RESEARCHES IN AMINOPHOSPHINES

by

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This thesis is the original work of the author except in those portions where it is specifically stated to the contrary.

It has not been submitted in whole or part for a degree at any other University.

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NOMENCLATURE.

The nomenclature of organophosphorus compounds is generally based on the Handbook for Chemical Society Authors (1960), this system being the result of an agreement between the British and American Societies. Using the Chemical Society recommendation, the compound Ph_2PNEt_2 would be called P:P-diphenylphosphinous N:N-diethylamide. It is felt, along with other authors, that this is not a satisfactory name for such a compound and that the tendency to describe such compounds as phosphine derivatives is more descriptive of their chemistry.

Compounds involving the P-N and N-P-N systems are considered to be phosphine derivatives: e.g.

Ph_2PNEt_2 is N:N-diethylaminodiphenylphosphine

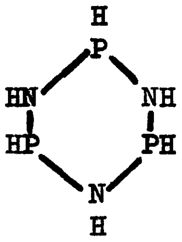
$PhP(NEt_2)_2$ is bisdiethylaminophenylphosphine

$PhP(NMe_2)NEt_2$ is diethylaminodimethylaminophenylphosphine

The two compounds reported which involve the P-N-P skeleton are considered to be tertiary amines: e.g.

$(Ph_2P)_2NMe$ is methylbis(diphenylphosphino)amine.

The naming of the compound $(PhPNEt)_3$ presents some difficulty. R. A. Shaw (1) has suggested that such compounds can be named as derivatives of the parent compound:-



cyclotriphospha (III) azane.

While this is a perfectly satisfactory method of nomenclature for this ring compound, it is felt that its relationship to the aminophosphines is not sufficiently emphasised and that the name Cyclotri-(N-ethylaminophenylphosphine) is more descriptive of the compound.

The nomenclature of the organophosphorus acids is complex, and although such compounds are only incidental to this work, a summary of their names is necessary: e.g.

$PhP(OH)_2$ - Phenylphosphonous acid.

Ph_2POH. - Diphenylphosphinous acid.

$PhPO(OH)_2$ - Phenylphosphonic acid.

$Ph_2PO(OH)$ - Diphenylphosphinic acid.

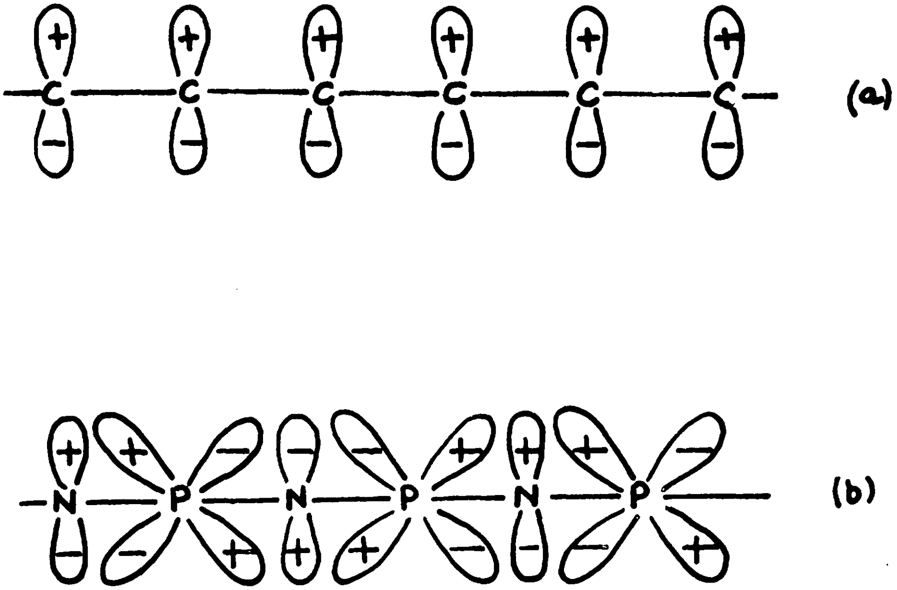
SURVEY.

