Studies in the reactions of N, N-Dimethyl chloramine and a variety of tri coordinate phospohorus compounds

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How to cite:

Khabbass, M.D. (1979) *Studies in the reactions of N, N-Dimethyl chloramine and a variety of tri coordinate phospohorus compounds*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9029/

ABSTRACT

In this work the reactions between various phosphorus (III) species and dimethyl chloramine have been studied. In all cases the phosphorous (III) species were oxidised to phosphorus (V), in most cases by chloramination, that is by the addition of the dimethylamino group to the phosphorus producing a phosphonium cation with chloride as the anion.

$$Me_2NCl + PX_3 \longrightarrow Me_2NPX_3^+ Cl^-$$

This reaction occurred in the cases of Me_2NPCl_2, $(Me_2N)_2PCl$, $(C_6H_5O)_3P$, $Me_2N(C_6H_5)PCl$, $(C_6H_5)_2PCl$ and $C_6H_5PCl_2$ although in the latter two cases the salt was too unstable to be isolated as the chloride but the systems could be stabalised as the tetrachloroborate or hexachloroantimonate salts. It is likely that dimethylchloramine chloraminated trimethyl phosphite to give a similar species, but this decomposed quickly giving chloromethane and $Me_2NPO(OMe)_2$.

In the case of $(Me_2N)_3P$ chlorination occurred giving $(Me_2N)_3PCl_2$ and $(Me_2N)_2$. Phosphorus trichloride seemed to be an intermediate case, as, in the presence of excess phosphorus trichloride the following reaction occurred:-

$$4PCl_3 + 3Me_2NCl \longrightarrow Me_2NPCl_4 + Me_2NPCl_3PCl_6 + Me_2NPCl_2$$

STUDIES IN THE REACTIONS OF N,N-DIMETHYL CHLORAMINE AND A VARIETY OF TRI COORDINATE PHOSPHORUS COMPOUNDS

A THESIS PRESENTED BY

N. D. KHABBASS

FOR THE DEGREE OF MASTER OF SCIENCE

OF THE

UNIVERSITY OF DURHAM

To my father and my mother.

ACKNOWLEDGEMENTS.

The author wishes to extend his sincere gratitude to Dr. C.J. Ludman of the Chemistry Department, University of Durham, for his invaluable guidance, his active interest and his continuous encouragement through this research.

I would also like to thank very sincerely Dr. K.B. Dillon of the Chemistry Department, University of Durham, and his team for their very fruitful cooperation.

I also thank Dr. A. Royston, the Senior Experimental Officer of the Chemistry Department, University of Durham, for training me on ^{31}Pnmr equipments. I would like to thank the staff of the analytical section for micro-analyses.

Many thanks to Mrs. E.K. Jones for photographing the spectra and the figures, and to Mrs. K.F. Smith for typing the manuscript.

I thank very much my father and my mother for supporting me through my academic career.

This work has been carried out during the period October, 1977, to October, 1978, in the Chemistry Department of the University of Durham, and submitted according to the regulations of the University of Durham.

CONTENTS

CHAPTER ONE

CHAPTER TWO

EXPERIMENTAL METHODS

CHAPTER THREE

THE REACTIONS OF DIMETHYL CHLORAMINE WITH TRI COORDINATE ALLIPHATIC PHOSPHINES.

CHAPTER FOUR

A. REACTIONS OF Me_2NCl WITH PHOSPHORUS ACID ESTERS

B. REACTIONS OF Me_2NCl WITH TRI COORDINATE AROMATIC PHOSPHINES.

CHAPTER FIVE

CHAPTER ONE

INTRODUCTION.

Introduction

The chemistry of N halamines is a very broad area which has attracted considerable attention since the coverage of some sides of inorganic chemistry by Mellor (1) and Gmelin (2), when they treated the subject of halogen derivatives of nitrogen. Later, because of the halamines in water purification, Berliner (3) wrote about the chloroderivatives of ammonia with the emphasis on chloramine. Snelders (4) has reviewed the discovery and early chemistry of nitrogen trichloride. A more recent review had been achieved by Drago (5), Colton and Jones (6), Theilaker and Wegner (7) on the chemistry of chloramine which is probably the best described N-halamine in the literature. The uses of N-halamines as precursors for the preparation of various classes of organic compound was compiled by Schmitz (8). An extensive survey of Hofmann-Loffer reactions was represented by Wolff (9), afterwards a comprehensive work, of the chemistry of N-halamines has been undertaken by Kovacic (10).

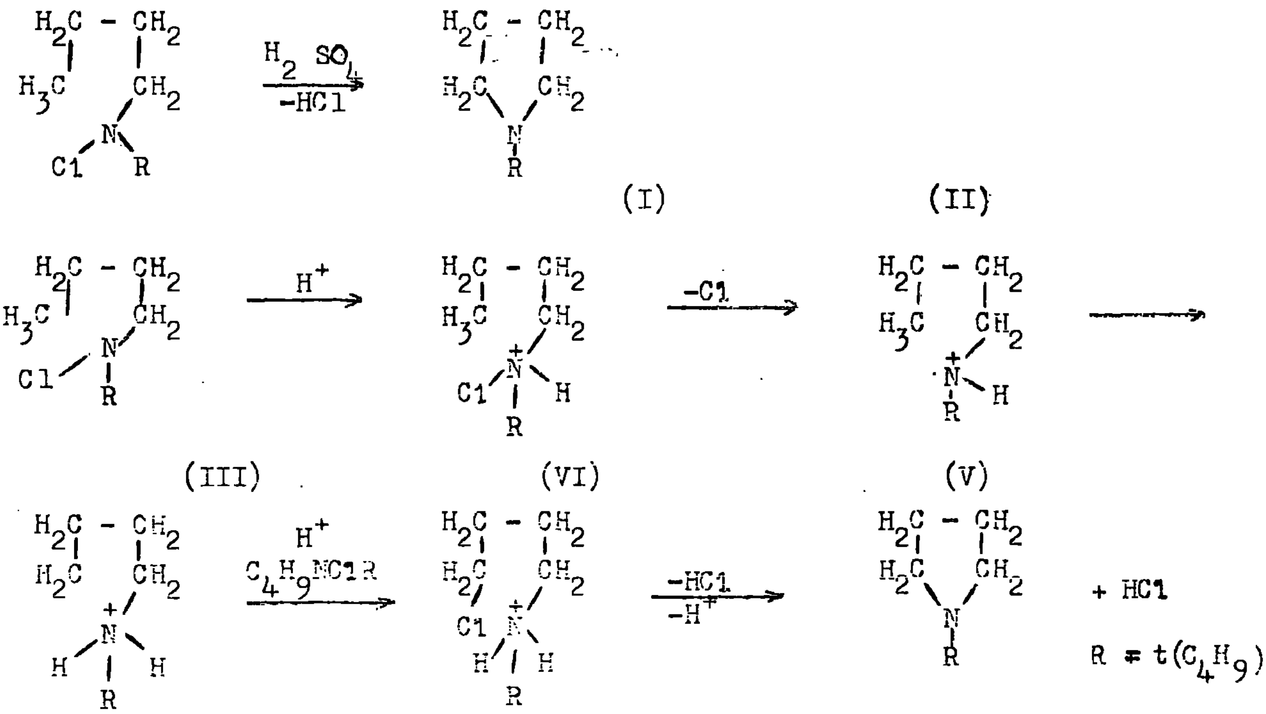
Some halamines are very toxic materials and some are explosive (10a), e.g. nitrogen trichloride which is notoriously unstable. It was used as a bleaching agent for flour until its bad effect on the activities of the body functions was realised (11). The explosion hazards of nitrogen trichloride has been recognised since the serious injury caused to one of the early investigators. Generally the explosion hazard is eliminated or greatly diminshed when an inert solvent is employed.

The chemical reactions of halamines can be typified into VI types.

1 - rearrangement, 2 - dehydrohalogenation, 3 - dealkylation, 4 - photolysis, 5 - halogenation agent, 6 - aminating agent.

1 - Rearrangement:

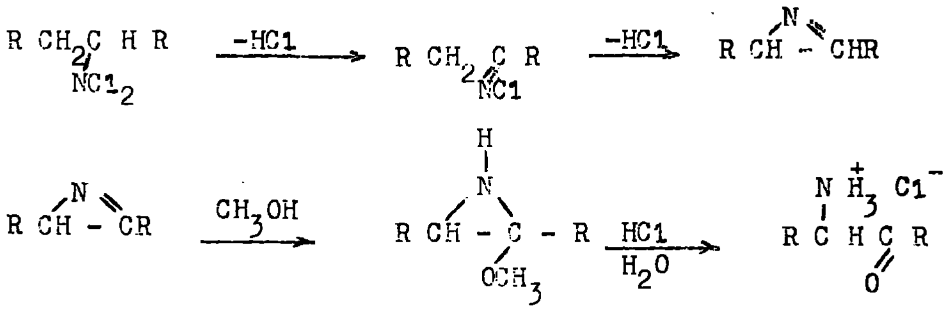
The Hofmann-Loffer reaction is the best known reaction by which N-halamines provide the synthesis of certain cyclic amines. A comprehensive review by Wolff (9) covers the literature through the first half of 1961. The mechanism of the reaction is illustrated by the following equation:



The salt of the N-chloramine is homolytically cleaved under the influence of heat, light or some other initiator to afford aminium radicals(II). This radical in turn intramolecularly abstracts a sterically favoured hydrogen to form an alkyl radical (III) which in chain reaction abstracts chlorine intermolecularly (IV). The alkyl chloride is then converted by alkali to the cyclic tertiary amine (V).

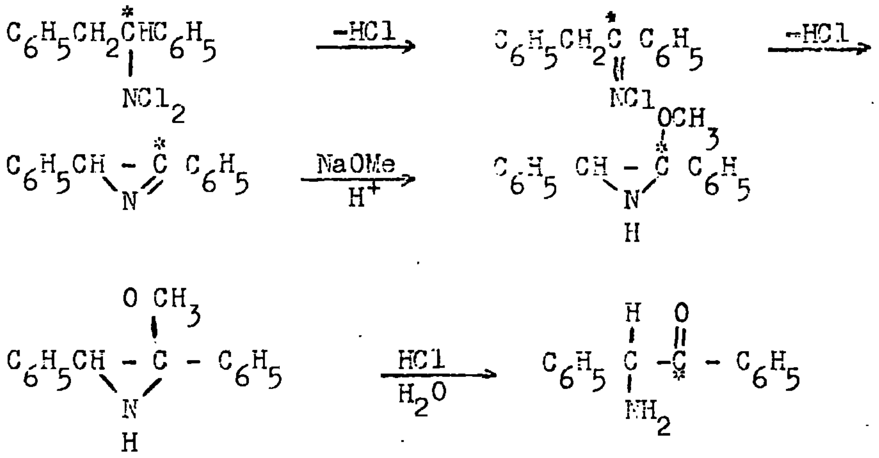
Further investigations of the mechanism of this reaction showed interesting results, like the isolation of 4-chlorodibutylamine from N-chlorodibutylamine, and served to support the proposal. The postulated scheme was also supported by the results of examining several features including stereochemistry, hydrogen isotope effect, initiation, inhibition, catalysis, intermediates and selectivity of hydrogen transfer.

The discovery of the rearrangement of N,N-dichloro-sec-alkylamines to α-amino keteones, provides another different type of rearrangement and a useful synthetic scheme. This rearrangement received the attention of a number of investigators so further studies broadened the scope and produced an improved procedure. N-halamine substrate was successively reacted with sodium methoxide and with dilute hydrochloric acid:-



Several pieces of evidence were provided to support the postulated mechanism, e.g. the isolation of N-chlorimine R CH_2 C(=NCl)R which was converted to the α-amino ketone.(17) An excellent mechanistic study of the labelled base (I) confirmed the original proposal. Exposure to the standard conditions resulted in the formation of desylamine. The application of two degradation procedures to the product provided unequivocal evidence that the labelled carbon atom was incorporated almost exlusively in the carbonyl group.

I



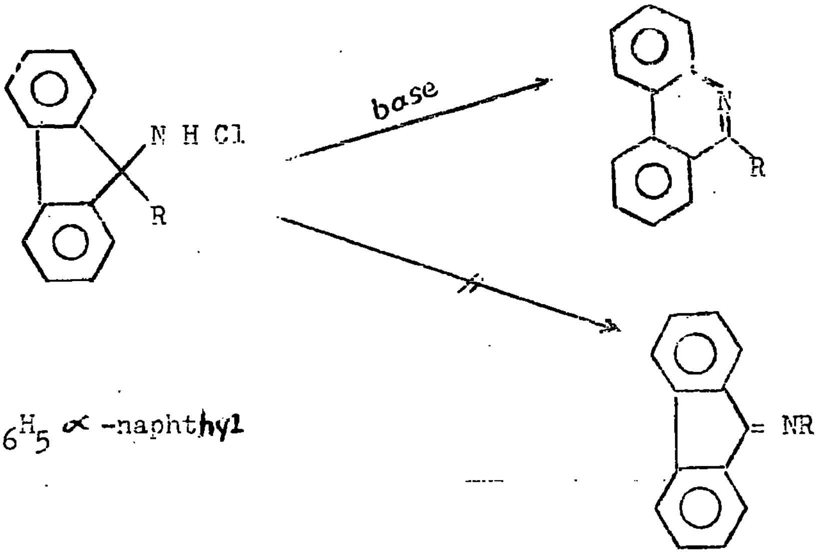
The Stieglitz rearrangement has received attention during a period of time extended to fifty years. The reaction involved the formation of nitrenes; for example during the rearrangement of N- halo and N, N- dihalotritylamines.(19,20) Benzophenone anil was observed from the thermal rearrangement of N,N-dichlorotritylamine.

$$(C_6H_5)_3\,C\,N\,Cl_2 \xrightarrow{\triangle} (C_6H_5)_2\,C = N\,C_6H_5$$

or from the treatment of the N-bromo derivative with base

$$(C_6H_5)_3\,C\,N\,Br_2 \xrightarrow{\text{Base}} (C_6H_5)_2\,C = N\,C_6H_5$$

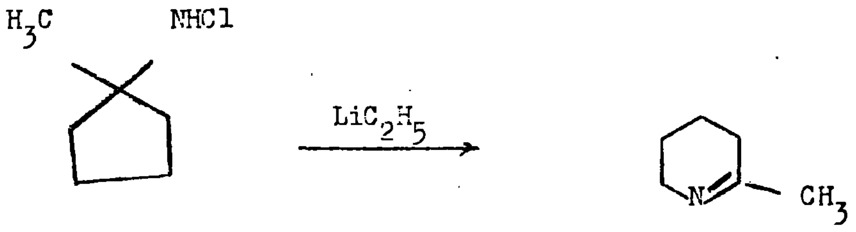
Another application of the Stieglitz method was the synthesis of substituted phenanthridines. The Stieglitz method caused rearrangement of various N-halo-9-aryl- and -alkyl- 9 - fluorylamines(21).



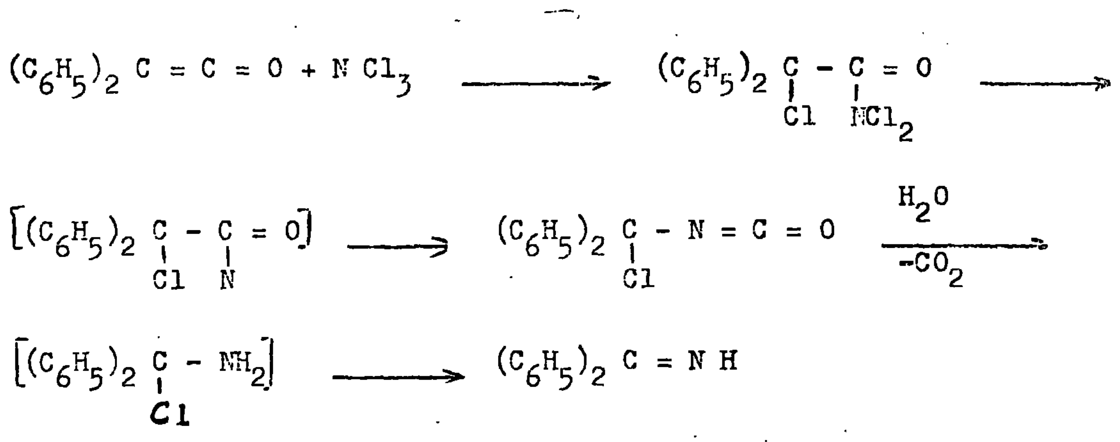
R = CH_3 C_6H_5 α -naphthyl

The causes of this rearrangement are clearly the relief of strain in the five-membered ring and the energy gained through extended conjugation.

A recent investigation showed that it is possible to synthesise a cyclic imine from the interaction of N-chloro-1-methyl-cyclopentylamine with ethyllithium(22).



A nitrene intermediate was proposed in the formation of 1,1-diphenylmethylenimine from the treatment of diphenylketene with nitrogen trichloride.(23)

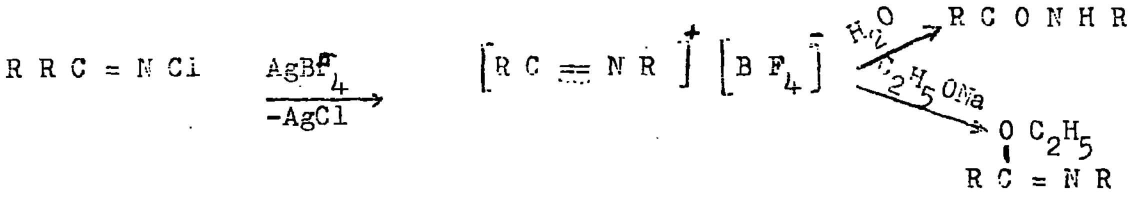


$$(C_6H_5)_2C=C=O+NCl_3 \longrightarrow (C_6H_5)_2\underset{Cl}{C}-\underset{NCl_2}{C}=O \longrightarrow$$

$$\left[(C_6H_5)_2\underset{Cl}{C}-\underset{N}{C}=O\right] \longrightarrow (C_6H_5)_2\underset{Cl}{C}-N=C=O \xrightarrow[-CO_2]{H_2O}$$

$$\left[(C_6H_5)_2\underset{Cl}{C}-NH_2\right] \longrightarrow (C_6H_5)_2C=NH$$

An interesting study showed that N-choroketimines react with silver tetrafluoroborate in aqueous dioxane to produce amides by rearrangement.(24)



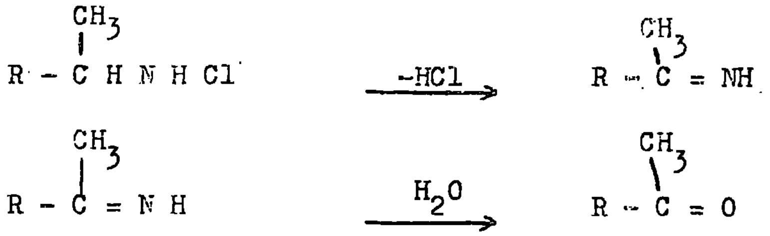
$$RRC=NCl \xrightarrow[-AgCl]{AgBF_4} \left[RC\equiv NR\right]^{+}\left[BF_4\right]^{-} \xrightarrow{H_2O} RCONHR$$

$$\left[RC\equiv NR\right]^{+}\left[BF_4\right]^{-} \xrightarrow{C_2H_5ONa} R\overset{OC_2H_5}{C}=NR$$

The nitrilium ion, postulated as an intermediate, was trapped with sodium ethoxide in aprotic solvent. The rate of the reaction was found to be increased with increasing solvent polarity. Considering R = C_6H_5 benzanilide was formed in yields of 65-70%.

2 - Dehydrohalogenation

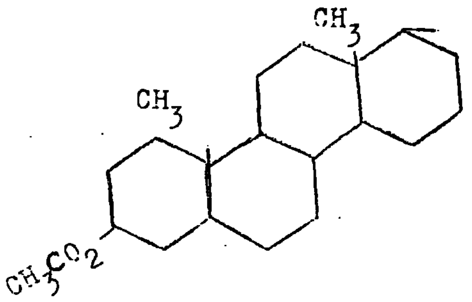
Several N-chloramines have been subjected to dehydrohalogenation agents and it was found that if the dehydrohalogenation is followed by hydrolysis (as is generally the case) it gives rise to carbonyl compounds. This method is illustrated by the conversion of N-chloroderivative of 3 β - acetoxy - 20 - amino - 5 pregnene to 5 pregnenolone.(25)



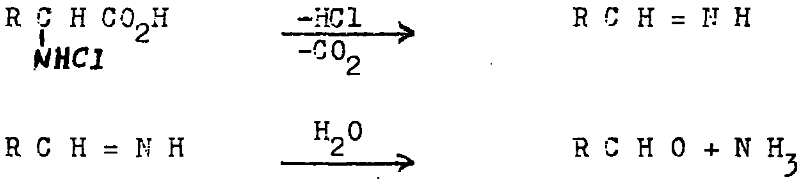
$$R-\overset{CH_3}{\overset{|}{C}}HNHCl \xrightarrow{-HCl} R-\overset{CH_3}{C}=NH$$

$$R-\overset{CH_3}{\overset{|}{C}}=NH \xrightarrow{H_2O} R-\overset{CH_3}{C}=O$$

where R =



Aldehydes also can be formed from α-aminoacids and the following mechanism is consistent with the original proposal of Langheld.(27)



$$R\underset{NHCl}{\underset{|}{C}}HCO_2H \xrightarrow[-CO_2]{-HCl} RCH=NH$$

$$RCH=NH \xrightarrow{H_2O} RCHO+NH_3$$

It is known that acetone and amonia are generated by the hydrolysis of N-chloroisopropylimine and that this occurred probably through the intermediary isopropylimine

$$(CH_3)_2\ CHNHCl \xrightarrow{-HCl} (CH_3)_2C=NH$$

$$(CH_3)_2\ C=NH \xrightarrow{H_2O} (CH_3)_2C=O+NH_3$$

Acetone and chloramine are formed when the product of the treatment of N, N-dichloroisopropylimine with aluminium chloride is hydrolysed.(28)

$$(CH_3)_2\ CHNCl_2 \xrightarrow[-HCl]{AlCl_3} (CH_3)_2\ C=NCl.$$

$$(CH_3)_2\ C=NCl \xrightarrow{H_2O} (CH_3)_2\ CO+NH_2Cl$$

Nitriles are formed from ald-chlorimines of the type shown by the following equation (by thermal decomposition or exposure to base)(29,30).

$$R\,CH = NCl \xrightarrow{-HCl} R\,C \equiv N.$$

and, N,N dihalamines containing at least β carbon atoms produce nitriles when treated with caesium fluoride.

$$R\,CH_2NCl_2 \xrightarrow{CsF} R\,C \equiv N.$$

N,N - dichloro-n-butylamine gave the nitrile in 90% yield.

