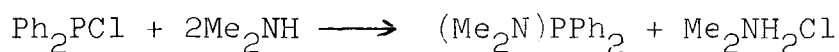
Because similar procedures were used for the preparation of these phosphines, only the preparations of I will be described in detail:

Diphenyl chloro phosphine (142 mmol) was syringed into a three-necked round bottom flask containing dry, degassed petroleum ether (50 cm^3). The flask was continuously pressurised with dry nitrogen through a tap fitted to a side neck. The central neck was fitted with a mechanical stirrer. The remaining neck was equipped with a dropping funnel, containing dry degassed petroleum ether (50 cm^3) and dimethylamine (295 mmol) under dry nitrogen. The flask was cooled to $-6^{\circ}C$ in an ice-salt mixture. The amine solution was then added dropwise with continuous stirring. Addition was completed after about an hour, but the stirring was con-tinued for a further 20 minutes to ensure complete reaction. The white precipitate formed (Me_2NH_2Cl) was isolated by filtration under a dry atmosphere of nitrogen and washed three times with ether. The filtrate containing I was collected in a clean conical flask and the solvent was pumped

away leaving a white solid.   The purities of I and II were
checked by [31]Pnmr spectroscopy and elemental analysis.   The
spectrum of the ethereal solution of I showed one sharp peak
only at -64.3 p.p.m. due to the formation of Ph_2PNMe_2 (60)
and that of II showed one sharp peak at -99.8 p.p.m. due to
the formation of $PhP(NMe_2)_2$ (60).   The elemental analysis
data are listed in tables 4.1 and 4.2:

Table 4.1

Element	Calculated for Ph_2PNMe_2	Found
C	73.36	72.15
H	6.99	7.20
N	6.12	6.22
P	13.54	13.46

Table 4.2

Element	Calculated for $PhP(NMe_2)_2$	Found
C	61.22	61.11
H	8.67	8.96
N	14.29	15.06
P	15.82	15.63

4.3   The chlorination of diphenyl dimethylamino phosphine

A sample of diphenyl dimethylamino phosphine (34.9 mmol)
prepared as described in Section 4.2 was dissolved in 40 cm^3
of dry and degassed dichloromethane.   This solution was
placed inside a three necked round bottom flask under an
atmosphere of dry nitrogen.   Dry chlorine was bubbled for
five minutes through the phosphine solution (coded to $-6^{o}C$
with an ice-salt mixture).   The flask was allowed to warm
to room temperature for half an hour under dry nitrogen and
then connected to the vacuum line.   The gas phase infrared
spectrum showed the presence of dichloromethane only.   The
solvent was pumped away leaving a white solid which was washed

three times with petroleum ether inside the dry box. The
^{31}Pnmr spectrum of the product dissolved in dichloromethane
showed one sharp peak at -74.9 p.p.m. figure (36) due to the
formation of $Me_2NPPh_2Cl^+.Cl^-$ which has been prepared by re-
acting Ph_2PCl with Me_2NCl (1). The infrared spectrum of
the product is shown in figure (10) and the elemental analysis
data are listed in table 4.3:

Table 4.3

Element	Calculated for $Ph_2PNMe_2Cl_2$	Found
C	56.01	56.21
H	5.34	5.57
N	4.67	4.26
P	10.34	16.33
Cl	23.64	22.98

These results indicate that simple chlorination of the
phosphine has occurred:

$$Ph_2PNMe_2 + Cl_2 \longrightarrow Ph_2PNMe_2Cl^+.Cl^-$$
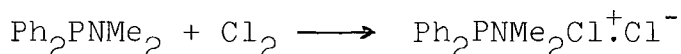
4.4   The bromination of diphenyl dimethylamino phosphine

Diphenyl dimethylamino phosphine prepared as described
in Section 4.2 was dissolved in 50 cm^3 of dry and degassed
dichloromethane inside a 250 cm^3 three necked round bottom
flask which was kept under a dry atmosphere of nitrogen. A
sample of bromine (42.8 mmol) was dissolved in 50 cm^3 of di-
chloromethane and added to the phosphine solution dropwise
with continuous stirring at 0°C. When the addition of the

bromine solution was completed the flask was stirred at room temperature under dry nitrogen for half an hour. The flask was then connected to the vacuum line. The gas phase infra- red spectrum showed the presence of dichloromethane only which was evaporated off leaving a yellow solid. This was washed three times with petroleum ether inside the dry box. The ^{31}Pnmr spectrum of the product dissolved in dichloro- methane showed one sharp peak only at -70.9 p.p.m. due to the formation of a phosphonium ion (figure 37). This chemical shift has not been reported previously, the elemental analysis results are listed in table 4.4:

Table 4.4

Element	Calculated for $Ph_2PNMe_2Br_2$	Found
C	43.21	43.01
H	4.12	4.38
N	3.60	3.71
P	7.97	8.06
Br	41.10	41.21

This result indicates that simple bromination of the phosphine had occurred:

$$Ph_2PNMe_2 + Br_2 \longrightarrow Ph_2PNMe_2Br^+.Br^-$$
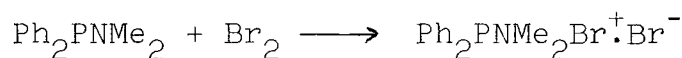
4.5 The chlorination of phenyl bis(dimethylamino)phosphine

Phenyl bis(dimethylamino)phosphine (38.3 mmol) prepared as described in section 4.2 was dissolved in 50 cm^3 of dry degassed dichloromethane inside a three necked round bottom

flask which was kept under dry nitrogen. The flask was cooled to $-6^{\circ}C$ and dry chlorine gas bubbled for three minutes through the phosphine solution which was being stirred continuously. The flask was allowed to warm to room temperature under dry nitrogen for half an hour and then connected to the vacuum line. The gas phase infrared spectrum showed the presence of dichloromethane only. The solvent was pumped away leaving a white solid, which was washed four times with petroleum ether inside the dry box. The ^{31}Pnmr spectrum of the product dissolved in dichloromethane showed one sharp peak at -67.8 p.p.m. due to the formation of a tetracoordinate phosphonium ion (figure 38), this chemical shift has not been previously reported. The infrared spectrum of the product is shown in figure (11) and the elemental analysis results listed in table 4.5:

Table 4.5

Element	Calculated for $PhP(NMe_2)_2Cl_2$	Found
C	44.96	45.01
H	6.37	6.46
N	16.49	10.55
P	11.62	11.41
Cl	26.56	26.37

These results indicate that simple chlorination of the phosphine had occurred:

$$PhP(NMe_2)_2 + Cl_2 \longrightarrow PhP(NMe_2)_2Cl^+Cl^-$$
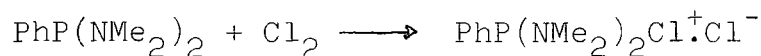
4.6 The bromination of phenyl bis(dimethylamino)phosphine

Phenyl bis(dimethylamino)phosphine (3.57 mmol) prepared as described in section 4.2 was dissolved in 50 cm^3 of dry and degassed dichloromethane inside a three necked round bottom flask. A sample of bromine (3.6 mmol) was dissolved in 60 cm^3 of dry degassed dichloromethane. The bromine solution was added to the phosphine solution dropwise, under an atmosphere of dry nitrogen at -6°C with continuous stirring. When the addition was completed the contents of the flask were allowed to warm to room temperature with continuous stirring. The flask was connected to the vacuum line and the gas phase infrared spectrum showed the presence of dichloromethane only. This was pumped away leaving an orange solid which was washed five times with petroleum ether, inside the dry box. The ^{31}Pnmr spectrum of the product showed one broad peak at -70.9 p.p.m. due to the formation of a tetracoordinate phosphonium ion. The infrared spectrum of this product is similar to that of PhP(NMe$_2$)$_2$Cl.Cl except for the absence of the P-Cl stretching frequency in the region of 570-520cm^{-1} and the presence of a band at 490cm^{-1} (79) attributable to the P-Br stretching frequency. The elemental analysis data are listed in table 4.6:

Table 4.6

Element	Calculated for PhP(NMe$_2$)$_2$Br$_2$	Found
C	33.72	33.52
H	4.78	4.99
N	7.87	8.02
P	8.71	8.61
Br	44.92	44.70

These results indicate that a tetracoordinate phosphonium ion was formed and the reaction can be represented by the following equation:

$$PhP(NMe_2)_2 + Br_2 \longrightarrow PhP(NMe_2)_2Br^+.Br^-$$
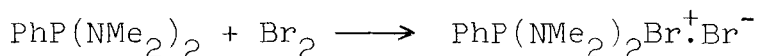
4.7 The preparation of dimethylamino dibromophosphine and bis(dimethylamino)bromophosphine

These phosphines were prepared by reacting phosphorus tribromide with dimethylamine but using different stoichiometric ratios (78) as follows:

1. $PBr_3 + 2Me_2NH \longrightarrow Me_2NPBr_2 + Me_2NH_2Br$

2. $PBr_3 + 4Me_2NH \longrightarrow [Me_2N]_2PBr + 2Me_2NH_2Br$
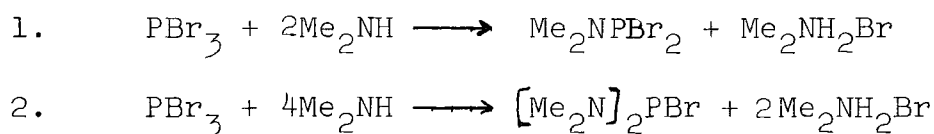
The procedures for the preparation of these phosphines were similar, consequently only the preparation of dimethylamino dibromophosphine will be described in detail.

Phosphorus tribromide (0.13 mole) was dissolved in 50 cm^3 of dry degassed ether, in a three necked round bottom flask, fitted with a mechanical stirrer, a tap (connected to source of dry nitrogen) and a dropping funnel which contained dimethylamine (0.27 mole) dissolved in cold dry degassed petroleum ether (60 cm^3). The flask was cooled to $-83^{\circ}C$ and the dimethylamine solution added dropwise to the phosphine solution with continuous stirring. The addition was completed after an hour and the contents of the flask were stirred at $-83^{\circ}C$ for a further 30 minutes. Then the cooling bath was removed and the stirrer kept on while the mixture

warmed to room temperature. The formation of a pale coloured solid, and an ethereal supernatant layer (containing dimethylamino dibromophosphine) was observed inside the flask. The pale yellow solid was isolated by filtration under dry nitrogen and washed three times with ether. The filtrate was placed in a clean dry conical flask, and ether was removed by evacuation leaving a pale yellow liquid, the infrared spectrum of which (thin film) is shown in figure 12. The elemental analyses results for Me_2NPBr_2 and $(Me_2N)_2PBr$ are listed in table 4.7 and table 4.8:

Table 4.7

Table 4.8

Element	Calculated for Me_2NPBr_2	Found
C	10.22	11.10
H	2.56	2.81
N	5.96	5.73
P	13.20	13.01
Br	68.06	67.92

Element	Calculated for $(Me_2N)_2PBr$	Found
C	24.13	23.97
H	6.03	6.40
N	14.08	14.62
P	15.59	15.33
Br	40.17	39.86

The $^{31}Pnmr$ spectrum of Me_2NPBr_2 showed one sharp peak at -176.5 p.p.m. and the $^{31}Pnmr$ spectrum of $(Me_2N)_2PBr$ showed one sharp peak at -170.9 p.p.m. The chemical shifts of these phosphines have not been reported in the literature.

4.8   The bromination of dimethylamino dibromophosphine

A dry degassed solution of dimethylamino dibromo phosphine (39.4 mmol) prepared as described in Section 4.7 was dissolved in petroleum ether (60 cm^3) and introduced into a three necked round bottom flask under dry nitrogen. A dry, degassed solution of bromine (39.1 mmol) dissolved in petroleum ether (50 cm^3) was added dropwise to the phosphine solution at $-6^{\circ}C$ with continuous stirring.   When the addition was complete the reactants were allowed to warm to room temperature with stirring for half an hour.   The formation of a yellowish orange solid was observed, which was isolated by evaporating the solvent *in vacuo*. The solid was washed three times with petroleum ether inside the drybox.   The ^{31}Pnmr spectrum of the solid showed a broad peak at -12.9 p.p.m. due to the formation of a tetracoordinate phosphonium ion figure 39 , the chemical shift of this compound has not been reported previously.   The infrared spectrum is shown in figure (13) and the elemental analyses data are listed in table 4.9:

Table 4.9

Element	Calculated for Me_2NPBr_4	Found
C	6.08	5.79
H	1.52	1.94
N	3.55	4.01
P	7.86	7.40
Br	81.00	82.18

These results indicate that the overall reaction was simple bromination of the phosphine:

$$Me_2NPBr_2 + Br_2 \longrightarrow Me_2NPBr_3^+ . Br^-$$
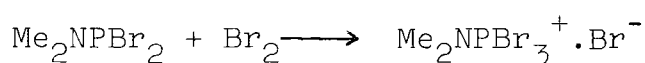
4.9   The bromination of bis(dimethylamino)bromo phosphine

In a three necked round bottom flask, a sample of bis
(dimethylamino) bromophosphine (42.7 mmol) as prepared in
Section 4.7) was dissolved in 50 cm^3 of dry degassed petrol-
eum ether.   A solution of bromine (42.7 mmol) in dry, de-
gassed petroleum ether (60 cm^3) was added dropwise with con-
tinuous stirring under dry nitrogen to the phosphine solution
(coded to -6°C).   When the addition was completed, the flask
was stirred under dry nitrogen for half an hour until the
contents reached room temperature.   The formation of a
yellow solid was observed, which was isolated by pumping
off the solvent.   The solid (after washing three times with
petroleum ether) showed a broad peak at -45.3 p.p.m. due to
the formation of a tetracoordinate phosphonium ion (figure 40);
the chemical shift of this ion has not previously been re-
ported.   The infrared spectrum is shown in figure (14)
and the elemental analyses are listed in table 4.10:

Table 4.10

Element	Calculated for $(Me_2N)_2PBr_3$	Found
C	13.38	12.92
H	3.35	3.53
N	7.81	7.71
P	8.64	8.80
Br	66.82	66.79

These results imply that $(Me_2N)_2PBr$ was brominated.   The
reaction can be represented by the following equation:

$$(Me_2N)_2PBr + Br_2 \longrightarrow (Me_2N)_2PBr_2^+.Br^-$$
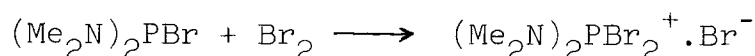
4.10 The bromination of tris(dimethylamino)phosphine

Tris(dimethylamino)phosphine (61.3 mmol) (prepared as described in Section 7.15) was dissolved in 50 cm^3 of dry degassed petroleum ether, and placed in a three necked round bottom flask. A sample of bromine (61.3 mmol) was dissolved in 60 cm^3 of dry degassed petroleum ether and added dropwise to the phosphine solution, while the flask contents were stirred under dry nitrogen at -6°C. After complete addition of the bromine solution the flask was warmed to room temperature over half an hour, with continued stirring. A yellowish orange solid was observed and this was isolated by evaporation of the solvent. The solid was washed three times with petroleum ether inside the drybox and pumped free of solvent *in vacuo*. The ^{31}Pnmr spectrum of the solid showed one broad peak at -48.3 p.p.m. due to the formation of a tetracoordinate phosphonium ion (figure 41). This chemical shift has not been reported in the literature. The infrared spectrum of the product is shown in figure (15) and the elemental analysis are listed in table 4.11:

Table 4.11

Element	Calculated for $(Me_2N)_3PBr_2$	Found
C	22.30	22.46
H	5.58	5.69
N	13.01	13.21
P	9.60	9.43
Br	49.51	48.97

These results indicate that simple bromination of the phosphine has occurred:

$$(Me_2N)_3P + Br_2 \longrightarrow (Me_2N)_3PBr^+Br^-$$
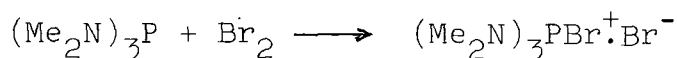
4.11 The iodination of tris(dimethylamino)phosphine

Tris(dimethylamino)phosphine (36.8 mmol) prepared as described in section 7.15 , was dissolved in 45 cm^3 of degassed dry petroleum ether ($30^{\circ}C$ - $40^{\circ}C$) and placed in a three necked round bottom flask under dry nitrogen. A sample of solid iodine (71.8 mmol) was added to the solution and the reactants stirred at reflux for five hours. A blackish grey solid was observed inside the flask which was isolated by evaporation of the solvent. The product was washed three times with dry ether inside the dry box and pumped dry. The ^{31}Pnmr spectrum of the solid showed one broad peak at -29.2 p.p.m. due to the formation of a tetracoordinate phosphonium ion. The chemical shift of this species has not been reported in the literature. The infrared spectrum is shown in figure (16) and the elemental analyses are listed in table 4.12:

Table 4.12

Element	Calculated for $(Me_2N)_3PI_2$	Found
C	17.27	16.83
H	4.32	5.02
N	10.08	10.41
P	7.44	7.40
I	60.89	60.59

These results indicate that simple iodination occurred and the overall reaction is:

$$(Me_2N)_3P + I_2 \longrightarrow (Me_2N)_3PI^+.I^-$$
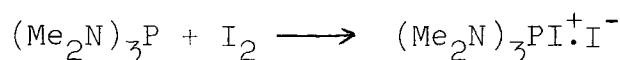
4.12 <u>The iodination of dimethylamino dibromophosphine</u>

Dimethylamino dibromophosphine (21.3 mmol) prepared as described in section 4.7, was dissolved in 16 cm^3 of dry degassed petroleum ether inside a two necked round bottom flask.   Iodine (14.1 mmol) was added to the solution which was kept under a blanket of dry nitrogen and continuously stirred.   In the flask the formation of two layers was observed, a supernatant ethereal layer and a heavy dark layer. The solvent was evaporated leaving a heavy black-brown liquid, the ^{31}Pnmr of which showed four peaks (assignments given in brackets) at 21.1 p.p.m. ($Me_2NPBrI_2^+.Br^-$), - 22.7 p.p.m. (($Me_2N)_2PBrI^+.I^-$) - 176.5 p.p.m. (Me_2NPBr_2; the starting material) and - 230.6 p.p.m. due to the formation of PBr_3 (reported δ -229 p.p.m. (80)).   The relative intensity for these peaks was 3:2:1:2 respectively.   After three hours the ^{31}Pnmr spectrum of the reaction mixture showed three peaks only at 21.1 p.p.m., -22.7 p.p.m. and at -229.3 p.p.m.   The integration ratio was 1:1:1.   This implied that the starting material Me_2NPBr_2 had reacted with the phosphorus species which has the chemical shift of 21.1 p.p.m. (most likely $Me_2NPBrI_2^+.Br^-$).   This is concluded because the relative intensity of the peak at 21.1 p.p.m. decreased as the peak due to the starting material (at -176.5 p.p.m.) disappeared. To confirm this result about 0.5 cm^3 of Me_2NPBr_2 was added to the reaction mixture.   The ^{31}Pnmr spectrum showed four peaks at 21.1 p.p.m. ($Me_2NPBr^+.Br^-$), -22.7 p.p.m. (($Me_2N)_2PBrI^+.I^-$), -229.3 p.p.m. (PBr_3), and -175.2 p.p.m. (Me_2NPBr_2), the integration ratio being 1:10:9:3 respectively.   This indicated that the phosphorus compound with a chemical shift of 21.1 ($Me_2NPBrI_2^+.Br^-$) reacts with Me_2NPBr_2.   This reaction is

discussed in section 4.14.

4.13 The reaction between phosphorus trichloride and methyl dichloramine

A sample of phosphorus trichloride (7.9 mmol) was condensed onto a reaction vessel (figure 2.2b). Dichloro methane (4cm^3) was condensed onto the phosphine solution at -196°C. The vessel was allowed to warm to room temperature and its contents were shaken to produce a homogeneous solution. The vessel was connected to the vacuum line and cooled to -196°C where the phosphine solution was degassed. Methyl dichloramine (3.1 mmol) was prepared as described in Section 2. and condensed onto the phosphine solution. The reaction vessel was held at -83°C for three hours, then it was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of phosphorus trichloride and dichloromethane. These were pumped away leaving a white solid. The ^{31}Pnmr spectrum of this solid dissolved in dichloromethane showed two sharp peaks (i) at 79.1 p.p.m. due to the formation of $(MeN=PCl_3)_2$ (δ = 79.2 p.p.m.) (81) (see Figure 42), and (ii) at 87.6 p.p.m. due to the formation of a penta-coordinate covalent phosphorus compound. The latter peak may have been due to the formation of PCl_5. The ^{31}Pnmr spectrum of the product was thus run without a solvent. This showed two peaks, at -85.8 p.p.m. (PCl_4^+) and at 298.2 p.p.m. (PCl_6^-) (see Figure 43). The infrared spectrum is shown in Figure 17. These results indicate that the reaction occurring can be written as:

$$MeNCl_2 + 2PCl_3 \longrightarrow (MeNPCl_3)_2 + PCl_5.$$
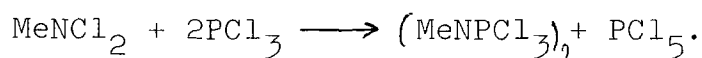
4.14 Results and discussion

The halogenation of $(Me_2N)_nPY_{n-3}$ (Y = Ph, Br and n = 1,2,3) with X_2 (X = Cl or Br) produced phosphonium salts of the following type $(Me_2N)_nPY_{n-3}X^+.X^-$. To explain these results let us take as an example the chlorination of diphenyl dimethyl amino phosphine. The product of this reaction was diphenyl dimethylamino chloro phosphonium chloride which might have been formed via an S_N2 attack by the phosphorus atom on a halogen atom:

$$Ph_2\overset{..}{P}NMe_2 + Cl-Cl \longrightarrow Ph_2PNMe_2Cl^+.Cl^-$$
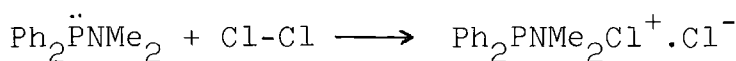
This mechanism is suggested in analogy with the mechanism proposed by Gerrard and Phillip to explain the chlorination of triisooctyl phosphite (82).

They proposed initial nucleophilic attack by the phosphorus atom on halogen, followed by an S_N2 attack by the chloride ion on the carbon atom linked to oxygen:

$$(C_8H_{17}O)_3P+Cl-Cl \longrightarrow (C_{18}H_{17}O)_2\overset{Cl}{\underset{}{P}}-O-\overset{H}{\underset{C_7H_{15}}{CH}}+Cl^- \longrightarrow (C_8H_{17}O)_2\overset{O}{P}Cl$$

$$+ C_{18}H_{17}Cl$$
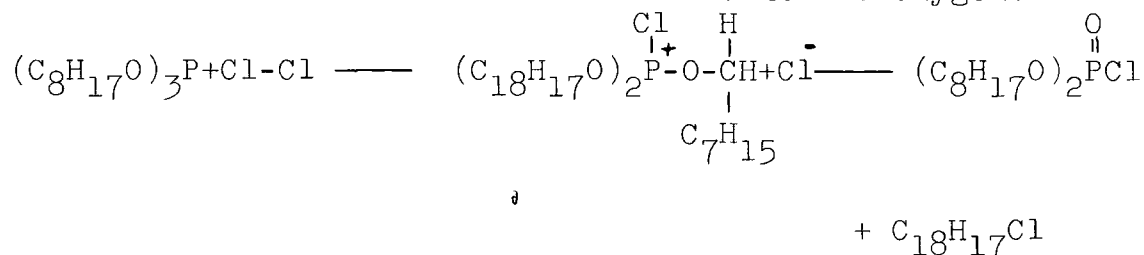
In the case of the reactions studied in this chapter the further reaction did not occur as there was no suitable nucleophilic site for the attack of the halide ion.

The results of the iodination of dimethylamino dibromo phosphine described in Section 4.12 can be represented by the following reactions:

1. $Me_2NPBr_2 + I_2 \longrightarrow Me_2NPBrI_2^+.Br^-$
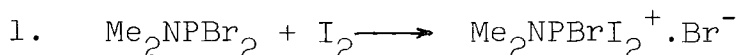
This initial product then reacted with the excess phosphine to give rearranged products.

2. $Me_2NPBrI_2^+.Br^- + Me_2NPBr_2 \longrightarrow (Me_2N)_2PBrI^+.I^- + PBr_3$
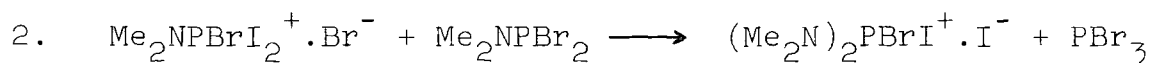
The initial product had a ^{31}P nmr chemical shift of

21.1 p.p.m. and therefore cannot be $Me_2NPBr_3^+.I^-$ because this

phosphonium ion has been prepared in this work by the bromin-

ation of Me_2NPBr_2 and its chemical shift is -12.9 p.p.m.

(Section 4.8).   The initial product was unlikely to have

been $Me_2NPI_3^+.Br^-$ as the chemical shift of this phosphonium

ion is most likely to be upfield of that of the reference.

If the initial product is $Me_2NPBr_2I^+.I^-$ and supposing that

it reacted with Me_2NPBr in the manner shown in equation number 2

then PBr_2I was most likely to have been formed instead of PBr_3.

The chemical shift of the initial product was observed in

the spectrum of the reaction between PI_3 and Me_2NBr as des-

cribed in Section 5.12.

The phosphorus species which was seen as a peak at

-22.7 p.p.m. could not be due to $(Me_2N)_2PBr_2^+$, because the

chemical shift of $(Me_2N)_2PBr_2^+.Br^-$ has been reported in this

work as -46.3 p.p.m. (Section 6.11).   The chemical shift of

-22.7 p.p.m. was unlikely to have been due to $(Me_2N)_2PI_2^+.Br^-$

as this unknown phosphonium salt is more likely to have a

positive chemical shift.   Neither can this chemical shift

be due to $(Me_2N)_3PBr^+.I$ because the chemical shift of

$(Me_2N)_3PBr^+.Br^-$ has been reported in this work (Section 4.10)

as -48.3 p.p.m.   Consequently the chemical shift of -22.7

p.p.m. is likely to have been due to $(Me_2N)_2PBrI^+.I^-$.   This

chemical shift was also observed in the spectrum of the re-

action between PI_3 and Me_2NBr as described in Section 5.12.

The third peak which appeared at -230.2 p.p.m. was due to

the formation of PBr_3.

The first spectrum of this reaction showed the peak at 21.1 p.p.m. as the major peak, with a minor peak due to the starting material Me_2NPBr_2. The second spectrum (taken after three hours) showed three peaks. at 21.1 p.p.m., -27.7 p.p.m. and -229.3 p.p.m. with integration ratios of 1:1:1. This implies that the starting material reacted with the phosphorus compound having the chemical shift of 21.1 p.p.m. To test this some Me_2NPBr_2 was added. The repeat spectrum showed that the peak at 21.1 p.p.m. became a minor one and the major peaks were at -27.7 p.p.m. and -229.2 p.p.m. with a fourth peak at -175.6 p.p.m. due to the excess of Me_2NPBr_2 added. This result implies that Me_2NPBr_2 reacted with the initial product until the reaction reached equilibrium.

The reaction between phosphorus trichloride and methyl dichloramine produced $(MeN=PCl_3)_2$ and phosphorus pentachloride. A likely mechanism for this reaction is:

$$MeNCl_2 + PCl_3 \longrightarrow \underset{\underset{Cl}{|}}{MeN} - PCl_3^+.Cl^-$$

$$\underset{\underset{Cl}{|}}{MeN}-\overset{+}{PCl_3} + PCl_3 \longrightarrow (MeNPCl_3)_2^+ PCl_4^+$$
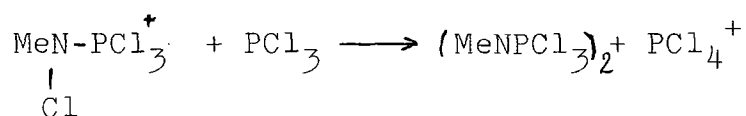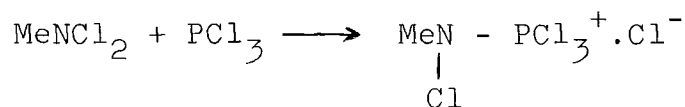
The ^{31}Pnmr spectrum of the product dissolved in methyl chloride (figure 42) showed two peaks at 79.1 p.p.m., due to $(MeN=PCl_3)_2$(81) and 85.5 p.p.m. due to PCl_5. The ^{31}Pnmr spectrum of the solid product showed two peaks at -85.9 p.p.m. due to PCl_4^+ and 298.2 due to PCl_6^-, the integration ratio of the two peaks being 1:1.