Organophosphorus compounds are involved in some way in most of the fundamental life processes and, as such, have been present on the earth's surface since the beginning of life on our planet. The chemical recognition of this group of compounds dates only from a century and a half ago, although it is likely that organic compounds of phosphorus were in fact prepared by the alchemists in the Middle Ages. The planned study of the organic compounds of phosphorus can be considered to have commenced in 1820 with the investigation of the esterification of dehydrated phosphoric acid by Lassaigne.

A development of the study of organophosphorus compounds has been the growth of an interest in phosphorus - nitrogen compounds. This interest, which was initially a medical one, developed rapidly beyond the scope of the medical chemist, but in recent years, the search for potential anti-cancer agents, and the general study of life processes has led to a renewal of the initial connection with medical science.

The trend of the bulk of recent research work in phosphorus - nitrogen chemistry has been particularly towards those compounds which have been variously called phosphinic nitrides, phosphazenes or phosphonitriles. These names all refer to the system of empirical formula PR_2N. Interest in these compounds has two origins. Firstly, the compounds present an academic problem in which the constitution, structure and bonding require clarification, as does the general chemistry. The second reason is that these compounds

Fig. i.



Overlap schemes for the formation of delocalised π-bonds from p-orbitals (a) or from alternate d- and p-orbitals (b).

may have potential commercial applications, since, due to the high thermal stability of some of the phosphonitriles, they may be of use as fluids in hydraulics, heat transfer, flame-proofing, as well as in the manufacture of solid polymers, in which, in theory, the P-N system could replace the C-C skeleton in our present polymers.

It is both interesting and relevant at this stage to consider the development of our knowledge of the phosphonitriles.

The first phosphonitrile was isolated by Liebig and Wohler in 1834 (2); however, it was not until much later that the correct molecular weight and empirical formula was determined. The trimeric phosphonitrilic chloride $(PCl_2N)_3$ has received the most attention. In 1943 Brockway and Bright studied this compound by electron diffraction in the gas-phase (3) and found it to have a six-membered planar ring, in which all the interatomic distances were equal and intermediate in length between a single and a double phosphorus - nitrogen bond. It was postulated that there was delocalisation of electrons within the ring and thus the ring was aromatic in character. A number of derivatives of the eight-membered ring compound $(PCl_2N)_4$ have been shown to be non-planar (4), (5), and there is recent X-ray evidence (5), (6), for the non-planarity of the six-membered ring, $(PCl_2N)_3$, when examined in the solid phase.

The type of bonding which occurs in the phosphonitriles, compared to that of the carbon-carbon double bond is best illustrated diagrammatically as shown in Fig. 1.

In derivatives of pentavalent phosphorus such as the phosphonitriles, all the 3p orbitals are involved in the formation of four tetrahedrally disposed obitals. The energy level of the phosphorus orbitals is such that the 3d orbitals, with their particularly suited directional properties, are capable of overlapping with the 2p nitrogen orbitals, and thus forming π bonds.

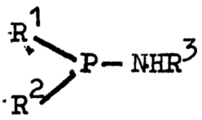
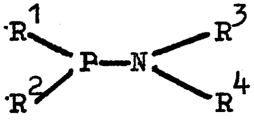
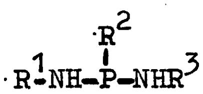
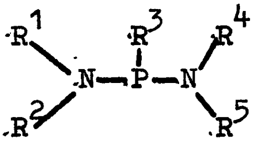
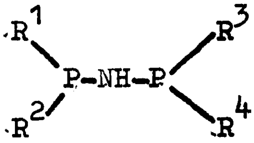
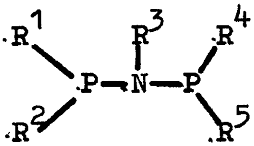
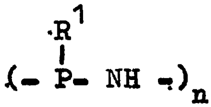
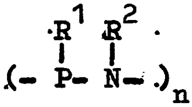
An important general feature is the tendency for elements such as silicon, phosphorus and sulphur to form polymer chains, rather than double bonds of the olefinic type. This state of affairs is illustrated by comparing the following pairs of compounds:-

CO_2	and	$(SiO_2)_n$
O_2	and	P_4O_6
N_2	and	white phosphorus P_4

Condensed products are the result of any attempt to prepare a phosphorus (III) analogue of a stable $C = C$ or $C = N$ monomer. This is exemplified by the fact that there is only one substantiated report of a $P(III) = N$ compound in the literature (7) viz. $(CH_3OC_6H_4N)_3P_2$. This inability of trivalent phosphorus to form double bonds is due to the fact that P(III) forms bonds involving pure p or hybridised sp^3 orbitals, and these are so diffuse that they are incapable of overlap with similar 3p and with 2p orbitals.