3 Dealkylations :

The dealkylation of N-haloalkylamines in acidic media is not reported in many papers in the literature, but in an investigation of the Hoffmann-Loffler reaction, non-radical disproportionation of $(n\text{-}Bu)_2NCl$ to $N\text{-}BuNCl_2$ was observed in the presence of sulphuric acid.(32) The indicated outline of the reaction pathway is presented in the following equations

$$Bu_2\overset{+}{N}HCl + H_2O \longrightarrow BuNHCl + H_3\overset{+}{O} + C_4 \text{ Fragment.}$$

$$BuNHCl + H^+ \rightleftharpoons Bu\overset{+}{N}H_2Cl$$

$$BuNHCl + Bu_2\overset{+}{N}HCl \longrightarrow BuNCl_2 + Bu_2\overset{+}{N}H_2$$

4 Photolysis :

The photochemistry of N - halamines has not been studied extensively and was concerned with the simple molecules such as chloramine and nitrogen trichloride. The photolysis of chloramine at -190° with ultraviolet light generates NH, (Nitrogen monohydride)(33); and NH was proposed as an intermediate in the thermal decomposition of NH_2Cl at 500° in the presence of carbon monoxide. Hydrogen cyanate is produced as the end product. Organic solvent can be chlorinated by nitrogen trichloride if the latter is exposed to light. In carbon tetrachloride the decomposition was of a simple type;(34) first order with an energy of activation of 32 kcal, giving rise to nitrogen and chlorine.(35) In the presence of an alcohol, the corresponding carbonyl compound was formed along with ammonium chloride and hydrogen cloride.(34) An extensive study of the photodecomposition of nitrogen trichloride in the presence of chlorine established that chlorine was acting as a photosensitizer and the chain mechanism is illustrated by the following equations which are of zero order :-

$$Cl_2 + hv \longrightarrow 2\,Cl$$

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

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

$$Cl + NCl_3 + X \rightleftharpoons NCl_4 + X$$

$$2\,NCl_4 \longrightarrow N_2 + 4Cl_2$$

5 Halogenation Agents

N-halamines have been used as halogenation agents for aliphatic and aromatic compounds. Alkanes as well as esters, alkyl halides, and ethers were found susceptible to facile chlorination (37,38,39) or bromination (37,40) with $(CH_3)_2NX$ (where X = Cl or Br) in the presence of sulphuric acid, usually with Fe(11) or light as the initiator. The proposed mechanism is essentially the same as for the Hoffmann Loffer reaction, except that the amine radical cation $(CH_3)_2N^{+}H$ abstracts a hydrogen atom intermolecularly from an alkane, forming the dimethylammonium cation and the radical R. In comparison to the Hoffmann Loffer reaction the aminium radical cation abstracts a hydrogen atom intramolecularly.

The suggested mechanism is postulated in the following equation:-(38)

$$(CH_3)_2\overset{+}{N}HX \xrightarrow[-FeCl^{2+}]{+Fe(II)} (CH_3)_2\ \overset{+}{N}H$$

$$(CH_3)_2\overset{+}{N}H + R\ H \longrightarrow (CH_3)_2\ \overset{+}{N}H_2 + R\cdot$$

The generated radical interacts with the protonated dimethylchloramine to form an alkyl halide and dimethylamine radical cation:

$$R\cdot + (CH_3)_2N^{+}HCl \longrightarrow RCl + (CH_3)_2\dot{N}^{+}H$$

Another study suggested that halogenation proceeded via the chlorine atom as the chain-propagation species, shown by the following equations:-

$$X\cdot + RH \longrightarrow HX + R\cdot$$

$$R_2\overset{+}{N}HX + HX \longrightarrow X_2 + R_2\overset{+}{N}H_2$$

$$R\cdot + X_2 \longrightarrow RX + X\cdot$$

This hypothesis was based on the isomer distribution from various metal-ion-initiated chlorinations by various chloramines. Also the orientation was similar to that obtained from photochlorination in which the chlorine atom in chain propagation was involved.

A more recent study supports the original mechanism(42) and shows that the chlorination process takes place by a radical chain process, in which aminium radicals are the principal hydrogen abstracting species, rather than considering the chlorine atom as the chain-propagation species. This evidence was achieved by Spanswick and Ingold through the investigation of N-halamine halogenation of 1 - chlorobutane in sulphuric acid - acetic acid. It was proved that a concurrent chlorine atom process could occur resulting from impurities in the N - halamine (molecular chlorine, hydrogen chloride, or chloride ion).

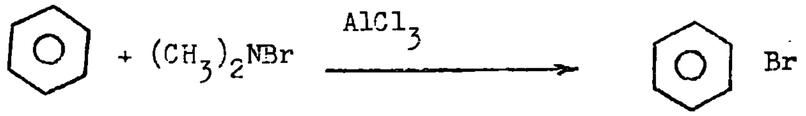
Benzylic chlorination occurs when ring substituted toluenes are exposed to N-chloropiperidine in sulphuric acid-acetic acid under photolytic conditions.

N-halamines have been reported as halogenation agents for olefins e.g. olefins combine with nitrogen trichloride to give β-chloroamines in low yield and unspecified amounts of dichloride.(44,23) In more recent work nitrogen trichloride has been shown to provide a simple means for the preparation of vicdichlorides in a very rich yield from certain types of olefins as shown by the following equations:-

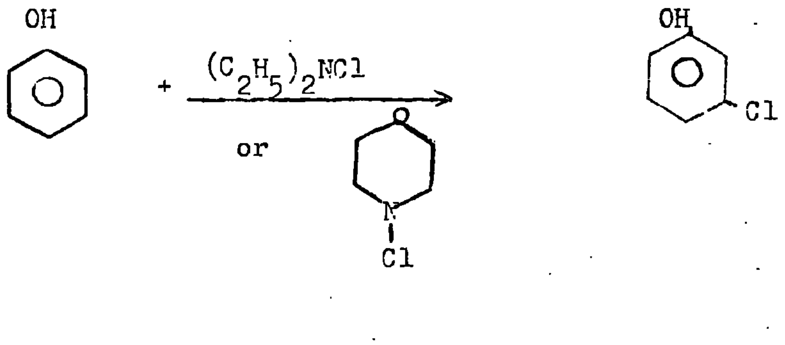
$$3RCH = CH_2 + 2NCl_3 \longrightarrow 3R\,CHClCH_2Cl + N_2$$

Acetylenes undergo chlorination with nitrogen trichloride to give vicdichloroalkenes predominantly.(46)

The interaction of N-chloramines and different types of aliphatic amines shows some interesting results since the interaction with primary and secondary amines occurs merely via an exchange reaction (H and X). In the case of tertiary amines there is some doubt. In the aromatic category the nuclear chlorination occurs as well as a side chain attack, as in the case of benzene and toluene with nitrogen trichloride.(50,51,52) Bromobenzene is formed from the reaction between benzene and N-bromodimethylamine and aluminium chloride:-



Phenol produces chlorophenol if it is treated with N-chlorodiethylamine(54) or with N - chloromorpholin:-(55)

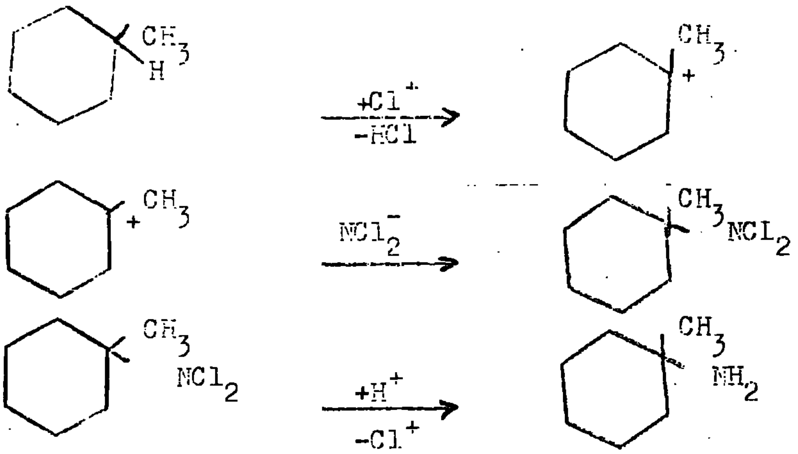


As in the already mentioned case protonated N-chloromorpholine is reported to be the actual agent involved(55).

6. Aminating Agent

N-halamines as aminating agents were found to react with several species of chemical compounds. One of the early experiments in this field was the amination of methylcyclohexane by nitrogen trichloride and aluminium chloride(56,57) to produce 1 -amino-1-methylcyclohexane (yield 70-80%). From the practical point of view it was important to add nitrogen trichloride to a mixture of methyl cyclohexane and aluminium chloride in the molar ratio 1:2:2(10a) ; the reaction is shown as in the following equations:-

$$Cl_3N + AlCl_3 \rightleftarrows Cl_3N\cdots AlCl_3 = \overset{\delta +}{Cl}(Cl_2N\overset{\delta -}{AlCl_3})$$



As shown in the equation above, Cl^+ affected the hydride ion abstraction, then nucleophilic attack occurred by the dichloroamide ion, followed by exchange reaction generating the product 1-amino-1-methylcyclohexane. Although the exact nature of the nitrogenous nucleophile is not known, isolation of N,N-dichlorocyclohexylamine from cyclohexane and N,N-dichloro-1-adamantylamine from adamantane suggests involvement of the dichloroamide ion. A similar reaction of nitrogen trichloride-aluminium chloride and alkyl halides produces primary and secondary amines and aziridines; depending upon the substrate used.(60,61) An example of this is the reaction between t -butylchloride and nitrogen trichloride - aluminium chloride; t-butylamine is produced in a 90% yield after the reduction of N,N-dirchloro t-butylamine which has been isolated.(60)

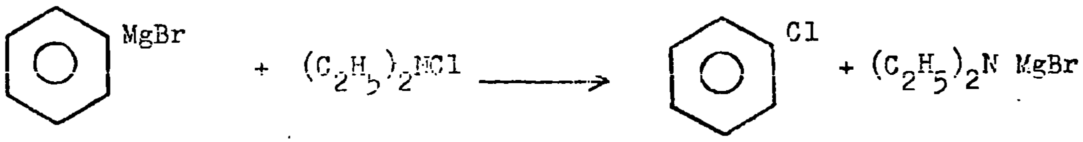
$$(CH_3)_3CCl \xrightarrow[-Cl^-]{AlCl_3} (CH_3)_3\overset{+}{C}\cdot \xrightarrow{NCl_2^-} (CH_3)_3CNCl_2 \xrightarrow[-Cl^+]{+\overset{+}{H}} (CH_3)_3CNH_2$$

The reactions between Grignard reagents and various N-halamines produce amines. The kind of amines produced either primary, secondary or tertiary depends on both the Grignard reagent and the N-halamine chosen. For example n-butylGrignard reagent and different types of N-halamine NH_2X(X=Cl,Br) produce primary amines,(62,63,64) $NHBr_2$ and nitrogen trichloride produce primary and secondary amines, when CH_3NCl_2 is treated with $(n\text{-}C_4H_9)$-Mg X it yields primary, secondary and tertiary amines.

N-chlorodialkylamines provide secondary and tertiary amines.

N-chloroalkylamines give primary and secondary amines.

The greatest amount of primary amine produced, near 90%, occurs when dialkylmagnesium compounds are treated with chloramine. Phenyl Grignard reagents give low yields of amine.(62) On attempting the reaction of phenyl magnesium bromide with several N-chlorodialkylamines, for example dimethyl and diethyl-chloramine, no aniline derivatives were obtained:-



It is found that the size of yield of amine derived from RMgX with variation is X is Cl>Br>I for a given N-halamine which may be a reflection of steric factors and the carbonionic character of R. The formation of amines presumably involves the halogen on the amine leaving as a negative entity through S_N2 attack. The following two equations were presented by Coleman and Hauser:-(62)

$$RMgX + NH_2Cl \longrightarrow RNH_2 + MgXCl$$

$$RMgX + NH_2Cl \longrightarrow RCl + MgXNH_2$$

The difference in the value of the yield of the primary amine when the N-halo-atom is changed was rationalised. Substitution of bromine for chlorine in monohalamine decreases the basicity of the nitrogen thereby discouraging the nucleophilic attack at that site. The absence of aniline derivatives when a phenyl Gringnard reagent is treated with dialkylchloramines is apparently due to steric factors and to the inductive effect of the alkyl substituents. If we return back to the previous two equations we can notice during the generation of amine that the halogen in the N-halamines is of a dual nature, exhibiting either anionic or a cationic character, whereas when the alkyl halide is obtained the amino-group is displaced. Both reactions occur together since ammonia production was found to increase with the decrease of the amine formation. Primary amine is formed from the reaction between organometallic compounds e.g. organo-lithium or organozinc compounds with N-halamines:-

$$RM + NH_2Cl \longrightarrow RNH_2 + MCl$$

where $M = Li, Zn$.

The treatment of zinc alkyl with nitrogen trichloride generates primary and secondary amines(70) whilst with dialkylhalamines hydrazine and tertiary amine formation occurs with alkyl potassium complexes:-

$$\begin{aligned}\left[(CH_3)_2CH\right]K + \left[(CH_3)_2CH\right]_2NCl \longrightarrow\ &\left[(CH_3)_2CH\right]_3N\\ &\left[(CH_3)_2CH\right]_2N\,N\left[(CH_3)_2CH\right]_2\end{aligned}$$

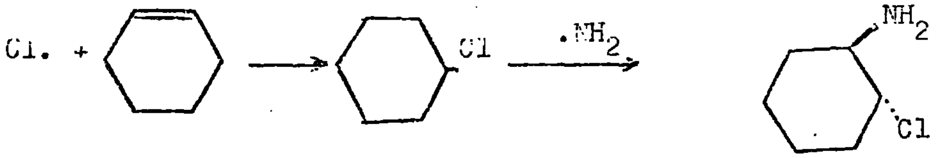
It has been found that the yields (3% amine and 4.5% hydrazine) are low.

The reaction of N-halamines with various unsaturated compounds such as: olefins, acetylenes, α,β-unsaturated ketones acids, and ketenes, involves addition to the double bond.

Coleman and co-workers made an extensive study of the reaction of nitrogen trichloride with carbon-carbon double bonds.(44,71,23) It was found that nitrogen trichloride added a molecule of chlorine to the following olefins:- 1 - and 2 - butene, ethylene, propylene, 2-pentene, isobutylene and cyclohexene. The products were β-chloroalkylamines which apparently were derived from the corresponding N,N-dichloro derivatives as the primary adducts. Treatment with concentrated hydrochloric acid effected the conversion to amino salt. Markovnikov's rule concerning unsymmetrical olefins was followed by chlorine being added to the least substituted carbon atom and by nitrogen becoming affixed to the other position.

Other work has been carried out on the addition of halamines to olefins by means of radical intermediates. The photochemical addition of chloramine to cyclohexene results in the production of trans-2-chlorocylcohexylamine (8[illegible]) and of neutral products.(72) The following mechanism was postulated:-

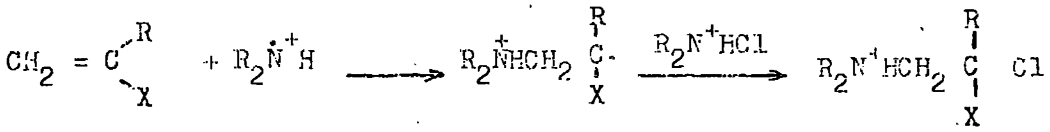
$$NH_2Cl \rightleftharpoons NH_2Cl^{*} \rightleftharpoons NH_2^{\bullet} + Cl^{\bullet}$$



The radical addition of N-chlorodialkylamines was found to occur with terminal olefins in a sulphuric acid-acetic acid medium:(73) two competing reactions are involved:-

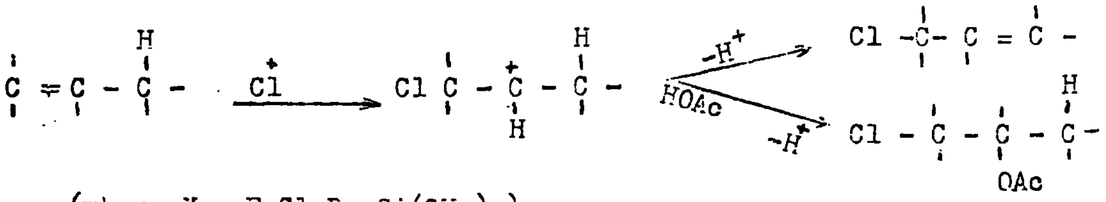
$$R_2NCl \xrightarrow[HOAc]{H_2SO_4} R_2\dot{N}^{+}H + Cl.$$

Then a free-radical addition of the ion radical $R_2\dot{N}^{+}H$ happened to the terminal olefin in a chain process as follows:-



$$CH_2 = C\begin{matrix} R \\ X \end{matrix} + R_2\dot{N}^{+}H \longrightarrow R_2\overset{+}{N}HCH_2\overset{R}{\underset{X}{\dot{C}}} \xrightarrow{R_2N^{+}HCl} R_2N^{+}HCH_2\overset{R}{\underset{X}{C}}Cl \cdot$$

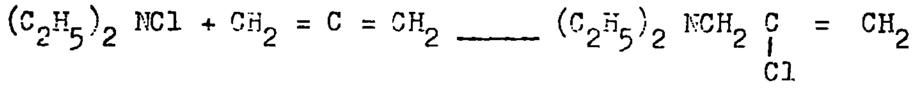
The other reaction proceeds via anionic chlorine attack.



(where X = F,Cl,Br,$Si(CH_3)_3$)

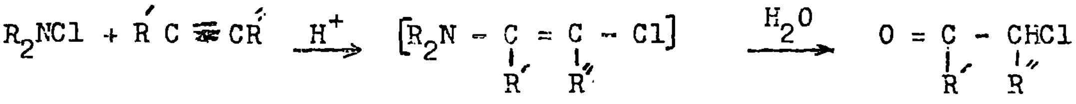
It is of interest to note that the aminium radical displayed little tendency to participate in the intermolecular hydrogen abstraction reaction.

R.S. Neale found that allenes undergo 1,2-radical addition with N-chlorodialkylamines in a sulphuric acid-acetic acid medium. Aminium radical attack results in nitrogen becoming affixed to the least substituted carbon atom, e.g. the reactions between N-diethylchloramine and allene produced 2 -chloroallylamines as shown in the following equation$^{(74,75)}$:



$$(C_2H_5)_2NCl + CH_2 = C = CH_2 \text{ —— } (C_2H_5)_2NCH_2\underset{\displaystyle Cl}{\underset{|}{C}} = CH_2$$

When R.S. Neale treated acetylenes with N-chloramines in some acidic media, α-chloro-carbonyl compounds were generated$^{(74,75)}$. One mechanistic possibility α entails the formation of an emamine via the participations of the aminium radical (the emamine not having been isolated):-



$$R_2NCl + R'C \equiv CR'' \xrightarrow{H^+} [R_2N - \underset{R'}{\underset{|}{C}} = \underset{R''}{\underset{|}{C}} - Cl] \xrightarrow{H_2O} O = \underset{R'}{\underset{|}{C}} - \underset{R''}{\underset{|}{CHCl}}$$

where R= Et, R' = H, R'' = n-C_4H_9 (45%)

R= R' = R'' = Et (59%)

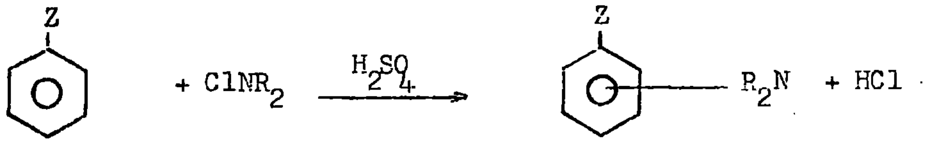
R= Et, R' = H, R'' = $(CH_3)_3C$ (60%)

A recent work on the amination of aromatic compounds with the N-halamines was achieved by three groups:- Bock and Kompa, Minisci and co-workers, and Koracic and co-workers.

Nuclearamination with the N-chlorodialkylamines has been investigated extensively by three principal techniques:-

1) Using 96% sulphuric acid

It was found that N-chlorodimethylamine and phenyl derivatives produced N,N-dimethylarylamines in a yield of 20-80% generally shown by the following equation(79):-



In the case of toluene the distribution of the product was ortho:meta: para = 9 : 53 : 38. No justification of the high meta content was shown. Two possibilities were suggested for the aminating species depending upon the sight of protonation as shown by the following two equations:-

1) $R_2NCl^{+}H \longrightarrow R_2N^{+} + HCl$

or

2) $R_2\overset{+}{\underset{H}{N}}\,Cl \longrightarrow R_2\hat{N}^{+}H + Cl^{\cdot}$

$\phantom{R_2\overset{+}{\underset{H}{N}}\,Cl} \longrightarrow R_2NH + Cl^{+}$

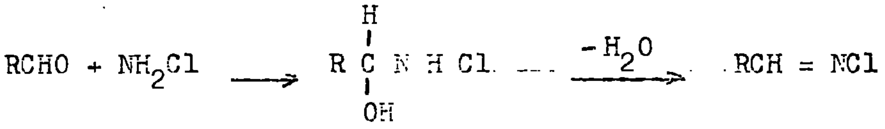
2) Photolysis

A mixture of N-chlorodialkylamine, cold sulphuric acid and toluene gave nuclear amination products in almost the same yield as for the thermal decomposition(77) of the same mixture. The orientation ortho:meta:para = 9 : 53 : 38 from the two routes suggests that the same reaction pathway is involved. Neither the formation of the chlorine nor the side-chain halogenation was noted. The same isomer distribution was obtained from the amination of toluene with N-chlorodimethylamine in a redox system, $R_2\overset{\circ +}{N}H$ was proposed to be the attacking species.

3) <u>Using excess of aluminium chloride and nitroalkanesolvent.</u>

The third method of nuclear amination involved N-chlorodialkylamine, excess aluminium chloride, toluene and nitroalkane solvent.(78) It was found that there was a difference in the orientation, an increase in the para isomer (at the expense of meta:). The orientation was ortho:meta: para = 14: 27: 59 which could be compared with the almost equal o- and p- content of the result of amination of toluene with amino sulphuric acid, (NH_2OSO_3H). With NCl_3, $AlCl_3$ as an aminating system 100% m-toluidene was formed,(81) and with other alkyl arenes similar orientation was found.(82) With N,N-dialkyl halamines although m-isomer was noted, the high m-orientated yields with NCl_3 were not reproduced. The decrease in the m-orientated product yield was attributed to electrophilic amination or free radical reactions, competing with the o- substitution reaction.