CHAPTER FIVE

<u>THE REACTIONS OF HALAMINES WITH</u>

<u>THE PHOSPHORUS TRIHALIDES</u>

5.1 Introduction

The reactions of halamines and phosphorus trihalides have not received much attention in the literature. The work done in this area comprises of only two reactions, namely the reaction between nitrogen trichloride and phosphorus trichloride which gives $(Cl_3-P-N=PCl_3)^+.PCl_6^-$; and the reaction between dimethylchloramine and excess trichloride (carried out in this laboratory (1)) which can be represented by the equation:

$$4PCl_3 + 3Me_2NCl \longrightarrow 2Me_2NPCl_3^+ + PCl_6^- + Me_2NPCl_2^+Cl^-.$$

The complexity of this reaction produced an interest in reacting the phosphorus trihalides with various halamines.

5.2 The reaction of phosphorus trichloride with excess dimethylchloramine

A sample of dry, degassed dimethylchloramine (7.4 mmol) was condensed into a modified nmr tube. Onto this was condensed $3cm^3$ of dry, degassed dichloromethane and the tube was allowed to warm to room temperature so that it could be shaken to form a homogeneous solution. Degassed phosphorus trichloride (3.1 mmol) was condensed onto this solution at $-196^\circ C$. After the tube had been kept at $-23^\circ C$ with occasional shaking for five hours, it was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethylchloramine and dichloromethane. A white precipitate was formed which was found to be insoluble in dichloromethane acetonitrile and nitrobenzene. The ^{31}Pnmr spectrum of this solid showed three peaks: a broad one at -51.6 p.p.m. due to the formation of $(Me_2N)_2PCl_2^+$ which

has been prepared by reacting Me_2NCl with Me_2NPCl_2 (1).

The second peak appeared as a shoulder on the first one at

-56.4 p.p.m. due to the formation of $Me_2NPCl_3^+$. (1). The

final peak was a broad one at 298.2 p.p.m. due to the formation

of PCl_6^- (it was difficult to measure the integration ratio,

because of the poor resolution of the two peaks at -56.4 p.p.m.

and -51.6 p.p.m.). This result implies that the reaction

can be written as:

$$3PCl_3 + 3Me_2NCl \longrightarrow Me_2NPCl_3^+ + (Me_2N)_2PCl_2^+ + PCl_6^- + Cl^-.$$
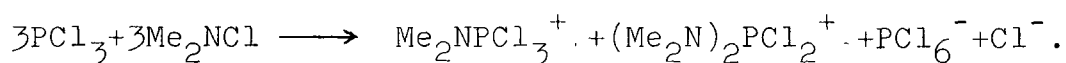
After the product had been hydrolysed by exposure to wet

nitrogen for twelve days it was noted that most of the sample

had been converted to a colourless liquid. Chloroform

(2 cm^3) was added to the sample and the ^{31}Pnmr spectrum of

the solution (figure 44) showed two sharp, minor peaks at

-58.6 p.p.m. due to unhydrolysed $Me_2NPCl_3^+.Cl^-$ and at -51.6

p.p.m. due to unhydrolysed $(Me_2N)_2PCl_2^+.Cl^-$. This spectrum

showed three other sharp peaks at -32.1 p.p.m. due to the

formation of $(Me_2N)_2POCl$ (2.2b) (produced as a result of

hydrolysis of $(Me_2N)_2PCl_2^+$).

A second peak was observed at -19.1 p.p.m. due to the

formation of Me_2NPOCl_2 (51) which was produced as a result

of hydrolysis of $Me_2NPCl_3^+$. A third peak was noted at -1.6

p.p.m. due to the formation of $POCl_3$ (83) which was produced

by the hydrolysis of PCl_6^-.

These hydrolysis further confirm the above equation

for the reaction of phosphorus trichloride with excess

dimethyl chloramine.

5.3   The reaction between phosphorus trichloride and $Me_2NPCl_3^+$

This reaction was performed to help to elucidate the reaction described in section 5.2.   A sample of the mixture (0.41g) $Me_2NPCl_3^+$, $(Me_2N)_2PCl_2^+$, PCl_6^-, Cl^- obtained as described in section 5.2, was placed inside a reaction vessel (figure 2.26) and 2 cm^3 of dry degassed dichloromethane was condensed onto it.   The vessel was shaken continuously at room temperature for 10 minutes.   Then 3 cm^3 of degassed phosphorus trichloride was condensed onto this slurry at $-196^{\circ}C$.   The vessel was allowed to warm to room temperature, but there was no indication that any reaction was occurring. The vessel was kept at room temperature for two hours, with occasional shaking.   The gas phase infrared spectrum of the most volatile fraction showed a mixture of phosphorus trichloride and dichloromethane.   These were pumped away leaving a white solid which had a similar $^{31}Pnmr$ spectrum to that of the original mixture, implying that the exchange re-action had not occurred:

$$Me_2NPCl_3^+ + PCl_3 \longrightarrow Me_2NPCl_2 + PCl_4^+$$
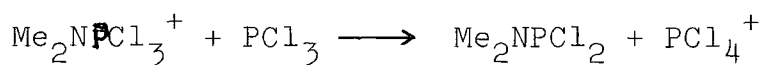
5.4   The reaction between phosphorus tribromide and dimethyl bromamine

A sample of dry degassed dimethyl bromamine (prepared as in section 2.9.3) was condensed onto 8.7 mmol of phosphorus tribromide dissolved in 3 cm^3 of petroleum ether in a reaction vessel (Figure 2.2 b)at $-196^{\circ}C$.   The reactants were kept at $-32^{\circ}C$ (the freezer temperature) for seven hours and then the cell was connected to the vacuum line and allowed to warm to room temperature.   The gas phase infrared spectrum of the

most volatile fractions showed a mixture of dimethyl
bromamine and petroleum ether.   These were evaporated,
leaving an orange solid inside the vessel.   The product
was washed three times with petroleum ether inside the dry-
box.   The ^{31}Pnmr spectrum of the solid product showed one
broad peak at -13.1 p.p.m.   This chemical shift (within
experimental error) is identical to that found for
$Me_2NPBr_3^+.Br^-$ prepared as described in section 4.8 .   The
infrared spectrum (Figure 13) showed the characteristic
peak for the phosphorus nitrogen bond at 720 cm^{-1} (84).
The elemental analysis results are shown in Table 5.1.

Table 5.1

Table 5.1

Element	Calculated for Me_2NPBr_4	Found
C	6.1	6.31
H	1.5	2.10
N	3.55	3.27
P	7.86	7.53
Br	81.00	81.72

These results indicate that the product of the reaction was
$Me_2NPBr_3^+.Br^-$ and that the reaction was a simple amination
of the phosphorus atom:

$$PBr_3 + Me_2NBr \longrightarrow Me_2NPBr_3^+.Br^-$$
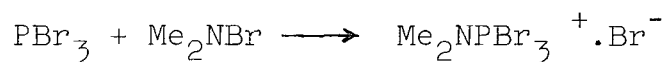
5.5 The reaction between phosphorus tribromide and dimethyl chloramine

A dry degassed sample of dimethyl chloramine (8.2 mmol) was distilled into 5.5 mmol of phosphorus tribromide dissolved in 3 cm^3 of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) at -196°C. The cell was allowed to warm to -37°C (the freezer temperature) for five hours and then warmed to room temperature. The gas phase infrared spectrum of the vessel contents showed a mixture of dimethyl chloramine and petroleum ether. A yellowish-white solid was left inside the vessel, after the volatile substances had been pumped away. The product was found to be hygroscopic and was washed with petroleum ether three times. One broad peak at -54.6 p.p.m. was found in the ^{31}Pnmr spectrum of this solid (figure 45). The infrared spectrum showed the formation of the phosphorus nitrogen bond by the presence of a peak at 720 cm^{-1} (Figure 18) (84). The elemental analysis results are given in Table 5.2.

Table 5.2

Element	Calculated for Me$_2$NPClBr$_3$	Found
C	6.85	6.17
H	1.70	2.01
N	4.00	3.88
P	8.85	8.96
Br	68.50	68.10
Cl	10.10	9.98

The elemental analysis results imply that the product has the following molecular formula Me$_2$NPClBr$_3$, and the ^{31}Pnmr result indicates that the product is a phosphonium ion and

it is not $Me_2NPBr_3^+.Cl^-$, because the chemical shift of this

phosphonium ion was found as -13.1 p.p.m. as described in

section 5.4, thus the produce is likely to be $Me_2NPClBr_2^+.Br^-$

and the overall reaction is most probably as the following:

$$Me_2NCl + PBr_3 \longrightarrow Me_2NPClBr_2^+.Br^-$$
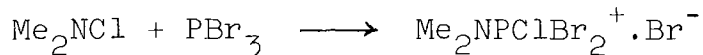
To confirm that the product is a bromide phosphonium salt

the following two experiments were carried out.

5.6   The reaction between $Me_2NPClBr_3$ and boron tribromide

Boron tribromide ($4 \ cm^3$) was condensed onto 5.3 mmol of

$Me_2NPClBr_3$ at $-196^\circ C$ inside a reaction vessel (Figure 2.2b).

The reactants were kept at $-32^\circ C$ (the freezer temperature)

for five hours.   The vessel was allowed to warm to $0^\circ C$ and

the gas phase infrared spectrum showed the presence of boron

tribromide only, which was pumped away leaving a yellowish-

orange solid inside the cell.   This solid was washed with

petroleum ether three times and the $^{31}Pnmr$ spectrum of the

solid showed one broad peak only at -54.2 p.p.m. due to the

presence of the same tetra coordinate phosphonium ion produced

by the reaction in the previous section.   The infrared spectrum

showed a broad band in the range of $700 \ cm^{-1}$: $750 \ cm^{-1}$, but

the spectrum was not clear enough to decide whether this band

was due to BBr_4^- or BBr_3Cl^-.

5.7   The reaction between $Me_2NPClBr_3$ and phosphorus pentachloride

A sample of $Me_2NPClBr_3$ (4.4 mmol) was dissolved in

$5 \ cm^3$ of dry degassed dichloromethane inside a modified Pnmr

tube (Figure 2.5) inside the dry box. Phosphorus penta-
chloride (7.2 mmol) was added to this solution and the Pnmr
tube was sealed and shaken vigorously for two hours. Three
peaks were found in the ^{31}Pnmr spectrum (Figure 46), one at
-219.3 p.p.m. corresponding to PCl_3 (57), a second at -54.1
p.p.m. (due to the phosphonium ion produced in section 5.5)
and a third at 298 p.p.m. due to PCl_6^-; in the ratio 1:2:2
approximately. The colour of the solution inside the tube
was brown, indicating the presence of bromine. K.B. Dillon
and his co-workers (85) have proved that if a bromide salt
is reacted with an excess of phosphorus pentachloride *then* bromine,
hexachlorophosphate and phosphorus trichloride will be pro-
duced. In the reaction described in this section bromine
and phosphorus trichloride have been found, thus it is likely
that the salt formed in section 5.5 is the bromide salt of
dimethylaminodibromo chlorophosphonium ion and that the re-
action occurring on addition of phosphorus pentachloride is:

$$2Br^- + 3PCl5 \longrightarrow Br_2 + PCl_3 + 2PCl_6^-$$
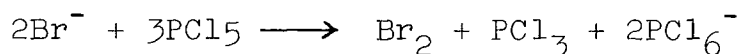
Thus the chloramination reaction that is described in
section 5.5 can be written as:

$$PBr_3 + Me_2NCl \longrightarrow Me_2NPClBr_2^+.Br^-$$
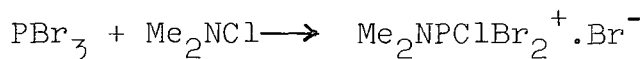
This represents not only amination of the phosphorus, but
also exchange of one of the halogens.

Presumably the reaction that is described in section 5.6
was the formation of the tetrabromoborate:

$$Me_2NPClBr_2^+.Br^- + BBr_3 \longrightarrow Me_2NPClBr_2^+ BBr_4^-$$
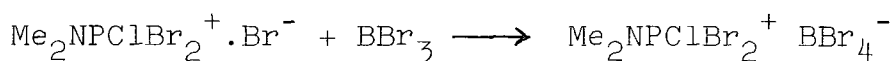
5.8 The reaction between phosphorus trichloride and dimethyl bromamine

A dry degassed sample of dimethyl bromamine (12.0 mmol) was condensed onto 19.6 mmol of degassed phosphorus tri-chloride dissolved in 3 cm^3 of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) at -196°C.   The tube was kept at -32°C (the freezer temperature) for twenty hours. After the vessel had been allowed to warm to room temperature, the gas phase infrared spectrum showed a mixture of petroleum ether and phosphorus trichloride.   The volatile substances were pumped away leaving a white substance inside the vessel. A sample of the product was transferred under dry nitrogen into a Pnmr tube.   The spectrum of the solid (Figure 47) showed three peaks:

(1)   A sharp peak at -175.2 p.p.m. which (within experimental error) corresponds to the chemical shift found for Me_2NPBr_2 as described in section 4.7);

(2)   A broad peak at -58.6 p.p.m. corresponding to $Me_2NPCl_3^+$ (1); and

(3)   A broad peak at 301.1 p.p.m. due to the formation of PCl_6^- (86).

The relative intensity of the three peaks was 1:2:1.   The product was washed with petroleum ether three times to remove Me_2NPBr_2 and the white solid remaining showed two peaks in the ^{31}Pnmr spectrum at -58.6 p.p.m. and 301.3 p.p.m. (intensity ratio 2:1).   The infrared spectrum of this solid was very similar to the infrared spectrum of $2Me_2NPCl_3^+$, PCl_6^-, Cl^- (1) (Figure 19).

The elemental analysis results are shown in Table 5.3.

Table 5.3

Element	Calculated for $(Me_2N)_2P_3BrCl_{12}$	Found
C	7.00	6.85
H	1.15	1.83
N	4.09	4.25
P	13.55	13.49
Br	61.90	60.41
Cl	11.65	11.27

These results indicate that the overall reaction was:

$$2Me_2NBr + 4PCl_3 \longrightarrow Me_2NPCl_3^+ \cdot Br^- + Me_2NPCl_3^+, PCl_6^- + Me_2NPBr_2$$
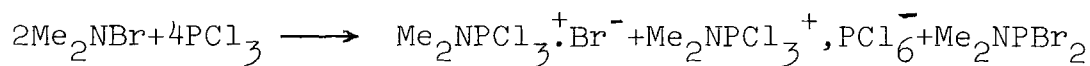
5.9 The preparation of phosphorus trifluoride

Phosphorus trifluoride was prepared as described by Booth and Bozarth by reacting antimony trifluoride with phosphorus trichloride using antimony pentachloride as a catalyst (87):

$$SbF_3 + PCl_3 \xrightarrow{SbCl_5} PF_3 + SbCl_3$$
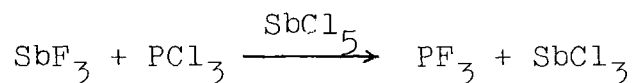
The purity of phosphorus trifluoride produced was checked by comparing its gas phase infrared spectrum with an authentic spectrum of the phosphine. The phosphine was stored in one of the bulbs of the fractionation section of the vacuum line (Figure 2.1) at liquid air temperature.

5.10 The reaction between phosphorus trifluoride and dimethylchloramine

Phosphorus trifluoride (23.9 mmol) as prepared in Section 5.9 was degassed and condensed onto 2 cm^3 of dichloromethane inside a silica nmr tube containing a constriction. A dry degassed sample of dimethylchloramine (38.6 mmol) was condensed onto this solution at -196°C and the tube sealed and allowed to warm to -23°C.   After one hour the colour of the contents was pale green.   The ^{31}Pnmr spectrum (Fig.47) showed four sets of peaks (i) a triplet centred at -21.1 p.p.m. (J = 1069 Hz) due to the formation of a tetra co-ordinate phosphonium ion, presumably $(Me_2N)_2PF_2^+$, this triplet also appeared in the spectrum of the reaction between Me_2NCl and Me_2NPF_2 (Figure 57); (ii) a heptet centred at 145.1 p.p.m. (J = 712 Hz) due to the formation of a PF_6^- (88); (iii) a sextet centred at 146.8 p.p.m. (J = 796 Hz) due to the formation of a hexa co-ordinate phosphate ion, where five fluorine atoms are attached to the phosphorus, there are two possibilities for this system, $PClF_5^-$ and $Me_2NPF_5^-$ but the first ion is known and its chemical shift is reported as   138 p.p.m. (J = 860 cps) (89   ), thus it is likely that the ion is $Me_2NPF_5^-$; (iv) a triplet centred at 30.7 p.p.m. (J = 980 Hz) due to the formation of the known PF_2Cl_3 molecular species (90).   Since the ^{31}Pnmr spectrum of the produce showed the presence of the four phosphorus species (described above) then it is possible to represent this reaction by the following equation:

$$9Me_2NCl + 7PF_3 \longrightarrow 4(Me_2N)_2PF_2^+ + PF_6^- + Me_2NPF_5^- + PF_2Cl_3$$
$$+ 2Cl^- + 2Cl_2$$
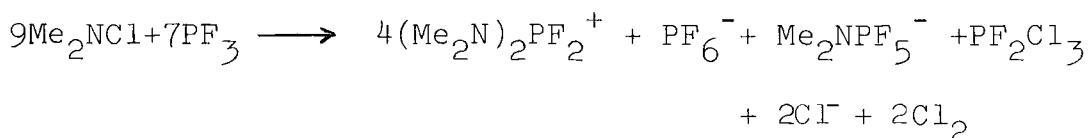
5.11 The reaction between phosphorus trifluoride and dimethylbromamine

Phosphorus trifluoride (17.1 mmol) as prepared in Section 5.9 was degassed and condensed on to 3 cm^3 of dry degassed dichloromethane inside a silica nmr tube, (figure 2.5). A dry degassed dimethylbromamine sample (42.7 mmol) was condensed onto the phosphorus trifluoride solution and the tube was sealed off and warmed to -23°C (carbon tetrachloride cooled bath). After an hour the reaction mixture had turned brown. The ^{31}Pnmr spectrum (figure 48) showed two sets of peaks: (i) a doublet centred at -41.2 p.p.m. (J = 976.5 H_z), this chemical shift is very close to the chemical shift of $(Me_2N)_3PF.^+Cl^-$ prepared by reacting $(Me_2N)_2PF$ with Me_2NCl as described in Section 5.15; (ii) a sextet centred at 148.3 p.p.m. (J = 782.1 cps) which is very close to the chemical shift of $Me_2NPF_5^-$ noted in the spectrum of the product of the reaction between phosphorus trifluoride and dimethyl chloramine, Section 5.10.

Then according to the ^{31}Pnmr spectrum which shows the presence of the species described above, it is possible to represent this reaction by the following equation:

$$4 \; Me_2NBr + 2 \; PF_3 \longrightarrow (Me_2N)_3PF^+.Me_2NPF_5^- + 2 \; Br_2$$
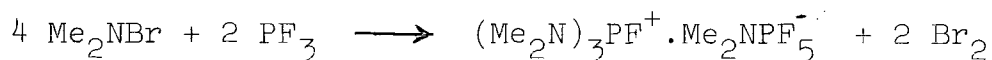
5.12 The preparation of phosphorus triiodide

Phosphorus triiodide was prepared by reacting phosphorus trichloride with potassium iodide (91) as follows: Inside a two-necked round bottomed flask and under an atmosphere of dry nitrogen, potassium iodide (30g) was made into a slurry with $50 cm^3$ of dry diethylether. Phosphorus trichloride ($5 cm^3$) was added and the reaction mixture was refluxed for 20 hours. The ether was then removed under vacuum and the phosphorus triiodide extracted with carbon disulphide. After the carbon disulphide had been pumped away a reddish solid remained. The ^{31}Pnmr spectrum of the solid dissolved in carbon disulphide showed one major peak at -177.0 p.p.m. due to phosphorus triiodide and a minor peak at -109.1 p.p.m. due to tetra iodobiphosphine. The integration ratio of the two peaks was 100:8. Tetra iodobiphosphine is generally produced as impurity when phosphorus triiodide is prepared.

5.13 The reaction between phosphorus triiodide and dimethylchloramine

This reaction was carried out four times as shown in Table 5.4. Carbon disulphide was used as a solvent for phosphorus triiodide. Dry dimethyl chloramine was degassed and condensed onto this solution inside a modified nmr tube (Figure 2.5). In each case the tube was connected to the vacuum line and the gas phase infrared spectrum determined. The vapour from the first experiment showed the presence of carbon disulphide only, while the spectra of the other experiments showed the presence of a mixture of dimethyl chloramine and carbon disulphide. These were pumped away leaving compounds as described in Table 5.4. The chemical shift of

the final product of the fourth experiment is $similar$
to that found for $(Me_2N)_3PCl^+.Cl^-$ ($\delta = -53.3$ p.p.m. (1)).
Thus it is likely that complete oxidation of all the P-I bonds
had occurred.

$$3Me_2NCl + PI_3 \longrightarrow (Me_2N)_3PCl^+.ICl_2^- + I_2$$
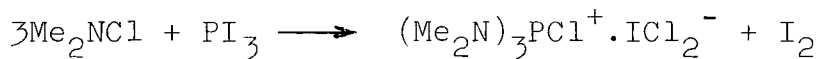
The presence of the iodide was implied by the dark metallic
colour of the product.

5.14 The reaction between phosphorus triiodide and dimethylbromamine

This reaction was carried out using the same technique
as described in the previous section.   Phosphorus triiodide
was dissolved in carbon disulphide and dimethylbromamine was
degassed before it was condensed onto the solution at $-196^{\circ}C$.
This reaction was performed four times under different con-
ditions as shown by Table 5.5.   The gas phase infrared
spectrum of the product of reaction No.1 showed the presence
of carbon disulphide only, while the gas phase infrared
spectrum of the volatile fractions of the other reactions
showed a mixture of carbon disulphide and dimethyl bromamine.
These were pumped away leaving substances as described in
Table 5.5.   The conditions and the ^{31}Pnmr spectra of these
reactions are shown in Table 5.5.   The chemical shift of
the final product of the fourth experiment is -48.3 p.p.m.
This chemical shift is consistent with that of $(Me_2N)_3PBr^+.Br^-$
prepared by the bromination of $(Me_2N)_3P$ as described in
Section 4.10 ($\delta = -48.3$ p.p.m.).   Thus it is probable that
complete oxidation occurred for all the P-I bonds:

$$3Me_2NBr + PI_3 \longrightarrow (Me_2N)_3PBr^+.IBr_2^- + I_2$$
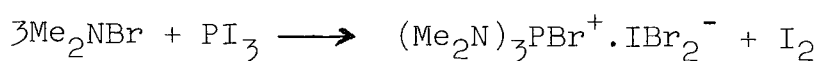
5.15 The reaction between tetra iodobiphosphine and dimethyl chloramine

Tetra iodo biphosphine was made by Dr. A. Platt using the method of M. Baudler.(92) The ^{31}Pnmr spectrum showed the presence of about 6% phosphorus triiodide. The reactions of the biphosphine with the chloramine were carried out four times applying the same technique used for the phosphorus triiodide reactions. Carbon disulphide was used as a solvent. The conditions and the spectra of these reactions are shown in Table 5.6. The gas phase infrared spectrum of the most volatile fraction of the first reaction showed the presence of carbon disulphide only, while in the case of the other reactions a mixture of dimethyl chloramine and carbon disulphide was seen. These were pumped away leaving substances as described in Table 5.6. These reactions will be discussed in Section 5.17.

5.16 The reaction between tetra iodobiphosphine and dimethyl bromamine

This reaction was performed four times by employing the same technique used in Section 5.13. The conditions and the spectra of these reactions are shown in Table 5.7. The gas phase infrared spectrum of the most volatile fraction of the first reaction showed the presence of carbon disulphide only, while the spectra of the other three reactions showed a mixture of dimethyl bromamine and carbon disulphide. These were pumped away leaving substances as described in Table 5.7. These reactions will be discussed in Section 5.17.

Table 5.4

The conditions and spectra of the reactions between phosphorus triiodide and dimethylchloramine

No.	Molar Ratio Me$_2$NCl/PI$_3$	Temp. °C	Time Min.	Pnmr/p.p.m.	Fig. 50	Integration ratios	Appearance
1	0.58	-23.0	30	0.0 -177.5 -208.4 -185.3	50.a	6: 2.5:1:1	an orange solid
2	1.95	-45.0	20	0.0 -27.4	50.b	1:15	a brown oily substance
3	2.53	-45.0	10	0.0 -27.4 -53.3	50.c	1:10:8	blackish brown oil substance
4	4.61	-45.0	15	-27.4 -53.3	50.d	1:3	blackish brown oily substance mixed with iodine looking powder
	4.61	-23.0	50	-53.3	50.e		

Table 5.5

The conditions and spectra of the reactions between phosphorus triiodide and dimethyl bromamine

No.	Molar Ratio Me_2NBr/PI_3	Temp. °C	Time Min.	Pnmr/p.p.m.	Integration ratios	Fig. 51	Appearance
1	0.63	-23.0	35	21.0 -177.3 -208.1 -185.3	9:5:3:1	51.a	an orange solid
2	1.79	-45.0	30	21.0 -21.1	1:7	51.b	dark brown oily substance
3	2.81	-45.0	15	21.0 -21.1 -48.3	1:3:1	51.c	black brownish oily substance
4	4.36	-45.0	25	-21.1 -48.3	1:2	51.d	black brownish oily substance mixed with
		-23.0	75	-48.3		51.e	iodine looking powder

Table 5.6

The conditions and spectra of the reactions
between P_2I_4 and Me_2NCl

No.	Molar Ratio Me_2NCl/P_2I_4	Temp. °C	Time Min.	Pnmr/p.p.m.							Integration ratios	Fig. 52	Appearance
1	0.73	-23.0	10	-208.4	-185.5	-109.1	-177.5				6:6:2:1	52.a	an orange solid
2	2.42	-45.0	15					0.0	-27.4		2:1	52.b	a brownish oily substance
3	4.61	-45.0	15					0.0	-27.4	53.3	1:5:2	52.c	blackish red oily substance
4	6.95	-23.0	20						-27.4	-53.3	1:6	52.d	blackish red oily substance
	6.95	-23.0	40							-53.3		52.e	mixed with iodine looking powder

Table 5.7

The conditions and spectra of the reactions
between P$_2$I$_4$ and Me$_2$NBr

No.	Molar Ratio Me$_2$NBr/P$_2$I$_4$	Temp. °C	Time Min.	Pnmr/p.p.m.							Integration ratios	Fig. 53	Appearance
1	0.69	-23.0	15				-109.1	-177.5	-185.3	-208.2	5:4:1:2	53.a	an orange solid
2	2.35	-45.0	20	21.0	-21.1						1:3	53.b	a deep brown oily substance
3	4.52	-45.0	20	21.0	-21.1	-48.3					2:5:1	53.c	blackish brown oily substance
4	6.38	-45.0	15		-21.1	-48.3					1:2	53.d	brownish black oily substance
	6.38	-23.0	50			-48.3						53.e	with iodine looking powder

5.17 Discussion of the reactions described in Sections 5.13, 5.14, 5.15 and 5.16

The reactions between PI_3 and Me_2NCl are listed in Table 5.4. The $^{31}Pnmr$ spectrum of the first reaction showed a major peak at 0.0 p.p.m. which is likely to be due to the formation of $Me_2NPClI_2^+.I^-$. It is unlikely to be due to the formation of $Me_2NPI_3^+.Cl^-$ because the chemical shift of the latter would be positive considering the chemical shift of $Me_2NPBr_3^+.Br^-$ which is -12.9 p.p.m., and it is known that replacing bromine atoms with iodine atoms will bring the *resonance upfield* of that of the reference. Two minor peaks were observed in the spectrum which could be due to the side reaction between Me_2NCl and P_2I_4 which was found as an impurity in PI_3. One peak was at -208.4 p.p.m. which is close to the reported value for PI_2Cl ($\delta = -208.$ p.p.m.) (93) and the second at -185.3 p.p.m. which is close to the chemical shift of Me_2NPI_2 (94). The fourth peak at -177.5 p.p.m. is due to excess PI_3.