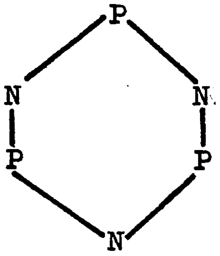
This thesis describes work in which a study of some simple tervalent phosphorus - nitrogen compounds has

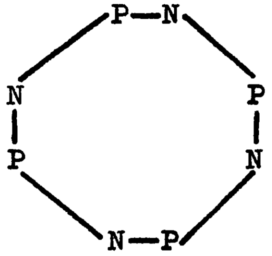
SIMPLE LINEAR P (III)-N SYSTEMS.

System	Abbreviation	System	Abbreviation
	P—NH		P-N
 $R^1NH-\overset{R^2}{P}-NHR^3$	NH-P-NH		N-P-N
	P-NH-P		P-N-P
 $(-\overset{R^1}{P}-NH-)_n$	$(P-NH)_n$	 $(-\overset{R^1}{P}-\overset{R^2}{N}-)_n$	$(P-N)_n$

been made. The aim of the research has been to investigate the possibility of building up tervalent phosphorus - nitrogen systems and to study the properties associated with such arrangements.

There are several possible combinations of P(III) with N, the simple linear systems being as shown opposite. Other more complex types would include such arrangements as P-N-P-P, N-P-P-N, P-N-N-P-P, etc. Ring systems could also arise, e.g.

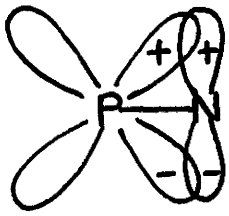




which would be derived from $(P-N)_n$. More complex ring systems can be envisaged with deviations from P-N alternation, or with cross linking, leading to 3-dimensional cage like structures. An example of the latter has been reported and will be referred to later.

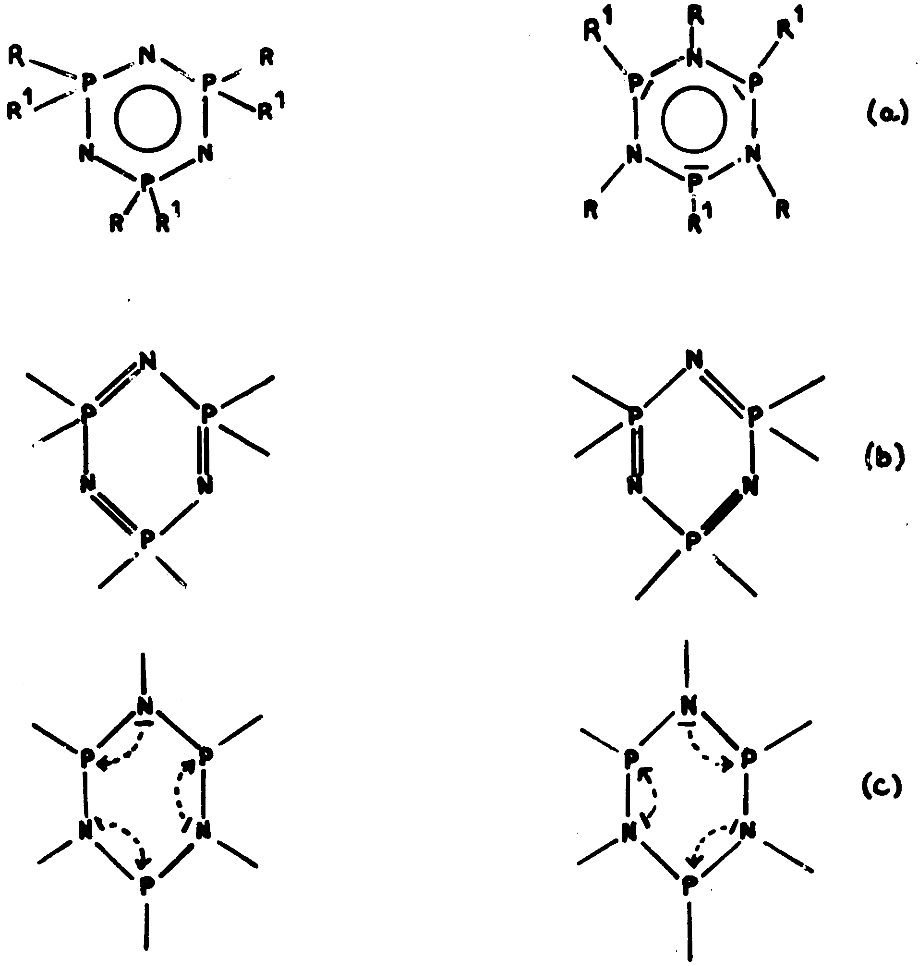
Stereochemical considerations will undoubtedly play a large part in determining the stability and ease of formation of many of the P (III)-N compounds. Bond angles would be expected to deviate somewhat from the tetrahedral angle associated with an sp^3 hybridised system through overcrowding and electronic effects. A model of $(Ph_2P)_2NMe$ shows clearly the severe overcrowding due to the bulky nature of the phenyl groups. The formation of rings must involve bond angle distortion and, or, non-planarity, even when relatively large numbers of phosphorus and nitrogen atoms are involved. Molecular detail, such as might be obtained from X-ray investigation of these compounds will be of the greatest value and one aim of this work is to provide material suitable for such studies.