The reaction of aldehydes and ketones with chloramines is an interesting practical work, since the ald-chlorimines are merely an example of the Schiff base reaction:-



$$RCHO + NH_2Cl \longrightarrow R\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}NHCl \xrightarrow{-H_2O} RCH = NCl$$

On reduction $RCH = NCl$ produce RCH_2NH_2.(84) Keto-chlorimines are prepared via the amination of the ketonic compound by NH_2Cl. The Keto-chlorimines formed generate primary amine by reduction:-

$$RCH = O + NH_2Cl \xrightarrow{-H_2O} RCH = NCl \xrightarrow{[H]} RCH_2NH_2.HCl$$

Keto-chlorimines are also prepared by the action of chlorine or alkyl hypochlorites on the compounds of the type $RR'C = NMgX$ as follows:-

$$RR'C = NMgX \xrightarrow[R''OCl]{Cl_2 \text{ or}} RR'C = NCl$$

A review by Drago(86) showed that hydrazines can be synthesised via the reaction of chloramine with amines as the following equations show:-

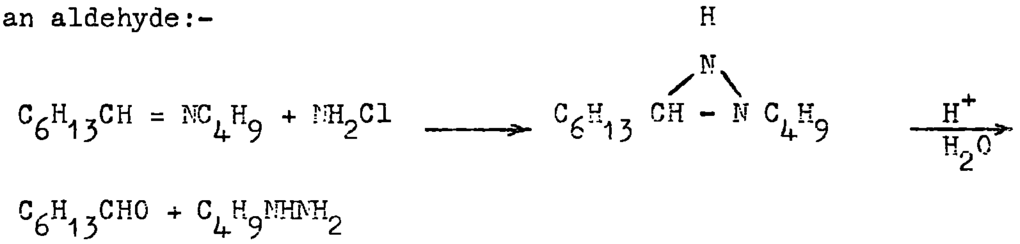
$$NH_2Cl + 2\ NH_3 \longrightarrow NH_2-NH_2 + NH_4Cl$$

$$NH_2Cl + 2\ R\ NH_2 \longrightarrow RNHNH_2 + RNH_3\ Cl$$

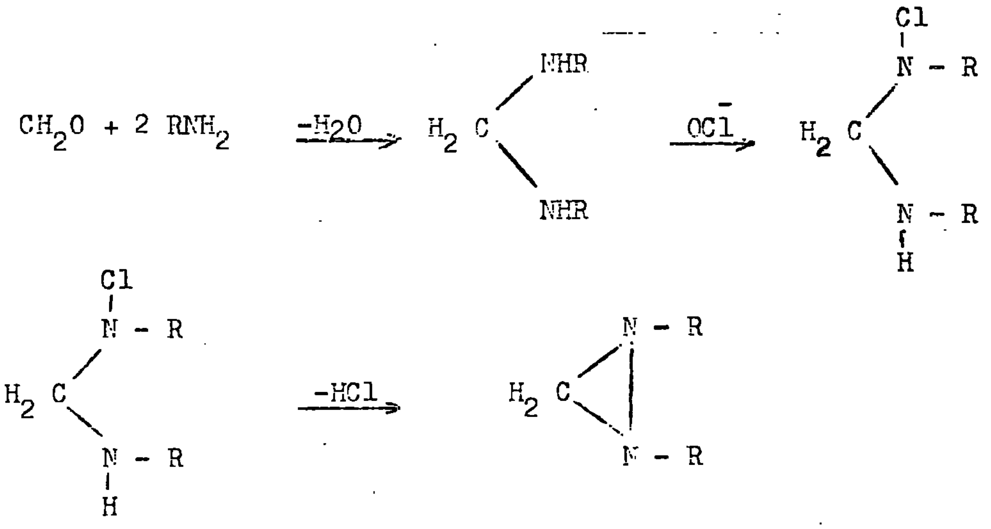
$$NH_2Cl + 2\ R_2NH \longrightarrow R_2NNH_2 + R_2NH_2Cl$$

$$NH_2Cl + R_3N \longrightarrow R_3NN\ \overset{+}{H_2}Cl^-$$

Schiff bases react with chloramine dissolved in ether to generate diaziridines which are cleaved by dilute acid to produce alkylhydrazine and an aldehyde:-



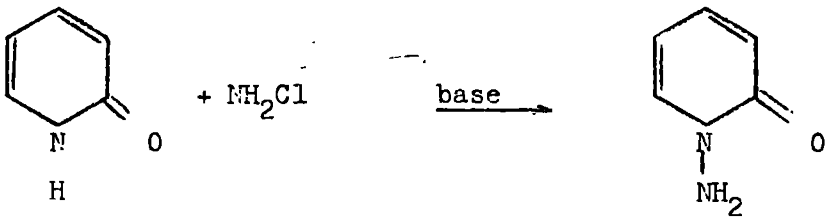
The reactions between formaldehyde in 2 N sodium hydroxide solution and the alkylamines with hypochlorite produce Diaziridines:-



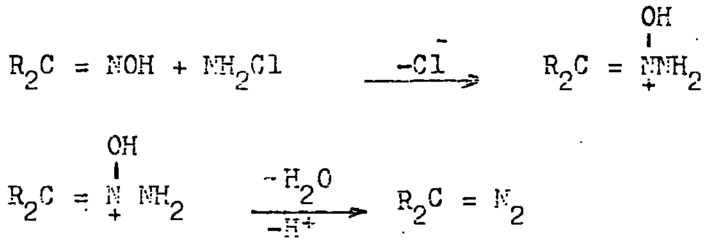
A gaseous mixture of ammonia and chloramine with 1,1-dialkyl hydrazine(88) generated triazanium as illustrated by the following equation:-

$$R_2NNH_2 + NH_2Cl \longrightarrow \left[H_2NNR_2NH_2\right]^+\ Cl^-$$

Chloramine reacts with 2- pyridone in the presence of a base to form a hydrazine derivative (89):-



A mixture of formaldehyde oxime and chloramine generated diazomethane in a sequence of steps commencing with the nucleophilic displacement taking place on the nitrogen of the chloramine:-



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

$$R_2C = \overset{\overset{OH}{|}}{\underset{+}{N}}\,NH_2 \xrightarrow[-H^+]{-H_2O} R_2C = N_2$$

The reaction of N-halamines with sulphur compounds is not an extensive study in the literature. The most common process appears to be nucleophilic substitution on halamine nitrogen by the sulphur compounds e.g. The reaction of N-monochloro derivatives of primary amines with metal mercaptides (91). This generates sulphinetriazine as a new ring compound (92):-

(93) Recent work shows that dialkyl sulphilimine hydrochloride precipitates when dialkyl sulphides are treated with chloramine in ether solution:-

$$R_2S + NH_2X \longrightarrow [R_2SNH_2]^+ X^-.$$

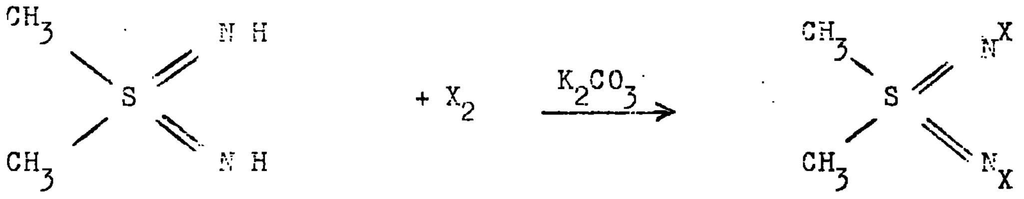
In alcoholic solvent sulphides react with chloramine and generate the hydrocloride of bis (iminodialkyl sulfilimine)(94):-

$$2\ R_2S + 4\ NH_2Cl \longrightarrow [(R_2\overset{+}{S}NH\overset{-}{N}H)_2]\ HCl + 3HCl.$$

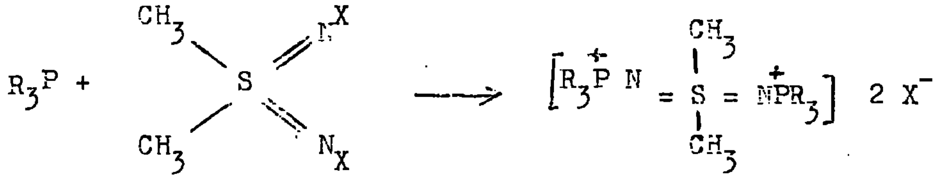
Nitrogen trichloride reacts with diphenylthioether to generate bis (diphenylsulphide) nitride trichloride(95):-

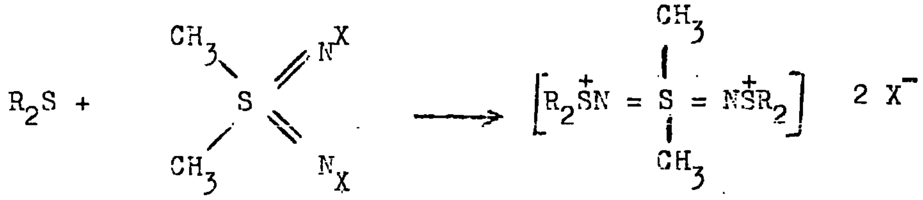
$$(C_6H_5)_2S + NCl_3 \longrightarrow [(C_6H_5)_2SNS(C_6H_5)_2]^+\ Cl_3^-$$

In a buffered aqueous solution a new type of N-halo compound (N,N-dihalogeno-S,S-dimethyl sulphur diimide) was prepared by halogenation of dimethyl sulphur diimide:-



With phosphines and sulphides:-





These compounds underwent nucleophilic substitution. Bock and Kompa generated various amino thiocyanates according to the following equation(97):-

$$RNCl_2 + 2\ NH_4SCN \longrightarrow RN(SCN)_2 + 2NH_4Cl$$

The chlorامination of arsenic compounds with chloramine and $(CH_3)_2NCl$ (99,100) was reported. The following equations show the reactions between NH_2Cl, $(CH_3)_2NCl$ and arsines containing As - H bonds (101):-

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

$$AsH_3 + (CH_3)_2NCl \longrightarrow As + (CH_3)_2NH_2Cl$$

$$CH_3AsH_2 + NH_2Cl \longrightarrow (CH_3As)_5 + NH_4Cl$$

$$CH_3AsH_2 + (CH_3)_2NCl \longrightarrow (CH_3As)_5 + (CH_3)_2NH_2Cl$$

$$(CH_3)_2AsH + NH_2Cl \longrightarrow (CH_3)_2As \cdot As(CH_3)_2 + NH_4Cl$$

$$(CH_3)_2AsH + (CH_3)_2NCl \longrightarrow (CH_3)_2AsAs(CH_3)_2 + (CH_3)_2NH_2Cl$$

The halamine abstracts the hydrogen from As-H bonds. Diphenylarsine and triphenylarsine reacts with chloramine to give aminoarsonium chlorides e.g:-

$$(C_6H_5)_3As \xrightarrow{NH_2Cl} \left[(C_6H_5)_3AsNH_2\right]Cl$$

Various substituted stibines combine with chloramine to produce compounds of the type $\left[R_3Sb(Cl)\right]_2NH$ as shown below:-

$$R_3Sb + NH_2Cl \longrightarrow R_3Sb(NH_2)Cl$$

$$2\,R_3Sb(NH_2)Cl \longrightarrow \left[R_3Sb(Cl)\right]_2NH + NH_3$$

Phosphorus compounds and N-halamines combine in a variety of ways. When an aryl phosphite is treated with N-chlorodialkylamine an addition compound is generated (102):-

$$(C_6H_5O)_3P + Et_2NCl \longrightarrow (C_6H_5O)_3P(NEt_2)Cl.$$

An alkyl phosphite reacts further:-

$$(EtO)_3\ P + Et_2NCl \longrightarrow Et_2NPO(OEt)_2 + EtCl$$

Trisubstituted phosphines and chloramine give quaternary aminophosphonium chlorides in a high yield which in some cases are hard to isolate because of facile hydrolysis:-(103)

$$R_3P + NH_2Cl \longrightarrow [R_3PNH_2]^+\ Cl^-$$

$$[R_3PNH_2]Cl + H_2O \longrightarrow R_3PO + NH_4Cl$$

Trishydroxymethylphosphine with diethylchloramine forms the corresponding aminophosphonium chloride in a 95% yield:_

$$P(CH_2OH)_3 + (C_2H_5)_2NCl \longrightarrow [(CH_2OH)_3\ PN(C_2H_5)_2]^+\ Cl^-$$

The product loses a molecule of formaldehyde and of hydrogen chloride when treated with triethylamine:-(104)

$$[(CH_2OH)_3\ PN(C_2H_5)_2]^+\ Cl^- \xrightarrow{(C_2H_5)_3N} (HOCH_2)_2\ PN(C_2H_5)_2 + CH_2O + (C_2H_5)_3\ N\ .\ HCl$$

Phenylphosphine and diphenylohospine fail to give the analogous addition products with diethylchloramine. This is attributed to the decomposition of the initially formed adducts:-

$$\phi_2PH + (C_2H_5)_2\ NCl \longrightarrow [\phi_2\overset{H}{P}N(C_2H_5)_2]^+\ Cl^- \longrightarrow$$

$$\phi_2PN(C_2H_5)_2 + HCl \longrightarrow \phi_2PCl + (C_2H_5)_2NH$$

Phenylphosphine and diphenylphosphine produce tetraphenylphosphetane and tetraphenylbiphosphine respectively when treated with dimethylchloramine or chloramine:-(105)

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

$$2\ (C_6H_5)_2PH + R_2NCl \longrightarrow (C_6H_5)_2PP\ (C_6H_5)_2 + R_2NH_2Cl$$

$(R = CH_3$ or $H)$

Phosphine gives elemental phosphorus with dimethylchloramine and polymeric phosphorus hydride with chloramine:-

$$2\ PH_3 + 3\ (CH_3)_2\ NCl \longrightarrow 2\ P + 3(CH_3)_2NH_2Cl$$

With nitrogen trichloride and triphenylphosphine as precursors, bis (triphenylphosphine) nitride trichloride is synthesised:-(106)

$$(C_6H_5)_3\ P + NCl_3 \longrightarrow [\{(C_6H_5)_3P\}_2N]^+\ Cl_3^-$$

Diphenylchlorophosphine combines with a mixture of chloramine and ammonia to form compounds, which on heating are converted to trimers and tetramers of the empirical formula $(C_6H_5)_2PN$.(107) The reaction of ammonia-free chloramine and diphenylchlorophosphine proceeds as illustrated:-

$$(C_6H_5)_2PCl + NH_2Cl \longrightarrow [(C_6H_5)_2P(Cl)NH_2]\ Cl \xrightarrow{-HCl}$$

$$(C_6H_5)_2P(NH_2)(Cl)NHP(Cl)_2(C_6H_5)_2$$

Pyrolysis of the product yields the trimer and tetramer,

$[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$ respectively.

Although theoretically, the reaction between aminophosphines and chloramine presents the possibility of either a nitrogen-nitrogen or a phosphorus-nitrogen bond being formed, amination always occurs at the phosphorus site:-

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

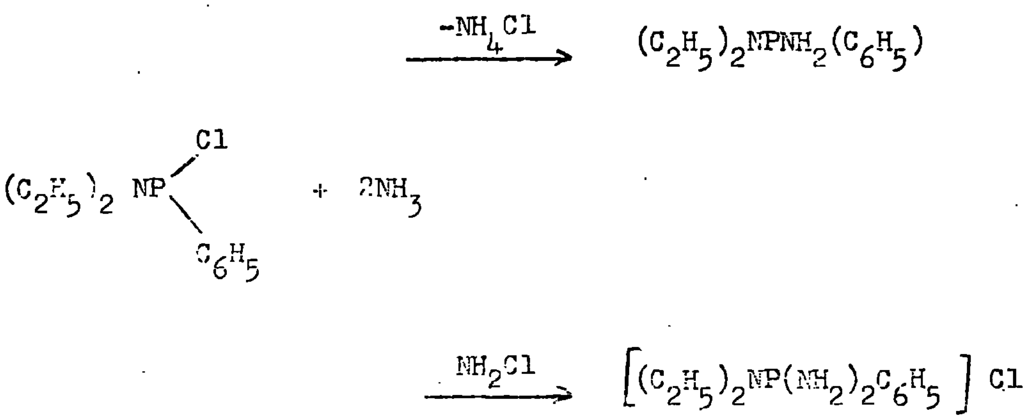
A similar pathway was followed with $(R_2N)_2\ P\ C_6H_5$ or $(R_2N)_3\ P$.

The yield of aminophosphonium chlorides range from 43 to 79%. Amination is shown to occur on phosphorus by the examination of the products obtained through basic hydrolysis of amino-t-butylaminodiphenylphosphonium chloride:-

$$[(H_2N)\ \{(t\text{-}C_4H_9)NH\}\ (C_6H_5)_2P]^+ + H_2O + OH^- \longrightarrow$$

$$(C_6H_5)_2P(O)OH + NH_3 + t\text{-}C_4H_9NH_2$$

If amination occurrs on nitrogen, t-butyl hydrazine will be generated instead of t-butylamine. According to the reaction between the mixed phosphine, $(C_2H_5)_2NP(Cl)(C_6H_5)$, and a mixture of chloramine and ammonia, the following equation is proposed, since P-Cl bonds are subject to rapid ammonolysis:-



$$(C_2H_5)_2NP(Cl)(C_6H_5) + 2NH_3 \xrightarrow{-NH_4Cl} (C_2H_5)_2NPNH_2(C_6H_5) \xrightarrow{NH_2Cl} [(C_2H_5)_2NP(NH_2)_2C_6H_5]Cl$$

Dimethylaminophosphines and dimethylchloramine behave analogously giving phosphonium salts(111):-

$$(CH_3)_2NP(CH_3)_2 + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_2P(CH_3)_2]Cl$$

$$[(CH_3)_2N]_2P(CH_3) + (CH_3)_2NCl \longrightarrow [\{(CH_3)_2N\}_3P(CH_3)]Cl$$

Amination takes place on the phosphorus atom of the hydrazinephosphines by chloramine:-

$$(C_6H_5)_2PN(CH_3)N(CH_3)_2 + NH_2Cl \longrightarrow [(C_6H_5)_2P(NH_2)N(CH_3)N(CH_3)_2]Cl$$

The amination of the phosphorousatoms in the aminophosphines and the hydrazinephosphines by chloramine demonstrates that the electron density on the phosphorus is increased in relation to the attached amino nitrogen atom; probably through $p_\pi - d_\pi$ bonding. Furthermore, the other nitrogen atom of the hydrazino group is a less preferred sight for reaction.

Nitrogen trichloride reacts with phosphorus trichloride to produce $[Cl_3P{=}N{-}PCl_3]^+ [PCl_6]^-$ (113)

Generally phosphines react with chloramine in the same manner as their nitrogen counterparts. Chloramine reacts in such a way that the chlorine atom takes on the role of a negative species. The formation of hydrazines is postulated to take place in an analogous fashion.

CHAPTER TWO

EXPERIMENTAL METHODS

The study of the reactions of dimethyl chloramine with the phosphines required the use of a variety of manipulative techniques.

Although the majority of the reagents used were not particularly volatile, a vacuum line allowed the quantitative transference of materials to be made under anhydrous conditions. The vacuum line also allowed investigations of the reaction products (which were volatile,) to be made. The vacuum line was beneficial in removing any excess of dimethyl chloramine from the vessel of the reaction. Also it was useful in fractional condensation for the purification of volatile substances for example Me_2NCl. In order to maintain anhydrous conditions throughout a series of reactions, or during washing of the products, a dry box was used.

This chapter will describe the vacuum and dry box systems and give details of the equipment associated with them. The methods employed to purify or prepare all the reactants used in the study are also explained and discussed.

1. The vacuum line (Figure 1)

The vacuum line was of the kind designed for general purposes, as shown diagrammatically in Figure 1. It could be split into four sections comprising of a pumping section (P), a general working section (W), a storage section (S), and a fractionating section (F).

The pumping section was comprised of 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 pumping capacity at 10^{-3} to 10^{-5}mm Hg. and could attain an ultimate vacuum of 3×10^{-7}mm Hg. The pump was heated electrically using a 320 watt wrap-round heating element. The critical backing pressure of

0.2mm Hg. was easily obtained using the two-stage rotary oil pump which was an Edwards "Speedivac" Model 2SC20A powered by an 0.25 horsepower motor; this provided a pumping speed of 22 litres per minute and an optimum vacuum better than 10^{-3}mm Hg.

The diffusion pump was situated between two cold traps, having been isolated from the rest of the line by large three-way tap (3a and Figure one) ensured that if chemicals reactive to hot mercury (e.g. Cl_2) were being handled in this section, no contamination would occur. An air bleed was provided via tap 1a to prevent oil suck-back when the oil pump was switched off. The connections between the rotary pump and the diffusion pump and the rest of the line were as large as possible.

The general working section consisted of a row of six taps terminating in B14 sockets to allow the attachment of the various pieces of apparatus, such as infra red gas cells or reaction vessels. It was found more convenient to have B 14 sockets rather than B 14 cones on this section, as reactions were carried out which often required the making and breaking of connections to this part of the line e.g. The weight analysis cell work, where the cleaning of vacuum grease from the demounted apparatus was facilitated by having a cone and not a socket. This section of the line was also equipped with a standard volume V. and a cold finger, C. The storage section provided a total capacity of 90 litres in the form of four 20 litre bulbs and two 5 litre bulbs. The storage bulbs were connected to the vacuum line via Rotaflo taps, which were found to be more satisfactory than greased ground glass taps for this particular purpose, since the seal provided was found to be, in general, more durable than that offered by a greased tap. The merits of this type of vacuum tap are discussed later.

For the investigation of volatile reaction products, or the purification of volatile reatants, the fractionation section was used. This consisted of six individualy isolated fractionation bulbs of a diameter making a close fit in the mouth of a "Thermos" dewar.

The fractionation section was demountable, for easy cleaning, and was equipped with it's own manometer (F M, Figure 1) so that slow distillation could be carried out whilst leaving the rest of the vacuum line free for other work. Access of this section was via B 14 sockets. Cold baths necessary for distillations were made up using organic liquids of suitable melting point, and liquid nitrogen (never liquid air). The temperatures of such baths are given in Table 1.

Table 1: Temperatures of a variety of cold baths.