The $^{31}Pnmr$ spectrum of the second reaction did not show an excess of PI_3 but a minor peak at 0.0 p.p.m., which could be due to unreacted $Me_2NPClI_2^+.I^-$, whilst the peak at -27.4 p.p.m. was the major one. This could indicate that the suggested initial product $Me_2NPClI_2^+.I^-$ (0.0 p.p.m.) reacted with a second molecule of Me_2NCl:

$$Me_2NPClI_2^+.I^- + Me_2NCl \longrightarrow (Me_2N)_2PClI^+.I_2Cl^-$$
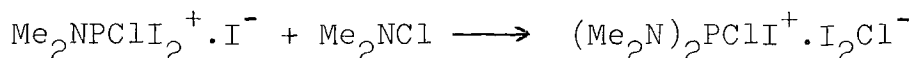
The peak at -27.4 p.p.m. is likely to be due to the formation of $(Me_2N)_2PClI^+$ and not due to the formation of $(Me_2N)_2PCl_2^+$, because the chemical shift of the latter was reported as -51.6 p.p.m. (1). Also this chemical shift of -27.4 p.p.m. is not likely to be due to the formation of $(Me_2N)_2PI_2^+$. which would have a positive chemical shift considering that the

chemical shift of $(Me_2N)_2PBr_2^+.Br^-$ is -46.3 p.p.m. (as
reported in Section 4.9). In the third reaction the $^{31}Pnmr$
spectrum showed the same two peaks as the second reaction.
In this case, however, rather more of the $Me_2NPClI_2^+$ had re-
acted as in this case more chloramine had been used. The
spectrum of the fourth reaction initially showed two peaks,
one at -27.4 p.p.m., as seen in reactions 2 and 3, due to
$(Me_2N)_2PICl^+$. and one at -53.3 p.p.m. which has the same
chemical shift as has been observed for $(Me_2N)_3PCl^+.Cl^-$
prepared by the reaction of $(Me_2N)_2PCl$ with Me_2NCl (1). After
this mixture had been at room temperature for a further 35
minutes the nmr spectrum showed only one peak at -53.3 p.p.m.
indicating that the removal of the final iodine atom from
the phosphonium occurs slowly. These results show that the
reaction between PI_3 and Me_2NCl is not a one-step reaction
but occurs in a series of reactions:

$$PI_3 + Me_2NCl \xrightarrow{S_N2} Me_2NPI_3^+.Cl^- \longrightarrow Me_2NPClI_2^+.I^-$$
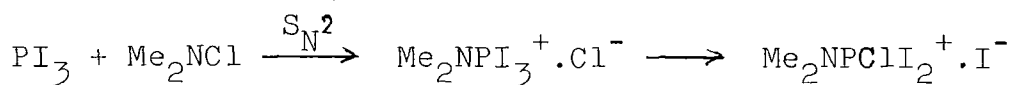
Then this iodo phosphonium salt reacts with another molecule
of Me_2NCl to replace the iodine atom attached to the phosphorus
by a dimethyl amino group:

$$Me_2NPClI_2^+.I^- + Me_2NCl \longrightarrow (Me_2N)_2PClI^+.I_2Cl^-.$$
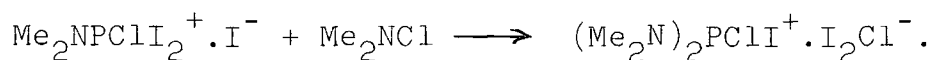
Then $(Me_2N)_2PClI^+.I_2Cl^-$ reacts further with Me_2NCl:

$$(Me_2N)_2PClI^+.I_2Cl^- + Me_2NCl \longrightarrow (Me_2N)_3PCl^+.ICl_2 + I_2.$$
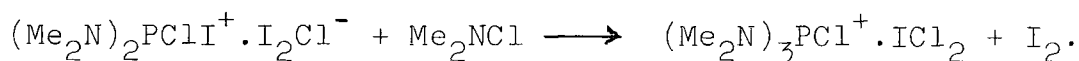
The side reaction between Me_2NCl and P_2I_4 which was found as
an impurity will be discussed later.

The reactions between PI_3 and Me_2NBr can be represented
as a similar set of reactions to those mentioned in the
chloramine case above:

$$Me_2NBr + PI_3 \longrightarrow Me_2NPBrI_2^+.I^- \quad (1)$$

Compounds can then react further with Me_2NBr and thus the intensity of the peaks at 21.0 p.p.m. decreased, while the other phosphonium ion formed showing a peak at -21.1 p.p.m.:

$$Me_2NPI_2Br.I + Me_2NBr \longrightarrow (Me_2N)_2PBrI^+.I_2Br^- \qquad (II)$$
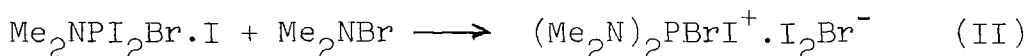
The chemical shift of -21.1 p.p.m. was also noted when Me_2NPBr_2 was iodinated, and it was thought to be due to the formation of $(Me_2N)_2PBrI^+.I^-$ as described in Section 4.14.

The compound $(Me_2N)_2PIBr^+.I_2Br$ presumably reacted further with Me_2NBr and the dimethylamino group replaced the last iodine atom linked to the phosphorus:

$$(Me_2N)_2PIBr.I_2Br + Me_2NBr \longrightarrow (Me_2N)_3PBr^+.I_2Br^- + IBr.$$
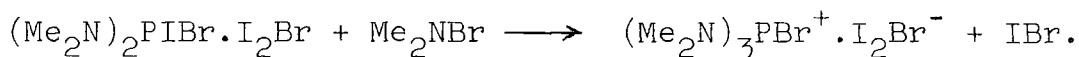
The formation of $(Me_2N)_3PBr^+$ is indicated by the spectrum of the fourth experiment which showed one peak only at -48.3 p.p.m. due to the formation of $(Me_2N)_3PBr^+$, the chemical shift of which has been reported in Section 4.10. The formation of IBr was indicated by the black colouration and the black solid suspended in the heavy oil. Neither the infrared spectra nor the Raman spectra of the products of these reactions have been studied due to the difficulty of isolating the compounds from the product mixture and as far as Raman is concerned due to the dark colour of the product.

The reactions between P_2I_4 and Me_2NCl are listed in Table 5.6. The $^{31}Pnmr$ spectrum of the first reaction shows four peaks, one at -208.4 p.p.m. due to the formation of PI_2Cl ($\delta = -208.0$ p.p.m. (93)): the second peak at -185.5 p.p.m. due to the formation of Me_2NPI_2 (94): the third peak at -109.1 p.p.m. is due to P_2I_4 (which was used in excess) and the fourth peak at -177.5 p.p.m. is due to PI_3 (which was

found as an impurity). This suggests that the reaction is a simple oxidation by the cleavage of P-P bond:

$$I_2P-PI_2 + Me_2NCl \longrightarrow Me_2NPI_2 + PI_2Cl$$
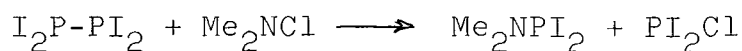
This reaction is similar to the reported cleavage of P-P bonds by alkylating agents (95):

$$R_2N(R)P-P(R)NR_2 + C_2H_5I \longrightarrow R_2N(R)PC_2H_5 + R_2N(R)PI.$$
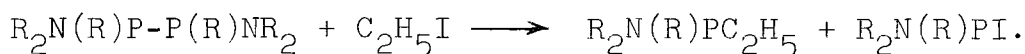
The ^{31}Pnmr spectrum of the second reaction showed two peaks only at 0.0 p.p.m. and at -27.4 p.p.m. these peaks have been observed in the spectrum of the reaction between Me_2NCl and PI_3 (Table 5.4). The peak at 0.0 p.p.m. was thought to be due to Me_2NPI_2Cl . and the one at -27.4 p.p.m. due to $(Me_2N)_2PClI^+$. as has been discussed above. These two phosphonium ions could be formed by the cleavage of the P-P bond as described above, followed by the amination of the two P(III) products:

$$PI_2Cl + Me_2NCl \longrightarrow Me_2NPI_2Cl^+.Cl^-$$

$$Me_2NPI_2 + Me_2NCl \longrightarrow (Me_2N)_2PICl^+.I^-$$
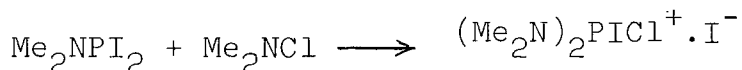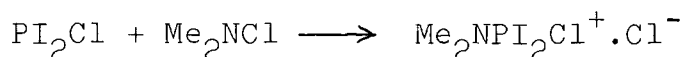
In the compound $Me_2NPI_2Cl^+.Cl^-$ an exchange of halogen atom could occur to produce $Me_2NPICl_2^+.I^-$, but it seems as if the reaction between $Me_2NPI_2Cl^+.Cl^-$ and dimethyl chloramine is faster and the appearance of new phosphorus species was not shown by the ^{31}Pnmr spectrum:

$$Me_2NPI_2Cl^+.Cl^- + Me_2NCl \longrightarrow (Me_2N)_2PICl^+.ICl_2^-$$
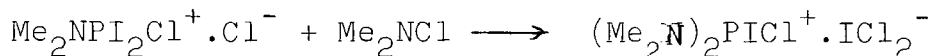
while $(Me_2N)_2PICl^+.I^-$ reacted with Me_2NCl as follows:

$$(Me_2N)_2PICl^+.I^- + Me_2NCl \longrightarrow (Me_2N)_3PCl^+.Cl^- + I_2$$
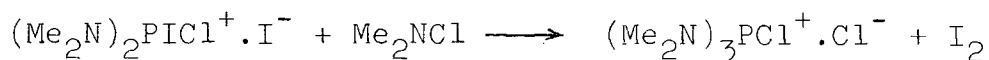
Thus the ^{31}Pnmr spectrum of the third reaction showed two peaks, a minor one at -27.4 p.p.m. ($(Me_2N)_2PICl^+.ICl_2^-$) and

a second peak being the major one at -53.3 p.p.m.   This chemical shift is identical to the chemical shift observed for $(Me_2N)_3PCl^+.Cl^-$ (δ =-53.3 p.p.m. (1)).   The ^{31}Pnmr spectrum of the fourth reaction showed one peak only at -53.3 p.p.m. due to $(Me_2N)_3PCl^+$ indicating that the chloramine has completed the oxidation of the last P-I bond in the previous two phosphonium ions:

$$(Me_2N)_2PICl^+.ICl_2^- + Me_2NCl \longrightarrow (Me_2N)_3PCl^+.ICl_2^-. + ICl$$

$$(Me_2N)_2PICl^+.I^- + Me_2NCl \longrightarrow (Me_2N)_3PCl^+.Cl^- + I_2.$$
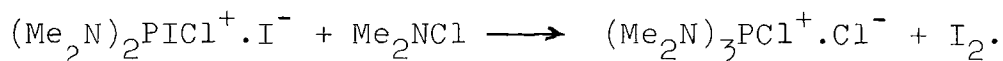
The reactions between P_2I_4 and Me_2NBr parallels the reaction between P_2I_4 and Me_2NCl.   The ^{31}Pnmr spectrum of the first reaction (Table 5.7), showed four peaks: one at -208.4 p.p.m. due to the formation of the known compound PI_2Br (δ = 208.2 p.p.m.(96)); the second peak at -185.3 p.p.m. due to the formation of Me_2NPI_2 (94); the third peak at -109.1 p.p.m. due to P_2I_4 which was used in excess; and the fourth peak at -177.5 p.p.m. is due to PI_3 which was found as an impurity in the starting material.   This result indicates that the reaction was simple oxidation by the cleavage of the P-P bond as shown in the following equation:

$$I_2P-PI_2 + Me_2NBr \longrightarrow PI_2Br + Me_2NPI_2.$$
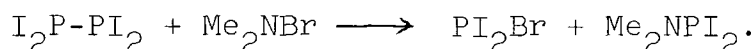
The ^{31}Pnmr spectrum of the second reaction (Table 5.7) showed two peaks at -21.1 p.p.m. and 21.0 p.p.m., these peaks were observed in the spectrum of the reaction between Me_2NPBr_2 and iodine (Section 4.12).   The assignment of the peaks at 21.0 p.p.m. and -21.1 p.p.m. as $Me_2NPI_2Br^+$. and $(Me_2N)_2PIBr^+$. respectively has been discussed in Section 4.14.   These

phosphonium ions could well have been formed according to the following equations:

$$PI_2Br + Me_2NBr \longrightarrow Me_2NPI_2Br^+.Br^-.$$

$$Me_2NPI_2 + Me_2NBr \longrightarrow (Me_2N)_2PIBr^+.I^-.$$
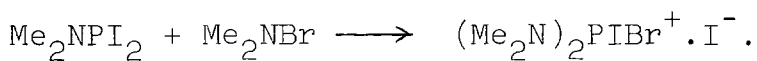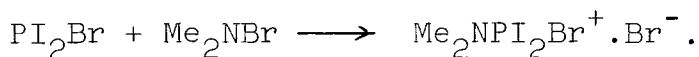
In the compound $Me_2NPI_2Br^+.Br^-$ the exchange of halogens seems not to occur to produce $Me_2NPIBr_2^+.I^-$, because, if this kind of halogen exchange occurred, then $Me_2NPBr_3^+.I^-$ could be produced and the latter was not observed in any of the spectra. It seems that the P-I bonds were replaced by $P-NMe_2$ bonds to produce $(Me_2N)_3PBr^+$ in both $Me_2NPI_2Br^+$ and $(Me_2N)_2PIBr^+$. This assumption is supported by the $^{31}Pnmr$ spectrum of the third reaction as shown in Table 5.7, where the peaks were observed; a minor one at -21.1 p.p.m. ($(Me_2N)_2PIBr^+$.) and a major peak at -48.3 p.p.m. which is identical to the chemical shift found for $(Me_2N)_3PBr^+.Br^-$ (-48.3 p.p.m., Section 4.10).

The $^{31}Pnmr$ spectrum of the fourth reaction which contained excess Me_2NBr (Table 5.7) shows one peak only at -48.3 p.p.m. which is due to the formation of $(Me_2N)_3PBr^+$. This indicates that all the iodine atoms linked to the phosphorus have been replaced by dimethyl amino groups:

$$Me_2NPI_2Br^+.Br^- + Me_2NBr \longrightarrow (Me_2N)_2PIBr^+.IBr_2^-.$$
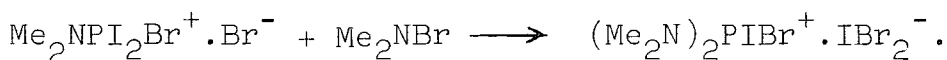
Thus a further replacement of P-I bond by $P-NMe_2$ bond:

$$(Me_2N)_2PIBr^+.IBr_2^- + Me_2NBr \longrightarrow (Me_2N)_3PBr^+.IBr_2^- + IBr.$$
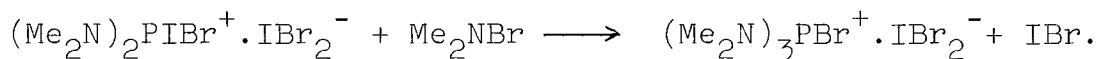
While the other phosphonium salt produced from the reaction between Me_2NPI_2 and Me_2NBr ($(Me_2N)_2PIBr^+.I^-$) will react further with Me_2NBr:

$$(Me_2N)_2PIBr^+.I^- + Me_2NBr \longrightarrow (Me_2N)_3PBr^+.Br^- + I_2$$
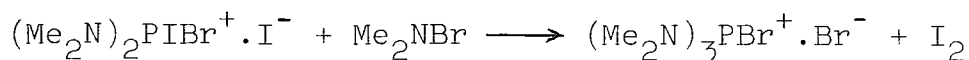
Thus eventually the reaction of excess Me_2NBr with PI_3 produces one kind of phosphonium ion $(Me_2N)_3PBr^+$. and this was confirmed by the $^{31}Pnmr$ spectrum of the fourth reaction as shown in Table 5.5. It was difficult to isolate the various products of the reaction, and it was difficult as well to run Raman spectra because of their very dark blackish colour.

5.18 Results and discussion of the reactions between Me_2NX and PY_3 (X = Cl or Br and Y = Cl, Br or F)

The reaction between dimethyl chloramine and excess phosphorus trichloride was carried out previously in this laboratory (1) and the overall reaction was found to be:

$$4 PCl_3 + 3Me_2NCl \longrightarrow 2 Me_2NPCl_3^+ + PCl_6^- + Cl^- + Me_2NPCl_2$$
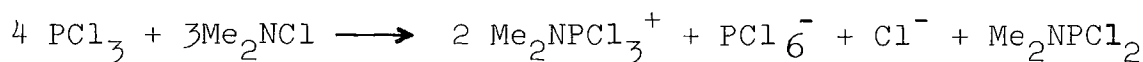
The mechanism suggested for this reaction was (i) initial fast amination of phosphorus trichloride:

$$PCl_3 + Me_2NCl \longrightarrow Me_2NPCl_3^+.Cl^-$$
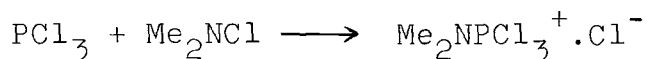
followed by (ii) a slow oxidation of phosphorus trichloride by the phosphonium ion formed in (i). Finally (iii) the tetrachloro phosphonium ion formed would react with chloride ion to generate hexachlorophosphate:

$$PCl_4^+ + 2Cl^- \longrightarrow PCl_6^-$$
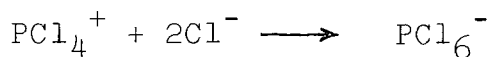
To further test this hypothesis in the present work the reaction was repeated with the chloramine in excess. The reaction was:

$$3PCl_3 + 3 Me_2NCl \longrightarrow Me_2NPCl_3^+ + (Me_2N)_2PCl_2^+ + PCl_6^- + Cl^-$$
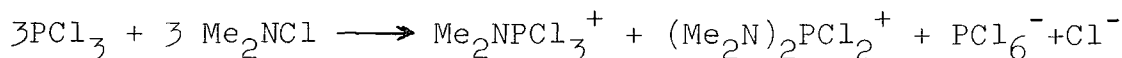
The products of this reaction paralleled those of the one above except that since dimethyl chloramine was in excess it reacted with the phosphine formed in step (ii) to produce phosphonium salt:

$$Me_2NPCl_2 + Me_2NCl \longrightarrow (Me_2N)_2PCl_2.Cl$$
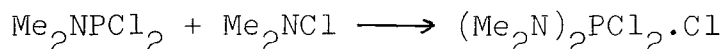
The reaction between solid $Me_2NPCl_3.Cl$ and PCl_3 was carried out and it was found that no reaction occurred. This result could be attributed to the insolubility of $Me_2NPCl_3.Cl$ and thus PCl_3 would not be able to react. Nevertheless the reaction could occur in the reaction series discussed above as the salt could react with the PCl_3 as soon as it had been formed in solution.

The reaction between phosphorus tribromide and dimethyl bromamine was a simple amination reaction which could well have occurred by the phosphine attacking the nitrogen of the chloramine in an S_N2 reaction. This reaction did not go any further. This may be due to the fact that PBr_3 does not react with bromine as vigorously as PCl_3 reacts with chlorine, consequently no further reaction would occur between PBr_3 and the phosphonium ion produced. This could also explain why the reaction between PBr_3 and Me_2NCl is a simple amination, but in this case halogen exchange occurred to produce the phosphonium bromide salt. This kind of halogen exchange occurred when Me_2NPBr_2 was reacted with Me_2NCl to produce the phosphonium bromide salt as described in Section 6.18

The reaction between PCl_3 and Me_2NBr was not a simple amination and the products were parallel to those of the reaction between PCl_3 and Me_2NCl:

$$3Me_2NBr + 4PCl_3 \longrightarrow 2Me_2NPCl_3^+ + Me_2NPBr_2 + Br^- + PCl_6^-$$
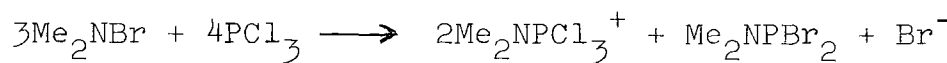
The reaction between dimethyl chloramine and phosphorus trifluoride was a complex one and a mixture of phosphorus species were formed. This may be attributed to the nature of the fluorine atom which is the smallest of the halogen atoms and the most electronegative and facile exchange reactions are known to occur involving phosphorus-fluorine bonds, particularly reactions that generate hexafluorophosphate (71). The initial steps of this reaction could be the haldmination of the phosphorus atom to produce dimethylamine trifluorochloro phosphorane:

$$PF_3 + Me_2NCl \longrightarrow Me_2NPF_3Cl$$
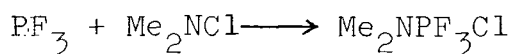
The phosphorane could then rearrange:

$$3 \, Me_2NPF_3Cl \longrightarrow (Me_2N)_2PF_2^+ \cdot Me_2NPF_5^- + PF_2Cl_3$$
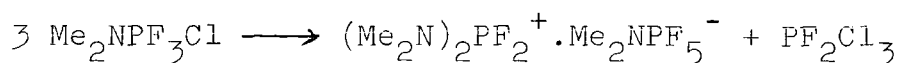
and the PF_2Cl_3 could disproportionate to give hexafluorophosphate.

The reaction between PF_3 and dimethyl bromamine produced a mixture of phosphorus species as shown in Section 5.11.

The suggested reaction pathway for this reaction is represented by the equations:

(i) $Me_2NBr + PF_3 \longrightarrow Me_2NPF_3Br$

(ii) $Me_2NPF_3Br + Me_2NBr \longrightarrow (Me_2N)_2PF_3 + Br_2$

(iii) $2(Me_2N)_2PF_3 \longrightarrow (Me_2N)_3PF^+ \cdot Me_2NPF_5^-$
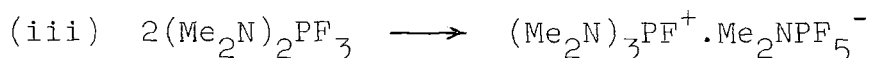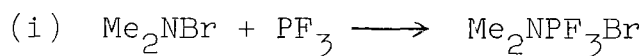
CHAPTER SIX

THE REACTIONS OF HALAMINES WITH

A VARIETY OF ORGANO HALO SUBSTITUTED PHOSPHINES

6.1 Introduction

The reactions which have been carried out between phosphorus trichloride and dimethyl chloramine and the parallel reaction with dimethyl bromamine as described in Chapter Five motivated interest towards a comparative study. Thus the reactions of dimethyl chloramine and dimethyl bromamine with halo substituted phosphine have been studied and reported in this chapter. The reactions of $(Me_2N)_nPF_{3-n}$ (n = 1,2,3) phosphines with the chloramine and the bromamine were performed to throw some light on the reaction of phosphorus trifluoride with dimethyl chloramine and the parallel reaction with dimethyl bromamine. This work has been also directed towards the expansion of the research in this field, since the study of very few reactions have been published in the course of the last thirty years (Section 1.2.1).

6.2 The reaction between dimethyl chloro phosphine and dimethyl chloramine

A reaction vessel (figure 2.2b) containing $3cm^3$ of dry degassed petroleum ether was connected to the vacuum line and 6.2 mmol dimethyl chlorophosphine condensed into it. The vessel was allowed to warm to room temperature to let the phosphine dissolve in the petroleum ether and then cooled to $-196^\circ C$, so that 8.8 mmol of dimethyl chloramine could be condensed onto the solution. After the cell had been kept at $-45^\circ C$ for five hours a white solid was observed. The gas phase spectrum of the most volatile fraction at room temperature showed the presence of dimethyl chloramine and

petroleum ether, which were pumped away.   The white solid
left inside the cell, when dissolved in dichloro methane,
gave a ^{31}Pnmr spectrum showing one peak at -103.3 p.p.m. as
shown in figure 54 indicating the formation of a tetra
coordinated cationic phosphorus species.   The infrared
spectrum is shown in figure 20 and the elemental analysis
results are listed in Table 6.1.

Table 6.1

Element	Calculated for $Me_2NPMe_2Cl_2$	Found
C	27.29	27.32
H	6.82	6.49
N	7.96	6.04
P	17.62	17.95
Cl	40.31	40.27

From these results it is likely that simple amination of
the phosphine occurred and that the reaction can be written
as:

$$Me_2PCl + Me_2NCl \longrightarrow Me_2NPMe_2Cl^+.Cl^-.$$
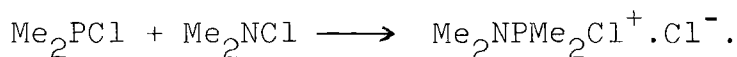
6.3   The reaction between dimethyl chloro phosphine and dimethyl bromamine

Dimethyl bromamine (7.2 mmol) was degassed and con-
densed onto a solution of 9.1 mmol of dimethyl chloro phosphine
dissolved in $4cm^3$ of dry degassed petroleum ether inside a
reaction vessel (figure 2.2b).   After the reactants had been
kept at $-30^{\circ}C$ (the freezer temperature) for eight hours the
formation of a white solid was observed.   The gas phase
infrared spectrum of the most volatile fractions showed a

mixture of dimethyl chloro phosphine and petroleum ether.
After pumping off the volatile substances a white solid
remained, which when dissolved in dichloromethane, showed
one sharp peak at -103.1 p.p.m. in the ^{31}Pnmr spectrum.
This chemical shift corresponds to the chemical shift for
$Me_2NPMe_2Cl^+.Cl^-$ (δ = -103.3 p.p.m.) (which was described in
Section 6.2). It is unlikely to be the $Me_2NPMe_2Br^+$ ion
as this would have an upfield chemical shift from the chloro
cation. The elemental analysis results are listed in
Table 6.2.

Table 6.2

Element	Calculated for $Me_2NPMe_2Cl.Br$	Found
C	21.28	20.39
H	5.45	6.02
N	6.35	6.55
P	14.07	14.10
Cl	36.26	36.13
Br	16.09	16.03

These results imply that simple amination of the product
has occurred and that the reaction can be written as:

$$Me_2PCl + Me_2NBr \longrightarrow Me_2NPMe_2Cl^+.Br^-.$$
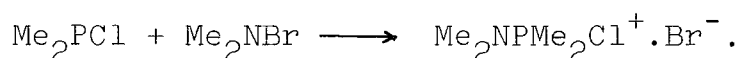
6.4 The reaction between methyl dichloro phosphine and dimethyl chloroamine

This reaction was carried out by condensing 5.7 mmol
of dimethyl chloroamine onto 4.9 mmol of methyl dichloro
phosphine dissolved in $3cm^3$ of dry degassed petroleum ether
inside a reaction vessel (figure 2.2b). The reactants were

kept at $-83^{\circ}C$ for eighteen hours and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl chloroamine and petroleum ether. These were pumped away leaving a white solid. The ^{31}Pnmr spectrum of this solid dissolved in dichloro methane showed one sharp peak only at -87.1 p.p.m. (figure 55) indicating the presence of a four coordinate phosphonium ion. The infrared spectrum of the product is shown in figure 21 and the elemental analysis results are listed in Table 6.3.

Table 6.3

Element	Calculated for $Me_2NPMe_2Cl_3$	Found
C	18.33	18.09
H	4.58	4.58
N	7.13	7.74
P	15.79	15.81
Cl	54.16	53.75

The above results indicate that simple amination of the phosphine has occurred and the overall reaction is as follows:

$$MePCl_2 + Me_2NCl \longrightarrow Me_2NPMeCl_2^+.Cl^-$$

6.5 The reaction between methyl dichloro phosphine and dimethyl bromamine

A degassed dry sample of dimethyl bromamine (6.9 mmol) was condensed onto 5.2 mmol of methyl dichloro phosphine dissolved in $2cm^3$ of dry degassed petroleum ether inside a reaction vessel (figure 2.2 b) at $-196^{\circ}C$. The reactants were

kept at -45°C with occasional shaking for an hour.   On
warming the cell to room temperature, the infrared spectrum
of the most volatile fraction showed a mixture of dimethyl
bromamine and petroleum ether.   A white solid was left in the
vessel when the volatile substances were pumped off through
the vacuum line.   This produce was washed with petroleum
ether inside the dry box and the ^{31}Pnmr spectrum run in
dichloro methane.   This showed one sharp peak only at -74.2
p.p.m. which indicated the formation of a tetra coordinate
phosphonium ion.   This chemical shift is similar to the
chemical shift found for $Me_2NPMeCl_2^+.Cl^-$ ($\varsigma = -87.1$ p.p.m.)
prepared as described in Section 6.4.   Thus the product is
likely to be $Me_2NPMe.Cl_2^+.Br^-$.   The infrared spectrum of
the product is shown in figure 22   and the elemental analysis
results are listed in Table 6.4.

Table 6.4

Element	Calculated for $Me_2NPMeCl_2.Br$	Found
C	14.95	14.68
H	3.74	4.01
N	5.81	5.96
P	12.87	12.77
Br	33.18	31.85
Cl	29.44	28.26

These results indicated that the phosphine was aminated by
dimethyl bromamine to produce phosphonium salt and the overall
reaction could be written as follows:

$$MePCl_2 + Me_2NBr \longrightarrow MePNMe_2Cl_2^+.Br^-.$$
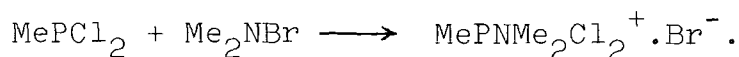
6.6 The reaction between dicyclohexyl chloro phosphine and dimethyl chloroamine

A dry degassed sample of dichloro methane ($3cm^3$) was distilled onto 6.8 mmol of dicyclohexyl chloro phosphine inside a reaction vessel (figure 2.2b). The tube was allowed to warm to room temperature and was shaken until the phosphine was completely dissolved. After cooling to $-196^{\circ}C$ a dry degassed sample of dimethyl chloroamine (9.5 mmol) was condensed onto the phosphine solution and the vessel kept at $-23^{\circ}C$ for five hours. After the tube had warmed to room temperature the infrared gas phase spectrum of the most volatile fraction was taken and showed a mixture of dichloro methane and dimethyl chloroamine. These were pumped away, leaving a white solid. The ^{31}Pnmr spectrum of this product dissolved in dichloro methane showed one sharp peak only at -104.7 p.p.m. (figure 56) due to the formation of a tetra coordinate cationic phosphorus species. The infrared spectrum of the product is shown in figure 23 and the elemental analysis results are listed in Table 6.5.