The juxtaposition of phosphorus and nitrogen atoms leads to the possibility of electronic arrangements more complex than those associated with the phosphorus and nitrogen atom in individual simple phosphines or amines. Phosphorus is a potential acceptor of electrons by virtue of its relatively low-energy vacant 3d orbitals and nitrogen might be expected to be capable of donation of its unshared pair of electrons to one of these orbitals. This would involve overlap of the nitrogen 2p and phosphorus $3d_{xy}$ orbital, with the resultant formation of a π bond.



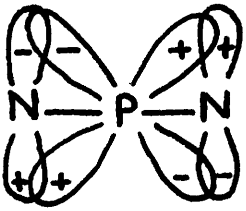
This bonding would have the effect of removing the nitrogen lone pair from external chemical interaction, such as its basic functions, methiodide formation, and its ability to act as a ligand atom, whilst the electron density on the phosphorus atom would be increased and the donor properties might thus be enhanced. This $p\pi - d\pi$ bond is evident in silicon - nitrogen chemistry, where its effect is in many ways similar.

Fig. ii.

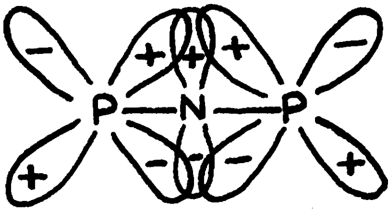


Possible electronic arrangements for (R_2PN).

Where the phosphorus atom is between two nitrogen atoms, the effect could operate simultaneously with both nitrogen atoms, although it might be that the effect is confined to only one of the nitrogen atoms.



Where the nitrogen is between two phosphorus atoms, the nitrogen donation could be confined to one phosphorus atom, or be shared. The latter would effectively produce a bonded system extended over the three atoms.



In linear $(P\text{-}N)_n$, the effect could likewise be localised to alternate P-N pairs or could be extended along the chain.

Ring $(P\text{-}N)_n$ also offers the possibility of intermolecular donor-acceptor bonding. There is an interesting parallel between the $(P\text{-}N)_n$ rings and the phosphonitriles in that they possess the same empirical formula, but with the substituents differently situated. Fig. iia illustrates the simple structures of the six-membered rings for both P(V) (phosphonitriles) and P(III) in which the

TABLE OF SOME REPORTED P (III)-N COMPOUNDS.