Cold bath component.	Temperature ($0^{\circ}C$)
Melting CCl_4	-23
Solid $CO_2/(CH_3)_2CO$	-84
Melting $C_6H_5CH_3$	-98

The cold traps used in the pumping section contained liquid nitrogen. The dewars used with the vacuum line were either wide necked dewars, most conveniently held in one pint oil cans, supported on cork rings, or standard quart "Thermos" flasks. The latter were used predominantly for freezing purified products on the fractionation train when such products could not be stored elsewhere, for example dimethly chloramine, since nitrogen evaporation losses were minimised by the narrow neck of the flask. The other dewars were used for holding the cold baths.

All parts of the line were connected, via various manifolds, either directly or indirectly to the main manometers M, (Figure 1), which were of the direct reading type and fabricated from 8mm bore tubing. Pressures were recorded using a cathetometer yielding a pressure reading to 0.01mm.

The standard volume situated in the working section of the line was calibrated using an external known volume; the volume of which was found by weight measurements full and empty of mercury, and the standard P, V and T relationships.

For vacuum checking, when the vacuum was observed to be better than 0.01mm from the manometer, a Tesla coil indicated a colour inside the vacuum line when the pressure had fallen below approximately 10^{-5}mm Hg. (a black vacuum), This condition was considered satisfactory when pumping out the reaction vessels or the joints between the line and the demountable pieces of apparatus. The use of the Tesla coil might induce the formation of "F" centres in alkalihalid infra red plates producing a blue colouration, and also causing the decomposition of some reactants such as $(CH_3)_2NCl$. Thus care was exercised in its use. It proved extremely useful in the detection of pinholes in the glass tubing of the vacuum line, but could also cause pinholes if sufficient care was not taken when checking thin walled containers such as the molecular weight bulbs.

In all cases Apiezon M grease was used for the joints which were broken, such as cones and sockets. Apiezon L grease was used for taps within the vacuum line, as this grade proved more convenient, especially when the ambient temperature was low, since it remained more fluid than the M grease at a lower temperature. Black Picein wax was used for the connections at the diffusion pump since this was considerably more permenent than either Apiezon L and M grease, and would also withstand the temperatures in this area. For experiments involving substances reactive towards Apiezon grease, such as chlorine, Kel-F 90, a fully fluorinated grease, was used.

Examples of different apparatuses used with the vacuum line are shown in Figure (2) an infra red gas cell and a gas molecular weight bulb. Figure (3) shows a storage ampoule and weight analysis cells. These equipments are fitted with the "Rotaflo" stopcock which is shown in the section in Figure (4) and consists of a "PTFE" plug attached to a plastic knurled knob; the whole fitting into a specifically designed glass tube. When the stopcock is closed the PTFE plug is clamped tightly onto the valve seat formed in the glass tube thus sealing the contents of the enclosed vessel off from the atmosphere. The seal at the other side of the stopcock is formed by expanding the PTFE plug along about 1cm of its own length by means of a resilient inside the PTFE plug.

The conditions of a good seal were obtained when both the PTFE and the glass contract 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 or this could cause leakage.

The use of a Tesla spark coil, for vacuum testing could degrade the PTFE around the valve seat area if care was not taken.

It was found that this type of stopcock had several advantages over the more standard greased, ground glass tap, in that it could be used quantitatively after long periods of time in contact with, for example, PCl_3. A conventional greased tap would have deteriorated.

Indeed, for weight analysis experiments, where the reaction studies involved materials whose boiling point was less than room temperature, the Rotaflo system offered ease of manipulation, the ability to be reproduced and safety.

It was found, however, that although a seal may be satisfactory at room temperature, this may not be so at e.g. -35°C in a freezer when the PTFE plug contracts. This does not represent a serious drawback since the contraction can be compensated for by pre-adjustment.

The use of the stopcock when formed into a storage ampoule is shown in Figure (4). Clearly the convenience of this method over a sealed pyrex ampoule need not be emphasised. Figure (2) shows two views of the infra red gas cell which was fabricated from a 25mm diameter tubing and has a path length of approximately 10cm. The cell was equipped with a short (approximately 3cm.) cold finger for the collection of small quantities of volatile materials, and was sealable by means of a Rotaflo stopcock. NaCl infra red plates were affixed to the ground glass ends by means of piceine wax (care being taken during the application of the plates to prevent cracking under the heat of an infra red lamp which was used to melt the black Piceine sealing wax). In some cases CsI plates were fixed in a similar way.

Figure (3b) shows a standard weight analysis cell formed from a B 24 cone and socket. The socket part of the cell contained a ground glass tap whereas the container part was formed from a cone. This was so that with careful greasing, materials could be weighed whilst in the cell without coming into contact with the grease around the cone and socket joint. The standard cell was only practical in the case of quantitative reactions, especially when solid materials were used. The Rotaflo weight analysis cell (Figure 3a) was used as a vessel for quantitative reactions, when one or both of the reactants were volatiles. The storage of some volatile chemical compounds in Rotaflo storage ampoules (Figure 3c) aided their intruductions into the vacuum line.

An ampoule of one hundred cm^3 capacity fitted to the B 14 cone was used as a container for the undistilled dimethlychloramine, during the process of distillation, by the use of the vacuum line (Figure 5)

A molecular weight bulb of $313cm^3$ capacity adapted with a B 14 cone and a Rotaflo stopcock was useful in quantitativly measuring gasses. In the case of volatile liquids, for example BCl_3 the compound was expanded into the molecular weight bulb at a known temperature and pressure this facilitating quantitative reaction. The nmr sample tubes of 8mm diameter were used, filled to a depth of about 2 cm (Figure 5a). For sealed tube reactions the nmr tube was fitted with a B 14 cone (Figure 5b), connected to a tap with a B 14 cone and socket (Figure 5c) which could be attached to the vacuum line. The merit of the above technique is that the sealed nmr tube which contained the reactant can be kept in the freezer at -35°C without any leakages, especially when the product is a highly hygroscopic material When using a Rotaflo weight analysis cell there is greater possibility of leakage, because of contraction of the metalic part of the tap. Using this technique the nmr spectrum can be run directly without any possible attack by moisture. In some cases it was necessary to break the sealed nmr tube inside the dry box in order to push the product towards the bottom of the nmr tube and after that stopper the tube by a rubber stopper surrounded by parafilm. This would improve the nmr signal. A heavy wall pyrex reactions ampoule of 16mm diameter (Figure 5d) was used to facilitate some sealed tube reactions.

2. The Dry Box.

The dry box was a standard box of approximately 30 litres capacity and is shown along with the associated humidity control equipment in Figure (6). The glove box was manufactured in 1970 at 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 infra red press.

An enclosed variable speed recirculating pump positioned inside the glove box, passed the box atmosphere approximately once every seven minutes through two cold traps (C), fitted in a parallel position. 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 drawn from central liquid nitrogen storage cylinder and was rated at less than 6ppm H_2O. The box itself was kept dry with dishes of phosphoric oxide placed in strategic positions around the box floor. The adequacy of this desiccation can be seen from the spectra of extremely moisture sensitive compounds such as $[(CH_3)_2N]_3PCl_2$. The entry and exit to and from the box was, for large objects, 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. For small items, such as infra red cells or analytical samples, the quick entry and exit port, Q, was used. This consisted of two brass B55 cones bolted back to back on the main port side of the box. B55 glass sockets equipped with Rotaflo taps were fitted over the cones and the whole of this could be evacuated to the water pump vacuum within minutes.

The box was also fitted with an electrical connection via a gland in the side wall terminating in a 13 amp socket. All none welded joints, for instance, at the large plastic window, were sealed with silicoset silicone rubber, and before commencing the box was purged with nitrogen for at least two weeks. Before use it was necessary to recirculate the box atmosphere through the cold traps, which were immersed in dewars of liquid air for at least four hours. Liquid air was used in this instance because with positive nitrogen pressure in the box, the box atmosphere may have condenced if liquid nitrogen was use.

3. nmr Technique.

All of the phosphorus compounds were examined by the 31 nmr spectrometer in the department; this is a modified P.E. R10 spectrometer. All 31p chemical shifts were reported, with respect to 85% aqueous phosphoric acid, as 0 ppm shift, with the upfield direction taken as positive. (Visual display unit page 44.) The phosphorus nmr machine error is ±1.4ppm. Various types of 8mm nmr tubes were used as described in Section II.1.

Preparation and purification of Reactants.

(a) Dimethyl chloramine.

The method employed here used the reaction between hypochlorite ions and alkylammonium halides (1.14) the modification being that:- (i) sodium hypochlorite is prepared according to the method of Sterling(113) and (ii) the alkylammonium chloride was added in solid form rather than solution.

$$(CH_3)_2\overset{+}{N}H_2 + Cl\bar{O} \longrightarrow (CH_3)_2NCl + H_2O$$

Temperature control during the addition of the dimethylammonium chloride was found to be very important, since any rise favoured the formation of dichloro-derivatives and possibly highly explosive nitrogen chloride.

The crude dimethyl chloramine was kept in the freezer mixed with calcium chloride as a drying agent.

Fractional condensation

Dimethyl chloramine was purified by fractionation on a vacuum line, the mixture being distilled through four traps cooled with baths:- at $-23^{o}C$ the melting point of carbontetrachloride two baths at $- 84^{o}C$ (acetone, solid carbon dioxide) and one at $-196^{o}C$. The majority of the product was collected at $- 84^{o}C$. The pure product, as shown by the gas infra red spectrum figure (IR p84) was pure dimethyl chloramine.

The dimethyl chloramine was kept in a Rotaflo storage ampoule in a freezer because dimethyl chloramine gives white solid decomposition products at room temperature.

(b) The preparation of Aminophosphines.

Tris(dimethylamino)phosphine $[(CH_3)_2N]_3P$, bis(dimethylamino) chlorophosphine $[(CH_3)_2N]_2$ PCl, dimethyl amino dichlorophosphine $(CH_3)_2N$ PCl_2 dimethyl amino phenyl chloro phosphine $(CH_3)_2N$ PCl ph can be obtained in a good yield from the reaction of phosphorous trichloride or phenyl dichlorophosphine with dimethylamine in stroichiometric proportions. The reactions are normally carried out in an inert solvent. The one which was used was a dry petroleum ether and proceeded according to the following equations:-

1. $PCl_3 + 2\ (CH_3)_2NH \longrightarrow (CH_3)_2NPCl_2 + (CH_3)_2NH_2Cl$ (115)

2. $PCl_3 + 4\ (CH_3)_2NH \longrightarrow [(CH_3)_2N]_2PCl + 2\ (CH_3)_2NH_2\ Cl$ (116)

3. $PCl_3 + 6\ (CH_3)_2NH \longrightarrow [(CH_3)_2N]_3\ P + 3\ (CH_3)_2NH_2\ Cl$ (117)

4. $PhPCl_2 + 2\ (CH_3)_2NH \longrightarrow PhPCl\ N(CH_3)_2 + (CH_3)_2\ NH_2\ Cl$ (116)

The purity of each of the phosphine reagents was checked by nmr as shown in the table:-

Number	Observed nmr Peaks p.p.m.	Reported nmr peaks p.p.m.	Molecular formula	References
1	-219.3	-219.4	PCl_3	118,119,120
2	-164.4	-166	$(CH_3)_2NPCl_2$	121,122.
3	-159.6	-159.7	$[(CH_3)_2N]_2PCl$	121,122
4	-122.5	-122.5	$[(CH_3)_2N]_3P$	123,124
5	-140	-140	$(CH_3O)_3P$	125,126
6	-127	-127	$(C_6H_5O)_3P$	126
7	- 82	- 81.5	$P(C_6H_5)_2Cl$	121
8	-161	-161.5	$P(C_6H_5)\ Cl_2$	127
9	-141.8	-141	$P(C_6H_5)N(CH_3)_2Cl$	123

Phosphorus trichloride was obtained from Fisons and after distillation stored in a Rotaflo storage ampoule. Trimethyl phosphite was obtained from Ralph N Emanuel, triphenyl phosphite from BDH, diphenyl chlorophosphine from Lancaster synthesis, and phenyl dichlorophosphine from Alfa-division.

(c) Other Chemicals.

1.) dimethylamine.

R_2NH was obtained in 250ml ampoules which were cooled in a freezer at -35°C; the top of the ampoule was cut off by a glass knife and the R_2NH was poured into a Rotaflo storage ampoule. The air was pumped off on the vacuum line while the amine was frozen at -196°C.

2.) HCl.

HCl as a gas was obtained from a cylinder and introduced into a 3 litre bulb connected to the fractionation section of the vacuum line and purified by fractionation.

3.) Cl_2 Chlorine.

Cl_2 as a gas was obtained from a cylinder.

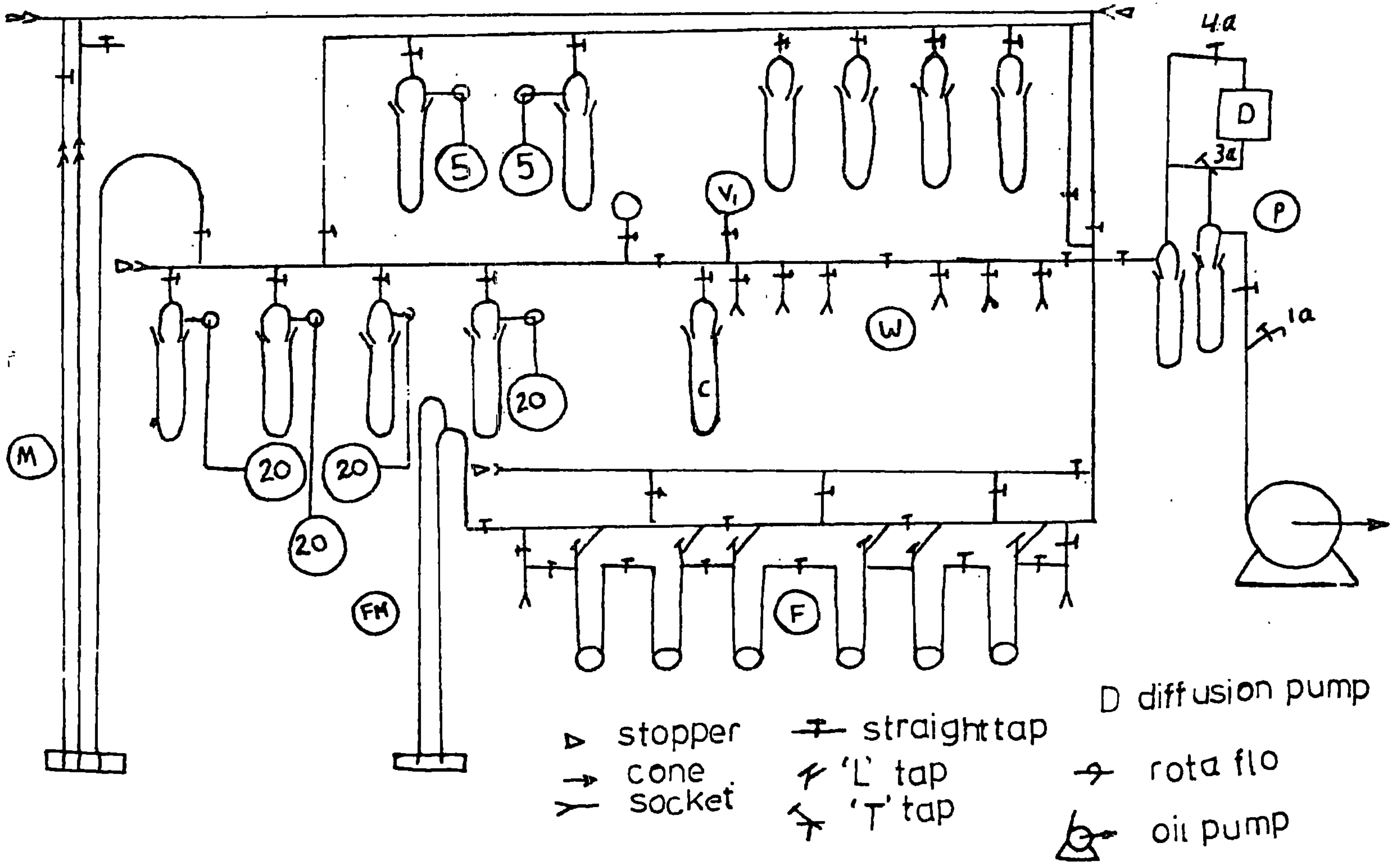
4.) Boron trichloride.

Pure redistilled BCl_3 was kept in a rotaflo storage ampoule.

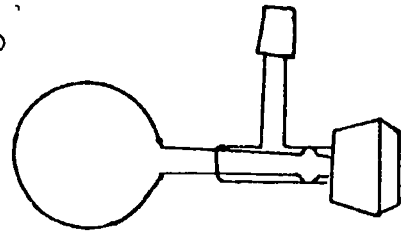
5.) Solvents.

Diethyl ether and petroleum ether were dried over fine sodium wire. Dichloro methane and carbontetrachloride were dried over a molecular sieve type 3A. The dried solvents were kept in well stoppered containers.

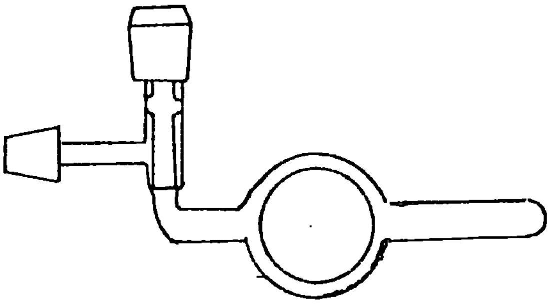
FIG 1



VACUUM LINE

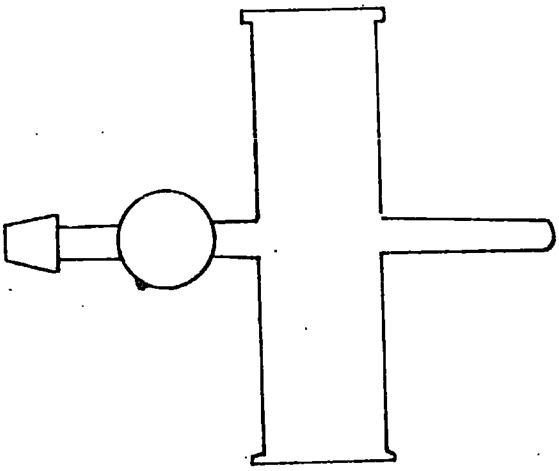


GAS MOLECULAR WEIGHT BULB



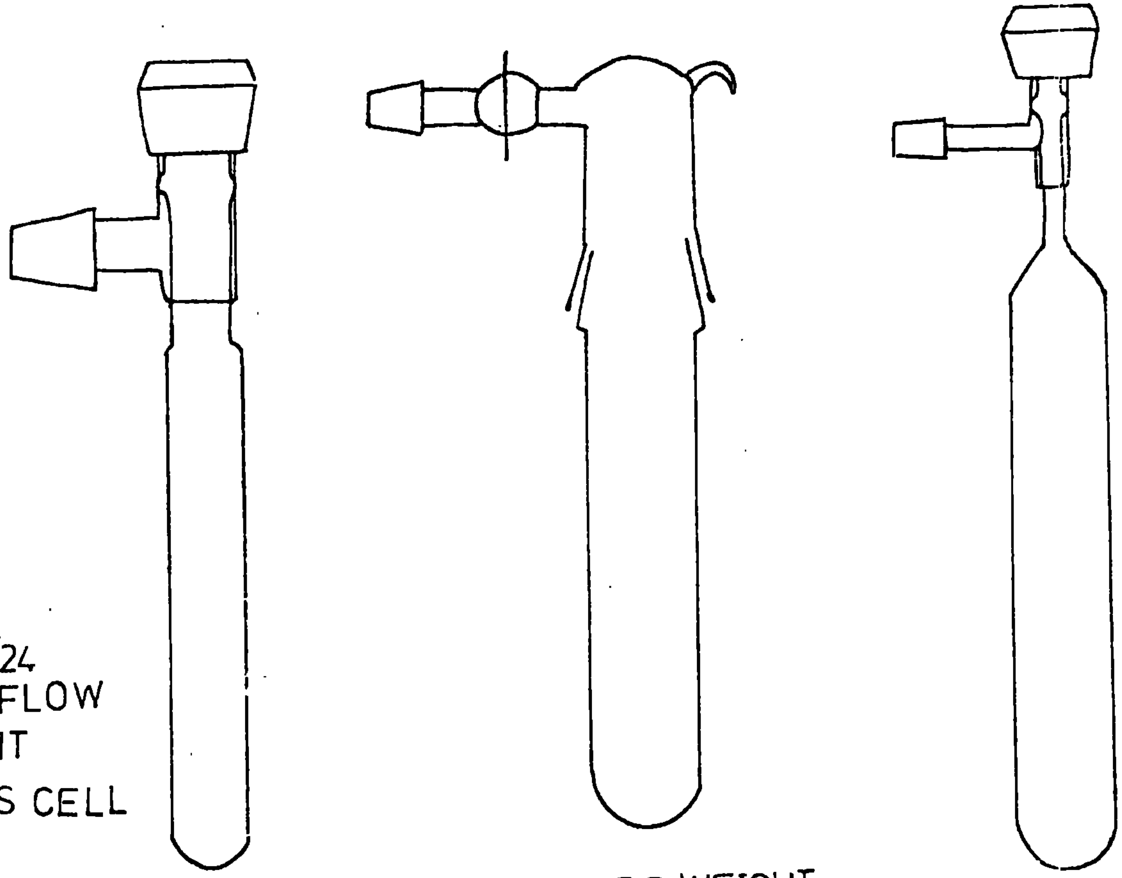
INFRA RED GAS CELL (SIDE VEIW)

FIG 2



INFRARED GAS CELL (PLAN)