Table 6.5

Element	Calculated for $(C_6H_{11})_2PNMe_2Cl_2$	Found
C	53.86	53.74
H	8.98	9.21
N	4.49	4.63
P	9.94	9.86
Cl	22.73	22.91

These results show that amination had occurred and that the reaction is as follows:

$$(C_6H_{11})_2PCl + Me_2NCl \longrightarrow Me_2NP(C_6H_{11})_2Cl^+ \cdot Cl^-$$
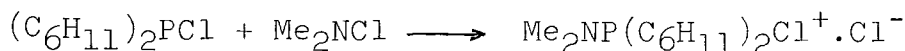
6.7 The reaction between dicyclohexyl chloro phosphine and dimethyl bromamine

Dicyclohexyl chloro phosphine (5.3 mmol) was dissolved in $3cm^3$ of dry degassed dichloro methane, inside a reaction vessel (figure 2.2b). The vessel was cooled to $-196^{\circ}C$, so that 6.8 mmol of dimethyl bromamine could be condensed onto the phosphine solution. The reactants were kept at $-45^{\circ}C$ for five hours, with shaking from time to time. The vessel was allowed to warm to room temperature and the infrared spectrum of the most volatile substances showed a mixture of dimethyl bromamine and dichloro methane. These were pumped away leaving a white solid. This was washed three times with petroleum ether inside the dry box. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane showed one sharp peak only at -104.3 p.p.m. This shift indicates the formation of a tetra coordinate phosphonium ion, and it is similar to the chemical shift found for $Me_2NP(C_6H_{11})_2$ $Cl^+.Cl^-$ ($\delta=104.7$ p.p.m.) which had been prepared as described in Section 6.6. This implies that the product is $Me_2NP(C_6H_{11})_2$ $Cl^+.Br^-$, however if the product was the bromo phosphonium salt the chemical shift would be shifted upfield in comparison with the chemical shift for the chloro salt. The elemental analysis results are listed in Table 6.6.

Table 6.6

Element	Calculated for $Me_2NP(C_6H_{11})_2ClBr$	Found
C	47.14	46.76
H	7.86	7.99
N	3.93	4.10
P	8.70	8.74
Cl	9.95	9.55
Br	22.42	21.75

These results indicate that simple amination has occurred
to produce a tetra coordinate phosphonium ion, thus the
overall reaction is:

$$(C_6H_{11})_2PCl + Me_2NBr \longrightarrow (C_6H_{11})_2PNMe_2Cl^+.Br^-$$
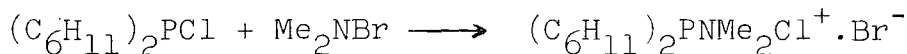
6.8 The reaction between bis(dimethylamino)chloro phosphine and dimethyl bromamine

A dry degassed sample of dimethyl bromamine (5.6 mmol)
was distilled into a solution of 4.2 mmol of bis(dimethylamino)
chloro phosphine dissolved in $4cm^3$ of dry degassed petroleum
ether inside a reaction vessel (figure 2.2b). The vessel
was kept at $-45^\circ C$ for four hours with occasional shaking.
A white solid formed. After the cell was allowed to warm
to room temperature, the infrared spectrum of the most volatile
fraction showed a mixture of petroleum ether and dimethyl
bromamine. These volatile substances were pumped away
leaving the white solid. The ^{31}Pnmr spectrum of this solid
dissolved in dichloro methane showed one sharp peak only at
-53.3 p.p.m. due to the formation of a tetra coordinate phos-
phonium ion. The chemical shift of this phosphonium ion is
identical to that of $(Me_2N)_3PCl^+.Cl^-$, which has been prepared
by reacting $(Me_2N)_2PCl$ with Me_2NCl (1).   Moreover,
the chemical shift of the bromo phosphonium ion $(Me_2N)_3PBr^+.Br^-$
which has been prepared by the bromination of $(Me_2N)_3P$
(Section 4.10) has a chemical shift of -48.3 p.p.m. This
suggests that the phosphonium ion produced is $(Me_2N)_3PCl^+$.
The chemical analysis results are shown in Table 6.7.

Table 6.7

Element	Calculated for $(Me_2N)_3PClBr$	Found
C	15.43	15.28
H	3.86	3.91
N	18.00	18.42
P	13.28	13.17
Br	34.24	33.21
Cl	15.19	14.73

From the above results it appears that simple amination of the phosphine occurred, the overall reaction being:

$$(Me_2N)_2PCl + Me_2NBr \longrightarrow (Me_2N)_3PCl^+.Br^-.$$
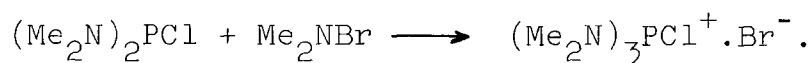
6.9 The reaction between dimethyl amino dichloro phosphine and dimethyl bromamine

A sample of degassed dimethyl bromamine (7.4 mmol) was condensed onto a dry degassed solution of *dimethyl amino dichloro* phosphine (6.5 mmol) in $4cm^3$ of petroleum ether inside a reaction vessel (figure 2.2b), at $-196^{\circ}C$. The vessel was kept at $-30^{\circ}C$ (the freezer temperature) for seven hours. A white solid formed and the gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl bromamine and petroleum ether. When the volatile substances were pumped away the white solid remained. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane showed one sharp peak only at -51.6 p.p.m. due to the formation of $(Me_2N)_2PCl_2^+$. This cation (as the chloride salt) has been prepared previously by the reaction between dimethyl chloramine and dimethyl amino dichloro phosphine (1), and gave a

^{31}Pnmr chemical shift of -51.6 p.p.m. in dichloro methane. The elemental analysis results are listed in Table 6.8.

Table 6.8

Element	Calculated for $(Me_2N)_2PCl_2Br$	Found
C	17.79	17.94
H	4.45	4.85
N	10.38	9.81
P	11.49	11.44
Br	29.28	29.02
Cl	26.28	25.75

These results indicate that simple amination of the phosphine has occurred and that the reaction can be represented by the following equation:

$$Me_2NPCl_2 + Me_2NBr \longrightarrow (Me_2N)_2PCl_2^+ \cdot Br^-$$
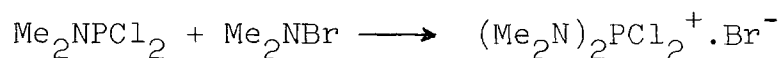
6.10 The reaction between bis(dimethylamino)bromo phosphine and dimethyl bromamine

A dry degassed sample of dimethyl bromamine (5.2 mmol) was condensed onto a solution of bis(dimethylamino)bromo phosphine (3.3 mmol) dissolved in 3cm^3 of dry, degassed petroleum ether, inside a reaction vessel (figure 2.2b) at -196°C. After the vessel had been kept at -30°C (the freezer temperature) for eighteen hours, an orange solid formed, and the vessel was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl bromamine and petroleum ether. These were pumped away leaving the orange solid. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane showed one sharp

peak only at -48.3 p.p.m. due to the formation of $(Me_2N)_3PBr^+.Br^-$ a phosphonium salt, which has been prepared by the bromination of tris(dimethylamino)phosphine, (Section 4.10), and gave a ^{31}Pnmr chemical shift of -48.3 p.p.m. (figure 41). The infrared spectrum of this solid was identical to that of $(Me_2N)_3PBr^+.Br^-$ shown in figure 15. The elemental analysis results are listed in Table 6.9.

Table 6.9

Element	Calculated for $(Me_2N)_3PBr_2$	Found
C	22.30	22.27
H	5.58	5.69
N	13.01	13.42
P	9.60	9.51
Br	49.50	50.11

These results imply that simple amination of the phosphine has occurred:

$$(Me_2N)_2PBr + Me_2NBr \longrightarrow (Me_2N)_3PBr^+.Br^-.$$
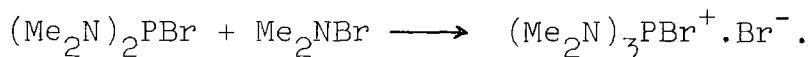
6.11 The reaction between dimethyl amino dibromo phosphine and dimethyl bromamine.

This reaction was carried out by the condensation of dry degassed dimethyl bromamine (5.21 mmol) onto a solution of dimethyl amino dibromo phosphine (4.75 mmol) dissolved in $5cm^3$ of dry, degassed petroleum ether inside a reaction vessel (figure 2.2b) at -196^oC. The reactants were kept at -45^oC for seven hours. After the vessel had been allowed to warm to room temperature the gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl bromamine

and petroleum ether. These were pumped away leaving a yellowish-orange solid. The ^{31}Pnmr spectrum of this solid showed one broad peak only at -46.3 p.p.m., due to the formation of $(Me_2N)_2PBr_2^+.Br^-$ which has been prepared by the bromination of bis(dimethyl amino) bromo phosphine (Section 4.9) and gave a ^{31}Pnmr chemical shift of -46.4 p.p.m. (figure 40). The infrared spectrum of the product is identical to the infrared spectrum of $(Me_2N)_2PBr_2^+.Br^-$ (figure 14) and the elemental analysis results are listed in Table 6.10.

Table 6.10

Element	Calculated for $(Me_2N)_2PBr_3$	Found
C	17.22	17.01
H	4.30	4.79
N	10.04	10.53
P	11.12	10.98
Br	57.32	57.05

These results indicate that simple amination occurred on the phosphorus atom:

$$Me_2NPBr_2 + Me_2NBr \longrightarrow (Me_2N)_2PBr_2.Br$$
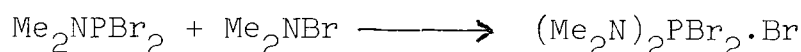
6.12 <u>The preparation of dimethylamino difluoro phosphine</u>

A sample of a dry, degassed dimethylamine was condensed into a calibrated cold finger (figure 2.5) at -196°C, then it was allowed to melt and the volume was measured as 8.3 cm^3 (126 mmol). This was condensed into the cold finger of a three litre bulb. A sample of phosphorus trifluoride (prepared as described in Section 5.9) was condensed into the

calibrated cold finger (figure 2.5) at -196°C.   This
sample was degassed, allowed to warm to -112.5°C and its
volume as a liquid was measured as 1.9cm^3 (84 mmol).   The
phosphorus trifluoride was condensed onto the amine inside
the cold finger of the bulb at -196°C.   The reactants were
allowed to warm to -112.5°C for twenty minutes and then to
-83°C for five hours.   A white solid (dimethyl ammonium
fluoride) was formed and the volatile contents of the bulb
were condensed into a modified ^{31}Pnmr tube (figure 2.5) at
-196°C.   After the tube had been allowed to warm to room
temperature a colourless liquid was observed.   The gas phase
infrared spectrum of this showed the absence of dimethylamine.
The ^{31}Pnmr spectrum of the liquid showed a triplet centred
at -143.5 p.p.m. (J = 1196.4 Hz).   This corresponds well
with the chemical shift reported for dimethylamino difluoro
phosphine (δ = 143.0 p.p.m., J = 1196.0 cps) (97,98).

6.13 The reaction between dimethylamino difluoro phosphine and dimethyl chloramine

A dry. degassed sample of dimethyl chloramine (6.1 mmol)
was distilled onto a dry, degassed sample of dimethylamino
difluoro phosphine (4.7 mmol) dissolved in 3cm^3 of dry,
degassed dichloromethane inside a modified ^{31}Pnmr tube
(figure 25) at -196°C.   The tube was held at -22°C for
40 minutes with occasional shaking, then it was allowed to
warm to room temperature.   The gas phase infrared spectrum
of the most volatile fraction showed a mixture of dimethyl
chloramine and dichloromethane.   The ^{31}Pnmr spectrum (figure
57) showed three major peak systems:

(1)   A doublet centred at -42.5 p.p.m. (J = 959.5 Hz)

due to $(Me_2N)_3PF^+$ phosphonium ion, which has been

prepared by reacting bis(dimethylamino)fluoro phosphine

with dimethyl chloramine as described in Section 6.15.

(2)   A triplet centred at -22.7 p.p.m. (J = 1060.3 Hz).

This indicates the formation of a tetra coordinate

phosphonium ion, in which two fluorine atoms are linked

to the phosphorus atom.   This phosphonium ion was

present among the products of the reaction between

dimethyl chloroamine and phosphorus trifluoride and

it is likely to be $(Me_2N)_2PF_2^+$.

(3)   A quartet centred at 154.8 p.p.m. (J = 944.1 Hz),   ·

due to the formation of $PCl_3F_3^-$ (99   ).

The integration ratios of the peaks forming the doublet,
triplet and the quartet are 2:3:1.

The overall reaction can be represented by the following
equation:

$$6Me_2NCl + 6\ Me_2NPF_2 \longrightarrow 3(Me_2N)_2PF_2^+ + 2(Me_2N)_3PF^+$$
$$+ PF_3Cl_3^- + 3Cl^- + F^-$$
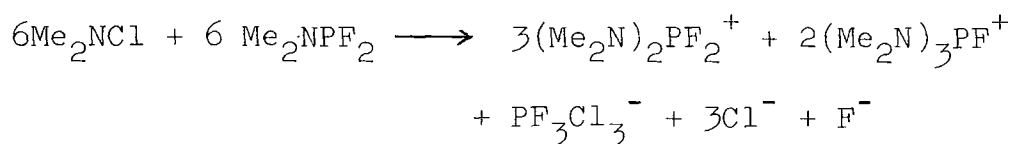
6.14 The preparation of bis(dimethylamino)fluoro phosphine

This preparation was first attempted by the reaction

of a stoichiometric quantity of dimethylamine with phosphorus

trifluoride in a sealed tube as described by Fleming and

Parry (100), but even when the reaction was warmed to $25^{\circ}C$

for two weeks incomplete amination occurred and the major

product was found to be dimethylamino difluoro phosphine.

Thus dimethylamino difluoro phosphine was first prepared as described in Section 6.12 and this product reacted with a slight excess of dimethylamine.

Dimethylamine (50 mmol) and dimethylamino difluoro phosphine (20 mmol) were condensed into a silica tube which was sealed and warmed to $-60^{\circ}C$.   After three weeks the sealed tube was allowed to reach room temperature and the formation of a considerable amount of white solid was noticed (dimethylammoniumfluoride).   The ampoule was fitted to an ampoule breaker (figure 2.3) and attached to the fractionation section of the vacuum line (figure 1).   The tube contents were fractionated through a train of cold traps at $-23^{\circ}C$, $-96^{\circ}C$ and $-196^{\circ}C$.   No liquid condensed at $-23^{\circ}C$, and a small amount was trapped at $-196^{\circ}C$.   The major product condensed at $-96^{\circ}C$ and showed two products in the ^{31}Pnmr spectrum; a doublet centred at -153.5 p.p.m. (J = 1050 cps) (101) due to the formation of $(Me_2N)_2PF$ and a singlet at -122.5 p.p.m. due to the formation of $(Me_2N)_3P$.   It was found difficult to separate the two phosphines by using the apparatus available in this laboratory.   The gas phase infrared spectrum of the fraction trapped at $-196^{\circ}C$ showed that it was dimethylamine.

6.15 The reaction between bis(dimethylamino)fluoro phosphine and dimethyl chloramine.

A sample of degassed dimethyl chloramine (3.5 mmol) was condensed onto a degassed solution of 2.8 mmol of bis(dimethylamino)fluoro phosphine (prepared as described in Section 6.14) and dissolved in $2cm^3$ of dry, degassed petroleum ether inside

a modified ^{31}Pnmr tube (figure 2.5) at -196°C.   After
the tube had been kept at -23°C for half an hour it was
allowed to warm to room temperature.   The gas phase infra-
red spectrum of the most volatile fraction showed the pre-
sence of dimethyl chloramine and petroleum ether.   These
were pumped away leaving a white solid.   The ^{31}Pnmr
spectrum of this solid (figure 26) dissolved in dichloro
methane showed the following signals:

1.   A singlet at -53.3 p.p.m.   This chemical shift is
     identical to that of $(Me_2N)_3PCl^+.Cl^-$ which was pro-
     duced by reacting Me_2NCl with $(Me_2N)_3P$ (1).
     The phosphonium salt $(Me_2N)_3PCl^+.Cl^-$ could be formed
     by a side reaction between Me_2NCl and the $(Me_2N)_3P$
     impurity.

2.   A doublet centred at - 42.6 p.p.m. (J= 1017.8 Hz) due to
     the formation of a tetra coordinate phosphorus species,
     which is likely to be $(Me_2N)_3PF^+$.

6.16 The reaction between bis(dimethylamino)fluoro phosphine and dimethyl bromamine

This reaction was carried out by applying the same
technique employed in Section 5.14.   The amount of the re-
actants were 2.15 mmol of bis(dimethylamino)fluoro phosphine
and 3.01 mmol of dimethyl bromamine. petroleum ether (2cm^3)
being used as a solvent.   The tube was kept at -45°C for
half an hour before it was allowed to warm to room temperature.
The gas phase infrared spectrum of the most volatile fraction
showed a mixture of dimethyl bromamine and petroleum ether.
These were pumped away leaving a creamish-yellow solid.   The

^{31}Pnmr spectrum of this solid dissolved in dichloro methane (figure 27) showed two sets of peaks:

1. A singlet at -48.3 p.p.m., this chemical shift is identical to the chemical shift of $(Me_2N)_3PBr^+.Br^-$ which was produced by reacting $(Me_2N)_3P$ and Me_2NBr as described in Section 4.10. This is therefore likely to have been produced from the impurity $P(NMe_2)_3$.

2. A doublet centred at - 42 p.p.m. ($J = 937.6$) due to the formation of a tetra coordinate phosphorus species. Since this doublet appeared also in the ^{31}Pnmr spectrum of the reaction between Me_2NCl and $(Me_2N)_2PF$ as well, then it is likely to be due to the formation of $(Me_2N)_3PF^+.X^-$ (X = Cl or Br).

Thus the reaction between Me_2NX and $(Me_2N)_2PF$ is a simple amination:

$$Me_2NX + (Me_2N)_2PF \longrightarrow (Me_2N)_3PF^+.X^-$$
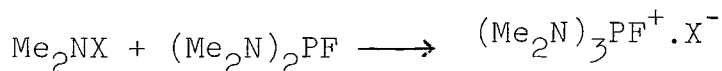
6.17 The reaction of dimethylamino difluoro phosphine with dimethyl bromamine

This reaction has been carried out by employing the same technique described for the reaction between dimethyl amino difluoro phosphine and the chloramines in Section 6.13. The amount of the bromamine used in this reaction was 7.4 mmol and the amount of the phosphine used was 5.1 mmol with dichloro methane as a solvent. The gas phase infrared spectrum of the most volatile fraction showed a mixture of dichloro methane and dimethyl bromamine. The colour of the solution was dark brown and its ^{31}Pnmr spectrum (figure 28) showed:

1. A doublet centred at -41.1 p.p.m. (J = 969.2 *Hz*)
    which indicates the formation of a tetra coordinate
    phosphonium ion with one fluorine atom linked to the
    phosphorus.   The chemical shift and the coupling
    constant of this compound are very close to those of
    $(Me_2N)_3PF^+$. which has been prepared by reacting $(Me_2N)_2PF$
    with Me_2NX (X = Cl or Br) as described in Sections
    6.15 and 6.16.

2. A quartet centred at 64.5 p.p.m. (J = 796.7 *Hz*) due
    to the formation of $(Me_2N)_2PF_3$ (δ = 64.5 p.p.m.,
    J = 758 *Hz*) (102   ).

    The integration ratio of the doublet to the quartet
    was 1:2.5.

    From the above result it is possible to represent

this reaction by the following equation:

$$2Me_2NPF_2 + 3Me_2NBr \longrightarrow (Me_2N)_3PF^+.Br^- + (Me_2N)_2PF_3 + Br_2$$
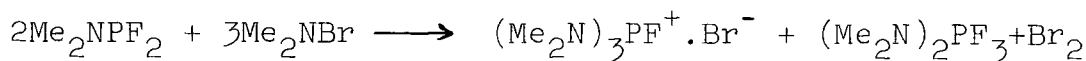
    This reaction will be discussed in detail in Section 6.19

6.18 The reaction between dimethylamino dibromo phosphine and dimethyl chloramine

A sample of dimethylamino dibromo phosphine (4.2 mmol)
prepared as described in Section 4.7 was dissolved in 4 cm^3
of degassed petroleum ether inside a reaction vessel (Fig.2.2b).
Dimethyl chloramine (6.8 mmol) was condensed onto the solution
at -198°C.   The vessel was kept at -45.6°C for seven hours
with occasional shaking and was then allowed to warm to room
temperature.   The gas phase infrared spectrum of the most

volatile fraction showed a mixture of dimethyl chloramine and petroleum ether. These were pumped away leaving an orange solid. The ^{31}Pnmr spectrum of the product dissolved in dichloromethane showed one sharp peak at -50.0 p.p.m. (Figure 29). Elemental analysis agreed with the theoretical results for $(Me_2N)_2PClBr_2$ as shown in Table 6.11.

Table 6.11

Element	Calculated for $(Me_2N)_2PClBr_2$	Found
C	15.27	14.76
H	3.82	4.35
N	8.91	8.99
P	9.86	9.73
Cl	11.31	11.14
Br	50.85	49.90

The nmr spectrum of the product indicated the formation of a tetra coordinate phosphonium ion, which would be generated by simple amination on the phosphorus atom. The nmr spectrum also indicated that the cation formed by this reaction is the chlorobromo species and not the dibromo as this cation has been prepared as its bromide salt (Section 4.9) and has a ^{31}Pnmr chemical shift of -46.7 p.p.m.

A possible course for this reaction is:

$$Me_2NPBr_2 + Me_2NCl \longrightarrow (Me_2N)_2PBr_2^+ . Cl^-$$
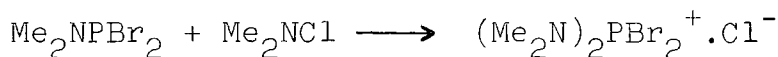
followed by halogen exchange:

$$(Me_2N)_2PBr_2^+ . Cl^- \longrightarrow (Me_2N)_2PBrCl^+ . Br^-$$
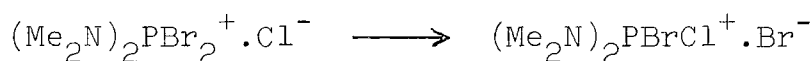
This is to be expected as the phosphorus chlorine single bond energy term is some 63 kJ mol^{-1} stronger than the phosphorus bromine bond energy term (125).

6.19 Results and Discussion

In the work described in this Chapter it was found that the reactions of Me_2NX (X = Cl or Br) with chloro or bromo substituted phosphorus were simple aminations. These reactions probably occurred by an S_N2 attack by the phosphorus atom on the nitrogen atom of the halo amine with loss of halide ion from the nitrogen.

$$Me_2PCl + Me_2NX \longrightarrow Me_2NPMe_2Cl^+.Cl^-$$
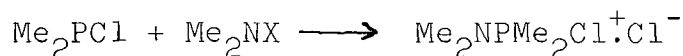
In contrast the reactions in which fluoro substituted phosphine occur were much more complex. The stoichiometry of the reaction between dimethylchloro amine and dimethyl-aminodifluoro phosphite can be written:

$$6Me_2NCl + 6Me_2NPF_2 \longrightarrow 3(Me_2N)_2PF_2^+ + 2(Me_2N)_3PF^+ + PCl_3F_3^-$$
$$+ 3Cl^- + F^-$$
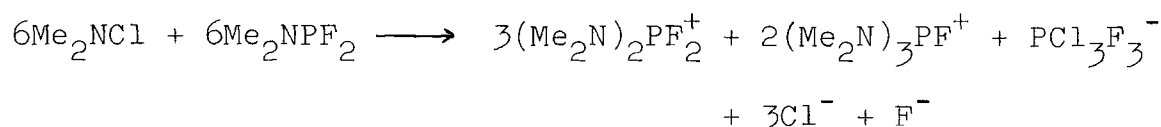
The first step in this reaction could be amination at the phosphorus:

$$Me_2NCl + Me_2NPF_2 \longrightarrow (Me_2N)_2PF_2Cl$$
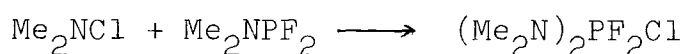
followed by rearrangement of the groups on the phosphorus V species:

$$2(Me_2N)_2PF_2Cl \longrightarrow (Me_2N)_3PF.^+Cl^- + Me_2NPF_3Cl$$
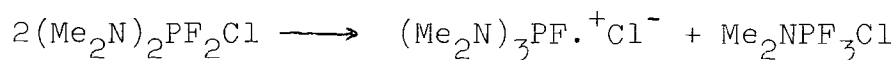
This type of rearrangement is well known in phosphorus V chemistry particularly in the presence of fluorine, e.g.:

$$2\ PCl_2F_3 \longrightarrow PCl_4^+. PF_6^- \quad (\ 71)$$
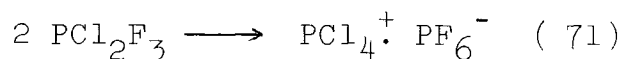
Similarly two molecules of Me_2NPF_3Cl could further rearrange

$$2\ Me_2NPF_3Cl \longrightarrow (Me_2N)_2PF_2^+.F^- + PF_3Cl_2$$
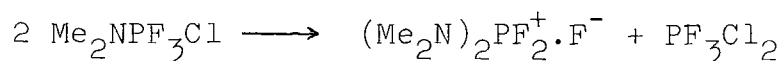
and the PF_3Cl_2 formed could react with chloride ion formed in the first reaction to give the octahedral anion:

$$PF_3Cl_2 + Cl^- \longrightarrow PF_3Cl_3^-$$
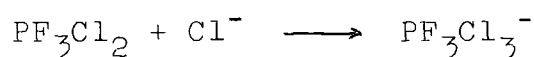
The reaction between dimethyl bromamine and dimethylamino difluoro phosphine was also found to be complex and the stoichiometry can be represented as:

$$5\ Me_2NPF_2 + 7Me_2NBr \longrightarrow 2(Me_2N)_3PF^+\cdot Br^- + 3(Me_2N)_2PF_3 + 3Br_2$$
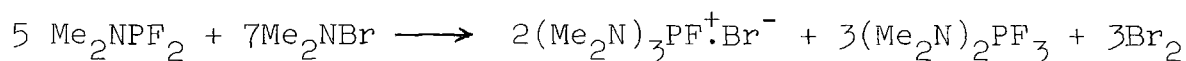
Here again one can envisage initial amination on the phosphorus followed by rearrangement of the phosphorus V species:

$$Me_2NPF_2 + Me_2NBr \longrightarrow (Me_2N)_2PF_2Br$$

$$2(Me_2N)_2PF_2Br \longrightarrow (Me_2N)_2PF_3 + (Me_2N)_2PFBr_2$$
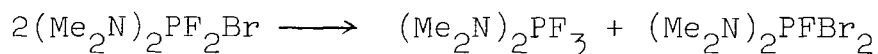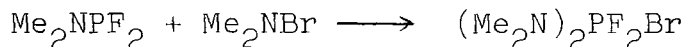
The dibromo species so formed could then be in equilibrium with the phosphine and bromine, similar to the equilibrium that exist between PBr_5 and PBr_3:

$$(Me_2N)_2PFBr \rightleftharpoons (Me_2N)_2PF + Br_2$$
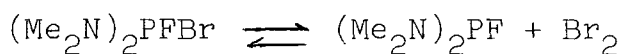
The phosphine would then react with the excess bromamine, as described in section 6.

$$(Me_2N)_2PF + Me_2NBr \longrightarrow (Me_2N)_3PF^+\cdot Br^-$$
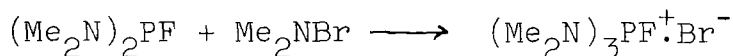
The formation of the bromine was shown by the presence of a brownish liquid.

The reactions between $(Me_2N)_2PF$ and Me_2NX (X = Cl or Br) produced a tetra coordinate phosphonium salt by simple amination on the phosphorus atom:

$$(Me_2N)_2PF + Me_2NX \longrightarrow (Me_2N)_3PF^+\cdot X^-$$
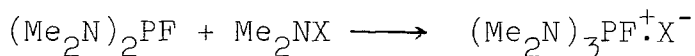
The spectra of these reactions showed a singlet due to the product of the side reaction between $(Me_2N)_3P$ (which was found on an impurity with the starting material and Me_2NX. The phosphorus compound produced when $(Me_2N)_3P$ was reacted with Me_2NCl was $(Me_2N)_3PCl_2$ (1) and that of the parallel reaction with Me_2NBr was $(Me_2N)_3PBr_2$ as described in section 7.16.