Compound.	Reference.
Cl_2 PNHR. (R=Et, Bu^{iso}, phenyl)	14
Cl_2 $PNEt_2$	10
Cl_2 PNR_2. (R=Et, Pr, Bu^{iso}, amyl)	14
Cl_2 PNPhMe.	14
Me_2 $PNMe_2$.	9
$(CF_3)_2$ PNH_2.	12
$(CF_3)_2$ PNHMe.	12
$(CF_3)_2$ $PNMe_2$.	12
(C_2H_5O) P $(NC_5H_5)_2$.	14
Et_2 $PNEt_2$.	10
Bu_2 $PNEt_2$.	10
$(Cyclohexyl)_2$ $PNEt_2$.	10
PhPCl (NEt_2).	15
PhP $(NC_5H_{10})_2$.	13
ClC_6H_4P $(N_5H_{10})_2$.	14
Ph_2PNHBu^t.	11
Ph_2PNH (2:6 EtC_6H_3).	11
Ph_2PN $(CH_2CH{=}CH_2)_2$.	11
Ph_2PN $(CH_2)_5$.	11

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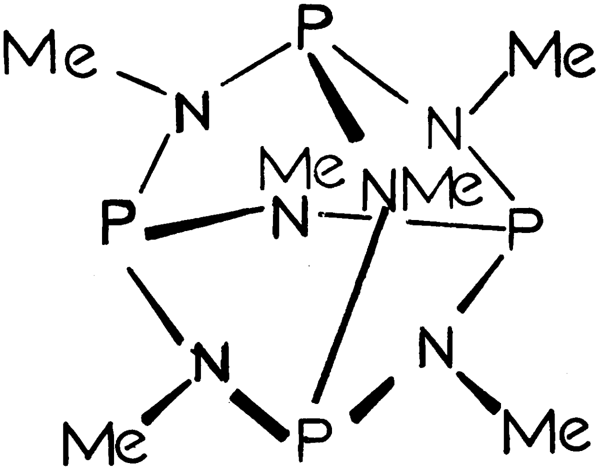
electrons are shown to be completely delocalised, as in benzene. Fig. iib shows the two possible electronic structures for the phosphonitriles and Fig. iic the corresponding $(P-N)_n$.

A list of the most important tervalent phosphorus - nitrogen compounds reported in the literature is given in the table opposite. The most outstanding worker in the field of organophosphorus - nitrogen chemistry must undoubtedly be Professor Carl Arnold August Michaelis, who was obviously a brilliant experimentalist, with a tremendous intuition for his subject, and who prepared, during the period 1890 - 1905, a vast number of compounds. The interpretation of some of his results can now be revised on the basis of modern chemical theory. Unfortunately, several authors have quoted interpretations directly from the papers of Michaelis without a re-assessment of the experimental evidence in the light of current theory. This has led to a considerable amount of confusion, which has prompted the following opinion expressed by Kosolapoff (8) in his book on organophosphorus chemistry:-

"Many of the rather interesting reactions used in the synthesis and interconversions of this family are very imperfectly understood. For this reason, a considerable confusion exists in the literature on this subject to the present day. The elimination of such confusion is extremely necessary, and its accomplishment is one of the great challenges in the field of organophosphorus compounds."

Van Wazer comments further (16) that Kosolapoff might have added that some of the structures assigned to a number of organic compounds involving phosphorus - nitrogen

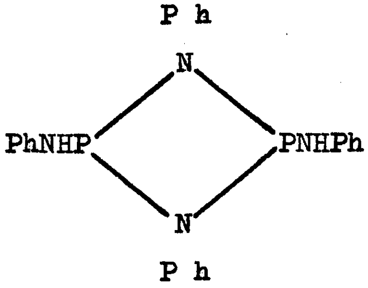
Fig. iii.



Product from reaction of PCl_3 and $MeNH_2$.

bonds are patently absurd!

After the work of Michaelis and his colleagues, there is a gap of about forty years in which there appears to be no published work of significance. In 1946 Grimmel and his co-workers (17) prepared the compound of empirical formula PhNHPNPh by reacting stoicheiometric quantities of aniline and phosphorus trichloride, the halide being added to the amine. Thus, the halide is effectively being added to an excess of amine. The compound was shown, by molecular weight determinations in dioxan, to be dimeric, and to it was assigned the ring structure shown, confirming the results of Michaelis.