FIG 3

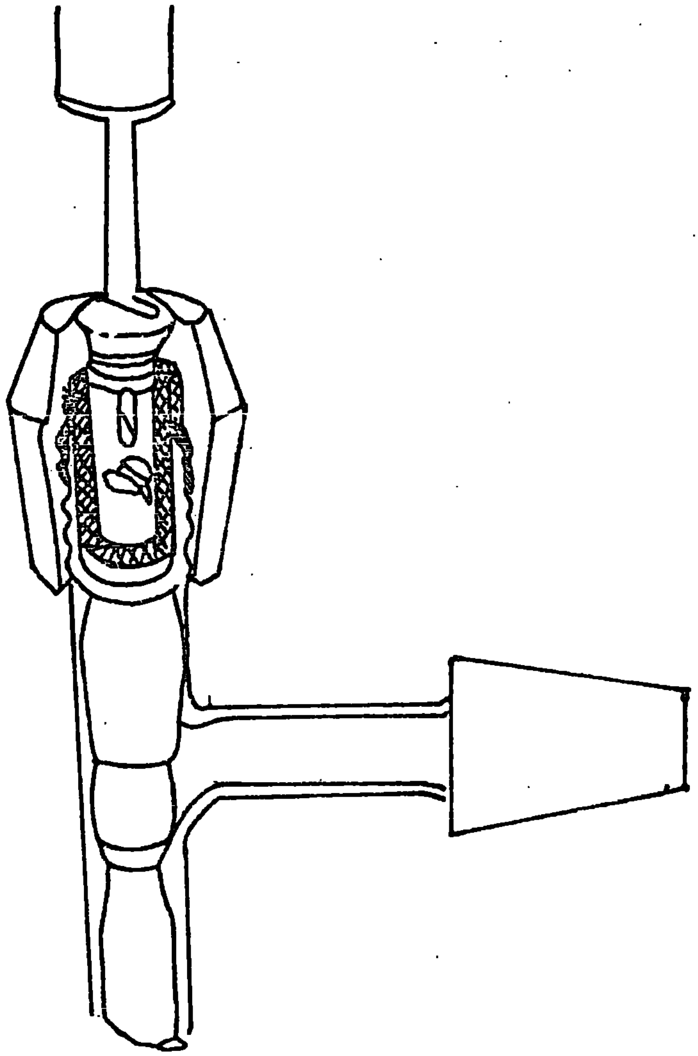


TF 16/24
ROTA FLOW
WEIGHT
ANALYSIS CELL

STANDARD WEIGHT
ANALYSIS CELL

TF 6/13
ROTA FLO STORAGE
AMPOULE

FIG 4



SECTIONAL VIEW OF THE
ROTA FLO STOP COCK

FIG 5

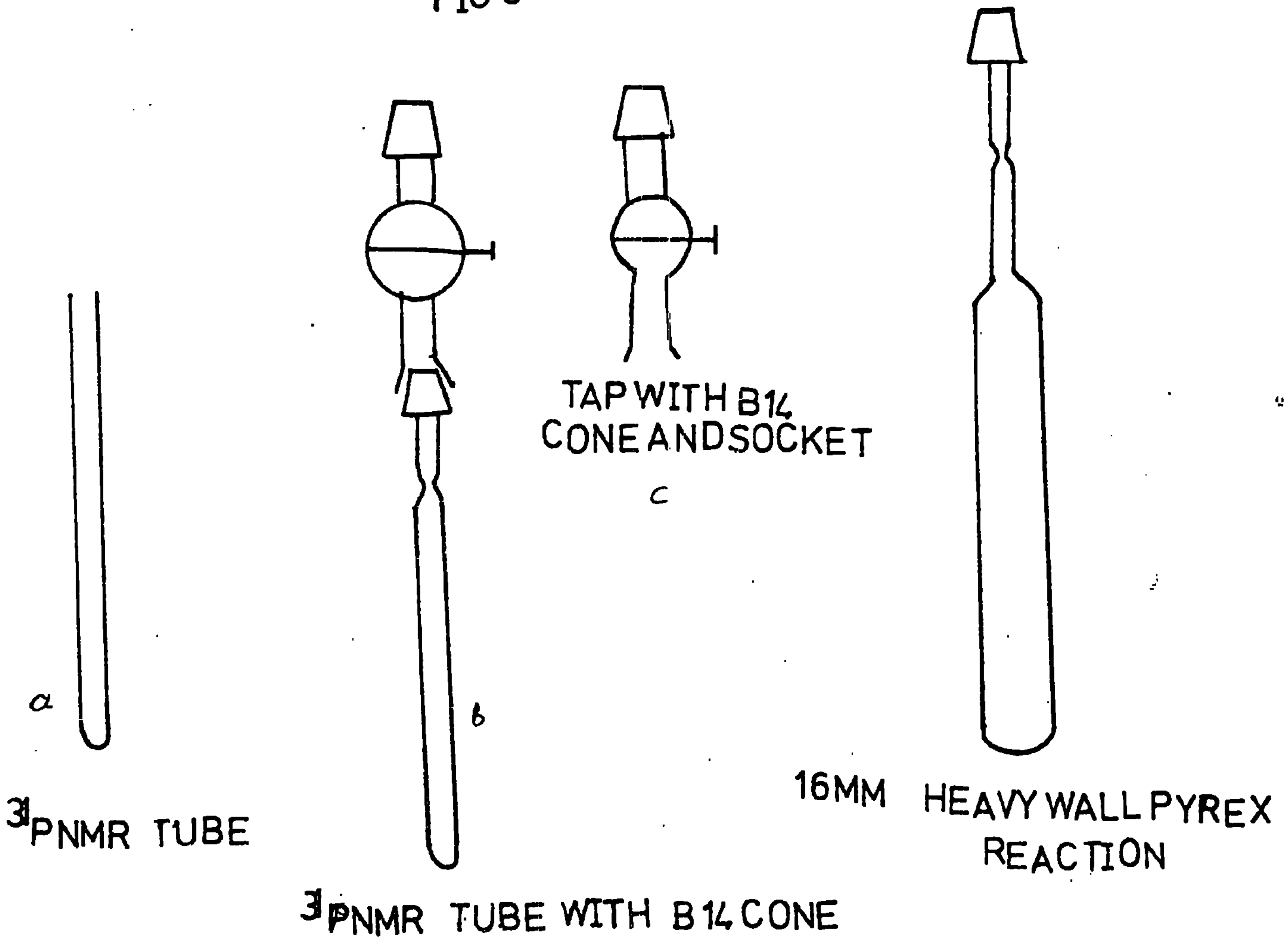
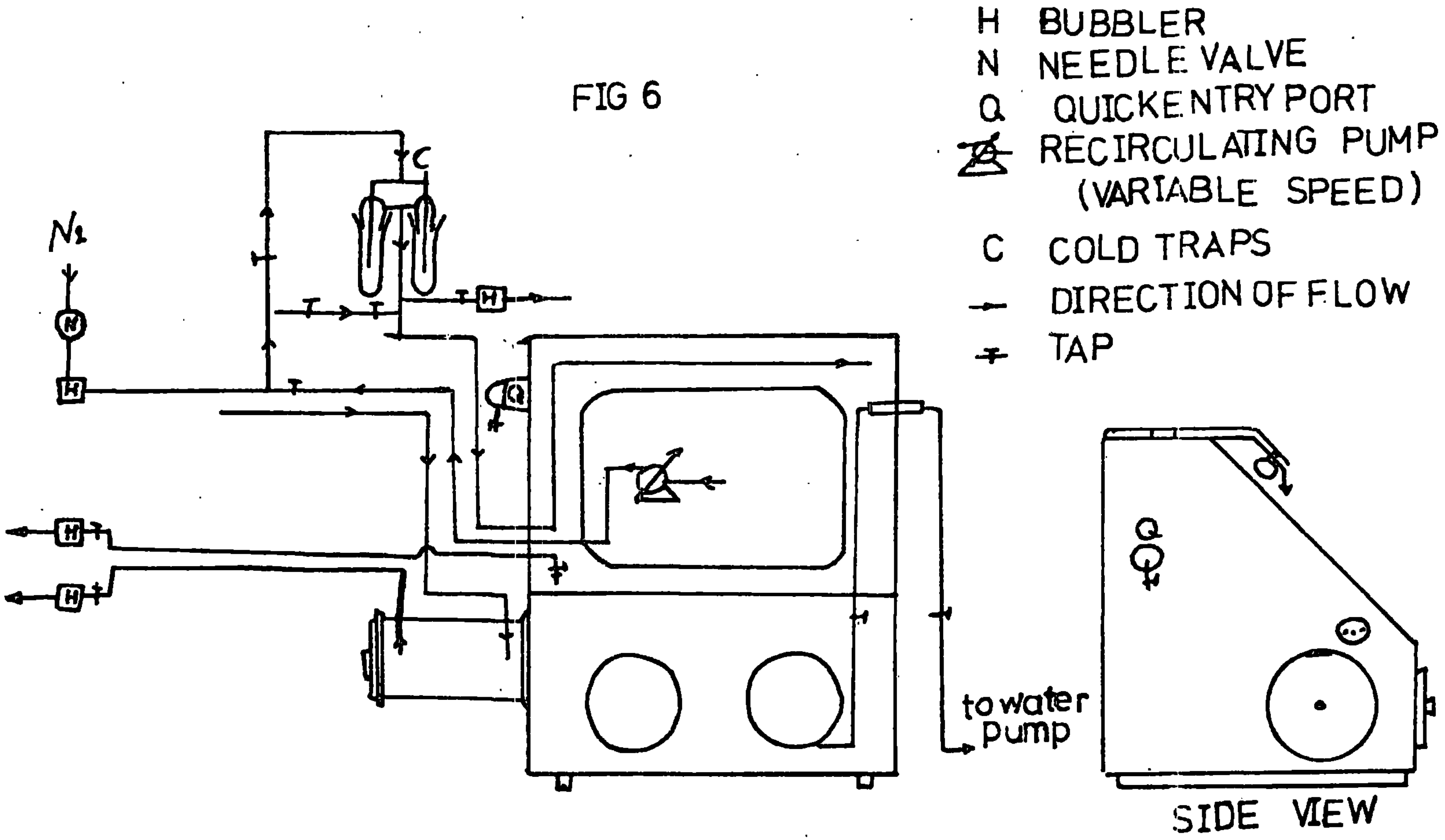
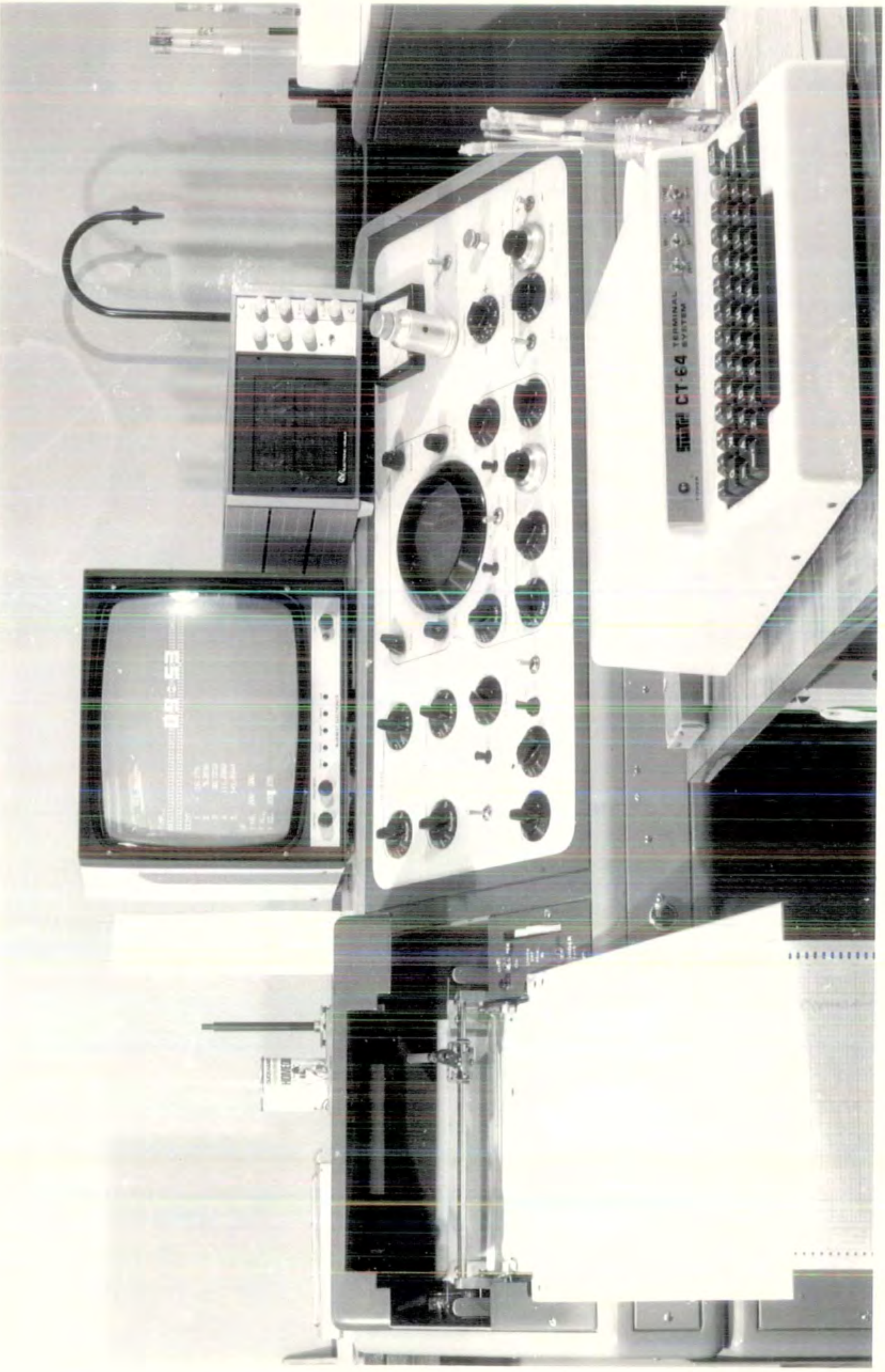

a
^{31}PNMR TUBE
b
^{31}PNMR TUBE WITH B14 CONE
TAP WITH B14
CONE AND SOCKET
c
16MM
HEAVY WALL PYREX
REACTION

FIG 6



THE DRY BOX GENERAL LAY OUT


SWTPC CT-64 TERMINAL SYSTEM

CHAPTER THREE

THE REACTIONS OF N.N. DIMETHYL CHLORAMINE WITH TRI COORDINATE ALEPHATIC PHOSPHINES.

Introduction:-

The initial purpose of this work was to determine whether dimethyl chloramine and the following compounds:-

Phosphorus trichloride (PCl_3), dimethyl amino dichloro phosphine (Me_2NPCl_2), bis (dimethyl amino)chlorophosphine $[(Me_2N)_2PCl]$ and tris (dimethylamino) phosphine $[(Me_2N)_3P]$, react to form addition compounds analogous to the reported reactions of chloramine with amines and phosphines(103) (Me = CH_3).

It was found that dimethyl chloramine reacted vigorously with phosphorus trichloride to produce 2 $(Me_2NPCl_3)^+$, Me_2NPCl_2 , Cl^- and PCl_6^-. It was found that dimethyl chloramine reacted with dimethylamine dichloro phosphine to produce $(Me_2N)_2PCl_2{}^+ . Cl^-$, and it reacted with bis (dimethyl amino) chlorophosphine to produce $[(Me_2N)_3P\,Cl]^+ . Cl^-$. The reaction between dimethyl chloramine and tris (dimethyl amino) phosphine was found to produce $[(Me_2N)_3PCl]^+ . Cl^-$ and tetramethyl hydrazine rather than producing $[(Me_2N)_4P]^+ . Cl^-$.

The reaction between Me_2NPCl_2 and molecular chlorine produce 2 $[Me_2NPCl_3]^+$, PCl_6^- , Cl^- and Me_2NPCl_2. This reaction was novel in that parallel reactions, such as the chlorination of tris(dimethylamino) phosphine $[(Me_2N)_3P]$produces $[(Me_2N)_3PCl]^+ . Cl^-$ the simple product.(130)

The reaction between phosphorus tri-chloride and dimethyl chloramine.

The typical reaction was performed by distilling 1.260g. of Me_2NCl (0.0 158 moles) under vacuum into a rotaflo weight analysis cell containing 5.65g of PCl_3 at -196°C. The vessel was kept in a freezer at -35°C for fifteen hours. The volatile fraction was distilled from the vessel and the gas infra red spectrum showed that it was PCl_3 only. The excess PCl_3 was pumped off. The product was weighed and the reaction was found to be completed in molecular ratio PCl_3 : Me_2NCl 1.34 : 1. It was found that the product was highly hygroscopic, so care was taken to eliminate moisture.

The reaction was performed 9 times using various ratios of the reactants (Table 1). In all cases a white solid formed after a few minutes at -35°C and seemed to be completed after twelve hours. The vessel was transferred to the dry box and the product isolated and studied by using nmr which showed a broad peak due to the solid phosphorus cation $Me_2NPCl_3^+$ (131) at -61.3 ppm. and another broad peak at 298.2ppm. corresponding to PCl_6^- (132) and a sharp third peak due to a liquid phosphorus compound which corresponded to Me_2NPCl_2 (121) at -164.4 ppm. Figure (1a).

The infrared spectrum of the sample showed a peak at 440 cm^{-1} due to PCl_6^- (133) and other peaks at:- 2845 cm^{-1}, 2920cm^{-1}, 1460 cm^{-1} 1300 cm^{-1}, 1170 cm^{-1}, 1055 cm^{-1}, 1010 cm^{-1}, 749 cm^{-1}, 730 cm^{-1}, 665 cm^{-1}, 510 cm^{-1}, 590 cm^{-1}, 490 cm^{-1}. (Figure 2b,4b).

The microanalysis results are shown in the following table:-

Element	Calculated data for $2(Me_2NPCl_3)^+.PCl_6^-$ Cl^- . $Me_2NPCl_2^{--}$	Found
C	9.14	9.31
H	2.28	3.23
N	5.33	5.29
P	15.7	14.57
Cl	67.5	66.62

The reaction between PCl_5 and Me_2NCl was achieved nine times. Table (1) summarises the reactions.

TABLE 1

Number	PCl_3/Me_2NCl The actual Molar ratio reacted.	Temperature ^{o}C	Time by Hours	pnmr signal and integration ratio (ppm)		
				Me_2NPCl_2	$Me_2NPCl_3^+$	PCl_6^-
1	1.34/1	-35	15	-164.4ppm 1.0	-61.3 ppm 1.95	298.2 ppm 1
2	1.3/1	-35	12	-166 " 1.0	-60.0 " 1.9	291.7 " 1
3	1.03/1	0	13	-166 " 0.9	-58.5 " 1.83	298.2 " 1
4	1.21/1	-35	13	-166 " 1.0	-59.7 " 1.94	299.8 " 1
5	1.01/1	-35	13	-164.4 " 1.0	-59 " 1.96	288.2 " 1
6	1.31/1	-35	16	-164.4 " 1.2	-58.8 " 2.0	289 " 1
7	Sealed tube	-35	12	-167.7 " 1.1	-59.3 " 2.0	302.9 " 1
8	Sealed tube	-35	15	-164.4 " 1.2	-59.9 " 2.2	302.9 " 1
9	1.33/1	-35	14	-166 " 0.9	-61.3 " 1.93	295 " 1

Therefore the reaction is:-

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

The reaction between Me_2NCl and PCl_3 using a sealed tube.

0.0093 mol of Me_2NCl was distilled through the vacuum line onto 0.015 mol of PCl_3 inside a nmr tube which was adapted to be connected to the vacuum line (Figure 1) and it was surrounded by a bath of liquid nitrogen (-196°C). The nmr tube which contained the reactants was sealed off and left in a freezer at -35°C for 15 hours. The tube was cut into two pieces inside a dry box and the product was pushed towards the bottom of the tube by using a glass rod. The tube afterwards was stoppered and protected by parafilm. The nmr spectrum of the product showed the presence of three phosphorus species as shown in Table 1, experiment number 8. Inside the dry box the product was removed from the nmr tube and identified again by infra red spectroscopy which was also the same as the spectrum of the product of the typical experiment.

Abstraction of the mixture $\left[2(Me_2NPCl_3)^+ + PCl_6^- + Cl^-\right]$

The mixture was obtained from the product of the reaction between PCl_3 and Me_2NCl $\left[2(Me_2NPCl_3)^+ + PCl_6^- + Cl^- + Me_2NPCl_2\right]$ after the removal of Me_2NPCl_2 by washing the product with dichloromethane inside the dry box, and the nmr showed two peaks, one at -61.3 ppm corresponding to $2\left[Me_2NPCl_3\right]^+$ and the other at 298.2 ppm corresponding to PCl_6^- (Figure 2a).

The reaction between HCl and the mixture.

Gaseous HCl was condensed at a temperature of -196°C in a standard weight analysis cell connected to the vacuum line and containing 0.103 g of the mixture.

The reactants were left for 30 minutes at room temperature. The excess of HCl was distilled off and a white solid left inside the vessel.

It was found that there was no change in the mass, and the infra red spectrum showed no change from the infra red of the mixture before. Presumable the dimethylamino trichloro phosphonium cation was not large enough to form a thermally stable hydrogen dichloride at room temperature, and that hydrogen chloride was not a strong enough proton acid to cleave the phosphorus nitrogen bond.

The reaction between the mixture $[2(Me_2NPCl_3^+).\ PCl_6^-\ .\ Cl^-]$ and BCl_3, HCl

A sample of the mixture 0.384g was placed in a standard weight analysis cell inside the dry box. The standard weight analysis cell was connected to the vacuum line. Gaseous HCl was condensed inside the standard weight analysis cell (2ml), which was surrounded by liquid nitrogen (-196°C). The mixture dissolved slowly in liquid HCl.

BCl_3 was condensed in the vessel at -196°C. The liquid nitrogen surrounding the vessel was replaced by a cooled bath of toluene. The reactants were kept at -96°C for 35 minutes, afterwards the excess of HCl and BCl_3 were distilled off. A white solid was obtained and the vessel was weighed.

The weight analysis cell which contained the product was transferred to the dry box. The nmr and the infra red were studied. The nmr showed one peak only at -85.5 ppm which corresponds to the PCl_4^+ cation.(134) (Figure 5a). The infra red spectrum of the product (Figure 5b) showed peaks at 3200cm^{-1} due to N-H vibration and a peak at 650 cm^{-1} for

PCl_4^+ (136), and a broad peaks at 630 cm^{-1} and 720 cm^{-1} for the vibration of BCl_4^- (137). It was noticed that the peak which corresponded to the vibration (Figure 4b) of PCl_6^- (440 cm^{-1}) disappeared. This reaction was achieved twice as in the Table (2)

TABLE 2

Number	BCl_3/Mixture	Temperature °C	Time by minute	nmr of the product PCl_4^+
1	2.98/1	-96	35	-85 ppm
2	5/1	-96	30	-80.7 ppm

So the reaction is :-

$$(Me_2NPCl_3)_2Cl \cdot PCl_6 + 4\ HCl + 5\ BCl_3 \longrightarrow 2\ Me_2\overset{+}{N}H_2\overset{-}{B}Cl_4 + 3PCl_4^+\ BCl_4^- .$$

The reaction between dimethyl amino-dichlorophosphine and chlorine.

Chlorine was bubbled gently through 0.0187 moles of Me_2NPCl_2 dissolved in dry dichloromethane for five minutes under an atmosphere of dry nitrogen. When external cooling to 0°C took place a white solid product was formed. The reaction was repeated under the same conditions.

Purification of the product.