From the above discussion it is possible to conclude that the reactions of the chloro or the bromo substituted organic phosphine with Me_2NX produced tetra coordinate phosphonium ions by simple amination.   The reaction of Me_2NPF_2 with Me_2NX were not simple amination reactions, this could be attributed to the nature of the fluorine atoms, which made it possible for the initially formed phosphorus species to rearrange and to produce both ionic and covalent compounds.

CHAPTER SEVEN

THE REACTIONS OF HALAMINES WITH

A VARIETY OF TRI(ORGANO)PHOSPHINES

7.1 Introduction

The reactions of tris(dimethylamino)phosphine and dimethyl bromamine described in this chapter were carried out in order to compare the results obtained with that of the parallel reaction with dimethyl chloramine (1), which has been found to be:

$$(Me_2N)_3P + 2Me_2NCl \longrightarrow (Me_2N)_3PCl.Cl + Me_2N.NMe_2$$
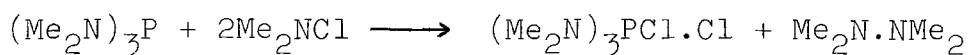
It was thought that the chloramine had failed to aminate tris(dimethylamino)phosphine because of the steric hindrance caused by the three dimethylamino groups linked to the phosphorus atom. Because of this the reactions of Me_2NX (X = Cl or Br) with tri(organo)phosphines (with bulky organic groups) were attempted such as the reaction between triphenyl phosphine and dimethyl chloramine, in order to determine whether other bulky groups cause parallel reactions.

7.2 The reaction between dimethyl chloramine and triphenyl phosphine

A sample of triphenyl phosphine (6.2 mmol), purchased from BDH chemicals Ltd. and recrystallised from dichloro methane, was dissolved in 3 cm^3 of dry degassed dichloro methane inside a reaction vessel (Figure 2.2b). Dimethyl-amine (8.1 mmol) was condensed onto the solution at -196°C. After the reactants had been held at -23°C for three hours. the vessel was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction was run. This identified a mixture of dimethyl chloramine and dichloro methane. These were pumped away leaving a white

solid, the ^{31}Pnmr spectrum of which (Figure 62) showed one peak only at -46.8 p.p.m.   This chemical shift indicated the formation of a new tetra coordinate phosphonium ion. The infrared spectrum of the product is shown in Figure 24 and the elemental analyses are listed below (Table 7.1).

Table 7.1

Element	Calculated for Ph_3PNMe_2Cl	Found
C	70.29	69.72
H	6.15	7.05
N	4.10	4.38
P	9.08	9.12
Cl	10.38	10.50

These results indicated that simple amination had occurred on the phosphorus atom and the overall reaction can be represented as:

$$Ph_3P + Me_2NCl \longrightarrow Ph_3PNMe_2^+ \cdot Cl^-$$
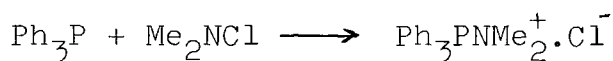
7.3   The reaction between $Ph_3PNMe_2 \cdot Cl$ and boron trichloride

A sample of $Ph_3PNMe_2 \cdot Cl$ (5.7 mmol), prepared as described in Section 7.2, was introduced into a reaction vessel (Figure 2.2b).   Boron trichloride (7.9 mmol) was condensed onto the phosphonium salt and cooled to -196°C.   The vessel was kept at -96°C for half an hour and then connected to the vacuum line.   The gas phase infrared spectrum of the most volatile fraction showed only the presence of boron trichloride which was pumped away, leaving a creamish-white solid.   The infrared spectrum of this solid (Figure 25) showed the characteristic broad band in the range 650-750 cm^{-1} due to the formation

of BCl_4^- (103).   The ^{31}Pnmr spectrum of the solid showed
one peak only at -48.8 p.p.m.   This chemical shift is very
close to that of $Ph_3PNMe_2^+.Cl^-$ reported in Section 7.2.   The
elemental analyses are listed in Table 7.2.

Table 7.2

Element	Calculated for $Ph_3PNMe_2^+.BCl_4^-$	Found
C	52.33	51.82
H	4.58	5.07
N	3.05	3.41
P	6.76	6.55
Cl	30.92	31.22

These results confirmed that $Ph_3PNMe_2.Cl$ is an ionic com-
pound and the reaction with boron trichloride was:

$$Ph_3PNMe_2.Cl + BCl_3 \longrightarrow Ph_3PNMe_2^+.BCl_4^-$$
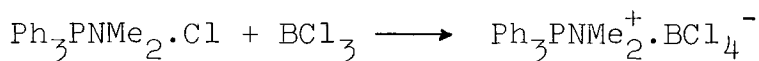
7.4   Attempted hydrolysis of $Ph_3PNMe_2.Cl$

A sample of $Ph_3PNMe_2.Cl$ (2.1 mmol) prepared as described
in Section 7.2 was dissolved in 2.5 cm^3 of distilled water,
producing a colourless solution.   The ^{31}Pnmr spectrum of
this solution showed one sharp peak only at -46.4 p.p.m.
This chemical shift is very close to that reported for
$Ph_3PNMe_2.Cl$ in Section 7.2.   This result showed that the
nitrogen phosphorus bond in this compound is not susceptible
to cleavage by water.

7.5 *Attempted* ₁ reaction between dimethyl bromamine and triphenyl phosphine.

Triphenyl phosphine (5.1 mmol) was dissolved in 4cm^3 of dry degassed dichloro methane inside a reaction vessel (Figure 2.2b). Dimethyl bromamine (6.8 mmol) was condensed onto the solution at -196°C. After having been kept at -46.7°C (chlorobenzene cooled bath) for an hour, the vessel was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction run showing a mixture of dichloromethane and dimethyl bromamine. These were pumped away leaving a pale yellow solid, the infrared spectrum of which is shown in Figure 2b. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane gave one sharp peak at -46.8 p.p.m. This chemical shift is identical to that found for $Me_2NPPh_3^+.Cl^-$ prepared by reacting Me_2NCl with Ph_3P as described in Section 7.2. The elemental analysis are shown in Table 7.3.

Table 7.3

Element	Calculated for $Me_2NPPh_3.Br$	Found
C	62.19	61.57
H	5.44	5.83
N	3.63	3.74
P	8.03	8.12
Br	20.71	20.50

These results indicate that the overall reaction is:

$$Ph_3P + Me_2NBr \longrightarrow Me_2NPPh_3.Br$$
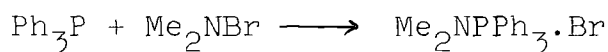
7.6 The reaction between Me_2NPPh_3Br and boron tribromide

A sample of Me_2NPPh_3Br (1.3 mmol) prepared as described in the previous section was introduced into a reaction vessel (Figure 2.2b), and boron tribromide ($5cm^3$) condensed onto it at $-196^{\circ}C$. The reactants were kept at $-23.2^{\circ}C$ for half an hour, and then allowed to warm to room temperature. The gas phase infrared spectrum showed the presence of boron tribromide only, which was pumped away leaving a pale yellow solid. The infrared spectrum of the solid showed the characteristic peak due to BBr_4^- in the range between 650 cm^{-1} and 760 cm^{-1}. The ^{31}Pnmr spectrum of the solid (dissolved in dichloromethane) showed one sharp peak at -46.8 p.p.m. This chemical shift is identical to the chemical shift found for $Me_2NPPh_3.Cl$ prepared by reacting Me_2NCl with Ph_3P as described in Section 7.2. The elemental analyses are listed in Table 7.5.

Table 7.5

Element	Calculated for $Me_2NPPh_3.BBr_4$	Found
C	37.71	36.98
H	3.3	3.88
N	2.2	3.01
P	4.87	4.62
Br	50.22	49.92

These results confirmed the ionic character of $Me_2NPPh_3.Br$ and showed that the reaction with boron tribromide was:

$$Me_2NPPh_3.Br + BBr_3 \longrightarrow Me_2NPPh_3^+.Br_4^-$$
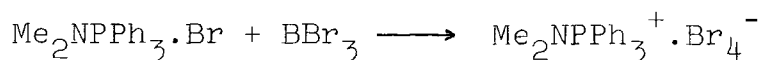
7.7 The hydrolysis of Me$_2$NPPh$_3$Br

A sample of Me$_2$NPPh$_3$Br (1.6 mmol) was introduced into a modified nmr tube (Figure 2.5). When distilled water (3cm^3) was added to the phosphorane, a pale yellow liquid was formed. The ^{31}Pnmr spectrum of this liquid showed one sharp peak only at -46.8 p.p.m. which was identical to the chemical shift found for Me$_2$NPPh$_3$.Br. Thus it is possible to conclude that water cleaved neither the N-P nor the C-P bonds.

7.8 The reaction between tri(n-butyl) phosphine and dimethylchloramine

A sample of tri(n-butyl)phosphine (3.1 mmol) obtained from BDH Chemicals Ltd., and used without further purification was dissolved in 4cm^3 of dry degassed petroleum ether inside the reaction vessel (Figure 2.2b). Dimethyl chloramine (4.6 mmol) was condensed onto the solution at -196°C. After the reactants had been kept at -23.2°C (carbon tetrachloride cold bath) for three hours, they were allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction was run showing a mixture of petroleum ether and dimethyl chloramine. These were pumped away leaving a white solid which was washed three times with petroleum ether inside the drybox. The infrared spectrum of the product is shown in Figure 27 . The ^{31}Pnmr spectrum of the product dissolved in dichloro methane showed one sharp peak at -67.8 p.p.m. The elemental analyses are listed in Table 7.6.

Table 7.6

Element	Calculated for $(C_4H_9)_3PNMe_2.Cl$	Found
C	59.69	59.53
H	11.73	12.15
N	4.97	5.01
P	11.01	11.23
Cl	12.60	12.49

These results show that simple amination had occurred at the phosphorus and that the overall reaction was:

$$(C_4H_9)_3P + Me_2NCl \longrightarrow Me_2NP(C_4H_9)_3^+.Cl^-$$

7.9 The reaction between tri(n-butyl)phosphine and dimethyl bromamine

Tri(n-butyl) phosphine (2.8 mmol) was dissolved in $4cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b). Dimethyl bromamine (5.2 mmol) was condensed onto the solution at -196^oC. The reactants were held at -30^oC (the freezer temperature) for five hours and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of petroleum ether and dimethylbromamine. These were pumped away leaving a yellow solid which was washed three times with petroleum ether inside the drybox. The infrared spectrum of the product was very similar to that of $Me_2NP(C_4H_9)_3.Cl$. The $^{31}Pnmr$ spectrum of the solid dissolved in dichloro methane showed one sharp peak only at -66.2 p.p.m. This chemical shift is very close to the chemical shift found for $Me_2NP(C_4H_9)_3^+.Cl^-$

which was prepared as described in Section 7.8. The elemental analyses are listed in Table 7.7.

Table 7.7

Element	Calculated for $(C_4H_9)_3PNMe_2Br$	Found
C	51.55	51.33
H	10.13	10.51
N	4.30	4.79
P	9.51	9.38
Br	24.52	24.20

These results indicate that simple amination occurred at the phosphorus atom of $(C_4H_9)_3P$ and that the overall reaction was:

$$(C_4H_9)_3P + Me_2NBr \longrightarrow Me_2NP(C_4H_9)_3^+ \cdot Br^-$$
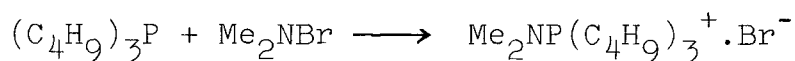
7.10 The hydrolysis of $(C_4H_9)_3PNMe_2Cl$ and $(C_4H_9)_3PNMe_2 \cdot Br$

Two samples, one of the $(C_4H_9)_3PNMe_2Cl$ salt and the other of the $(C_4H_9)_3PNMe_2Br$ salt were introduced into two ^{31}Pnmr tubes. Then they were exposed to wet nitrogen for three hours. The spectrum of each sample dissolved in dichloro methane showed two sharp peaks, one due to the unhydrolysed phosphonium salt and a second peak at -43.5 p.p.m. due to the form of the known phosphine $(C_4H_9)_3$ PO oxide (104). This indicates that both phosphonium salts were slowly hydrolysed by water as follows:

$$(C_4H_9)_3PNMe_2 \cdot X + H_2O \longrightarrow (C_4H_9)_3PO + Me_2NH_2 \cdot X$$

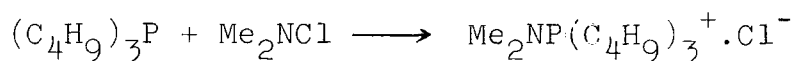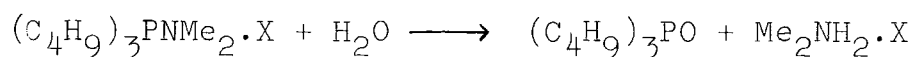## 7.11 The reaction between trimethyl phosphine and dimethyl chloramine

A sample of trimethyl phosphine (3.1 mmol) obtained from FluoroChemicals Limited and purified by vacuum fractionation was distilled into a reaction vessel (Figure 2.2b) and degassed petroleum ether ($3cm^3$) was condensed onto the phosphine at $-196^{\circ}C$. The vessel was allowed to warm to room temperature and shaken to dissolve the trimethyl phosphine into the ether. Dimethyl chloramine (5.7 mmol) was condensed onto the solution at $-196^{\circ}C$ and the reactants were kept at $-83^{\circ}C$ (dry ice-acetone mixture) for five hours. After this time the vessel was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl chloramine and petroleum ether. These were pumped away leaving a white solid which was washed three times with petroleum ether inside the drybox. The infrared spectrum of the product is shown in Figure 28. The ^{31}Pnmr spectrum of the solid product showed a broad peak at -74.2 p.p.m. and the elemental analyses are listed in Table 7.8.

Table 7.8

Element	Calculated for $Me_3PNMe_2 \cdot Cl$	Found
C	38.60	38.44
H	9.65	10.06
N	9.0	9.34
P	19.94	19.72
Cl	22.81	22.80

These results indicate that simple amination occurred at the phosphorus atom of Me_3P. This reaction can be represented by the following equation:

$$Me_3P + Me_2NCl \longrightarrow Me_3PNMe_2 \cdot Cl$$

7.12 The reaction between trimethyl phosphine and dimethyl bromamine

Trimethyl phosphine (3.5 mmol) was distilled into a reaction vessel (Figure 2.2b) at $-196^{\circ}C$. A dry degassed sample of petroleum ether ($5cm^3$) was condensed onto the phosphine at $-196^{\circ}C$ and the vessel allowed to warm to room temperature so that after shaking the trimethyl phosphine would dissolve in the petroleum ether. A sample of dry degassed dimethyl bromamine (4.9 mmol) was condensed onto this solution and the reactants kept at $-46.7^{\circ}C$ (chlorobenzene cold bath) for four hours. The vessel was then allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction run which showed a mixture of petroleum ether and dimethyl bromamine. These were pumped off leaving a yellow solid which was washed three times with petroleum ether inside the drybox. The infrared spectrum of the product is very similar to that of $Me_3PNMe_2 \cdot Cl$. The ^{31}Pnmr spectrum of the solid showed one broad peak at -75.8 p.p.m. The elemental analyses are listed in Table 7.9.

Table 7.9

Element	Calculated for $Me_2NPMe_3 \cdot Br$	Found
C	30.02	29.79
H	7.50	7.83
N	7.00	7.21
P	15.51	15.43
Br	39.97	39.86

These results indicate that simple amination occurred
at the phosphorus of the trimethyl phosphine to produce a
four coordinate phosphonium salt.   The overall reaction
was as follows:

$$Me_3P + Me_2NBr \longrightarrow Me_3PNMe_2^+.Br^-$$
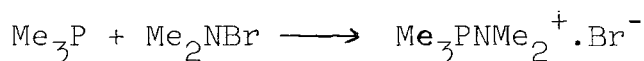
7.13 The hydrolysis of $Me_3PNMe_2.X$ (X = Cl or Br)

Samples of the two phosphonium salts were introduced
into two Pnmr tubes and exposed to wet nitrogen for three
hours.   These samples were each dissolved in $1.5cm^3$ of
dichloro methane and the ^{31}Pnmr spectra showed two sharp
peaks in each case, one at -76.4 p.p.m. (due to unhydrolysed
$Me_3PNMe_2.X$) and the other peak at -50.1 p.p.m. (due to the
formation of $Me_3P=O$).   This result implies that water cleaved
the P-N bond of phosphonium salts and that the hydrolysis can
be represented by the following equation:

$$Me_3P-NMe_2.X + H_2O \longrightarrow Me_3P=O + Me_2NH_2 X$$
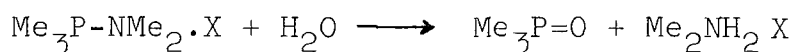
7.14 The reaction between tri(cyclohexyl)phosphine and dimethylchloramine

Tri(cyclohexyl)phosphine (2.6 mmol) obtained from
Floro Chemicals Limited and recrystallised from dichloro
methane was dissolved in $4cm^3$ of dry degassed dichloromethane
inside the reaction vessel (Figure 2.2b).   Dimethyl chloramine
(3.8 mmol) was degassed and condensed onto the solution at
$-196^{\circ}C$ and the reactants were warmed to $-23.2^{\circ}C$ (carbon tetra
chloride cold bath) for an hour.   After this time the vessel

was allowed to warm to room temperature and the gas phase infrared spectrum run, which showed a mixture of dichloro methane and dimethyl chloramine. These were pumped away leaving a white solid. The solid started to liquify and after five minutes had the appearance of a gel. The ^{31}Pnmr spectrum of this substance showed six peaks at -90.1 p.p.m., -82.5 p.p.m., -65.1 p.p.m., -32.7 p.p.m., -18.4 p.p.m. and at 9.2 p.p.m.

This reaction was repeated with some modification. Tri(cyclohexyl)phosphine (1.5 mmol) was dissolved in 2cm^3 of dry degassed dichloro methane inside a modified ^{31}Pnmr (Figure 2.5). Dimethyl chloramine (2.9 mmol) was degassed and condensed onto the solution at -196°C. The tube was kept at -83°C (dry ice-acetone mixture) for two hours and then cooled to -196°C and fitted into the probe of the ^{31}Pnmr spectrometer for a short run. The spectrum showed one sharp peak at -94.6 p.p.m. but when the tube was allowed to warm to room temperature for about five minutes the spectrum contained six peaks (as reported in the first experiment).

This result implies that the reaction initially produced a phosphonium salt which has the chemical shift of -94.6 p.p.m. and it is likely to be the product of simple amination:

$$(C_6H_{11})_3P + Me_2NCl \longrightarrow (C_6H_{11})_3PNMe_2 \cdot Cl$$
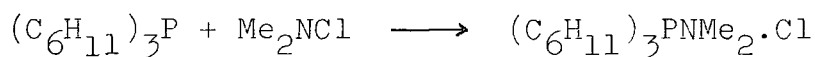
Then this phosphonium salt decomposed to produce a mixture of phosphorus compounds.

7.15 The preparation of tris(dimethylamino)phosphine

This phosphine was prepared as described by A. Michaelis (105) using the reaction:

$$PCl_3 + 6Me_2NH \longrightarrow (Me_2N)_3P + 3Me_2NH_2Cl$$
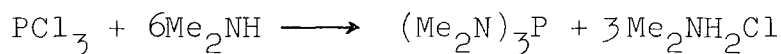
Two modifications were made to improve the yield of the reaction. The first was that the addition of the amine solution to the phosphine solution was carried out at $-83^{\circ}C$ so as to get more efficient cooling than that obtained by using crushed ice. This was important so as to control the exothermic reaction and to stop any loss of the amine by evaporation. The second modification was to leave the reaction mixture overnight at room temperature to give more time for the reaction to be completed.

The purity of the product was determined by ^{31}Pnmr spectroscopy and elemental analysis (see Table 7.10 below). The spectrum showed one sharp peak only at -122.6 p.p.m. due to the formation of $(Me_2N)_3P$ (reported value -123.p.p.m. (53).

Table 7.10

Element	Calculated for $C_6H_{18}N_3P$	Found
C	44.17	44.11
H	11.04	11.47
N	25.77	25.89
P	19.02	19.00

7.16 The reaction between tris(dimethylamine)phosphine and dimethylbromamine

Dimethylbromamine (5.1 mmol) was degassed, distilled through the vacuum line (Figure 2.1), and condensed onto a degassed sample of tris(dimethylamino)phosphine (3.7 mmol) dissolved in 3ml of dry degassed petroleum ether into a reaction vessel (Figure 2.2b) at $-196^{\circ}C$. The reactants were kept at $-23.2^{\circ}C$ (carbon tetrachloride cold bath) for four hours and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fractions showed a mixture of dimethyl bromamine, petroleum ether and a substance which could have been tetramethyl hydrazine. These were pumped away leaving a yellowish-orange solid. This was washed three times with petroleum ether inside the drybox and dried *in vacuo* . The infrared spectrum of this solid was identical to the infrared spectrum of $(Me_2N)_3PBr^+.Br^-$ (Figure 15) which has been prepared by the bromination of tris(dimethylamino)phosphine as shown in Section 4.10 . The $^{31}Pnmr$ spectrum showed one broad peak at -48.3 p.p.m. which was identical to the chemical shift found for $(Me_2N)_3PBr^+.Br^-$ (Figure 41). The elemental analyses are listed in Table 7.11

Table 7.11

Element	Calculated for $(Me_2N)_3PBr_2$	Found
C	22.30	21.73
H	5.58	5.96
N	13.01	13.41
P	9.60	9.54
Br	49.50	49.27

These results indicate that this reaction produced

$(Me_2N)_3PBr^+ \cdot Br^-$ and a volatile substance which could be

tetramethyl hydrazine.   This reaction was carried out

with modifications so as to prove the presence of tetra-

methyl hydrazine.   A dry degassed sample of dimethyl-

bromamine (4.9 mmol) was condensed onto a degassed sample

of tris(dimethylamino)phosphine (5.3 mmol) inside a reaction

vessel (Figure 2.2b) at -196°C.   The reactants were held

at -83°C (dry ice-acetone mixture) for eight hours, with

occasional shaking.   When the vessel was allowed to warm

to room temperature, a yellowish-orange solid was apparent.

The gas phase infrared spectrum of the most volatile fractions

showed tetramethyl hydrazine only, which was pumped away.

The ^{31}Pnmr spectrum of the product showed two peaks, a sharp

one at -122.5 p.p.m. due to tris(dimethylamino)phosphine (53)

and a broad peak at -48.3 p.p.m. due to the formation of

$(Me_2N)_3PBr^+ \cdot Br^-$.   The product was washed five times with

petroleum ether inside the drybox to remove tris(dimethylamino)

phosphine and the yellowish-orange solid was dried under vacuum.

Its infrared spectrum was identical to $(Me_2N)_3PBr^+ \cdot Br^-$ from

the first preparation.   The elemental analyses are listed in

Table 7.12.

Table 7.12

Element	Calculated for $(Me_2N)_3PBr_2$	Found
C	22.30	21.90
H	5.58	6.25
N	13.01	13.29
P	9.60	9.48
Br	49.50	49.38

These results indicate that the overall reaction was as follows:

$$2Me_2NBr + (Me_2N)_3P \longrightarrow (Me_2N)_3PBr^+ \cdot Br^- + Me_2N-NMe_2$$
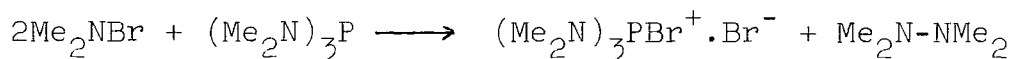
7.17 Results and Discussion

It is possible to conclude from the results of the reactions described in this chapter that in most cases simple amination occurred on the phosphorus atom to produce phosphonium salts in a nucleophilic substitution reaction, e.g.:

$$Ph_3P + Me_2NCl \longrightarrow Ph_2PNMe_2^+ \cdot Cl^-$$
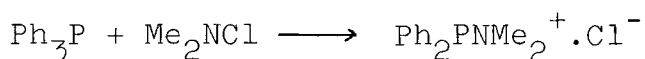
Simple amination did not take place on the phosphorus atom of tris(dimethylamino)phosphine when it was reacted with dimethyl bromamine, instead bromination of the phosphine occurred. This result parallels that found by H.H. Sis ler when he reacted dimethyl chloramine with tris(dimethyl*amino*) phosphine (4) and the same result found by Khabbass (1) when the chlorophosphorane and tetramethyl hydrazine were isolated.

This result could be explained by the steric hindrance caused by the three dimethyl amino groups linked to the phosphorus. This would make it difficult for the phosphorus atom to attack the nitrogen of the bromamine to produce $(Me_2N)_4P^+$. The alternative site of attack by phosphorus is the bromine atom:

$$(Me_2N)_3P + Me_2NBr \longrightarrow (Me_2N)_3PBr^+ + Me_2N^-$$
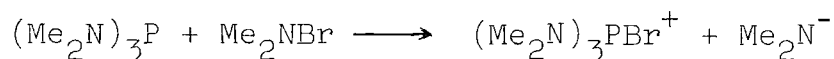
It is unlikely that the dimethylamide ion could have any real existence in the system, but it would attack a second bromamine molecule in a concerted reaction:

$$Me_2N^- + Me_2NBr \longrightarrow Me_2N\text{-}NMe_2 + Br^-$$
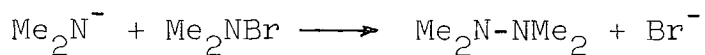
The result of this reaction is parallel to that of the reaction between triphenyl phosphite and phenyl sulphenyl chloride (61,62).

$$(PhO)_3P + PhSCl \longrightarrow (PhO)_3PCl_2 + PhS\text{-}SPh$$

although triphenyl phosphite reacts with halamines to give amination products (Section 7.2,7.5).

The reaction between tricyclohexyl phosphine and dimethyl chloramine initially produced phosphonium salts as implied by the ^{31}Pnmr spectrum, but this salt seemed to rearrange to produce a mixture of unknown species, as was shown by the ^{31}Pnmr spectrum when the product was allowed to warm to room temperature.

CHAPTER EIGHT

THE REACTIONS OF HALAMINES WITH

A VARIETY OF ORGANO PHOSPHINES

8.1 Introduction

In this Chapter the reactions of a variety of alkyl and aryl substituted phosphines with dimethyl chloramine and dimethyl bromamine are described. This study was performed in order to determine whether the reaction of trisdimethylaminophosphine with halamines, which gives the corresponding dihalo species and tetramethyl hydrazine (Section 7.16, (1)), has any parallel with the reactions of alkyl substituted phosphines with bulkyalkyl groups. Also various phosphines partially substituted with the cyclohexyl group were oxidised to see if any parallel reaction to the fast decomposition of the tricyclohexyl dimethylamino phosphonium salts, described in Section 7.14 could be discovered, thus shedding further light on that reaction.

8.2 The reaction between diphenyl methyl phosphine and dimethyl chloramine

Diphenyl methyl phosphine (8.7 mmol) (FluoroChemicals Limited) was dissolved in $4cm^3$ of dry petroleum ether inside a reaction vessel (Figure 2.2b) and 9.9 mmol of dry dimethyl chloramine condensed onto it. The vessel was kept at $-23^{\circ}C$ for five hours and then was allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed the presence of petroleum ether and dimethyl chloramine. These were pumped away through the vacuum line leaving a white solid which was removed from the cell and washed twice with petroleum ether inside the drybox. The $^{31}Pnmr$ spectrum (Figure 63) of the product dissolved in dichloro methane showed one sharp peak only at -51.6 p.p.m. due to the formation of a tetra coordinate phosphonium ion which is likely to be

Me_2NPPh_2 Me Cl.   This cation and its chemical shift have not been reported before.   The infrared spectrum of the product is shown in Figure 29   and the elemental analyses appear in Table 8.1.

Table 8.1

Element	Calculated for Me_2NPPh_2MeCl	Found
C	64.41	63.94
H	6.80	7.11
N	5.01	5.24
P	11.09	11.12
Cl	12.70	12.58

These results indicate that simple amination occurred to the phosphorus atom and the overall reaction can be represented by the following equation:

$$Ph_2PMe + Me_2NCl \longrightarrow Me_2NPPh_2Me.Cl$$
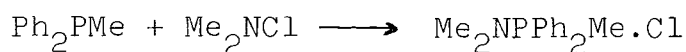
8.3   The reaction between diphenyl methyl phosphine and dimethyl bromamine

A sample of diphenyl methyl phosphine (7.3 mmol) was degassed and dissolved in $3cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b), and dry degassed dimethyl bromamine (9.1 mmol) condensed onto it at $-196^{o}C$. The vessel was held at $-23^{o}C$ for seven hours and then allowed to warm to room temperature.   The gas phase infrared spectrum showed a mixture of petroleum ether and dimethyl bromamine. These were pumped away leaving a yellow solid, which was washed three times with petroleum ether inside the drybox.   The [31]Pnmr spectrum of the product dissolved in dichloro methane

showed one sharp peak only at -51.6 p.p.m.   This chemical shift is identical to that of $Me_2NPPh_2Me.Cl$ prepared as described in Section 8.2.   The elemental analyses are given in Table 8.2.