After this thesis work was started, Sisler and Smith (11) published the investigation of derivatives of monoaminophosphine, in which various aminodiphenylphosphines were synthesised (see table). As a direct result, the investigation of the simple (P-N) compounds was curtailed.

Holmes and Forstner (18) reported the reaction between phosphorus trichloride and methylamine carried out at low temperature, using the amine as solvent. From this, they obtained the interesting product shown in Fig. iii. This is another example of a reaction in which condensation has taken place, not as in carbon chemistry, by a controlled catalyzed reaction, but by spontaneous condensation of an unstable monomer.

Burg and Slota (9) prepared the compound N:N-dimethylaminodimethylphosphine, Me_2PNMe_2, from the chlorocompound, Cl_2PNMe_2, and methylmagnesium bromide. The report of this preparation is of particular interest, since it discusses the properties of the P (III) - N bond.

There are a limited number of ways in which a phosphorus (III) - nitrogen bond can be formed. The first and most common method, which has been used throughout this work, is by interaction of a halophosphine with a primary or secondary amine, resulting in the elimination of hydrogen chloride, which is removed by reaction with excess amine. Benzene, ether or the amine itself have been found to be suitable solvents for this reaction.

The second method of formation of the phosphorus (III) - nitrogen bond, which has only been reported in one instance (11) is by reaction of an alkali metal salt of an amine with a halophosphine.

Two routes to amino-organophosphines are available, differing in the sequence of formation of the P-N and P-C bonds. Initial P-N bond formation leads to aminohalogenophosphines, which can be converted to amino-organophosphines by suitable organo-metallic reagents. This reaction can be complicated by the attack of the P-N bond by the organo-metallic compound leading to low yields of the aminophosphine (9). Initial P-C bond formation requires the synthesis and separation of organohalogenophosphines, which are not always readily handled or purified. Initially, synthesis of the phenylchlorophosphines in this work was undertaken, but subsequently it was possible to obtain these compounds commercially. The ready availability of these reagents has to some extent determined the compounds so far investigated, however, not wholly, since the phenyl group is the obvious first choice as a substituent by reason of its tendency to yield solid products and, more important, the stability to oxidation of aryl compounds is markedly greater than that of the alkyl.

There are varying reports as to the precautions which have to be taken to eliminate side reactions due to the presence of moisture and oxygen. Although throughout this work, unless otherwise specified, reactions have been carried out in dry solvents under an atmosphere of dry nitrogen, there is no indication that such precautions are essential.

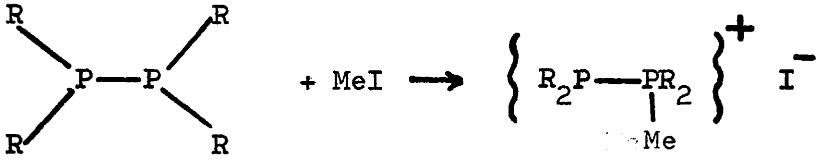
CHAPTER I.

THE PREPARATION AND PROPERTIES OF N:N-DIETHYLAMINODIPHENYLPHOSPHINE

INTRODUCTION.

The compound N:N-diethylaminodiphenylphosphine, Ph_2PNEt_2, is analogous to the derivatives of both diphosphine and hydrazine and, as such, it might be expected to have similar properties.

In the diphosphines and the hydrazines there are two neighbouring atoms, each possessing a lone pair of electrons. In theory, each of these atoms should be capable of donating its lone pair to an electrophilic centre. However, it has been shown that for these compounds only one electron pair is donated in quaternisation reactions. Thus, for tetralkyldiphosphines reacting with methyl iodide, only a 1:1 adduct has been obtained (10).