The volatiles were distilled from the vessel by a vacuum line. The product was hygroscopic material therefore, inside the dry box, samples were taken to study nmr and infra red. The nmr showed three peaks, a sharp one at -167.7 ppm due to Me_2NPCl_2, the second one was broad at -61.3 ppm corresponding to $[Me_2NPCl_3]^+$, and the third one was a broad peak at 298.2 ppm due to PCl_6^- , Table (3), Figures(3a, 4a)

The infra red spectrum of the product compared favourable with the infra red spectrum of the reaction between phosphorus trichloride and Me_2NCl (Figure 3b)

TABLE 3

Number	Time: Minutes	Temperature °C	nmr signal and integration ratio		
			$Me_2NPCl_3^+$	PCl_6^-	Me_2NPCl_2
1	5	0	ppm -61.3 2.08	ppm 298.2 1	ppm -167.7 0.98
2	8	0	-58 2.01	293.5 1	-166 1

The elemental analysis results are shown in the following table:-

The Element	Calculated data for $2Me_2NPCl_3^+ . PCl_6^- + Cl^- . Me_2NPCl_2$	Found
C	9.14	10.23
H	2.28	3.7
N	5.33	4.85
P	15.7	14.15
Cl	67.5	67.47

When Me_2NPCl_2 was removed from the product by washing it with dry dichloromethane in the dry box its nmr showed two peaks, one at -61.3 ppm due to $Me_2NPCl_3{}^+$ and another one at 298.2 ppm due to PCl_6^-, Figure (4a). A possible reaction is:-

$$3\ Me_2NPCl_2 + 4\ Cl_2 \longrightarrow (Me_2NPCl_3)_2\ Cl.\ PCl_6 + Me_2NCl.$$

since the chlorination of Me_2NPCl_2 was believed to be as the following:-

$$4\ Me_2NPCl_2 + 4\ Cl_2 \longrightarrow 4\ Me_2NCl + 4\ PCl_3$$

$$4\ PCl_3 + 3\ Me_2NCl \longrightarrow 2\left[Me_2NPCl_3\right]^+ + PCl_6^- + Cl^- + Me_2NPCl_2$$

The reaction between dimethyl chloramine and dimethyl amino dichloro phosphine.

2.1 mmol of Me_2NCl were distilled through the vacuum line and condensed on 2.32 mmol of Me_2NPCl_2 inside a standard weight analysis cell at - 196°C. The reactants were kept at 0°C for fourteen hours. By using a manometer connected to a vacuum line it was found that there was no volatile substances produced by the reaction.

The product was removed from the vessel in the dry box since it was highly hygroscopic material. The nmr showed one peak at -27.5 ppm, (Figure 6a). The infra red spectrum is shown in (Figure 6b). The micro analysis results for the compound $\left[(Me_2N)_2PCl_2\right]^+.\ Cl^-$ are shown in Table (4)

TABLE 4

The element	Theoretical data $(Me_2N)_2PCl_3$	Practical results.
C	21.3 %	21.72 %
H	5.32 %	5.53 %
N	12.42 %	12.38 %
P	13.75 %	13.42 %
Cl	47.19 %	46.75 %

The reaction is:-

$$Me_2NCl + Me_2NPCl_2 \longrightarrow [(Me_2N)_2PCl_2]^+ . Cl^-$$

The reaction between bis (dimethylamino)chlorophosphine and dimethylchloramine.

In a typical reaction 3.1 mmol of Me_2NCl was distilled into 1.5 mmol of $(Me_2N)_2PCl$ inside a standard weight analysis rotaflo at -196°C. The vessel which contained the reactants was kept in a freezer at -35°C for eighteen hours. A white solid was formed. On opening the tube, warmed to room temperature, no pressure was recorded on the manometer; since the product was highly hygroscopic material it was taken out of the vessel inside the dry box.

Purification of the product.

The product was washed by dry petroleum ether and kept inside a vacuum discator. The nmr of the product before being washed by dry petroleum ether showed two peaks, one at −159.6 ppm due to the excess of the reagent, and the other at −53.3 ppm, due to the product (Figure 7a) The infra red spectrum of the compound, is shown in (Figure 7b). The results of the elemental analysis are illustrated by Table (5).

TABLE 5

The elements	Calculated data for $(Me_2N)_3PCl_2$	Found
C	30.7	29.83
H	7.69	8.2
N	17.95	18.1
P	13.25	13.1
Cl	30.31	30.4

This indicates that the compound is $[(Me_2N)_3PCl]^+ . Cl^-$ and the equation for the reactions is:-

$$(Me_2N)_2PCl + Me_2NCl \longrightarrow [(Me_2N)_3PCl]^+ . Cl^-.$$

This reaction was performed six times, (Table 6)

TABLE 6

Number	Actual Mol ratio of the react. $(Me_2N)_2PCl/Me_2NCl$	Temp. ^oC	Time Hours	nmr by ppm
1	0.92/1	-35	14	-53.3
2	1/1	0	16	-51.6
3	1.07/1	0	12	-53.3
4	1.1/1	-35	15	-52.5
5	1/1	0	15	-53.3
6	0.97/1	-35	12	-53.3

Hydrolysis of the product $[(Me_2N)_3PCl]^+ . Cl^-$

The product was kept under an atmosphere of wet nitrogen for two weeks. The product $[(Me_2N)_3PCl]^+ . Cl^-$ became colourless liquid. The nmr showed one sharp peak only at -25.8 ppm due to $(Me_2N)_3PO$ (139) as is shown in Figure 9a.

The hydrolysis equation is:-

$$[(Me_2N)_3PCl]^+ . Cl^- + H_2O \longrightarrow (Me_2N)_3 PO + 2 HCl.$$

The reaction between dimethyl chloramine and tris (dimethyl amino) Phosphine.

0.008 moles of dimethyl chloramine were distilled through the vacuum line and condensed on 0.009 moles of $(Me_2N)_3P$ dissolved in 3ml of dry petroleum ether inside a standard weight analysis rotaflo, surrounded by a bath of liquid nitrogen -196°C.

The vessel was left for twenty hours at 0°C. A white solid product was formed. The solvent was pumped off. The gas infra red showed a spectrum of a mixture of petroleum ether and another substance which might have been tetramethyl hydrazine. The volatiles were condensed inside a vessel at -196°C then allowed to warm to room temperature in order to melt; for 3ml of the liquid a few drops of concentrated HCl were added. After five minutes the excess of HCl was pumped off, and a few drops of concentrated NaOH were added. Two aqueous layers were noticed. The supernatant layer was pumped off by a vacuum line. The gas infra red of the remaining liquid showed that the substance was tetramethyl hydrazine.

Purification of the solid product.

The product was a hygroscopic material therefore it was taken from the vessel inside the dry box and it was washed with dry petroleum. The nmr for the solid product of the typical reaction showed one peak only at -53.3 ppm which is equal to the position of the peak for the compound $[(Me_2N)_3PCl]^+ . Cl^-$ which was prepared by the reaction between $(Me_2N)_2PCl$ and Me_2NCl, Figure (8a).

The infra red spectrum of the product coincided with the infra red spectrum of the compound $[(Me_2N)_3PCl]^+ . Cl^-$. The result of the elemental analysis are shown in Table (7).

TABLE 7

The element.	Calculated data for $(Me_2N)_3PCl_2$	Found
C	30.7	31.4
H	7.69	8
N	17.95	17.93
P	13.25	12.8
Cl	30.31	30.1

The reaction was performed four times as shown by Table (8)

TABLE 8

Number	Actual mol. ratio for the reactants $(Me_2N)_3P/Me_2NCl$	Temp. °C	Time: Hours	nmr by ppm
1	1/1.98	-35	12	-53.2
2	1/1.86	0	15	-51.6
3	1/2.01	0	14	-53.3
4	1/1.94	0	12	-53.3

The results indicated that the reaction was:-

$$2\ Me_2NCl + (Me_2N)_3P \longrightarrow [(Me_2N)_3PCl]^+ . \bar{Cl} + Me_2N-NMe_2.$$

Hydrolysis of $[(Me_2N)_3PCl]^+ Cl^-$.

The substance was kept under a wet atmosphere of nitrogen for twelve days. It was converted to a colourless liquid which gave one peak by testing its nmr at -27 ppm. This corresponded to $(Me_2N)_3PO$ (138) chemical shift.

CHAPTER FOUR

A. THE REACTIONS OF DIMETHYL CHLORAMINE WITH PHOSPHORUS ACID ESTERS.

B. THE REACTIONS OF DIMETHYL CHLORAMINE WITH TRI COORDINATE AROMATIC PHOSPHINES.

A The reaction between trimethyl phosphite and dimethyl chloramine.

0.021 mol of dimethyl chloramine was distilled by the vacuum line into 0.014 mol of trimethyl phosphite at -196°C. The standard weight analysis rotaflo which contained the reactants was kept at -35°C for 18 hours. The contents of the vessel were allowed to warm to room temperature. The volatiles were pumped off on the vacuum line. The infra red spectrum of the most volatile fraction showed that it was methyl chloride, the less volatile fraction showed the presence of excess dimethyl chloramine as shown in Figure(8b).

The presence of MeCl was noticed by characteristic absorption bands at 716 cm^{-1},(139) and 745 cm^{-1}, and other two bands at 1340 cm^{-1} and 1370 cm^{-1}, as shown in Figure (10b). A colourless liquid was left in the vessel. On running the nmr of this liquid the spectrum showed one sharp peak at -8.2 ppm corresponding to a tetra coordinate phosphorus compound as shown in Figure (10a).

The thin film infra red of the product as shown in Figure(9b) showed the presence of a P=O bond by giving a characteristic absorption in the 1260 - 1250 cm^{-1} region(140), and the formation of $P - N\overset{C}{\underset{C}{<}}$ which was represented by a peak at 700 cm^{-1} (141).

The elemental analysis results agreed with the molecular formula $NMe_2PO(OMe)_2$.

Element	Calculated %	Found %
C	30.4	31.3
H	8.4	8
N	8.2	8.8
P	20.3	20.0

This reaction was repeated using the same technique where 0.013 mol of dimethylchloramine was condensed into a standard weight analysis cell containing 0.024 mol of trimethyl phosphite at -35°C for 17 hours. The infra red of the volatiles showed MeCl, and the nmr spectrum showed the 2 sharp peaks:- one corresponding to liquids at 140.2 ppm, (the starting material,) and the other peak at -8.8 ppm (the product). These observations can be explained by the following reaction:-

$$(MeO)_3P + Me_2NCl \xrightarrow{\hspace{2em}} Me_2N\overset{\nearrow O}{P}-(OMe)_2 + MeCl.$$

The preparation was attempted in a sealed nmr tube, but the pressure of methyl chloride burst the tube.

The reaction between Triphenyl phosphite and dimethyl chloramine.

In a typical reaction between triphenyl phosphite and dimethyl chloramine 0.0089 mol of dimethyl chloramine was distilled by using the vacuum line into the solution of 0.065mol of triphenyl phosphite dissolved into 2ml. of dry petroleum ether at -196°C in a standard weight analysis cell. The reaction was kept for 15 hours at -35°C and the contents of the vessel were allowed to warm to room temperature.

The gas infra red spectrum of the volatiles showed a mixture of dimethylchloramine and petroleum ether. The volatiles were pumped off; a white solid was left in the vessel and the vessel weighed. It was found that the reaction was completed by a moler ratio 1/1.007 $(PhO)_3P$ $/Me_2NCl$. The product was hygroscopic therefore all the precautions for handling such a substance were applied.

Purification of the product.

The product was washed by dry petroleum ether (60ml) inside the dry box and kept in a vacuum discator for fifteen minutes. A sample of the product was placed in a nmr tube and the spectrum showed one peak at 18.5 ppm as shown in Figure (11a). The elemental analysis results shown in the table agree well with the theoretical results for $(PhO)_3PNMe_2Cl$.

Element	Calculated %	Found %
C	61.6	60.4
H	5.4	6.1
N	3.6	2.9
P	7.9	8.2
Cl	9.1	9.4

The infra red spectrum showed absorption bands (Figure 11b) in the region 438 cm^{-1} - 565 cm^{-1} corresponding to P-Cl,(142) and another absorption band at 700 cm^{-1}, corresponding to $PNMe_2$. These results indicated that the reaction is:-

$$(PhO)_3P + NMe_2\,Cl \longrightarrow (PhO)_3\,P\,NMe_2 .\,Cl$$

where Ph = C_6H_5

B The reactions of dimethyl chloramine with tricoordinate aromatic phosphines.

1. The reaction between diphenyl chlorophosphine and dimethylchloramine.

0.0032 mol of dimethyl chloramine was distilled into a standard weight analysis cell containing 0.0015 mol of diphenyl chlorophosphine dissolved in 3 ml of dry petroleum ether at -193°C by using the vacuum line. The vessel was kept at -35°C for 17 hours. The contents of the tube were allowed to warm to the room temperature. The volatiles were pumped off. The gas infra red spectrum showed that it was the excess of dimethyl chloramine mixed with petroleum ether. The product was a white solid which, by exposure to the room temperature for twenty minutes, started to pyrolyse and changed in colour to yellowish white.

The nmr spectrum for the pyrolysed product showed a major peak at -70.9 ppm (Figure 12a) and a minor peak at -65 ppm, and a major peak at -37 ppm. This reaction was repeated using a different technique; the nmr tube with a B 14 cone adapted to a B 14 tap socket and a B 14 cone. Inside the dry box 0.0028 mol of Ph_2PCl dissolved in 2 ml of dry petroleum ether were placed inside the specially made tube. The contents of the tube were degasefied by using the vacuum line technique. 0.0017 mol of Me_2NCl was distilled into the tube at -196°C. The tube was kept at -35°C for eighteen hours. The product was allowed to warm to the room temperature for about three minutes; by this time all the volatiles were pumped off.

The infra red spectrum showed that it was petroleum ether. The white solid product was left inside the tube, cooled to -196°C, and the nmr measured as it warmed to room temperature. A run of fifty scans with three seconds delay produced a spectrum which showed two peaks, one sharp peak corresponding to the phosphorus starting material at -82 ppm and another broadish peak at -70.9 ppm due to the product. The product was allowed to be pyrolysed at room temperature for four hours and during that time no volatile species were produced (Figure 13a).

The reaction between the product of the above reaction and boron trichloride.

Inside the dry box 0.0015 mol of Ph_2PCl was syringed inside a standard weight analysis cell which contained 3 ml of dry petroleum ether. The contents of the vessel were degasefied. 0.004 mol of dimethyl chloramine was distilled into the vessel at -196°C by using a vacuum line technique. The cell, which contained the reactants was kept at -35°C for nineteen hours. The product was allowed to warm to room temperature for about three minutes and afterwards all the volatiles were pumped off. The vessel was weighed and the infra red spectrum of the volatiles showed that they were Me_2NCl and petroleum ether. The reaction was completed and from the masses the molecular ratio of the reactants was 1/1.006 Ph_2PCl/Me_2NCl. By using vacuum line technique a large excess of boron trichloride was distilled into the vessel at -95°C and then it was kept at the same temperature for three hours. The contents were allowed to warm to room temperature. The volatiles were pumped off and the infra red spectrum showed that this was the excess boron trichloride.

The vessel was re-weighed and there was an increase in mass. The product was stable at room temperature.

Purification of the product.

The product was very hygroscopic and was washed with 100 ml of dry petroleum ether in the dry box.

The nmr spectrum showed one peak at -71.8ppm, corresponding to a tetracoordinate cationic phosphorus species.

The elemental analysis results agreed with the molecular formula

$[Ph_2PClNMe_2]^+ + BCl_4^-$

where $Ph = C_6H_5$

%	Calculated	Found
C	40.26	39.5
H	3.8	4.5
N	3.35	2.9
P	7.43	7.48
Cl	42.4	41.6

The infra red spectrum(137) showed a broad absorption band at 656 cm^{-1}, corresponding to BCl_4^-.

These results indicate that the initial reaction is:-

$$Ph_2PCl + NMe_2Cl \longrightarrow Ph_2PClNMe_2^+ \ Cl^-.$$

and the reaction with boron trichloride is:-

$$[Ph_2PClNMe_2]^+ .Cl^- + BCl_3 \longrightarrow [Ph_2PClNMe_2]^+ .BCl_4^-$$

2. <u>The reaction between phenyl dichlorophosphine and dimethylchloramine.</u>

On the vacuum line 0.0024 mol of dimethylchloramine was condensed at -196°C into a vessel containing 0.0019 mol of phenyl dichlorophosphine which had been dissolved in 3 ml of dry petroleum ether in the dry box. The reaction was kept at -35°C for 20 hours.

The product was presumed to be hygroscopic so the usual means of moisture and air elimination were followed. The product was allowed to warm to room temperature and after twenty minutes a change in colour from white to greenish yellow was noted.

The nmr spectrum showed a major peak at -72.6ppm and other minor peaks at -66.2ppm, -35ppm and at 202ppm, (Figure 19a and 15a).

The vessel was connected again to the vacuum line but the manometer showed no increase in pressure.

This reaction was repeated using 0.011 mol of Me_2NCl to react with 0.0020 mol of $PhPCl_2$ dissolved in 2ml of dry petroleum ether. The modified nmr tube (Figure 5), which contained the reactants, was kept at -35°C for seventeen hours and the product was allowed to warm to room temperature for three minutes. Afterwards the volatiles were pumped off. The infra red spectrum of the volatiles showed that they were petroleum ether. The tube was cooled to -196°C and the nmr spectrum of fifty scans with three seconds delay was run. The spectrum showed one sharp peak at -160ppm, corresponding to the starting meterial and another broadish peak at -72.6ppm due to the product, (Figure 16a).

The reaction between the above product and boron trichloride.

The reaction between dimethylchloramine and phenyldichlorophosphine was performed using the same technique as above with excess Me_2NCl. A moler ratio 1/1.003 $PhPCl_2/Me_2NCl$ was found to have reacted. An excess of boron trichloride was distilled under vacuum into the standard weight analysis cell which contained the product at -95°C, and the cell was kept at -95°C for four hours. The contents of the vessel were allowed to warm to room temperature and the volatiles were distilled off. The infra red spectrum showed that it was boron trichloride. The cell was weighed and it was found that there was an increase in mass, but after about forty minutes the product started to decompose and change in colour at room temperature and the nmr spectrum showed (Figure 17a) one major peak at -72.6 ppm, and other minor peaks at -65ppm, -41ppm, -35.4ppm and at -25ppm.

The infra red showed a broad absorption band at 657 cm^{-1} due to BCl_4^- (137).

It was proposed that the cationic species synthesised above was $[PhPCl_2NMe_2]^+.Cl^-$. A second route to this cation was attempted via $PhPClNMe_2$.

The reaction between $PhPClNMe_2$ and $SbCl_5$.

Inside the dry box 0.016 mol of $SbCl_5$ was pipetted into a round bottomed flask containing 15ml of dry petroleum ether. 0.008 mol of $PhPClNMe_2$ (prepared as described in Chapter Two) was dissolved in twenty ml of dry petroleum ether and added to the solution of $SbCl_5$ drop by drop under and atmosphere of dry nitrogen, and with continuous shaking. The product was purified by washing with dry petroleum ether inside the dry box. The infra red spectrum of the product (Figure 14b) (whereCsI plates protected by polythene sheets were used) showed an absorption band at 337 cm^{-1} which is characteristic of $SbCl_6^-$.(143) Another infra red spectrum of the product (where NaCl plates were used) is shown in Figure 13b. The nmr spectrum showed one peak at -74 ppm which was the same chemical shift as for the product of the reaction between $PhPCl_2$ and Me_2NCl (the slight difference was due to the difference in the anion). (Figure 18a)

The reaction is:-

$$PhPClNMe_2 + 2\,SbCl_5 \longrightarrow [PhPCl_2NMe_2]^+ \,.\, SbCl_6^- + SbCl_3$$

and consequentyly the reaction between $PhPCl_2$ and Me_2NCl is:-

$$PhPCl_2 + Me_2NCl \longrightarrow [PhPCl_2NMe_2]^+ \,.\, Cl^-$$

and the formation of the tetrachloroborate:-

$$[PhPCl_2NMe_2]^+ \,.\, Cl^- + BCl_3 \longrightarrow [PhPCl_2NMe_2]^+ \,.\, BCl_4^-$$

3. The reaction between dimethylamino pheyl chlorophosphine and dimethyl chloramine.

Inside the dry box 0.004 mol of $PhPClNMe_2$ was syringed into a standard weight analysis cell containing 3 ml. of dry petroleum ether. The contents of the vessel were degassed by using the vacuum line technique. 0.0075 mol of dimethylchloramine was distilled into the vessel and the reaction was kept at -35°C for eighteen hours. The product was hygroscopic so moisture elimination was carried out.

The contents of the vessel were allowed to warm to room temperature and the volatiles were pumped off and found to be petroleum ether by infra red spectroscopy. The solid product was pale yellow.

Purification of the product.

Part of the product was purified by washing with 45ml. of dry petroleum ether and kept in a vacuum discator for twenty minutes. The other part was used to study the nmr which showed two peaks, one at -145 ppm corresponding to the phosphorus starting material and another peak at -66.2ppm due to the product of the reaction (Figure 21a)

The elemental analysis results agreed with the molecular formula $PhPCl(NMe_2)_2Cl$. as shown in the following table:

The element	Calculated	Found
C	44.96	43.89
H	6.36	7.07
N	10.40	9.74
P	11.61	11.50
Cl	26.56	26.98

The infra red spectrum, was as shown in (Figure 15b). These results indicated that the reaction is:-

$$Me_2NPPhCl + Me_2NCl \longrightarrow [(Me_2N)_2PPhCl]^+ . Cl^- .$$

CHAPTER FIVE

RESULTS AND DISCUSSION

nmr spectra

Infra red spectra

Bibliography.

The molecule of phosphorus trichloride did not undergo thermal or electrolytic dissociation under normal condition. Its chemical reactivity thus arose, primarily, from the strong polar P-Cl bonds, since the electronegativity of the phosphorus atom = 2.1 on Pauling's scale while the electronegativity of the chlorine atom, according to the same scale was 3.0. This difference in electronegativity let the electronic cloud be shifted towards the chlorine atom via the σ bond and caused partial positive charge on the phosphorus atom and thus made it prone to nucleophilic attack, and allowed donor-acceptor reactions.

The chemistry of dimethylchloramine is very diversified, not only because both the nitrogen and chlorine act as reaction sights, but also because of the different modes by which these functionalities react. Examples of the latter have been given in the first chapter. It is known that the bond between N-Cl in dimethylchloramine is not strong. This might be explained by the electronegativity of both the chlorine and the nitrogen being equal according to the Pauling scale (3.0); this bond is easily cleaved.