Table 8.2

Element	Calculated for Me_2NPPh_2MeBr	Found
C	55.57	55.01
H	5.87	6.20
N	4.32	4.64
P	9.57	9.49
Br	24.67	23.99

Thus the overall reaction is simple amination of the phosphorus atom:

$$Ph_2PMe + Me_2NBr \longrightarrow Me_2NPPh_2Me.Br$$
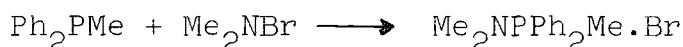
8.4   The preparation of dicyclohexylphenyl phosphine and cyclohexyl diphenyl phosphine

These phosphines were prepared by reacting cyclohexyl magnesium chloride with the corresponding chlorophenyl phosphine (106).

8.4.1   The preparation of cyclohexyl magnesium chloride

This compound was prepared by employing the general Grignard reaction procedure as described previously (107).

8.4.2   The preparation of dicyclohexyl phenyl phosphine

In a typical preparation cyclohexyl magnesium

chloride (195 mmol), was kept in the three-necked flask in which it had been prepared and $40cm^3$ of dry degassed ether was introduced into the flask. The central neck of the flask was equipped with a mechanical stirrer, one of the side necks was connected to a dry nitrogen line via a tap, and the third neck was equipped with a dropping funnel which was kept under dry nitrogen. Phenyl dichloro phosphine (195mmol), dissolved in $50cm^3$ of dry degassed ether, was syringed into the dropping funnel. This phosphine solution was added (over 30 minutes) to the Grignard solution, cooled to -6^oC, stirring continuously. When the addition was completed the mixture was refluxed for about 20 minutes and cooled by using an ice-salt bath. The dropping funnel was charged with about $60cm^3$ of saturated aqueous ammonium chloride solution, which was added dropwise to the reaction mixture with continuous stirring. It was observed that the reaction mixture formed two layers, with the upper, ethereal layer containing the phosphine. This layer was isolated by filtration inside the drybox, and the solvent was removed by distillation. A white solid remained in the flask which, when dissolved in petroleum ether, showed one sharp peak in the ^{31}Pnmr spectrum at -1.5 p.p.m. due to the formation of $PhP(C_6H_{11})_2$ ($\delta=2.5$ p.p.m.) (59). The analysis, shown in Table 8.3, is also in agreement with this formulation.

Table 8.3

Element	Calculated for $C_6H_5P(C_6H_{11})_2$	Found
C	78.83	78.40
H	9.85	10.01
P	11.31	11.22

8.4.3 <u>The preparation of cyclohexyl diphenyl phosphine</u>

This preparation followed the procedure described in Section 8.4.2 for the preparation of dicyclohexyl phenyl phosphine except that 166.7 mmol of cyclohexyl magnesium chloride and 166.7 mmol of diphenyl chloro phosphine were used. Also at the end of the preparation, when the solvent was removed the product in this case was purified by re-crystalisation, to produce a white solid. The ^{31}Pnmr of this (dissolved in ether) showed one sharp peak only at 3.2 p.p.m. in good agreement with the literature value for $Ph_2PC_6H_{11}$ ($\delta = 4.4$ p.p.m.) (59).

The result of elemental analysis of this phosphine is given in Table 8.4.

Table 8.4

Element	Calculated for $(C_6H_5)_2PC_6H_{11}$	Found
C	82.13	81.89
H	6.08	6.41
P	11.79	11.68

8.5 <u>The reaction between diphenyl cyclohexyl phosphine and dimethyl chloramine</u>

Diphenyl cyclohexyl phosphine (6.4 mmol) was dissolved in $3cm^3$ of dry degassed petroleum ether, inside a reaction vessel (Figure 2.2b) and dry degassed dimethyl chloramine (8.1 mmol) condensed onto it at $-196°C$. The cell was held at $-45°C$ for five hours, with occasional shaking, and then allowed to warm to room temperature. The gas phase infrared spectrum of the most volatile fraction showed a mixture of

petroleum ether and dimethyl chloramine. These were pumped
away leaving a white solid, which was washed with petroleum
ether three times inside the drybox. The ^{31}Pnmr spectrum
of the product dissolved in dichloromethane (Figure 64)
showed one sharp peak only at -56.5 p.p.m. indicating the
formation of a phosphonium ion. The chemical shift of this
ion has not been reported before. The infrared spectrum of
the product is shown in Figure 30 and the elemental analyses
appear in Table 8.5.

Table 8.5

Element	Calculated for $Me_2NPPh_2(C_6H_{11})Cl$	Found
C	69.07	69.1
H	7.78	7.53
N	4.03	4.41
P	8.92	8.76
Cl	10.20	9.91

These results indicate that the reaction is a simple amination
of the phosphorus atom:

$$Ph_2P(C_6H_{11}) + Me_2NCl \longrightarrow Me_2NPPh_2(C_6H_{11}).Cl$$

8.6 The reaction between diphenyl cyclohexyl phosphine and dimethyl bromamine
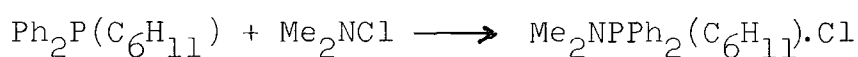
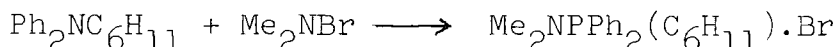Diphenyl cyclohexyl phosphine was dissolved in $4cm^3$ of
dry degassed petroleum ether inside a reaction vessel (Figure
2.2b) and 7.2 mmol of dry degassed dimethyl bromamine con-
densed onto it. The cell was isolated and kept at $-23^{\circ}C$
for five hours with occasional shaking and then warmed to
room temperature. The infrared spectrum of the most volatile
fractions showed a mixture of petroleum ether and dimethyl

bromamine, which were pumped away through the vacuum line leaving an orange solid. This solid was washed three times with petroleum ether inside the drybox and its ^{31}Pnmr spectrum (when dissolved in dichloro methane), showed one sharp peak only at -56.3 p.p.m. due to the formation of a tetra coordinate phosphorus species. This chemical shift is very close to that found for $Me_2NPPh_2(C_6H_{11}.Cl$ (δ =-56.5 p.p.m.) (Section 8.5). The elemental analyses are listed in Table 8.6.

Table 8.6

Element	Calculated for $Me_2NPPh_2(C_6H_{11})Br$	Found
C	61.24	60.79
H	6.89	7.21
N	3.57	3.94
P	7.91	7.83
Br	20.39	20.16

Thus the overall reaction is likely to be simple amination in the phosphorus atom:

$$Ph_2NC_6H_{11} + Me_2NBr \longrightarrow Me_2NPPh_2(C_6H_{11}).Br$$

8.7 The reaction between phenyl dicyclohexyl phosphine and dimethyl chloramine

Phenyl dicyclohexyl phosphine (5.3 mmol) was dissolved in $3cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 6.4 mmol of dry degassed dimethyl chloramine condensed onto it at $-196^\circ C$. The vessel was held at $-23^\circ C$ for five hours with occasional shaking and, at this temperature, the formation of a white precipitate was observed. After the cell had been warmed to room temperature, the gas phase infrared spectrum showed a mixture of

of petroleum ether and dimethyl chloramine.   These were
pumped away through the vacuum line leaving a white solid
which was washed three times with petroleum ether inside the
drybox.   The ^{31}Pnmr spectrum of this solid (dissolved in
dichloromethane) showed one sharp peak at -63.0 p.p.m.
(Figure 65).   This chemical shift indicates the formation
of a tetra coordinate phosphonium ion.   The infrared spectrum
of the product is shown in Figure 31   and the elemental
analyses appears in Table 8.7.

Table 8.7

Element	Calculated for $Me_2NPPh(C_6H_{11})_2Cl$	Found
C	67.90	66.98
H	9.34	10.02
N	3.96	4.21
P	8.77	8.73
Cl	10.03	10.11

These results support the following reaction:

$$PhP(C_6H_{11})_2 + Me_2NCl \longrightarrow Me_2NPPh(C_6H_{11})_2Cl$$

8.8   The reaction between phenyl dicyclohexyl phosphine and dimethyl bromamine
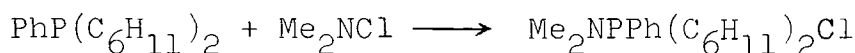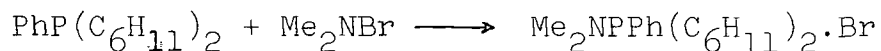
Phenyl dicyclohexyl phosphine (7.1 mmol) was dissolved
in 4cm^3 of dry degassed petroleum ether inside a reaction
vessel (Figure 2.2b) and 7.9 mmol of dry degassed dimethyl
bromamine was condensed onto it at -196°C.   The tube was
kept at -45°C for five hours with occasional shaking and during
this time the formation of a yellow precipitate was observed.
The vessel was allowed to warm to room temperature and the
gas phase infrared spectrum of the most volatile fraction was

run, which showed a mixture of petroleum ether and dimethyl bromamine. These were pumped away through the vacuum line leaving a yellow solid, which was washed three times with petroleum ether inside the drybox. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane showed one sharp peak at -62.9 p.p.m., this chemical shift is within experimental error of the chemical shift found for $Me_2NPPh(C_6H_{11})_2 \cdot Cl$ (δ = -62.9 p.p.m., Section 8.7). The infrared spectrum of the product is very similar to that of $Me_2NPPh(C_6H_{11})_2 \cdot Cl$. The elemental analysis results are listed in Table 8.8.

Table 8.8

Element	Calculated for $Me_2NPPh(C_6H_{11})_2 \cdot Br$	Found
C	60.32	59.89
H	8.29	8.56
N	3.52	3.82
P	7.79	7.68
Br	20.08	19.21

These results indicate that the reaction is a simple amination of the phosphorus

$$PhP(C_6H_{11})_2 + Me_2NBr \longrightarrow Me_2NPPh(C_6H_{11})_2 \cdot Br$$
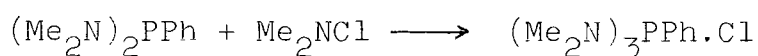
8.9 The reaction between bis(dimethylamino)phenyl phosphine and dimethyl chloramine

Bis(dimethylamino)phenyl phosphine (5.3 mmol) was dissolved in 4cm^3 of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 6.6 mmol of dimethyl chloro-amine was condensed onto the mixture at -196°C.   The cell was held at -45°C for five hours with occasional shaking and during this time the formation of a white precipitate was observed.   The cell was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction showed a mixture of petroleum ether and dimethyl chloramine.   These were pumped away leaving a white solid which was washed three times with petroleum ether inside the drybox.   The ^{31}Pnmr spectrum of the solid dissolved in di-chloro methane (Figure 66) showed one sharp peak only at -51.6 p.p.m. which is in the expected region for a four co-ordinate phosphonium ion and is within experimental error of the value found for $(Me_2N)_3PPh.Br$ (δ = -51.4 p.p.m., (Section 8.10)).   The infrared spectrum of the product is shown in Figure 32 and the elemental analyses are listed in Table 8.9.

Table 8.9

Element	Calculated for $(Me_2N)_3PPh.Cl$	Found
C	52.28	52.10
H	8.35	8.74
N	15.25	15.62
P	11.25	11.22
Cl	12.87	12.71

These results indicate that the overall reaction is:

$$(Me_2N)_2PPh + Me_2NCl \longrightarrow (Me_2N)_3PPh.Cl$$

8.10 The reaction between bis(dimethylamino)phenyl phosphine and dimethyl bromamine

Bis(dimethylamino)phenyl phosphine (6.2 mmol) was dissolved in $5cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 7.3 mmol of dry and de-gassed dimethyl bromamine was condensed onto this mixture at -196°C. The vessel was kept at -45°C for five hours, with occasional shaking and during this time the formation of a yellow precipitate was observed. The cell was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction was run, which showed a mixture of petroleum ether and dimethyl bromamine. These were pumped away through the vacuum line leaving a yellow solid which was washed four times with petroleum ether inside the drybox. The ^{31}Pnmr spectrum of the solid dissolved in dichloromethane showed one sharp peak only at -51.4 p.p.m., which is within experimental error of the chemical shift found for $(Me_2N)_3PPh.Cl$ (δ = -51.6 p.p.m., section 8.9). The elemental analyses are listed in Table 8.10.

Table 8.10

Element	Calculated for $(Me_2N)_3PPhBr$	Found
C	45.01	44.72
H	7.19	7.51
N	13.13	13.38
P	9.70	9.59
Br	24.98	24.59

These results indicate that simple amination of the phosphorus atom has occurred.

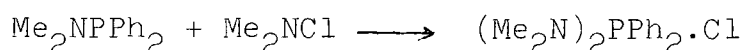$(Me_2N)_2PPh + Me_2NBr \longrightarrow (Me_2N)_3PPh.Br$
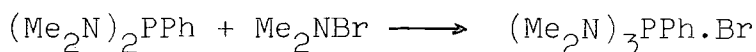
8.11 <u>The reaction between dimethylamino diphenyl phosphine and dimethyl chloramine</u>

A sample of dimethylamino diphenyl phosphine (4.9 mmol) was dissolved in $4cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 5.5 mmol of dimethyl chloromine was condensed onto the phosphine at $-196^{\circ}C$. The vessel was kept at $-23^{\circ}C$ for five hours during which time a white precipitate formed. The cell was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction was run, which showed a mixture of dimethyl chloramine and petroleum ether. These were pumped away through the vacuum line leaving a white solid, which was washed three times with petroleum ether inside the drybox. The ^{31}Pnmr spectrum of this solid dissolved in dichloromethane showed one sharp peak at -50.0 p.p.m. (Figure 67) which indicates the formation of a phosphonium cation and is within experimental error of the chemical shift found for $(Me_2N)_2PPh_2^+.Br$ as described in Section 8.12. The elemental analyses are shown in Table 8.11.

Table 8.11

Element	Calculated for $(Me_2N)_2PPh_2Cl$	Found
C	62.25	61.98
H	7.13	7.49
N	9.08	9.87
P	10.05	10.14
Cl	11.49	11.47

These results imply that simple amination has occurred on the phosphorus atom:

$$Me_2NPPh_2 + Me_2NCl \longrightarrow (Me_2N)_2PPh_2.Cl$$
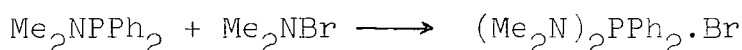
8.12 <u>The reaction between dimethylamino diphenyl phosphine</u>
<u>and dimethyl bromamine</u>

A sample of dimethylamino diphenyl phosphine (6.1 mmol) was dissolved in 5cm^3 of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 7.5 mmol of dry degassed dimethyl bromamine was condensed onto the phosphine at -196°C. The vessel was kept at -45°C for five hours with occasional shaking during which time a yellow precipitate was observed. The vessel was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction showed a mixture of dimethyl bromamine and petroleum ether. These were pumped away leaving a yellow solid which was washed four times with petroleum ether in the drybox. The $^{31}\text{Pnmr}$ spectrum of the solid dissolved in dichloromethane showed one sharp peak at -51.6 p.p.m. This chemical shift is (within experimental error) that of $(Me_2N)_2PPh_2Cl$ ($\delta = 50.0$ p.p.m., Section 8.11). The elemental analyses are listed in Table 8.12.

Table 8.12

Element	Calculated for $(Me_2N)_2PPh_2$.Br	Found
C	54.41	53.62
H	6.23	6.66
N	7.93	8.02
P	8.78	8.74
Br	22.64	22.53

Thus the overall reaction is:

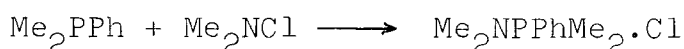$$Me_2NPPh_2 + Me_2NBr \longrightarrow (Me_2N)_2PPh_2.Br$$

8.13 The reaction between dimethyl phenyl phosphine and dimethyl chloramine

A sample of dimethyl phenyl phosphine obtained from Fl**uovo**Chemicals Limited (7.2 mmol) was dissolved in $4cm^3$ of dry degassed petroleum ether inside a reaction vessel (Figure 2.2b) and 8.4 mmol of dry degassed dimethyl chloramine was condensed onto the phosphine at $-196^{\circ}C$. The cell was kept at $-23^{\circ}C$ for five hours with occasional shaking and then allowed to warm to room temperature. The infrared gas phase spectrum of the most volatile fraction showed the presence of a mixture of petroleum ether and dimethyl chloramine. These were pumped away through the vacuum line leaving a white solid which was washed three times with petroleum ether under dry nitrogen. The $^{31}Pnmr$ spectrum of the product dissolved in dichloro methane showed one sharp peak only at -56.5 p.p.m. which indicates the formation of a phosphonium ion and is within the experimental error of the value found for $Me_2NPPhMe$ Br (δ = -54.9 p.p.m. Section 8.14). The elemental analyses appear in Table 8.13.

Table 8.13

Element	Calculated for $Me_2NPPhMe_2$.Cl	Found
C	55.19	53.98
H	7.82	8.11
N	6.44	6.62
P	14.26	14.30
Cl	16.30	16.47

These results indicate that the reaction is:

$$Me_2PPh + Me_2NCl \longrightarrow Me_2NPPhMe_2.Cl$$

8.14 The reaction between dimethyl phenyl phosphine and dimethyl bromamine

A degassed sample of dimethul phenyl phosphine (5.8 mmol) was dissolved in $5cm^3$ of dry degassed petroleum ether in a reaction vessel (Figure 2.2b) and 6.6 mmol of dry degassed dimethyl bromamine was condensed onto it at $-196^{\circ}C$. The vessel was kept at $-45^{\circ}C$ for five hours with occasional shaking and the formation of a yellow precipitate was observed. The vessel was allowed to warm to room temperature and the gas phase infrared spectrum of the most volatile fraction was run, which showed a mixture of dimethyl bromamine and petroleum ether. These were pumped away through the vacuum line leaving a yellow solid which was washed three times with petroleum ether inside the drybox. The ^{31}Pnmr spectrum of the solid dissolved in dichloro methane showed one sharp peak only at -54.9 p.p.m. which is (within experimental error) the value for $Me_2NPPhMe_2$.Cl (δ = -56.5 p.p.m. Section 8.13). The elemental analyses are listed in Table 8.14.

Table 8.14

Element	Calculated for $Me_2NPPhMe_2Br$	Found
C	45.82	45.51
H	6.49	6.87
N	5.35	5.94
P	11.84	11.79
Br	30.51	29.98

These results indicate that simple amination had occurred on the phosphorus atom to produce a phosphonium salt:

$$Me_2PPh + Me_2NBr \longrightarrow Me_2NPPhMe_2.Br$$
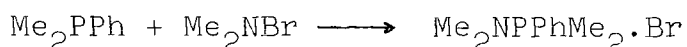
8.15 The reaction between excess white phosphorus and dimethyl chloramine

A sample of white phosphorus (12.5 mmol), (Fisons Scientific Ltd.) was dissolved in 4 cm^3 of degassed carbon disulphide inside a reaction vessel (Figure 2.2b). Dimethyl chloramine (5.3 mmol) was condensed onto the mixture at -196°C. The vessel was kept at -30°C (the freezer temperature) for seventeen days. The gas phase infrared spectrum of the most volatile fraction showed the presence of carbon disulphide only. The ^{31}Pnmr spectrum of the product dissolved in carbon disulphide showed three peaks, one at -164.6 p.p.m. due to the formation of Me_2NPCl_2 (51), a second peak at -53.3 p.p.m. due to the formation of $(Me_2N)_3PCl^+.Cl^-$ (1) and a third peak at 468 p.p.m. due to the white phosphorus. This result implies that the overall reaction is:

$$4 \ Me_2NCl + \tfrac{1}{2}P_4 \longrightarrow (Me_2N)_3PCl.Cl + Me_2NPCl_2$$
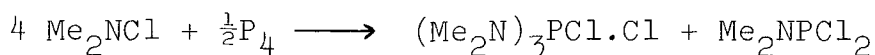
8.16 The reaction between white phosphorus and excess dimethyl chloramine

The reaction was carried out by using the same technique described in Section 8.15. The amounts of the reactants were 3.7 mmol of white phosphorus and 19.4 mmol of dimethyl chloramine. After the vessel had been kept at -30°C for two weeks (with occasional shaking), it was allowed to warm to room temperature and the gas phase infrared spectrum was run of the most volatile fraction. This showed the presence of a mixture of Me_2NCl and CS_2. These were pumped away leaving a white solid, the ^{31}Pnmr spectrum of which (dissolved in dichloromethane) showed one peak at -53.3 p.p.m. The

elemental analysis was consistent with the formula $(Me_2N)_5P_2Cl_5$ as shown in Table 8.15.

Table 8.15

Element	Calculated for $(Me_2N)_5P_2Cl_5$	Found
C	26.13	25.01
H	6.53	7.8
N	15.24	15.64
P	13.50	13.21
Cl	38.60	36.19

These results imply the formation of a mixture of $(Me_2N)_3PCl_2$ and $(Me_2N)_2PCl_3$ the chemical shifts of which are very close to each other and have been observed at -53.3 p.p.m. and -51.6 p.p.m. (1). To confirm this a sample of the product was exposed to wet nitrogen for 6 days. In this way the sample was converted to a colourless liquid, the nmr of which showed two sharp peaks only at -22.5 p.p.m. due to the formation of $(Me_2N)_3P=O$ (108) and at -30.7 p.p.m. due to the formation of $(Me_2N)_2POCl$ (109).

This result proved that the reaction of excess Me_2NCl with white phosphorus produced an equivalent mixture of $(Me_2N)_3PCl^+Cl^-$ and $(Me_2N)_2PCl_2^+Cl^-$. These, when hydrolysed produced $(Me_2N)_3P=O$ and $(Me_2N)_2POCl$. It is possible to represent the overall reaction as:

$$\tfrac{1}{2}P_4 + 5Me_2NCl \longrightarrow (Me_2N)_2PCl_2^+ \cdot Cl^- + (Me_2N)_3PCl^+ \cdot Cl^-$$
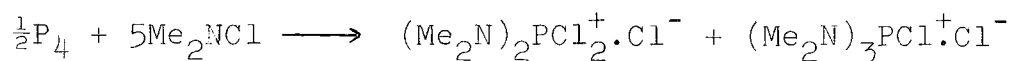
8.17 Results and Discussion

The results of the reactions described in this chapter imply that the phosphines have been aminated by the halamines possibly via an S_N2 attack by the phosphorus atom on the nitrogen of the halamine, e.g.:

$$PhP(C_6H_{11})_2 + Me_2NX \longrightarrow PhP(NMe_2)(C_6H_{11})_2 \cdot X$$

$$PhP(NMe_2)_2 + Me_2NX \longrightarrow PhP(NMe_2)_3 \cdot X$$
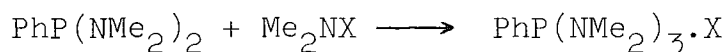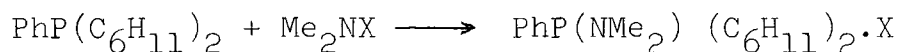
Even when $(C_6H_{11})_3P$ was reacted with Me_2NCl as described in the previous chapter it produced initially a phosphonium ion (most likely by amination) which decomposed rapidly at room temperature. This is most likely because no tetramethylhydrazen was detected in the product. None of the reactions described in this chapter was parallel to the reactions between $(Me_2N)_3P$ and Me_2NBr described in Chapter Seven. This may be attributed to the steric factor more than the electronic factor, since the tris(dimethylamino)phosphine is more bulky than any one of the phosphines reacted with Me_2NX as described in Chapters Seven and Eight, but it is not the most basic one. That is because some of the phosphines which were reacted with Me_2NX in Chapter Seven are more basic, e.g. Me_3P and Ph_3P (110).

In the tris(dimethylamino)phosphine molecule there are three dimethylamino groups linked to the phosphorus causing greater steric hindrance than that produced around the phosphorus atoms of the phosphines used in the reactions described in Chapter Eight. Thus it is most likely that steric effects play a significant role in determining the course of the reaction.

The reaction between white phosphorus (P_4) and Me_2NCl produced $(Me_2N)_3PCl.Cl$ and Me_2NPCl_2 when white phosphorus was used in excess. The white phosphorus molecule (P_4) has a strained tetrahedral structure. This will make the cleavage of the P-P bond by dimethyl chloramine relatively easy. This reaction could be in some stage parallel to the iodination of P_4 to produce P_2I_4 (92), i.e.

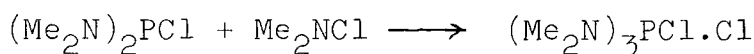$$\frac{1}{2}P_4 + 2Me_2NCl \longrightarrow Me_2N\overset{Cl}{-}P - \overset{Cl}{P}NMe_2$$

The P-P bond is very weak and it has been reported that halogen readily cleaves it (111):

$$R_2P - PR_2 + X_2 \longrightarrow R_2PX$$
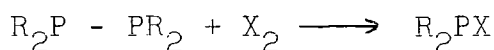
Consequently it is assumed that Me_2NCl reacted with the bisphosphine as:

$$Me_2N\overset{Cl}{-}P\overset{Cl}{-}P\text{-}NMe_2 + Me_2NCl \longrightarrow (Me_2N)_2PCl + Me_2NPCl_2$$
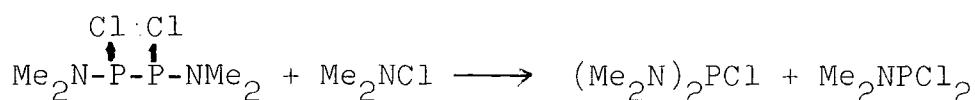
Since $(Me_2N)_2PCl$ is more basic than Me_2NPCl_2 it will react first with Me_2NCl to produce $(Me_2N)_3PCl.Cl$ (1).

$$(Me_2N)_2PCl + Me_2NCl \longrightarrow (Me_2N)_3PCl.Cl$$

Thus the $^{31}Pnmr$ spectrum of the reaction between excess white phosphorus and dimethyl chloramine showed the presence of $(Me_2N)_3PCl.Cl$, Me_2NPCl_2 and white phosphorus, but it did not show a peak due to the biphosphine which is likely to be more reactive towards the chloramine than the white phosphorus. When this reaction was carried out using excess of the chloramine the phosphine observed before reacted with the chloramine (1):

$$Me_2NPCl_2 + Me_2NCl \longrightarrow (Me_2N)_2PCl_2.Cl$$

Consequently the overall reaction was represented by the equation:

$$\frac{1}{2}P_4 + 5Me_2NCl \longrightarrow (Me_2N)_3PCl.Cl + (Me_2N)_2PCl_2.Cl$$
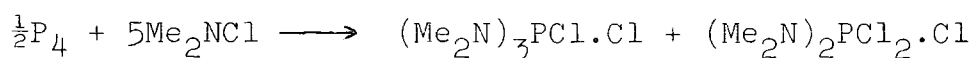
CHAPTER NINE

THE EFFECT OF LIQUID HYDROGEN CHLORIDE ON

A VARIETY OF P-N PHOSPHONIUM SALTS

9.1   Introduction

During previous studies in this laboratory (1) it has been found that liquid hydrogen chloride at $-98^{\circ}C$ dissolved $Me_2NPCl_3^+$ PCl_6^- but did not cleave the P-N bond since the same species was recovered when the hydrogen chloride was evaporated. Presumably the anion reacted to form the tetrachloro phosphonium ion as has been demonstrated by Raman spectroscopy (112).

$$PCl_6^- + 2HCl \longrightarrow PCl_4^+ + 2HCl_2^-$$
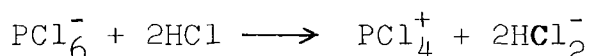
It was found that the P-N bond was cleaved when the acidity of the system was increased by the addition of boron trichloride:

$$Me_2NPCl_3^+ + 2HCl + BCl_3 \longrightarrow Me_2NH_2^+ + PCl_4^+ + BCl_4^-$$
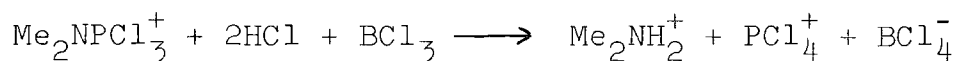
Consequently it was decided to study the stability of other systems containing P-N bonds and some other phosphorus species to see how substituents on the phosphorus changed the stability of the cation to react with hydrogen chloride.

## 9.2   The Purification of hydrogen chloride

A bulb of ten litre capacity with a cooled finger was evacuated and connected separately to a mercury bubbler and to a hydrogen chloride cylinder (BOC special gases). The valve of the cylinder was released gently so that hydrogen chloride replaced the air and filled the connections between the cylinder and the valve of the bulb and pass out through the bubbler. The valve of the bulb was then slowly opened to allow the hydrogen chloride to fill it. When the bulb was full of gas it was connected to the fractionation section

of the vacuum line (Figure 2.1) and the hydrogen chloride
degassed.   The hydrogen chloride was fractionated through
traps at -83°C, -112.5°C and -196°C.   It was noted that a
considerable amount was trapped at -112.5°C while about 0.5
cm³ of colourless liquid of relatively high boiling point
was trapped at -83°C which was presumably hydrogen chloride
hydrate.   No significant quantity of material was trapped
at -196°C.   The gas phase infrared spectrum of the fraction
trapped at -112.5°C showed bands due to hydrogen chloride
only.   The purified HCl was stored either in the ten litre
bulb or inside one of the traps of the fractionation section
at liquid air temperature.

9.3   The reaction between liquid hydrogen chloride and dimethyl amino-triphenyl phosphonium chloride

Inside the drybox a sample of dimethylaminotriphenylphosphonium
chloride (1.6 mmol) which had been prepared by reacting
dimethyl chloramine with triphenyl phosphine as described
in Section 7.2, was introduced into a modified nmr tube made
of silica with a constriction (Figure 2.5).   A sample of the
purified HCl was condensed into a calibrated cooled finger
(Figure 2.5) and warmed to -112.5 in order to measure its
volume (2.8 cm³).   The liquid hydrogen chloride was trans-
ferred onto the phosphonium salt and the tube sealed off under
vacuum and allowed to warm to room temperature inside a steel
cylinder placed inside a fumes hood.   The tube was warmed
to 40°C for five minutes to make sure that it could stand the
pressure at that temperature (the temperature of the nmr probe).
A clear colourless solution was observed and its ^{31}Pnmr spectrum

showed one sharp peak only at -66.2 p.p.m. due to the formation of Ph_3PCl^+ (δ =-66.2 p.p.m. (113)). This result shows that liquid HCl had cleaved the phosphorus nitrogen bond of the cation and that the overall reaction was:

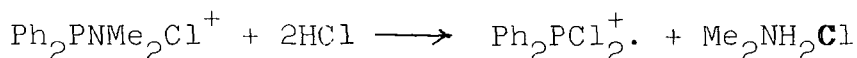$$Ph_3PNMe_2.Cl + 2HCl \longrightarrow Ph_3PCl^+.Cl^- + Me_2NH_2Cl$$
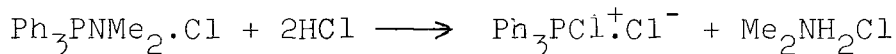
9.4 The reaction between liquid hydrogen chloride and bis(dimethylamino)diphenyl phosphonium chloride

This reaction was carried out using the same technique as described in Section 9.3. The amounts of the reactants used were 1.3 mmol of the phosphonium salt prepared by reacting diphenyl dimethylamino phosphine with dimethyl chloramine as described in Section 4.8 and 2.5 cm^3 of purified HCl. The ^{31}Pnmr spectrum of the solution run after the ampoule had been kept at room temperature for three hours showed one sharp peak at -71.5 p.p.m. due to the formation of $Ph_2PNMe_2Cl^+$ which had previously been prepared by the chlorination of Ph_2PNMe_2 as described in Section 4.3 when its chemical shift had been found to be -70.9 p.p.m. in solution in dichloromethane. This result shows that liquid hydrogen chloride cleaved one of the P-N bonds:
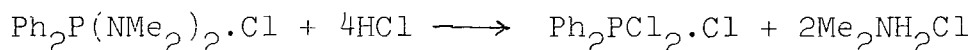
$$Ph_2P(NMe_2)_2^+. + 2HCl \longrightarrow Ph_2PNMe_2 Cl^+ + Me_2NH_2Cl$$
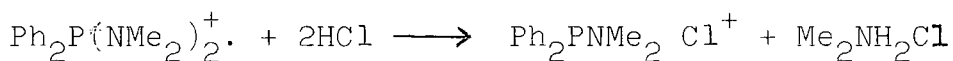
After the tube had been left at room temperature for fifteen hours, the ^{31}Pnmr spectrum of its contents showed one sharp peak only at -93.5 p.p.m. due to the formation of $Ph_2PCl_2^+$ (δ = -93.5 p.p.m.)

This result indicates that hydrogen chloride slowly cleaved the second phosphorus nitrogen bond at room temperature:

$$Ph_2PNMe_2Cl^+ + 2HCl \longrightarrow Ph_2PCl_2^+. + Me_2NH_2Cl$$

and that the overall recation could be represented as:

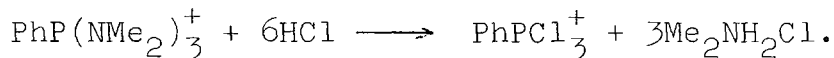$$Ph_2P(NMe_2)_2.Cl + 4HCl \longrightarrow Ph_2PCl_2.Cl + 2Me_2NH_2Cl$$

9.5 The reaction between tris(dimethylamino)phenyl phosphonium chloride and liquid hydrogen chloride

The reaction between tris(dimethylamino)phenyl phosphonium chloride and liquid hydrogen chloride was carried out by employing the technique described in Section 9.3. The phosphonium salt was prepared by reacting bis(dimethylamino) phenyl phosphine with dimethyl chloramine as described in Section 8. 9. The amounts of the reactants used were 1.5 mmol of the phosphonium salt and 3.2 cm^3 of the purified hydrogen chloride. A clear colourless solution was noted and its $^{31}Pnmr$ spectrum run shortly after the tube had been warmed to room temperature showed one sharp peak at -51.6 p.p.m. due to the starting material. After the tube had been left at room temperature for two days the $^{31}Pnmr$ spectrum showed two sharp peaks; a major one at -51.6 p.p.m. due to the starting material and a minor one at -72.1 p.p.m. due to the formation of $PhP(NMe_2)_2Cl^+$. This phosphonium ion had previously been prepared by the chlorination of $Ph\ P(NMe_2)_2$ as described in Section 4.5, and its chemical shift had been measured as -74.1 p.p.m. in solution in dichloromethane. The tube was kept at room temperature for fourteen days and its $^{31}Pnmr$ spectrum showed one sharp peak only at -101.0 p.p.m. due to the formation of $PhPCl_3^+$ (δ = -103.1 p.p.m.) [113]. This result shows that liquid hydrogen chloride had cleaved the phosphorus nitrogen bond of $PhP(NMe_2)_2Cl.Cl$:

$$PhP(NMe_2)_2Cl^+ + 4HCl \longrightarrow PhPCl_3^+ + 2Me_2NH_2 \cdot Cl$$
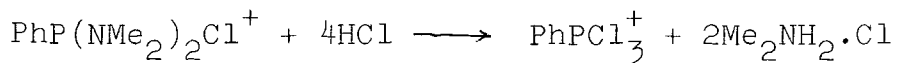
and that the overall reaction between $PhP(NMe_2)_3 \cdot Cl$ and HCl could be represented as:

$$PhP(NMe_2)_3^+ + 6HCl \longrightarrow PhPCl_3^+ + 3Me_2NH_2Cl.$$

## 9.6 The reaction between tris(dimethylamino)chloro phosphonium chloride and liquid hydrogen chloride

This reaction was carried out by applying the same technique employed in reacting dimethylamino triphenyl phosphonium chloride with liquid hydrogen chloride as described in Section 9.3. Tris(dimethylamino)chloro phosphonium chloride was prepared by reacting bis(dimethylamino)chloro phosphine with dimethyl chloramine (1). The amounts of the reactants were, 1.2 mmol of the phosphonium salt and 3.2 cm^3 of purified HCl. A colourless solution was noted inside the tube and the ^{31}Pnmr spectrum of the solution showed one sharp peak only at -53.3 p.p.m. due to the starting material. The tube was kept at room temperature for sixteen hours and the ^{31}Pnmr spectrum showed that no change had occurred. The ^{31}Pnmr spectrum of the solution was run after 35 days and still no change was observed in the spectrum. This result implies that liquid hydrogen chloride did not cleave any of the three P-N bonds of this phosphonium salt.

9.7 The reaction between hexamethyl phosphoramide and liquid hydrogen chloride

This reaction was carried out by applying the same technique as described in Section 9.3. Hexamethylphosphoramide was purchased from BDH Ltd. and its purity checked by ^{31}Pnmr. The amounts of reactants used were 0.8 cm^3 of the amide and 2.5 cm^3 of liquid hydrogen chloride. The ^{31}Pnmr spectrum of the reaction mixture showed one sharp peak only at -30.3 p.p.m. due to the formation of $(Me_2N)_2POCl$. This result implies that liquid hydrogen chloride cleaved one of the three phosphorus nitrogen bonds of the amide:

$$(Me_2N)_3PO + 2HCl \longrightarrow (Me_2N)_2POCl + Me_2NH_2Cl.$$
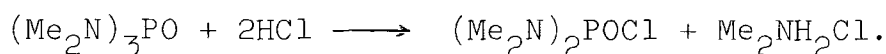
The tube had been left at room temperature for 24 hours and the ^{31}Pnmr spectrum showed two peaks, a major one at -30.3 p.p.m. due to $(Me_2N)_2POCl$ and a minor one at -15.8 p.p.m. due to the formation of Me_2NPOCl_2, the integration ratio being 7:1. This result indicates that a further slow solvolysis of $(Me_2N)_2POCl$ was occurring:

$$(Me_2N)_2POCl + 2HCl \longrightarrow Me_2NPOCl_2 + Me_2NH_2Cl.$$
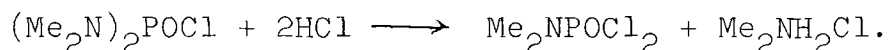
After five days the ^{31}Pnmr spectrum showed one sharp peak at -15.6 p.p.m., indicating that further reaction with hydrogen chloride to produce phosphorus oxychloride was not occurring significantly. The tube was kept at room temperature for a further 21 days and the ^{31}Pnmr spectrum showed one sharp peak only at -1.6 p.p.m. due to the formation of $POCl_3$:

$$Me_2NPOCl_2 + 2HCl \longrightarrow POCl_3 + Me_2NH_2.Cl$$
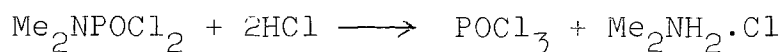
Thus the final conclusion is that liquid hydrogen chloride slowly cleaves the three phosphorus nitrogen bonds of the amide; the rate of reaction falling off markedly as the amine

group is substituted by chlorine:

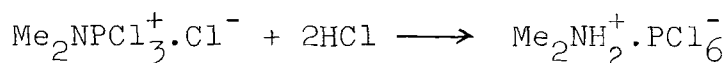$$(Me_2N)PO + 6HCl \longrightarrow POCl_3 + 3MeNH_2Cl.$$
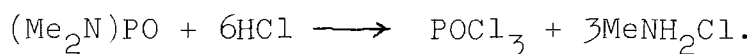
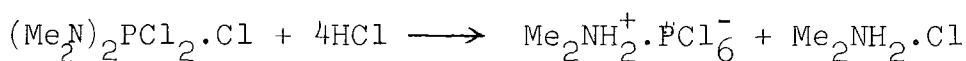## 9.8 The reaction between bis(dimethylamino)dichloro phosphonium chloride and liquid hydrogen chloride

The technique used for the reaction between bis(dimethyl-amino)dichloro phosphonium chloride and liquid hydrogen chloride parallels that described in Section 9.3. The phosphonium salt was prepared by reacting dimethylamino dichloro phosphine with dimethyl chloramine (1). The amounts of the reactants used were 1.01 mmol of the phosphonium salt and 2.9 cm^3 of purified liquid hydrogen chloride. A clear colourless solution was observed inside the tube and its ^{31}Pnmr spectrum showed one sharp peak only at -51.6 p.p.m. due to the starting material $P(NMe_2)_2Cl_3$. The tube was kept at room temperature for 6 days and the nmr spectrum showed a minor peak at -61.3 p.p.m. due to the formation of the dimethyl amino trichloro phosphonium ion (1,   ), whereas the major peak was one due to the starting material. The integration ratio was 1:11. After a month the nmr spectrum showed two peaks, one at -51.6 p.p.m. due to the starting material and another peak of the same intensity at -60.3 p.p.m. due to the formation of $Me_2NPCl_3^+$. This result indic-ated that some of the starting material had reacted with liquid HCl cleaving one of the phosphorus nitrogen bonds of the phosphonium ion in a slow reaction:

$$2HCl + (Me_2N)_2PCl_2^+ \xrightarrow{slow} Me_2NPCl_3^+ + Me_2NH^+.Cl^-$$
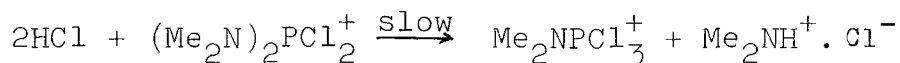
When the tube had been left for a further two weeks a large amount of white crystalline solid was observed to fill 3/4 of the volume of the tube and the ^{31}Pnmr spectrum showed the presence of the following phosphorus species (i) a peak at -51.6 p.p.m. due to the starting material, (ii) a peak at -60.3 p.p.m. due to the formation of $Me_2NPCl_3^+.Cl^-$, (iii) a peak at 302.1 p.p.m. due to the formation of PCl_6^- ($\delta = 300$ p.p.m.)(115). The previous three peaks were broad ones due to a solid phase spectrum. The result implies the P-N bond of $Me_2NPCl_3^+$ was cleaved by liquid hydrogen chloride. The rate of this reaction would be faster if the reactants were not in a solid phase. The overall reaction can be represented as:

$$Me_2NPCl_3^+.Cl^- + 2HCl \longrightarrow Me_2NH_2^+.PCl_6^-$$

Thus it is possible to write the following equation to represent the reaction between bis(dimethylamino)dichloro phosphonium chloride and liquid hydrogen chloride:

$$(Me_2N)_2PCl_2.Cl + 4HCl \longrightarrow Me_2NH_2^+.PCl_6^- + Me_2NH_2.Cl$$

The results obtained above show that liquid hydrogen chloride cleaved the phosphorus nitrogen bonds of $(Me_2N)_2PCl_2^+$.

9.9 The reaction between trimethyl dimethylamino phosphonium chloride salts and liquid hydrogen chloride

This reaction has been carried out by applying the technique described in Section 9.3. Trimethyl dimethylamino phosphonium chloride salt was prepared by reacting trimethyl phosphine and dimethyl chloramine as described in Section 7.11. The amounts of the reactants used are 1.4 mmol of the phosphonium
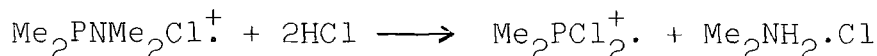
salt and 2.6 cm^3 of the purified liquid hydrogen chloride.
The ^{31}Pnmr spectrum of the liquid inside the tube showed
one sharp peak at -8 8 p.p.m. due to the formation of Me$_3$PCl$^+$. (113)
This implies that liquid hydrogen chloride cleaved the P-N
bond of the phosphonium salt:

$$Me_3P-NMe_2^+ + 2HCl \longrightarrow Me_3PCl^+ + Me_2NH_2^+ \ Cl^-$$

9.10 The reaction between dimethylamino dimethylchloro phosphonium chloride salt and liquid hydrogen chloride

The reaction between dimethylamino dimethyl chloro
phosphonium chloride salt and liquid hydrogen chloride was
carried out by employing the same techniques described in
Section 9.3.   The phosphonium salt was prepared by reacting
dimethyl chloramine with dimethyl chloro phosphine as des-
cribed in Section 6.2 .

The amount of the phosphonium salt used was 1.9 mmol
and that of liquid hydrogen chloride was 2.4 cm^3.   The ^{31}Pnmr
spectrum of the colourless liquid observed inside the tube
showed one sharp peak at -131.6 p.p.m. due to the formation
of Me$_2$PCl$_2^+$ ($\delta = -121.0$ p.p.m. (113)).   This result shows that
liquid hydrogen chloride had cleaved the phosphorus nitrogen
bond of the phosphonium salt:

$$Me_2PNMe_2Cl^+ + 2HCl \longrightarrow Me_2PCl_2^+. + Me_2NH_2.Cl$$

9.11 The reaction between dimethylamino methyl dichloro phosphonium chloride and liquid hydrogen chloride

This reaction was carried out using the same technique
described in Section 9.3.   The phosphonium salt was prepared

by reacting dimethyl chloramine with methyl dichloro phosphine as described in Section 6.4. The amount of dimethylamino methyl dichloro phosphonium chloride used was 1.5 mmol and that of hydrogen chloride was 2.5 cm^3. A colourless liquid was observed inside the tube, the ^{31}Pnmr spectrum of this liquid showed one sharp peak at -122.1 p.p.m. due to the formation of Me-PCl$_3^+$ (δ =-120.0 p.p.m. (113)). This result indicated that liquid hdryogen chloride had cleaved the P-N bond of the phosphonium salt and the overall reaction was:

$$MePNMe_2Cl_2^+ + 2HCl \longrightarrow MePCl_3^+. + Me_2NH_2Cl.$$
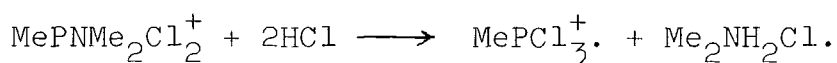
9.12 The reaction between tris(methoxy)phosphine oxide (methyl phosphate) and liquid hydrogen chloride

The reaction between tris(methoxy)phosphine oxide and liquid hydrogen chloride was carried out by employing the same technique described in Section 9.3. The amounts of the reactants used were 0.9 cm^3 of the phosphine oxide used as purchased, the purity having been checked by ^{31}Pnmr, (Ralph N. Emmanuel Ltd.) and 3.2 cm^3 of the purified liquid hydrogen chloride. The initial ^{31}Pnmr spectrum of the reaction mixture showed one sharp peak at 1.5 p.p.m. (116) due to the starting material. The tube was kept at room temperature for one day and the ^{31}Pnmr spectrum still showed only the peak due to the starting material. The ^{31}Pnmr spectra were studied daily for three weeks and no change was observed. This result implies that liquid hydrogen chloride does not react with tris(methoxy)phosphine oxide.

9.13 Results and Discussion

It is possible to conclude from the work described in this chapter that liquid hydrogen chloride reacted with the phosphonium salts of the molecular formula $Y_{(4-n)}P(NMe_2)_n^+$, (n=1,2,3 and Y=Ph,Me, or Cl) where it was found that the P-N bond or bonds were cleaved producing $Y_{(4-n)}PCl_n^+$ and dimethyl ammonium chloride. The one exception to this is the reaction between tris(dimethylamino)chloro phosphonium chloride and liquid hydrogen chloride. The likely mechanism of this reaction is an S_N2 attack on the phosphorus atom by chloride ion, prece ded perhaps by protonation of one of the nitrogens:

$$Me_3PNMe_2^+ + HCl \xrightarrow{\text{fast}} Me_3PNHMe_2^{2+} + Cl^-$$

$$Me_3PNHMe_2^{2+} + Cl^- \xrightarrow{\text{slow}} \underset{\underset{Cl}{|}}{Me_3P}-NHMe_2^+$$

$$\underset{\underset{Cl}{|}}{Me_3P}-NHMe_2^+ \longrightarrow Me_3PCl^+ + Me_2NH$$

$$Me_2NH + HCl \longrightarrow Me_2NH_2^+.Cl^-$$
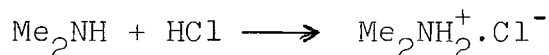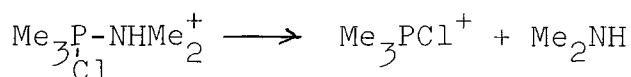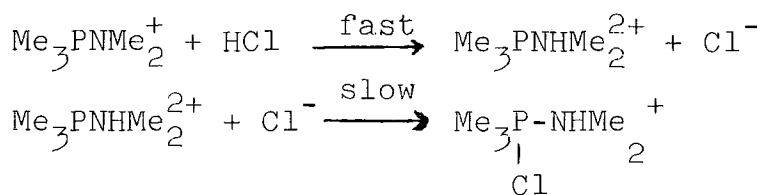
In order to suggest that protonation occurs before the chloride ion attacks the phosphorus in an S_N2 mechanism, $(Me_2N)_3PO$ and $(MeO)_3PO$ were reacted with liquid hydrogen chloride. The reaction between $(Me_2N)_3PO$ and liquid HCl occurred and the final products are:

$$(Me_2N)_3PO + 6HCl \longrightarrow POCl_3 + 3Me_2NH_2Cl.$$
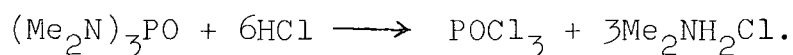
The dimethylamino groups are electron donating, and the lone pair of electrons on each nitrogen atom would interact with 3d orbitals of the phosphorus atom.

This would make the bond between P-N partially a π bond P-N due to delocalisation of the lone pair of electrons.

Despite this partial delocalization of the lone pairs of electrons of the nitrogen atoms they were vulnerable to protonation.

When $(MeO)_3P=O$ was reacted with liquid HCl no reaction was observed. The MeO is electron withdrawing group, thus there will be no electron interaction between the lone pairs of electrons of the oxygen atoms and 3d orbitals of the phosphorus atom. This would help in making the phosphorus atom of $(MeO)_3PO$ to be in a more vulnerable position to chlorination than that of $(Me_2N)_3P=O$, yet no reaction occurred. This result indicated that cleavage of the P-N bond by liquid HCl must be initiated by protonation of the nitrogen atom as illustrated above. It was observed that the more the dimethylamino groups linked to the phosphorus atom the slower the reaction rate was, e.g. the reaction between $Ph_3PNMe_2^+$ and liquid HCl is faster than the parallel reaction with $Ph_2P(NMe_2)_2^+$, which itself was faster than the reaction of $PhP(NMe_2)_3^+$. This may be attributed to the fact that the more dimethylamino groups linked to the phosphorus atom the more the interaction between the electrons and the 3d orbitals of the phosphorus atom and this would slow down the rate of the chlorination of the phosphorus atoms by the chloride ions. In the reaction between $(Me_2N)_3PCl^+$ and liquid HCl there was no reaction - this could be attributed to the nitrogen lone pairs interacting with the 3d orbitals of the phosphorus atom, with the presence of three-dimethyl amine groups enhancing this factor. When $(Me_2N)_2PCl_2^+$ was reacted with HCl the reaction occurred and it was a slow one as described in Section 9.7. This reaction probably occurred because there are two dimethylamino groups only and the phosphorus atom is linked

to the chlorine atoms which will withdraw the electronic
cloud around the phosphorus atom through the δ bonds making
the phosphorus atom on a good site to be attacked by the
partially negative charged chlorine of HCl.

CHAPTER TEN

<u>THE PREDICTION OF THE CHEMICAL SHIFTS FOR</u>

<u>A VARIETY OF PHOSPHONIUM IONS</u>

10.1 Introduction

Different workers have shown in their studies of the nmr spectra of several types of compounds, that the chemical shift of the central nuclei are pairwise additive with respect to the substituent groups (117), Vladimiroff and Malinowski (118) have produced a theoretical justification for this relationship.

Several teams of workers have used this rule to predict the chemical shift of compounds, and to distinguish between cis and trans geometic isomers. The chemical shifts of the mixed tetrahaloaluminate ions were measured by Kidd and Truax (119) and they found that each halogen did not introduce a constant increment to the aluminium shielding. They explained this variation by suggesting that the contribution of each halogen is dependent upon the other substituents bonded to aluminium, but no explanation about the nature of this dependency was offered. Malinowski (117) succeeded in proving that Al^{27} shifts of the tetrahaloaluminate ions obeyed pairwise additivity.

Boron-11, fluorine-19 (118), germanium-73 (120) and carbon -13 (121) were also found to obey the pairwise additivity rule.

The other benefit of applying this rule was utilised when its use was extended from predicting the chemical shift of four-coordinate species to identifying, in solution, the presence of specific geometric isomers of six-coordinate complexes, by predicting their chemical shifts. Examples for this application are the identification of hexahaloniobate V (126) and hexachlophosphates $PF_nCl_{6-n}^-$ (89) isomers.

10.2 The prediction of chemical shifts of phenyl chloro substituted phosphonium ions $Ph_nPCl_{4-n}^+$ (n=1,2,3)

It is possible to predict the chemical shift of these phosphonium ions if the values of pairwise parameters for following substituents are known $\eta Ph,Ph$, $\eta Ph,Cl$ and $\eta Cl,Cl$. The values of these substituents can be obtained by applying the pairwise additive rule to Ph_4P^+, Ph_3PCl^+ and PCl_4^+ as shown in Table 10.1

Table 10.1

The Phosphonium ion	Reported δ p.p.m.	Pairwise Additivity	Substituents	Pairwise η parameters p.p.m.
Ph_4P^+	-20.8	$6\eta Ph,Ph$	Ph,Ph	-3.47
Ph_3PCl^+	-66	$3\eta Ph,Ph+$ $3\eta Ph.Cl$	Ph,Cl	-18.53
PCl_4^+	-87	$6\eta Cl,Cl$	Cl,Cl	-14.5

By applying the pairwise additivity model it is possible to predict the chemical shift of $Ph_2PCl_2^+$:

The chemical shift of $Ph_2PCl_2^+ = 4\eta Ph,Cl + \eta Cl,Cl + \eta Ph,Ph$

$$of\ Ph_2PCl_2^+ = 4(-18.53)+(-3.47) = 92.09\ \text{p.p.m.}$$
$$+ (-14.5)$$

The reported chemical shift is -90 p.p.m. the difference between the predicted and the reported chemical shift could be within the area of the experimental error.

The chemical shift of $PhPCl_3^+ = 3\eta Cl.Cl + 3\eta Ph,Cl$

$$= 3(-14.5) + 3(-18.53) = -99.09\ \text{p.p.m.}$$

The predicted chemical shift is in good agreement with the reported one at -100.0 p.p.m. *(113)*.

10.3 The prediction of the chemical shifts of some $Me_nPCl^+_{(4-n)}$ (n=1,2,3) cations

It is possible to predict the chemical shift of these phosphonium ions, when the values of the following pairwise parameters are calculated: nCl,Cl, nMe,Cl and $nMe.Me$ as shown in Table 10.2.

Table 10.2

(alc.	Phosphonium ion	Reported δ p.p.m.	Reference	Substituent used in calculation	Pairwise parameter, np.p.m.
	PCl^+_4	-87	122	Cl,Cl	-14.5
	Me_4P^+	-24	123	Me,Me	-4.0
	$MePCl^+_3$	-117	113	Me,Cl	-24.5
-116.5	$Me_2PCl^+_2$	-121	113		
-85.5	Me_3PCl^+	-87	113		

The chemical shift of $Me_2PCl^+_2 = 4\,nMe,Cl + nCl,Cl. + nMe,Me$

$$= -116.5 \text{ p.p.m.}$$

The chemical shift of $Me_3PCl^+ = 3nMe,Me + 3nMe,Cl = -88.5$ p.p.m.

It is apparent from the data that $Me_nPCl^+_{(4-n)}$ phosphonium ions obey the pairwise additivity rule.

10.4 The prediction of the chemical shift of $PhPNMe_2Me^+_2$

It was interesting to attempt to apply the pairwise additivity rule to some groups of phosphonium ions prepared as described in the present work. Table 10.3 shows the chemical shift of some of these phosphonium ions and the values of the pairwise interaction parameters needed to predict the chemical shift of $PhPNMe_2Me^+_2$.

Table 10.3

Calc	Phosphon- ium ion	Observed δ p.p.m.	Reported δ p.p.m.	Reference	Substituent used in calculation	Pairwise parameter p.p.m.
	PMe_4^+		-24	123	Me,Me	-4
	Ph_4P^+		-20.8	124	Ph,Ph	-3.47
	$Ph_3PNMe_2^+$	-46.7		125	Ph,NMe$_2$	-12.1
	Ph_3PMe^+		-23	123	Ph,Me	-4.2
	$Ph_2PNMe_2Me^+$	-51.6			Me_2N,Me	-15.53
-55.6	$PhPNMe_2Me_2^+$	-56.5				

The chemical shift of $PhPNMe_2Me_2^+ = 2\eta Ph,Me + 2\eta Me_2N,Me + \eta Me,Me$

$$+ \eta Ph,NMe_2$$

$$= -55.6 \text{ p.p.m.}$$

The predicted chemical shift is in very good agreement with that found practically ($\delta = -56.5$ p.p.m.). This implies that the phosphonium ions listed in Table 10.3 obey the pairwise additivity rule.

10.5 The prediction of the chemical shift of $(Me_2N)_3PCl^+$

To predict the chemical shift of tris(dimethylamino) chloro phosphonium ion by employing the pairwise additivity rule it is necessary to know the values of the pairwise parameter (p.p.m.) of the following substituents $\eta Cl,Cl$, $\eta Me_2N,Cl$ and $\eta Me_2N,NMe_2$. Table 10.4 shows the phosphonium ions and their chemical shifts used in calculating the values of the pairwise parameters of the substituents mentioned above.

Table 10.4

Calc.