It was found that the reaction between phosphorus trichloride and dimethylchloramine was quite vigorous. The products were $Me_2NPCl_3^+ . Cl^-$., hexachlorophosphate and dimethyl amino dichlorophosphine.

A reasonable first step in the reaction of phosphorus trichloride with dimethyl chloramine might be an addition reaction to generate $Me_2NPCl_3^+ . Cl^-$. The reaction was quite fast, as a solid product was noticed after three minutes at -35°C. Some $Me_2NPCl_3^+$ cation reacted with the excess of phosphorus trichloride forming the tetrachlorophosphonium cation $\overset{+}{P}Cl_4 . Me_2N\overset{+}{P}Cl_3$ was reduced to dimethyl amino dichlorophosphine. The presence of dimethyl amino dichlorophosphine was shown by the nmr since a peak at -166ppm clearly showed its presence as did the infra red spectrum. The PCl_4^+ formed reacted with chloride ions forming hexachlorophosphate. The presence of hexachlorophosphate was shown by nmr as a peak at 298.2 ppm and by its infra red spectrum. It was therefore, proposed that the reaction between phosphorus trichloride and dimethyl chloramine proceeded in three steps:-

The first, which was fast and was an addition reaction to produce the phosphonium chloride salt:-

$$Me_2NCl + PCl_3 \longrightarrow [Me_2NPCl_3]^+ . Cl^-$$

The second step was the oxidation of PCl_3 to PCl_4^+ in a slow reaction:-

$$[Me_2NPCl_3]^+ + PCl_3 \xrightarrow{\text{slow}} Me_2NPCl_2 + PCl_4^+$$

The third stage was the nucleophilic reaction between PCl_4^+ and the chloride ions:-

$$PCl_4^+ + 2Cl^- \longrightarrow PCl_6^-.$$

Thus the stoichiometry for the reaction is:

$$4PCl_3 + 3Me_2NPCl_2 \xrightarrow{-35^{\circ}C} 2[Me_2NPCl_3]^+ + PCl_6^- + Cl^- + Me_2NPCl_2$$

In the reaction between $[2Me_2N\overset{+}{P}Cl_3 , PCl_6^- , Cl^-]$ and HCl. it was found that no change had occurred on removing the hydrogen chloride. This was clear from the lack of change in mass and the infra red spectrum. This implied that it was impossible for the hydrogen chloride to cleave the N-P bond. It has been suggested that the P-N bond can be easily cleaved by the action of hydrogen halides, and as an example of this, the reaction between tris dimethyl amino phosphine and hydrogen chloride to give bis dimethyl amino chlorophosphine can be considered:-(116)

$$(Me_2N)_3 P + 2HCl \longrightarrow (Me_2N)_2 PCl + (Me_2NH_2) .Cl.$$

It is known that $(Me_2N)_3P$ is considered as a Lewis base and its basicity was demonstrated by the stability of its borane adduct. The characteristic feature of this compound is the presence of a lone electron pair which is situated on each of the mutually adjacent principal atoms. Accordingly, Lewis acid can attack electrophilically either the phosphorus or the nitrogen atoms. In the case of a species like $Me_2N\overset{+}{P}Cl_3$ there is no lone pair of electrons on the phosphorus atom, but there is a lone pair on the nitrogen atom. The doner bonding power of the nitrogen atom is weakened by the interaction of its lone electron pair with a 3d orbital of the phosphorus atom.

The reaction with hydrogen chloride was repeated but using boron trichloride to increase the acidity of the system. The results showed that the bond between N-P was cleaved. Tetrachlorophosphonium cation was formed. The nmr spectrum of the product (Figure 5a) showed only one peak at -85.5ppm. The infra red spectrum showed the presence of PCl_4^+, $Me_2\overset{+}{N}H_2$, BCl_4^-, but not PCl_6^-.

An attempt was made to prepare the compound $[Me_2N\text{-}PCl_3]^+ . Cl^-$ by the chlorination of dimethyl amino dichloro phosphine with chlorine and by bubbling chlorine into a solution of the phosphine in dry petroleum ether. The product contained two phosphorus compounds, as shown by the nmr in Figure 3a, with an integration ratio of 2 : 1 at the positions of -61.3 ppm and of 298.2 ppm. The first peak corresponded to $Me_2N\overset{+}{P}Cl_3$ and the second one to PCl_6^-. A third peak on the integration ratio one corresponded to the phosphorus reagent dimethyl amino dichloro phosphine at -164.4ppm.

This indicated that Cl_2 cleaves the bond between the nitrogen and the phosphorus atom in $Me_2N\text{-}PCl_2$ and thus produces Me_2NCl and PCl_3 which reacts to give $2\ [Me_2NPCl_3]^+ + Cl^- + PCl_6^- + Me_2NPCl_2$.

The bromination of dimethyl amino dibromophosphine which has been reported generated dimethyl amino phosphorus tetrabromide.

The reaction between dimethyl amino dichloro phosphine and dimethyl chloramine was a vigorous exothermic one. An addition compound was generated $[(Me_2N)_2PCl_2]^+ \cdot Cl^-$. The nmr of the product showed only one peak at -27.5 ppm corresponding to tetra coordinate phosphorus cation.

Concerning this reaction it was noticed that the P-N bond in the compound $(Me_2N)_2PCl$ was left intact. Thus the chloramination of the phosphorus atom of the dimethyl amino dichloro phosphine produced the expected addition compound $[(Me_2N)_2PCl_2]^+ \cdot Cl^-$.

In the reaction between bis (dimethyl amino) chlorophosphine and dimethyl chloramine, chloramination took place at the phosphorus atom generating the addition product $[(Me_2N)_3PCl]^+ \cdot Cl^-$. The nmr of the product showed one peak at-53.3 ppm which corresponded to the phosphorus atom in $[(Me_2N)_3PCl]^+$ cation, and as mentioned before, the elemental analysis and the infra red spectrum agreed with the formulation. The nmr of the hydrolysis product of the compound showed one peak at -25.7 ppm, corresponding to $(Me_2N)_3PO$.

The reaction between tris (dimethyl amino) phosphine and dimethyl chloramine did not produce the expected addition product, the tetra kis (dimethylamino) chlorophosphonium ion. The product was $[(Me_2N)_3PCl]^+ Cl^-$ and tetra methyl hydrazine. It was clear that the bond between nitrogen and chlorine in dimethyl chloramine was cleaved, and as a result of this, double chlorination took place at the phosphorus atom to produce $(Me_2N)_3PCl^+ Cl^-$. The amination did not take place at the phosphorus atom, presumably because of steric hinderance. The attack on the phosphorus by the chlorine of dimethyl chloramine produced a negative polarity on the nitrogen atom. This could then attack a second dimethyl chloramine molecule to give tetra methyl hydrazine and chloride ion:-

$$(Me_2N)_3P + 2\ Me_2NCl \longrightarrow [(Me_2N)_3PCl]^+ \cdot Cl^- + Me_2N\text{-}NMe_2$$

The following are chemical equations for the reactions performed:-

1. $4\ PCl_3 + 3\ Me_2NCl \longrightarrow 2[Me_2NPCl_3]^+ + PCl_6^- + Cl^- + Me_2NPCl_2$

2. $Me_2NPCl_2 + Cl_2 \xrightarrow{\text{Fast}} Me_2NCl^- + PCl_3 \longrightarrow 2[Me_2NPCl_3]^+ + PCl_6^- + Cl^- + Me_2NPCl_2$

3. $2[Me_2NPCl_3]^+ + PCl_6^- + Cl^- \xrightarrow{HCl}$ no reaction

4. $[2Me_2N\overset{+}{P}Cl_3] + PCl_6^- + Cl^-] + 5\ BCl_3 + 4\ HCl \longrightarrow 2\ Me_2NH_2{}^+ . BCl_4^- + 3\ PCl_4{}^+ .\ BCl_4^-$

5. $Me_2NCl + Me_2NPCl_2 \longrightarrow [(Me_2N)_2PCl_2]^+ .\ Cl^-$

6. $Me_2NCl + (Me_2N)_2\ PCl \longrightarrow [(Me_2N)_3PCl]^+ .\ Cl^-$

7. $Me_2NCl + (Me_2N)_3P \longrightarrow [(Me_2N)_3PCl]^+ .\ Cl^- + Me_2N\text{-}NMe_2$

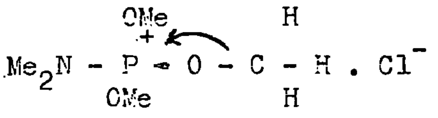
Dimethylchloramine reacted in different ways with triphenyl phosphite and trimethyl phosphite, an addition compound was formed by the reaction between dimethylchloramine and triphenyl phospite:-

$$(C_6H_5O)_3P + Me_2NCl \longrightarrow (C_6H_5O)_3\ PNMe_2Cl$$

It is obvious that chloramination took place at the phosphorus atom. The reaction of dimethylchloramine with trimethyl phosphite produced a covalent phosphorus compound with loss of methyl chloride:-

$$(MeO)_3P + Me_2NCl \longrightarrow Me_2NPO(OMe)_2 + MeCl.$$

It is likely that the reaction between trimethyl phosphite and dimethyl chloramine passes through an intermediate compound $[(RO)_3P.NMe_2]^+ .\ Cl^-$. This is followed by the chloride ion attacking the O-C bond in S_N2 reaction since $Me_2NPO(OMe)_2$ is a good leaving group.



$$Me_2N - \underset{OMe}{\overset{OMe}{\overset{+}{P}}} \leftarrow O - \underset{H}{\overset{H}{C}} - H\ .\ Cl^-$$

This was similar to the reaction between $CH_3 - Cl$ and OH^- to generate CH_3OH by S_N2 reaction.

In the case of the reaction between dimethyl chloramine and triphenyl phosphite the product was:-

$$Me_2NP(OPh)_3 \ . \ Cl$$

The chlorine anion cannot easily attack the bond between the benzene ring and the oxygen atom. The phenyl derivatives are known to be unreactive towards nucleophelic reactions such as:-

$+ Cl^- \longrightarrow$ No substitution reaction.

The reaction between diphenyl chlorophosphine and dimethyl chloramine generated an unstable product which was shown by the change in the intensity and in the number of peaks in the nmr spectrum (Figure 12a), where the major peak is at -70.0,/ppm. The product changed in colour from white to yellowish white, from yellowish white to yellow, and from yellow to a brownish-colour. The infra red spectrum showed a very broad undefined band. This reaction was repeated and the product was kept at -196°C. A quick scan on the nmr machine showed one peak at -70.0ppm corresponding to the product, and another one at -82ppm due to the starting material (Figure 13a).

Since it was found to be impossible to run a good infra red spectrum or to achieve the elemental analysis, an attempt was made to make the product of the reaction between Me_2NCl and diphenyl chlorophosphine react with boron trichloride as a Lewis acid. The product of this reaction was stable and the nmr spectrum showed one peak at 71.8ppm, (Figure 14a); the slight difference in the chemical shift was due to the difference in the anion. The infra red spectrum showed an absorption band at 656 cm^{-1} (Figure 12b) corresponding to

BCl_4^- (137). The elemental analysis was consistant with the molecular formula $Ph_2\overset{+}{P}ClNMe_2 . BCl_4^-$. The evidence indicated that the product of the reaction between dimethyl chloramine and diphenyl chlorophosphine is $[Ph_2PClNMe_2]^+ Cl^-$ and that the reaction was an addition one by chloramination onto the phosphorus atom.

The reaction between phenyl dichlorophosphine and dimethylchloramine produced a product which decomposed at room temperature. The nmr spectrum, (Figure 15a) showed a peak at -159ppm corresponding to the starting material. (One at -72.5ppm, a minor one at -66.2ppm, and one at -35.5ppm.) When this reaction was repeated again with the product kept at -196°C, the nmr spectroscopy was operated for a short time. It showed two peaks (Figure 16a), one at-151ppm corresponding to the phosphorus starting material, $PhPCl_2$, and another broad one (at -72.6ppm) due to the product. Again, as in the case of the product of the reaction between Ph_2PCl and Me_2NCl, it was impossible to obtain and good elemental analysis or an infra red spectrum. When this product was reacted with boron trichloride it was noticed to be unstable. The nmr (Figure 17a) showed one major broad peak at -72.6ppm and other minor ones at:- -66.2ppm, -41ppm, -35.4ppm and -25ppm. The infra red of this compound, (Figure 12b) showed a broad absorption band in the region between 700 - 650cm^{-1} corresponding to BCl_4^-.

As a second route to this cation dimethyl amino phenyl chlorophosphine was prepared and the nmr spectrum (Figure 20a) showed that it was pure by producing one peak at -141.8ppm. Dimethylamino phenyl chlorophosphine was reacted with $SbCl_5$ as a strong Lewis acid and as a chlorinating agent, similar to reactions performed by Ruff and his colleagues. Since this reaction would be expected to produce $Ph_2\overset{+}{P}Cl_2NMe_2.\overset{-}{Sb}Cl_6$ and $SbCl_3$, it was assumed that there would be one peak in the nmr spectrum which had the same chemical shift of the cationic species resulting from the reaction between $PhPCl_2$ and Me_2NCl. The product of the reaction between dimethy aminophenyl chlorophosphine ($PhPClNMe_2$) and $SbCl_5$ which was studied by the nmr technique and the spectrum (Figure 18a) showed one peak at -74ppm. The slight difference from the chemical shift of the product of Me_2NCl and $PhPCl_2$ was due to the difference in the anion. The infra red of the product (Figure 14a), showed an absorption peak at 337cm^{-1}, corresponding to $SbCl_6^-$.

The reaction between $PhPClNMe_2$ and $SbCl_5$ is:-

$$PhPClNMe_2 + 2SbCl_5 \longrightarrow PhPCl_2N\overset{+}{M}e_2 . SbCl_6^- + SbCl_3$$

Since the cationic species of this product has the same chemical shift as that of the reaction between Me_2NCl and $PhPCl_2$, this result can be considered a synthetical proof that the reaction between $PhPCl_2$ and Me_2NCl is:-

$$PhPCl_2 + Me_2NCl \longrightarrow [PhPCl_2NMe_2]^+ . Cl^-$$

Here again the reaction produced an addition compound where the phosphorus atom was chloraminated by dimethyl chloramine.

The decomposition products of $Ph_2PClNMe_2.Cl$, and $PhPCl_2NMe_2.Cl$ showed quite an interesting nmr spectrum. It was found that $Ph_2PClNMe_2.Cl$ decomposed at room temperature and that after five days the nmr spectrum showed the following peaks:-

-70.0ppm due to undecomposed part of the compound $[Ph_2PClNMe_2]^+ .Cl^-$,

-65ppm, corresponding to the Ph_2PNMe_2 (145) which may be generated,

-37ppm due to the Ph_2POCl (121).

Two more peaks appeared, by warming the tube at 118ppm and at 128ppm which were thought to be due to the two isomeric forms of $Ph_2PCl_4^-$. This may be formed by the chloronation of the starting material Ph_2PCl by the chlorine which is assumed to be formed from the—

decomposition of $Ph_2PNMe_2Cl_2$ to Ph_2PNMe_2. It was predicted that $Ph_2PCl_4^-$, which was not known(146), whould have lower chemical shifts than $PhPCl_5^-$ and that the transisomer would have a lower shift than the cis isomer. The nmr of the decomposition product of $PhPCl_2NMe_2Cl$ (Figure 19a) showed the following peaks:-

-158ppm due to the starting material,

-72.9ppm due to the undecomposed part of the compound,

-66.2ppm corresponding to $[PhPCl(NMe_2)_2]^+.Cl^-$, which had been prepared in the laboratory,

-35.5ppm, corresponding to $PhPOCl_2$(147), a peak at 202ppm, which corresponds to $PhPCl_5^-$ (148).

It's possible that a series of reactions between phenyl dichlorophosphine and dimethylchloramine produced $[PhPCl_2NMe_2]^+.Cl^-$; two molecules of the product interacted to produce $PhPCl_5^-$ and $[PhPCl(NMe_2)_2]^+$.

The reaction of dimethyl chloramine with dimethylamiophenyl chlorophosphine was an addition reaction and chloramination took place on the phosphorus atom and $[PhPCl(NMe_2)_2]^+.Cl^-$ was generated as a stable compound. Its nmr spectrum (Figure 21a) showed two peaks, one at -145ppm, corresponding to the starting material, and the other one at -66.2ppm corresponding to the product.

According to the previous work done on the reaction of dimethylchloramine and the tricoordinate phosphines mentioned before, it was found that dimethylchloramine reacted as an oxidation reagent in different ways:-

1. Oxidation by chloramination and chlorination:-

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

2. Oxidation by chloramination only.

This was the case with dimethylamino dichlorophosphine, bis(dimethylamino) chlorophosphine, tri-phenyl phosphite, diphenyl chlorophosphine, phenyl dichlorophosphine and dimethylamino phenylchlorophosphine:-

$$Me_2NPCl_2 + Me_2NCl \longrightarrow [(Me_2N)_2PCl_2]^+ . Cl^- .$$

$$(Me_2N)_2PCl + Me_2NCl \longrightarrow [(Me_2N)_3PCl]^+ . Cl^-$$

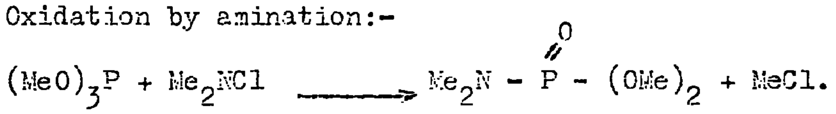
$$(PhO)_3P + Me_2NCl \longrightarrow [(PhO)_3PNMe_2]^+ . Cl^-$$

$$Ph_2PCl + Me_2NCl \longrightarrow [Ph_2PClNMe_2]^+ . Cl^-$$

$$PhPCl_2 + Me_2NCl \longrightarrow [PhPCl_2NMe_2]^+ . Cl^-$$

$$PhPClNMe_2 + Me_2NCl \longrightarrow [PhPCl(NMe_2)_2]^+ . Cl^-$$

3. Oxidation by amination:-



$$(MeO)_3P + Me_2NCl \longrightarrow Me_2N - \overset{O}{\overset{/\!/}{P}} - (OMe)_2 + MeCl.$$

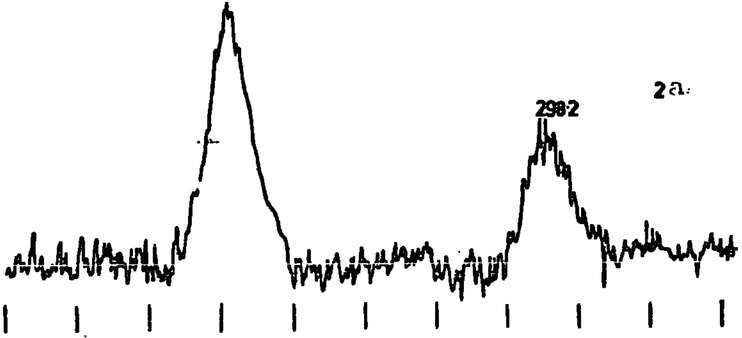
4. Oxidation by chloronation only:-

$$(Me_2N)_3P + 2\ Me_2NCl \longrightarrow [(Me_2N)_3PCl]^+ Cl^- + Me_2N\text{-}NMe_2$$

It was found that HCl was not able to attack the N-P bond in the mixture (2 $Me_2N\text{-}PCl_3^+$, PCl_6^- , Cl^-). This contradicted the generally known belief that hydrohalogen has the ability to cleave the bond between P-N. An interesting result was that Me_2NPCl_2, on chlorination, does not produce the expected addition product whilst $(Me_2N)_3P$, on chlorination and Me_2NPBr_2, on chlorination does. It is interesting to suggest further work in this field by reacting dichloromethylamine with the previous variety of tricoordinate phosphines.