Phosphonium ion	Observed δ p.p.m.	Reported δ p.p.m.	Reference	Substituent used in calculation	Pairwise parameter, p.p.m.
PCl_4^+	-87.0	-87.1	122	Cl,Cl	-14.5
$Me_2NPCl_3^+$	-61.3	-61.3	1 114	Me_2N,Cl	-5.93
$(Me_2N)_2PCl_2^+$	-51.6			Me_2N,NMe_2	-13.38
$(Me_2N)_3PCl^+$ *-57.9*	-53.3				

The chemical shift predicted for $(Me_2N)_3PCl^+ = 3\eta Me_2N,NMe_2$

$$+ 3\eta Me_2N,Cl$$

$$= -57.9 \ \ p.p.m.$$

This result is in good agreement with the observed chemical shift for $(Me_2N)_3PCl^+$ ($\delta = -53.3$ p.p.m.)

10.6 The prediction of the chemical shift of $Me_3PNMe_2^+$ and $MePNMe_2Cl_2^+$

The chemical shifts of these phosphonium ions were predicted when the values of the pairwise parameters of the following substituents were known:

$\eta Me,Me$, $\eta Cl,Me$, $\eta Cl,Me_2N$ and $\eta Me,NMe_2$ as shown in Table 10.5.

Table 10.5

Calc.	Phosphon-ium ion	Observed δ p.p.m.	Reported δ p.p.m.	Reference	Substituent used in calculation	Pairwise parameter, p.p.m.
	Me_4P^+		-24	123	Me,Me	-4
	$Me_2NPMe_2Cl^+$	-103.3		113	Me_2N,Me	-21.04
	$Me-PCl_3^+$		-120		Cl,Me	-24.5
	$Me_2NPCl_3^+$	-61.3	-61.3	1,114	Me_2N,Cl	-5.93
-75.1	$Me_2NPMe_3^+$	-74.2				
-96.3	$Me_2NPMeCl_2^+$	-87.1				

The calculated chemical shift of $Me_3PNMe_2^+ = 3\eta Me,Me + 3\eta Me_2N,Me$

$$= -75.1 \ p.p.m.$$

The value of the predicted chemical shift of $Me_3PNMe_2^+$ is in very good agreement with that of the observed chemical shift ($\delta = -74.2$ p.p.m.)

The calculated chemical shift of $MePNMe_2Cl_2^+ =$

$2\eta Cl,Me + 2\eta Me_2N,Cl + \eta Cl,Cl + \eta Me_2N,Me = -96.3 \ p.p.m.$

The predicted chemical shift of $MePNMe_2Cl_2^+$ is not in very good agreement with the observed chemical shift. This could be attributed to the fact that the pairwise additivity rule assumes that the pairwise parameter value of substituents is the same regardless of the other atoms linked to the central nucleus, i.e. the pairwise parameter value of $\eta Cl,Cl$ in PCl_4^+ is the same as that for $\eta Cl,Cl$ in $MePNMe_2Cl_2^+$.

10.7 The calculation of the chemical shifts of $PhPNMe_2Cl_2^+$ and $Ph_2PNMe_2Cl^+$

To predict the chemical shifts of $PhPNMe_2Cl_2^+$ and $Ph_2PNMe_2Cl^+$ the values of the parameters of the following substituents were needed, $\eta Cl,Cl$, $\eta Ph,Ph$, $\eta Ph,Cl$, $\eta Cl,NMe_2$ and $\eta Ph,NMe_2$. These values are deduced from the chemical shifts of the phosphonium ions listed in Table 10.6.

Table 10.6

Calc.	Phosphonium ion	Observed δ p.p.m.	Reported δ p.p.m.	Reference	Substituent used in calculation	Pairwise parameter, p.p.m.
	PCl_4^+	-87.1	-87	122	Cl,Cl	-14.5
	$PhPCl_3^+$	-103.1	-100	113	Ph,Cl	-18.83
	$Me_2NPCl_3^+$	-61.3	-61.3	1,114	Me_2N,Cl	-5.93
	$Me_2NPPh_3^+$	-46.7			Ph,NMe_2	-12.1
-76.1	$PhPNMe_2Cl_2^+$	-74.9				
-71.3	$Ph_2PNMe_2Cl^+$	-70.9				

The value of $\eta Ph,Ph$ was deduced from the chemical shift of Ph_4P^+ (Table 10.3).

The predicted chemical shift for $PhPNMe_2Cl_2^+ = 2\,\eta Cl,Ph$

$$+ 2\eta Cl,NMe_2 + \eta Cl,Cl + \eta Ph,NMe_2 = -76.12 \text{ p.p.m.}$$

The predicted chemical shift for $Ph_2PNMe_2Cl^+ = 2\eta Ph,Cl$

$$+ 2\eta Ph,NMe_2 + \eta Ph,Ph + \eta NMe_2,Cl = -71.26 \text{ p.p.m.}$$

The predicted and the observed chemical shifts of the two ions are in good agreement.
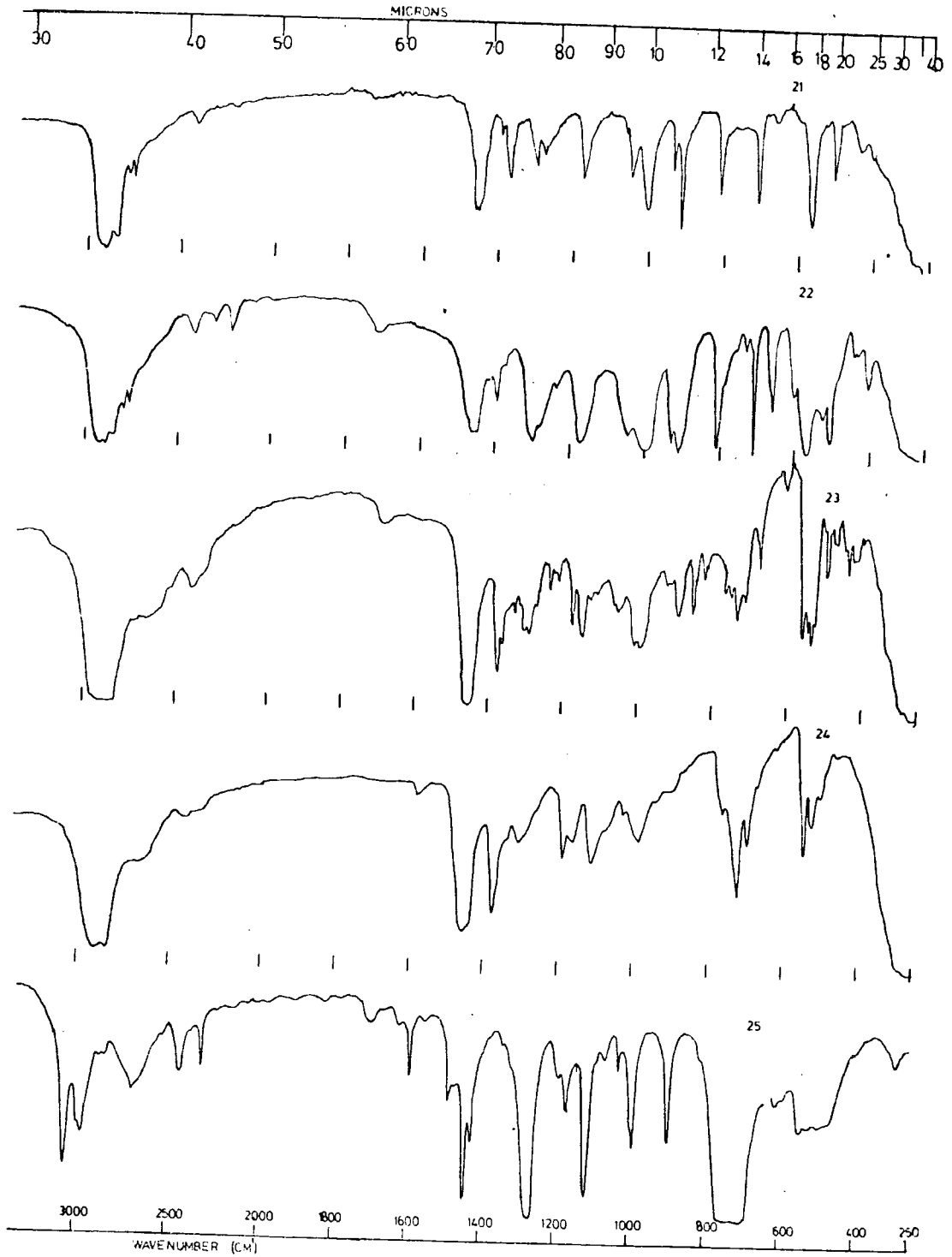
10.8 Conclusion

From the work described in this chapter it is possible to point out that the pairwise additivity rule is a good method to predict the chemical shifts of the phosphonium ions, which helps in confirming their formation.   The greatest error found occurred for the $Me_2NPMeCl_2^+$ ion (Section 10.6) and was only slightly over 10%.
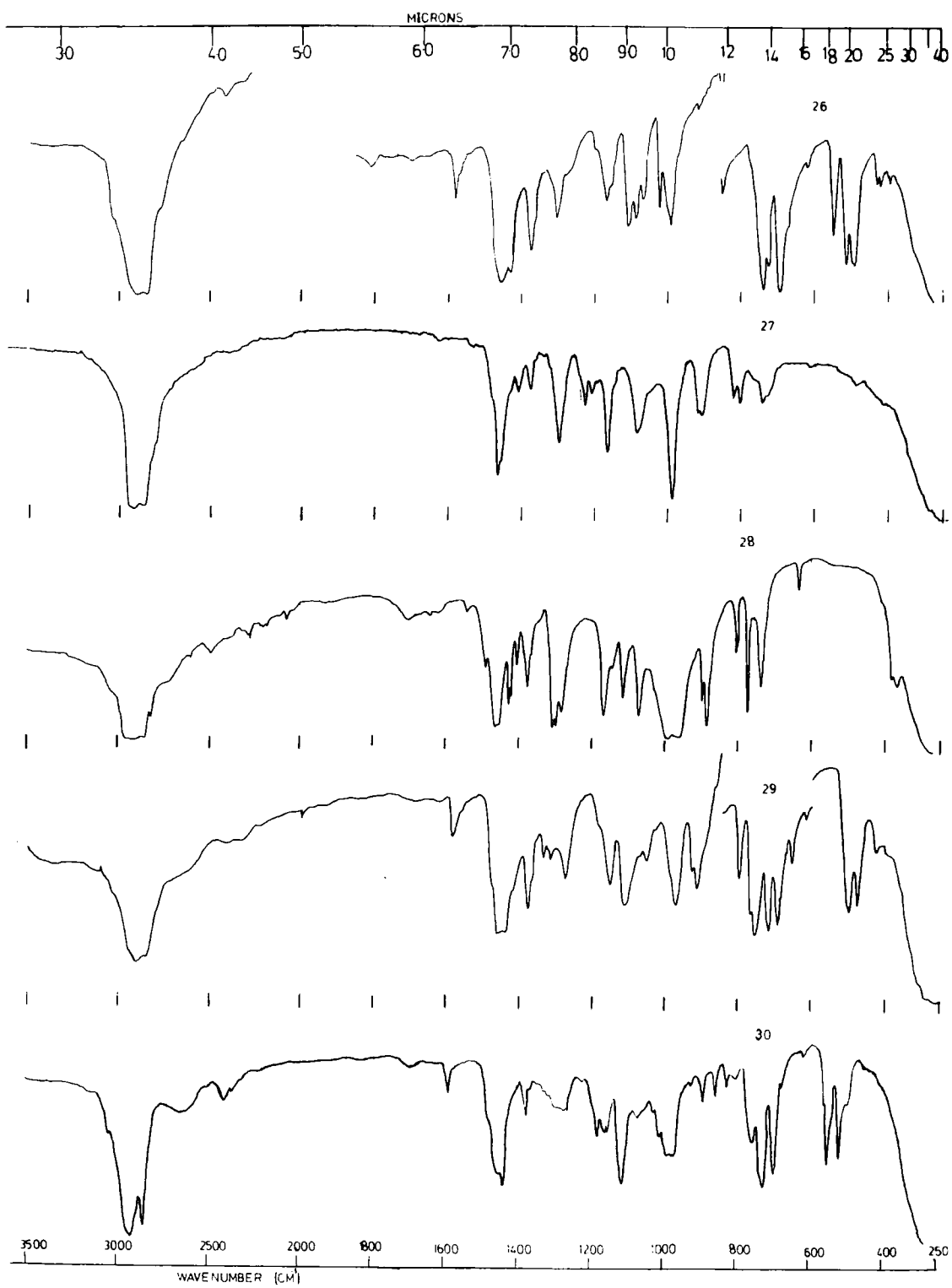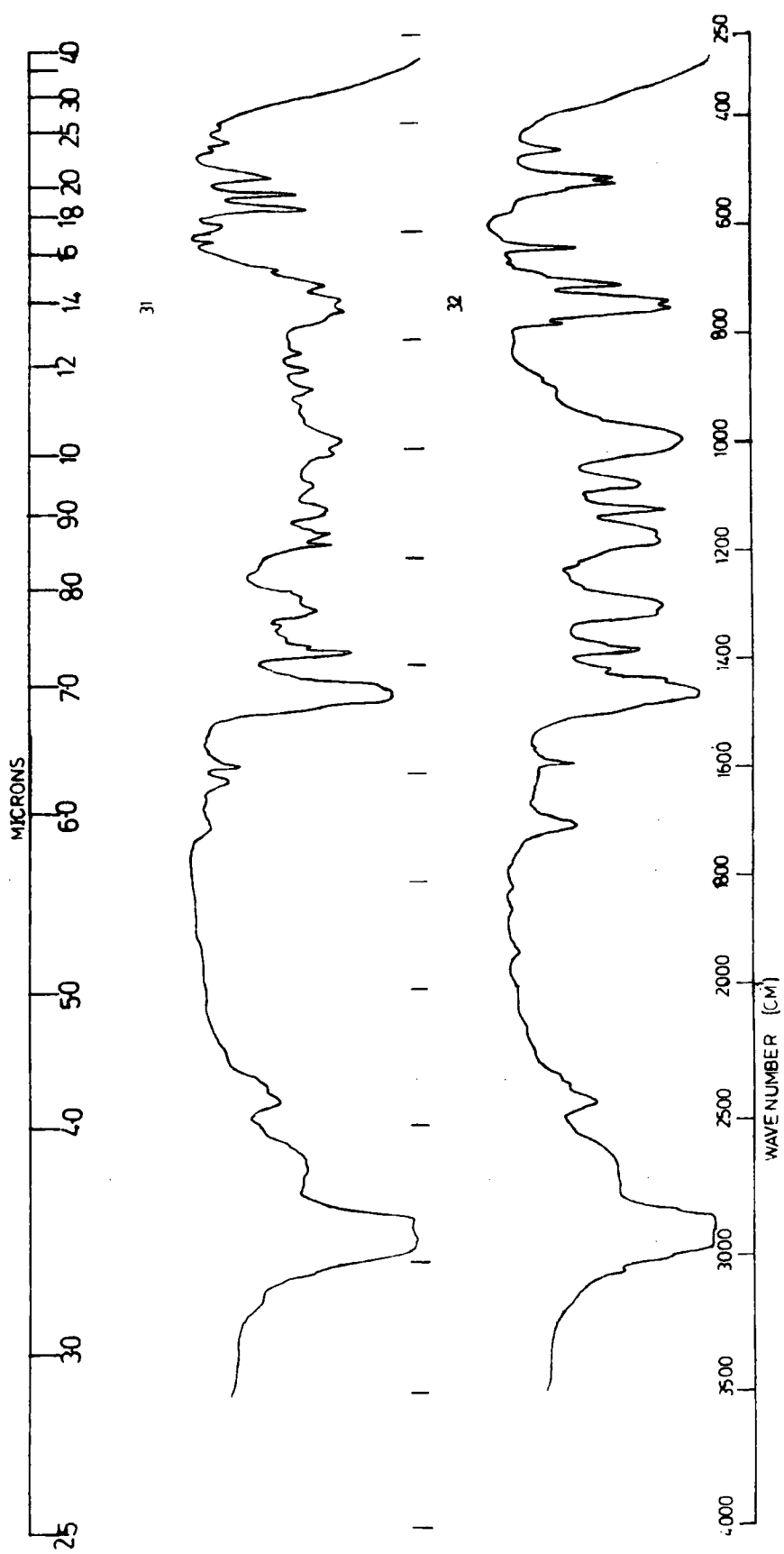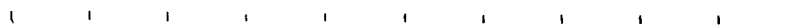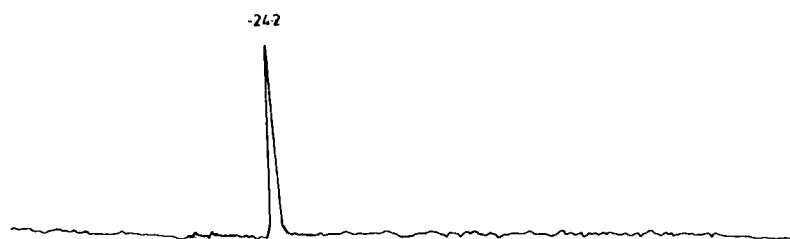
Microns

Wavenumber (Cm⁻¹)

Microns

33

-24.2

34

-19.3

35

-19.7

36

-7.9

37

-70.9

-298.5 PPM

-298.5 PPM

-2985 PPM

SWEEP WIDTH 400 C/S

48

-298.5 P.PM

SWEEP WIDTH 800 C/S

49

-298.5 P.PM

-298 PPM

50.e
-533

50.d
-533
-274

50.c
0.0
-533
-274

50.b
0.0
-27.4

50.a
-185.3
-208.3
177.5
0.0

200

51·a

51·b

51·c

51·d

51·e

-298·5 PPM

-208.2
-185.3
-177.5
-109.1
53-a

-21.0
21.1
53-b

-21.1
-48.3
21.0
53-c

-48.3
-21.1
53-d

-48.3
53-o

-298 PPM

54

-103.3

-87.1

55

-104.7

56

-22.7

SWEEP WIDTH 400 C/S

57

-62.2

-66.2

2H

9.6

134.8

174.9

212.8

58

-63.5 -21.6

6.33

-2985 PPM

59

60

61

62

63

-298.5 P.P.M

-56·5

64

-63

65

-51·4

66

-50·0

67

-298·5 P.P.M.

APPENDIX III

DEPARTMENTAL COLLOQUIA AND FIRST YEAR INDUCTION COURSE
FOR POSTGRADUATES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the writer's residence as a postgraduate student;

(b) all research conferences attended and papers read out by the writer of the thesis, during the period when the research for the thesis was carried out; and

(c) details of the first-year induction course.

Events in (a) which were attended are marked ✶

Research Colloquia, Seminars and Lectures

I. University of Durham Chemistry Colloquia

Academic Year 1977-78

<u>19 Oct</u>. Dr. B. Heyn (U. of Jena, D.D.R.), "Sigma-organo molybdenum complexes as alkene polymerisation catalysts".

✶ <u>27 Oct</u>. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.), "Reactions of organic compounds with xenon fluorides".

✶ <u>2 Nov</u>. Dr. N. Boden (U. of Leeds), "N.m.r. spin-echo experiments for studying structure and dynamical properties of materials containing interacting spin Y_2-pairs".

9 Nov. Dr. A.R. Butler (U. of St. Andrews), "Why I lost faith in linear free energy relationships".

7 Dec. Dr. P.A. Madden (U. of Cambridge), "Raman studies of molecular motions in liquids".

✷ 14 Dec. Dr. R.O. Gould (U. of Edinburgh), "Crystallography to the rescue in ruthenium chemistry".

25 Jan. Dr. G. Richards (U. of Oxford), "Quantum Pharmacology".

I Feb. Professor K.J. Ivin (Queens U. Belfast), "The olefin metathesis reaction, mechanism of ring opening polymerisation of cycloalkenes".

✷ 3 Feb. Dr. A. Hartog (Free U., Amsterdam), "Surprising recent studies in organomagnesium chemistry".

✷ 22 Feb. Professor J.D. Birchall (Mond Division, I.C.I.), "Silicon in the biosphere".

I Mar. Dr. A. Williams (U. of Kent), "Acyl group transfer reactions".

✷ 3 Mar. Dr. G. van Koten (U. of Amsterdam), "Structure and reactivity of aryl-copper cluster compounds".

15 Mar. Professor G. Scott (U. of Aston), "Fashioning plastics to match the environment".

✷ 22 Mar. Professor H. Vahrenkamp (U. of Freiburg, Germany), "Metal-metal bonds in organometallic complexes".

19 Apr. Dr. M. Barber (UMIST), "Secondary ion mass spectra of surfaces and adsorbed species".

16 May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface plasma waves and adsorbed species on metals".

18 May Professor M. Gordon (U. of Essex), "Three critical points in polymer chemistry".

22 May Professor D. Tuck (U. of Windsor, Ontario), "Electrochemical synthesis of inorganic and organometallic compounds".

✦ 24 & 25 May Professor P. von Schleyer (U. of Erlangen, Nurnberg),

I "Planar tetra-coordinate methanes, perpendicular ethenes, and planar allenes".

II "Aromaticity in three dimensions".

III "Non-classical carbo-cations".

21 June Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime cobalt complexes - catalytic black boxes".

23 June Professor G. Mateescu (Case Western Reserve U., Ohio), "A concerted spectroscopy approach to the characterisation of ion and ion-pairs: facts, plans, and dreams".

8 Sept. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical behaviour of electrode surface bonded molecules".

15 Sept. Professor W. Siebert (Marburg, W. Germany), "Boron heterocycles".

✩ 22 Sept. Professor T. Fehlner (Notre Dame, U.S.A.), "Ferraboranes: synthesis and photochemistry".

Academic Year 1978-79

I2 Dec. Professor C.J.M. Stirling (U. of Bangor), "Parting is such sweet sorrow - the leaving group in organic chemistry".

3I Jan. Professor P.D.B. de la Mare (U. of Auckland, New Zealand), "Some pathways leading to electrophilic substitution".

I4 Feb. Professor B. Dunnel (U. of British Columbia), "The application of n.m.r. to the study of motions of molecules in solids".

I4 Mar. Dr. J.C. Walton (U. of St. Andrews), "Pentadienyl radicals".

28 Mar. Dr. A. Reiser (Kodak Ltd.), "Polymer photography and the mechanism of cross-link formation in solid polymer matrices".

✶ 25 Apr. Dr. C.R. Patrick (U. of Birmingham), "Chlorofluorocarbons and statospheric ozone: an appraisal of the environmental problem".

I May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state chemistry of indigoid dyes".

✶ 2 May Dr. J.D. Hobson (U. of Birmingham), "Nitrogen-centred reactive intermediates".

8 May Professor A. Schmidpeter (Inst. of Inorg. Chem., Munich U.), "Five-membered Phosphorous heterocycles containing dicoordinate phosphorous".

✶ 9 May Professor G. Maier (Lahn Giessen U.), "Tetra-tert-butyltetrahedrane".

*   9 May Dr. A.J. Kirkby (U. of Cambridge), "Structure and reactivity in intramolecular and enzymic catalysis".

*   16 May Dr. J.F. Nixon (U. of Sussex), "Some recent developments in platinum-phosphine complexes".

   23 May Dr. B. Wakefield (U. of Salford), "Electron transfer in reaction of metals and organometallic compounds with polychloropyridine derivatives".

   13 June Professor I. Ugi (U. of Munich), "Synthetic uses of super nucleophiles".

+ 25 Sept. Professor R. Soulen (Southwestern U., Texas), "Applications of HSAB theory to vinylic halogen substitution reactions and a few copper coupling reactions".

Academic Year 1979-80

*   21 Nov. Dr. J. Muller (U. of Bergen), "Photochemical reactions of ammonia".

   28 Nov. Dr. B. Cox (U. of Stirling), "Macrobicyclic cryptate complexes: dynamics and selectivity".

   5 Dec. Dr. G.C. Eastmand (U. of Liverpool), "Synthesis and properties of some multicomponent polymers".

   12 Dec. Dr. C.I. Ratcliffe, "Rotor motions in solids".

*   18 Dec. Dr. K.E. Newman (U. of Lausanne), "High pressure multinuclear n.m.r. in the elucidation of mechanism of simple fast inorganic reactions".

✶ 30 Jan. Dr. M.J. Barrow (U. of Edinburgh), "The structures of some simple inorganic compounds of silicon and germanium - pointers to structural trends in group 4".

6 Feb. Dr. J.M.E. Quirke (U. of Durham), "Degradation of chlorophyll - a in sediments".

✶ 23 Apr. B. Grievson B.Sc. (U. of Durham), "Halogen radio-pharmaceuticals".

14 May Dr. R. Hutton (Waters Associates), "Recent developments in multi-milligram and multi-gram scale preparative high performance liquid chromatography".

21 May Dr. T.W. Bentley (U. of Swansea), "Medium and structural effects on solvolytic reactions".

✶ 10 July Professor D. Des Marteau (U. of Heidelberg), "New developments in organonitrogen fluorine chemistry".

2. Durham University Chemical Society

Academic Year 1977-78

13 Oct. Dr. J.C. Young and Mr. A.J.S. Williams (U. of Aberystwyth), "Experiments and considerations touching colour".

✶ 20 Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and crime".

3 Nov. Dr. G.W. Gray (U. of Hull), "Liquid crystals - their origins and applications".

24 Nov. Mr. G. Russel (Alcan), "Designing for social acceptability".

✧ **I Dec.** Dr. B.F.G. Johnson (U. of Cambridge), "Chemistry of binary metal carbonyls".

2 Feb. Professor R.A. Raphael (U. of Cambridge), "Bizarre reactions of acetylenic compounds".

I6 Feb. Professor G.W.A. Fowles (U. of Reading), "Home winemaking".

9 Mar. Professor H. Suschitzky (U. of Salford), "Fruitful fissions of benzofuroxans".

✻ **4 May** Professor J. Chatt (U. of Sussex), "Reactions of coordinated dinitrogen".

9 May Professor G.A. Olah (Case Western Reserve U., Ohio), "Electrophilic reactions of hydrocarbons".

Academic Year I978-79

IO Oct. Professor H.C. Brown (U. of Purdue), "The tool of increasing electron demand in the study of cationic processes".

✧ **I9 Oct.** Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is death in the pot".

26 Oct. Professor W.J. Albery (Imperial College, London), "Photogalvanic cells for solar energy conversion".

9 Nov. Professor A.R. Katritsky (U. of East Anglia), "Some adventures in heterocyclics".

I6 Nov. Dr. H.C. Fielding (Mond Division, I.C.I.), "Fluorochemical surfactants and textile finishes".

✧ **23 Nov.** Dr. C. White (Sheffield U.), "The magic of Chemistry".

I8 Jan. Professor J.C. Robb (Birmingham U.), "The plastics revolution".

✧ **8 Feb.** Mr. C.G. Dennis (Vaux Ltd.), "The art and science of brewing".

*   <u>I Mar</u>. Professor H. Mason (Govt. Scientific Advisor), "The scientist in defence policy".

<u>IO May</u> Professor G. Allen (Chairman S.R.C.), "Neutron scattering for polymer structures".

<u>Academic Year 1979-80</u>

<u>I8 Oct</u>. Dr. G. Cameron (U. of Aberdeen), "Synthetic polymers - twentieth century polymers".

<u>25 Oct</u>. Professor P. Gray (U. of Leeds), "Oscillatory combustion reactions".

<u>I Nov</u>. Dr. J. Ashby (I.C.I. Toxicological Laboratory), "Does chemically-induced cancer make chemical sense".

<u>8 Nov</u>. Professor J.H. Turnbull (R.M.C. Shrivenham), "Luminescence of drugs".

*   <u>I5 Nov</u>. Professor E.A.V. Ebsworth (U. of Edinburgh), "Stay still, you brute: the shape of simple silyl complexes".

*   <u>24 Jan</u>. Professor R.J.P. Williams (U. of Oxford), "On first looking into biology's chemistry".

<u>I4 Feb</u>. Professor G. Gamlen (U. of Salford), "A yarn with a new twist - fibres and their uses".

<u>2I Feb</u>. Dr. M.L.H. Green (U. of Oxford), "Synthesis of highly reactive organic compounds using metal vapours".

*   <u>28 Feb</u>. Professor S.F.A. Kettle (U. of East Anglia), "Molecular shape, structure and chemical blindness".

<u>6 Mar</u>. Professor W.D. Ollis (U. of Sheffield), "Novel molecular rearrangements".

Research Conferences Attended

3rd Annual Congress of the Chemical Society, Durham,
9-11 April 1980.

First Year Induction Course

In each part of the course, the use and limitations of
the various services available are explained by the
people responsible for them.

Departmental organisation	Dr. E.J.F. Ross
Safety matters	Dr. M.R. Crampton
Electrical appliances and infra-red spectroscopy	Mr. R.N. Brown
Chromatography and microanalysis	Mr. T.F. Holmes
Library facilities	Mr. W.B. Woodward (Keeper of science books)
Atomic absorptiometry and inorganic analysis	Mr. R. Coult
Mass spectrometry	Dr. M. Jones
N.m.r. spectroscopy	Dr. R.S. Matthews
Glassblowing techniques	Mr. W.H. Fettis and Mr. R. Hart

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