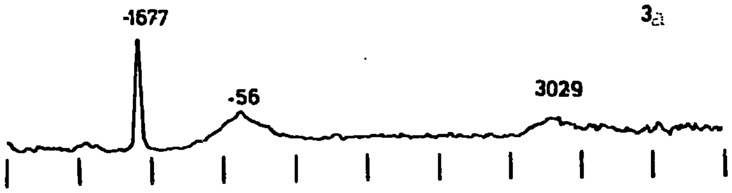
1 a

31pnmr spectrum of PCl_3, Me_2NPCl_2, $Me_2NPCl_3^+$ and PCl_6^-



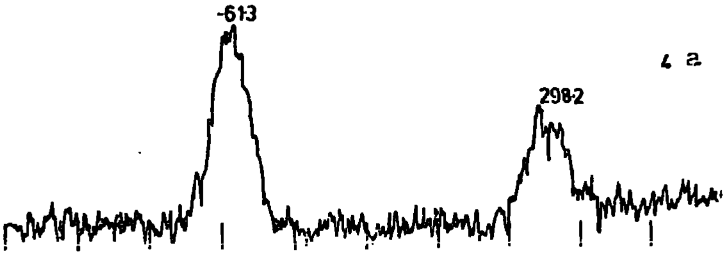
2 a

31pnmr spectrum of $Me_2NPCl_3^+$ and PCl_6^-



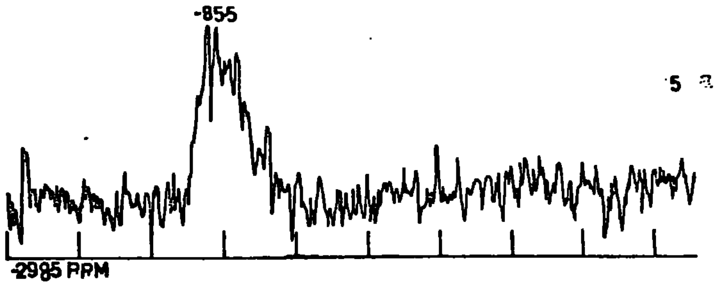
3 a

31pnmr of Me_2NPCl_2, $Me_2NPCl_3^+$ and PCl_6^-



4 a

31pnmr of $Me_2NPCl_3^+$ and PCl_6^-

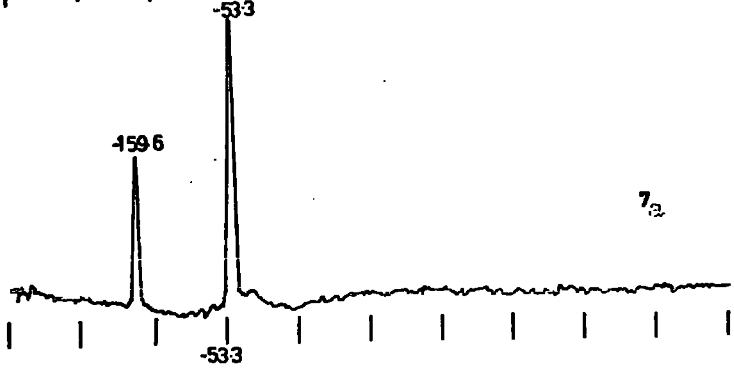


5 a

31pnmr of PCl_4^+

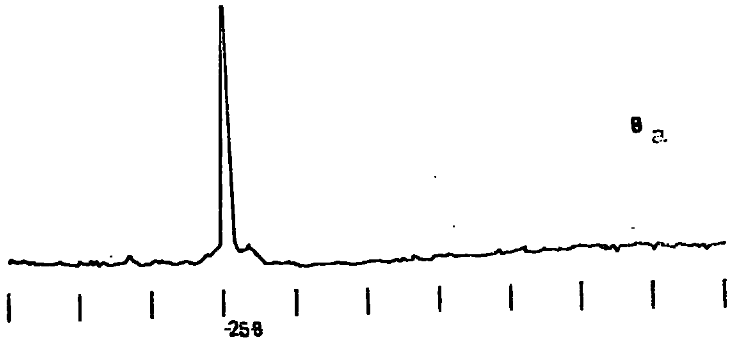
6a

31pnmr spectrum of $(Me_2N)_2PCl_2.Cl$



7a

31pnmr spectrum of $(Me_2N)_2PCl$ and $(Me_2N)_3PCl_2.C$

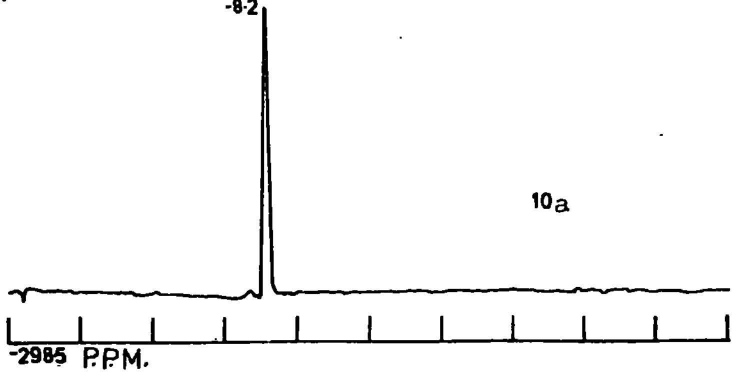


8a

31pnmr spectrum of $(Me_2N)_2PCl_2.Cl$

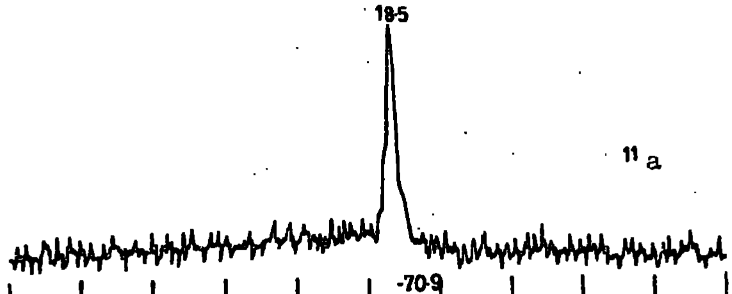
9a

31pnmr spectrum of $(Me_2N)_3PO$



10a

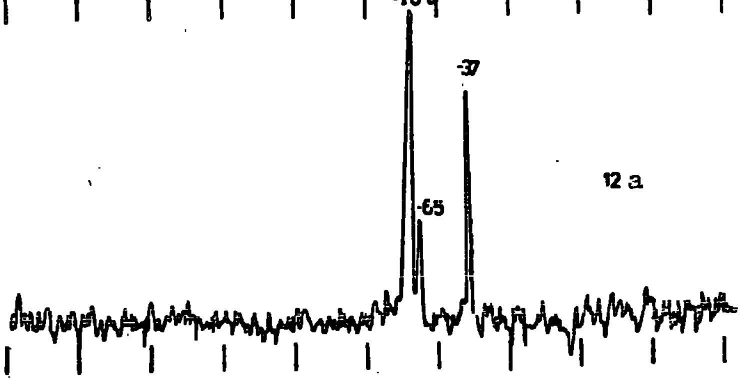
31pnmr spectrum of $Me_2NPO(OMe)_2$



11 a

31pnmr of

$(PhO)_3PNMe_2.Cl$

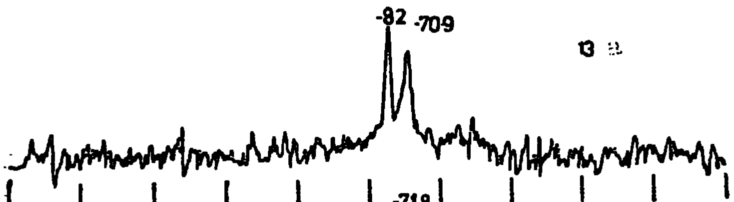


12 a

31pnmr of

$Ph_2PClNMe_2.Cl$

decomposition

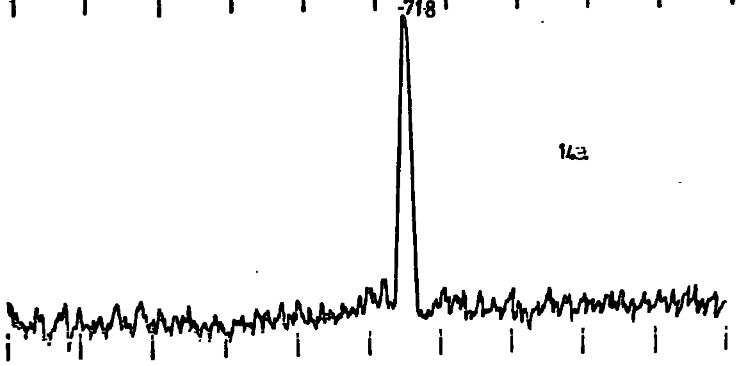


13 a

31pnmr of

Ph_2PCl and

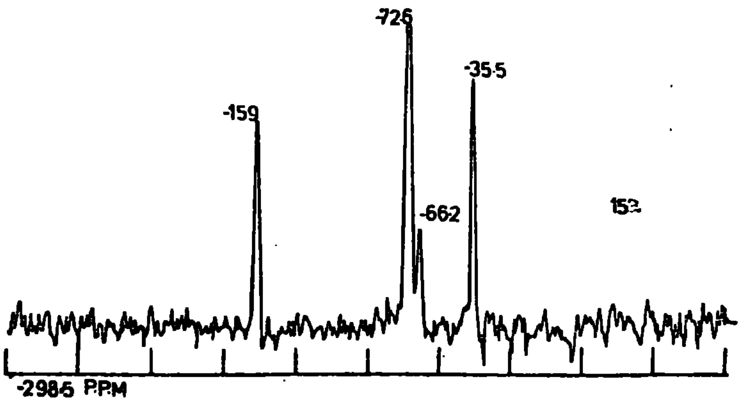
$Ph_2PClNMe_2.Cl$.



14a

31pnmr of

$Ph_2\overset{+}{P}ClNMe_2.\overset{-}{BCl_4}$

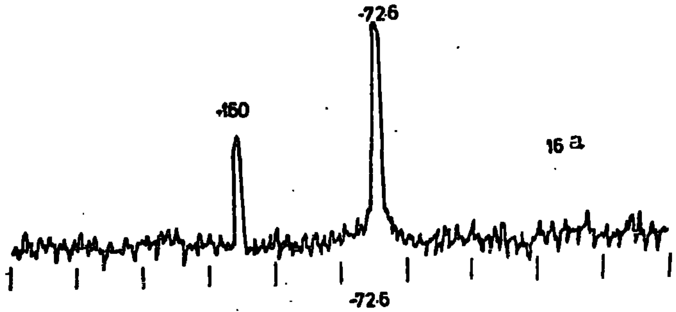


15a

31pnmr of

$PhPCl_2$ and $PhPCl_2NMe_2.Cl$.

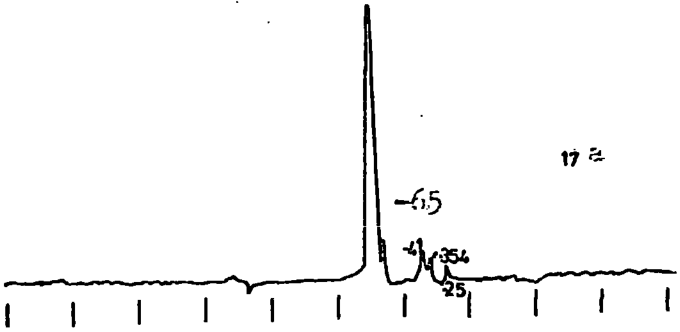
decomposition.



16 a

31pnmr spectrum of

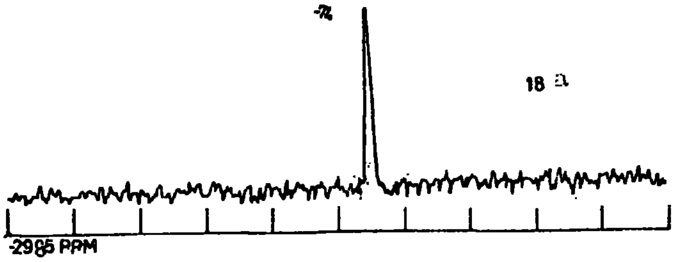
$PhPCl_2$ and
$PhPCl_2NMe_2 \cdot Cl$.



17 a

31pnmr spectrum of the decomposition product of

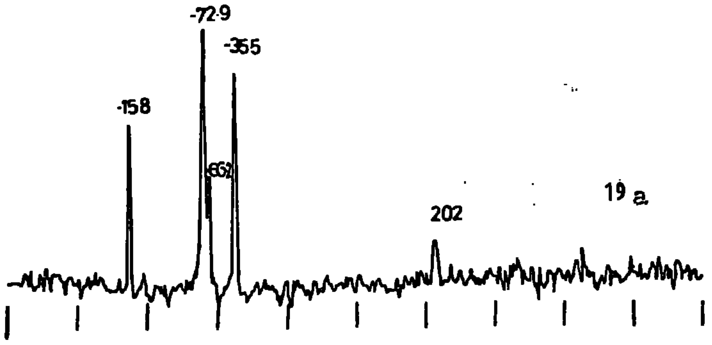
$Ph\overset{+}{P}Cl_2NMe_2 \cdot \overset{-}{B}Cl_4$



18 a

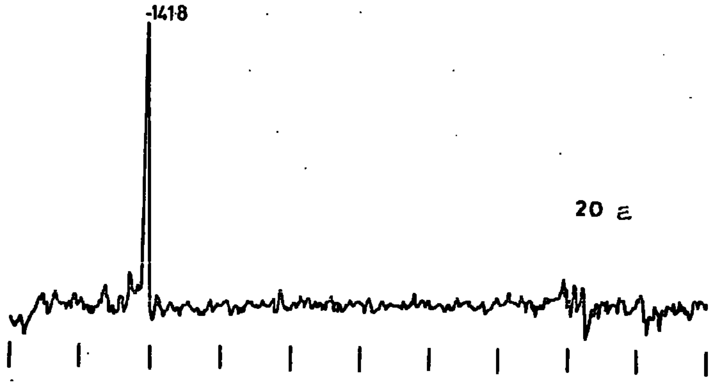
31pnmr spectrum of

$Ph\overset{+}{P}Cl_2NMe_2 \cdot \overset{-}{Sb}Cl_6$



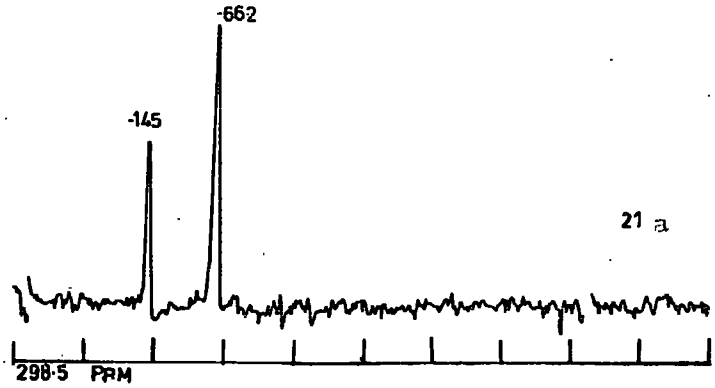
19 a

31pnmr spectrum of $PhPCl_2$ and $PhPCl_2NMe_2.Cl$ using 800 sweeps



20 a

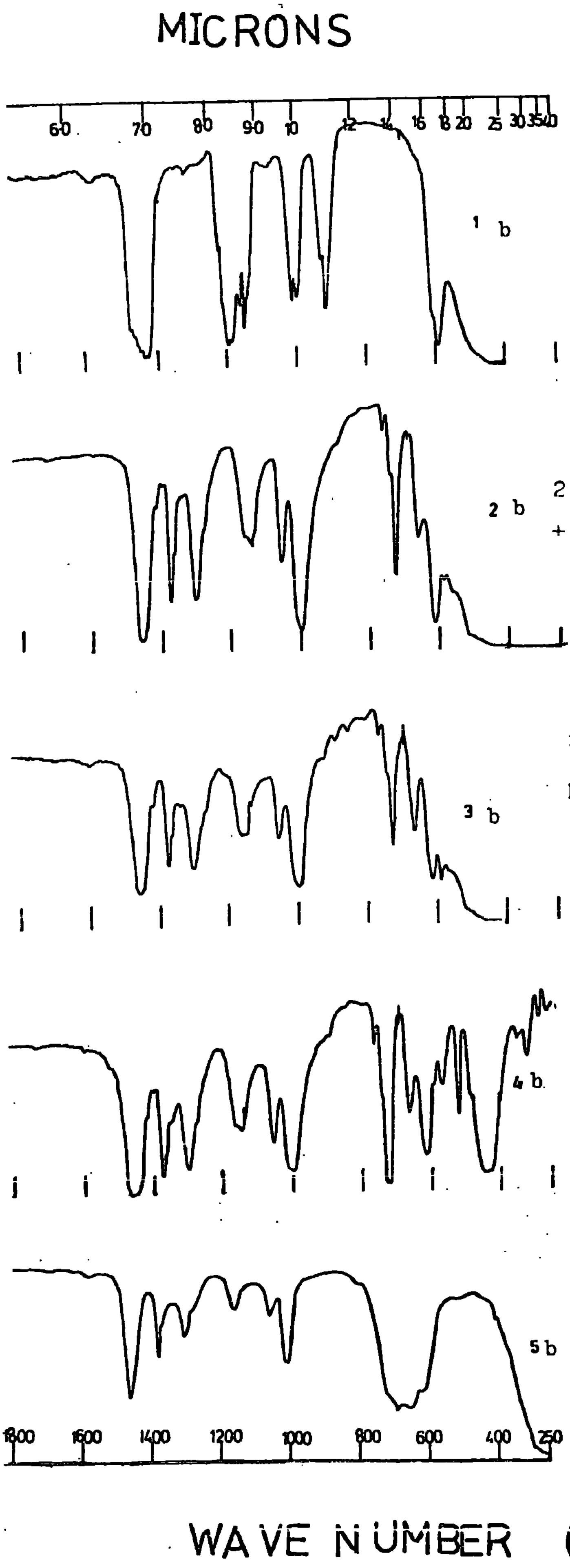
31pnmr spectrum of $PhPClNMe_2$.



21 a

31pnmr spectrum of $PhPClNMe_2$ and $PhPCl(NMe_2)_2.Cl$

The solvent used for the solid samples was Nujol



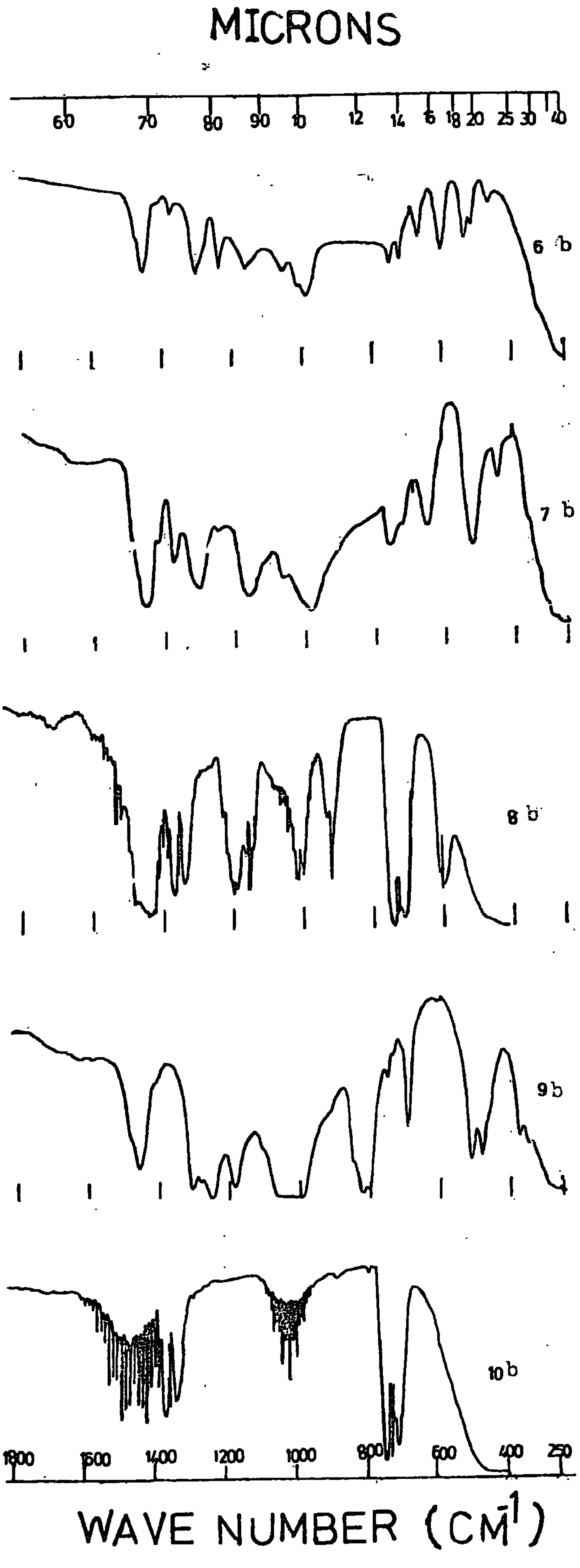
i.r. of
Me$_2$NCl

i.r. of
2 Me$_2$NPCl$_3^+$ + Cl$^-$ + PCl$_6^-$
+ Me$_2$NPCl$_2$

i.r. of
Me$_2$NPCl$_2$ chlorination

i.r. of
2 Me$_2$NPCl$_3^+$ + Cl$^-$ +
PCl$_6^-$ + Me$_2$NPCl$_2$

i.r. of
Me$_2$NH$_2$BCl$_4$ +
PCl$_4^+$.BCl$_4^-$



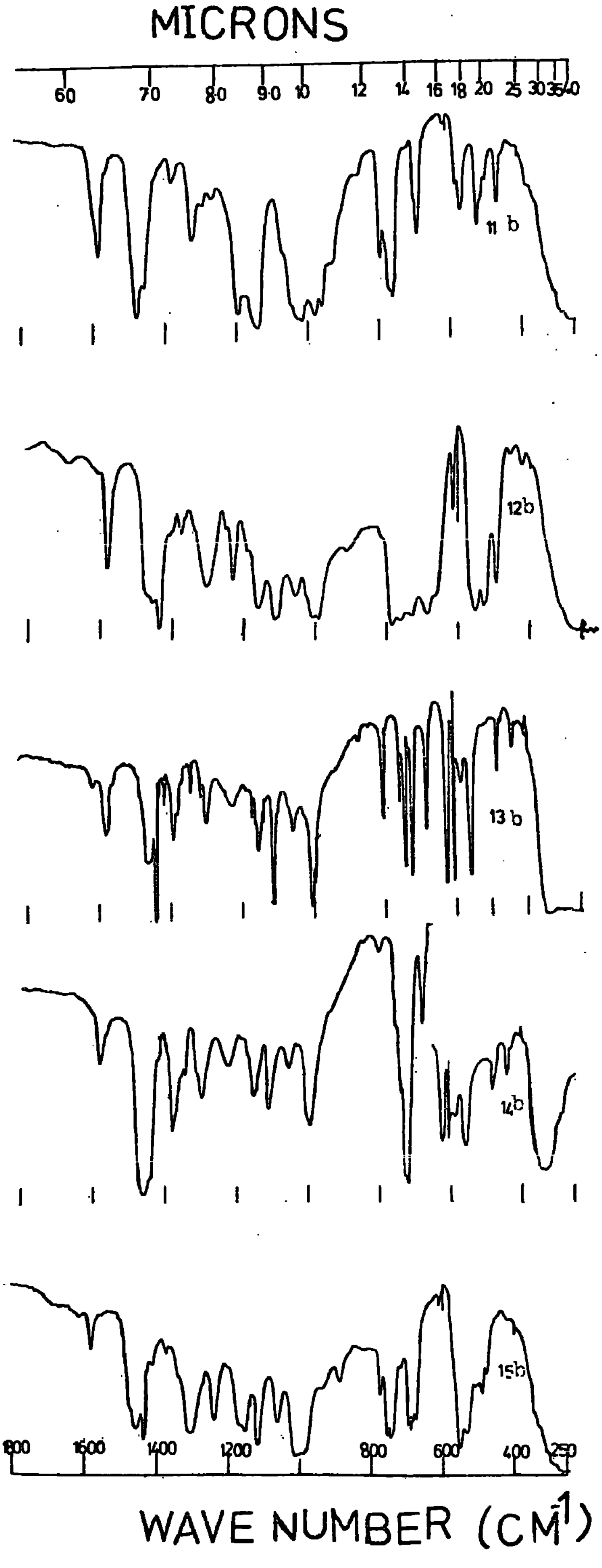
i.r. of $(Me_2N)_2P.Cl_3$

i.r. of $(Me_2N)_3PCl_2$

i.r. of $Me_2NCl + MeCl$

i.r. of $Me_2N\overset{O}{\overset{\|}{P}} - (OMe)_2$

i.r. of MeCl



i.r. of

$(PhO)_3PNMe_2.Cl$

i.r. of

$Ph_2\overset{+}{P}ClNMe_2\overset{-}{B}Cl_4$

i.r. of

$Ph\overset{+}{P}Cl_2NMe_2 . \overset{-}{Sb}Cl_6$

+ $SbCl_3$ Prep. 1

i.r. of

$Ph\overset{+}{P}Cl_2NMe_2.\overset{-}{Sb}Cl_6$

+ $SbCl_3$ Prep. 2

i.r. of

$PhPCl(NMe_2)_2.Cl$

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