$R = C_2H_5, C_4H_9.$

It appears that the uptake of methyl iodide is restricted to one mole due to the presence in the 1:1 adduct of a positive charge, which reduces the basicity of the neighbouring atom. Treatment of tetracyclohexyldiphosphine with an excess of methyl iodide results in scission of the phosphorus - phosphorus bond according to the equation:-

$$\begin{tikzcd} R_2P\text{-}PR_2 + MeI \arrow[r] & R_2PI \arrow[d, "MeI"] & + & MePR_2 \arrow[d, "MeI"] \\ & R_2MePI_2 & & (R_2Me_2P)\ I \end{tikzcd}$$

Diamines form only 1:1 methyl iodide adducts if there is conjugation between the donor atoms (20), although 2:1 adducts form in other cases.

From these properties of the diphosphines and the diamines we might expect N:N-diethylaminodiphenylphosphine to be capable of acting only as a monobase and to function as a monodentate ligand. Further, the phosphorus to nitrogen bond might undergo scission under certain conditions with alkyl halide.

In the synthesis and study of tervalent phosphorus - nitrogen compounds carried out by Michaelis, Burg and Slota, and by Sisler and Smith the phosphorus to nitrogen bond has been formed by the reaction of a phosphorus (III) halide with an amine by the elimination of hydrogen chloride. An exception to this is the preparation of N:N-diphenylaminodiphenylphosphine, Ph_2PNPh_2, from diphenylchlorophosphine and the sodium salt of diphenylamine.

This chapter describes the preparation of N:N-diethylaminodiphenylphosphine, the identification of this compound, and a study of some of the derivatives which it forms with methyl iodide, cuprous iodide and mercuric iodide. The study of the monoaminophosphines was not as full as originally intended, in view of the publication of Sisler and Smith covering the preparation and properties of a variety of diphenyl derivatives.

RESULTS AND DISCUSSION.

The preparation of N:Ndiethylaminodiphenylphosphine.

When diphenylchlorophosphine was reacted with an excess of dry diethylamine in sodium dried benzene, an almost quantitative yield of diethylamine hydrochloride was obtained. The benzene solution yielded a waxy solid from which, on distillation in vacuo, a liquid, b.p. 126°/0.1 mm., was obtained. This liquid had traces of crystals present in it, but on redistillation a clear liquid was obtained which analysed for N:N-diethylaminodiphenylphosphine. The reaction had thus gone according to the equation:-

$$Ph_2PCl + 2Et_2NH \longrightarrow PH_2PNEt_2 + Et_2NH.HCl.$$

However, the final yield of product corresponded to only 38% of that expected from the above equation, and it must be assumed that secondary reactions take place, possibly during distillation. This is supported by the fact that as well as the liquid product described above, a solid was obtained which tended to sublime at 150°.

Subsequent work showed that compounds with phosphorus - phosphorus bonds were obtained as by products in certain circumstances in the preparation of some phosphorus - nitrogen compounds. It is possible that such a side reaction is the cause of the low yield of N:N-diethylaminodiphenylphosphine in the above preparation.

The properties of N:N-diethylaminodiphenylphosphine.

N:N-Diethylaminodiphenylphosphine is stable to aerial oxidation and, as such, can be handled quite conveniently under normal atmospheric conditions, although its typically phosphine smell makes it unpleasant. It is a colourless liquid, which did not crystallise on cooling to -170°, was insoluble in hot and cold water and appeared to be unattacked by hot and cold aqueous sodium hydroxide. It is soluble in benzene, chloroform, ether, petroleum ether and alcohols.

On addition of carbon tetrachloride to the liquid, a green colour was produced, rapidly changing to yellow and then to reddish-brown. The reddish-brown product separated as an oil. This type of addition reaction between carbon tetrachloride and phosphines (21), phosphites (22) and amines (23) has been commented upon by other workers, but its exact nature is still unknown. Recently Babinowitz and Marcus (24) have postulated a mechanism for the reaction between triphenylphosphine and carbon tetrachloride, for which the net reaction is:-

$$CCl_4 + 2Ph_3P \longrightarrow (Ph)_3PCl_2 + Ph_3P{=}CCl_2.$$

This reaction with N:N-diethylaminodiphenylphosphine and carbon tetrachloride, appears to be even more complex and has not been pursued further.

The addition of dilute hydrochloric acid to the aminophosphine lead to complete solution and, on removal of excess reagent and water, a residue, whose infra-red spectrum indicated the presence of a mixture of diphenylphosphinic acid, Ph_2PO_2H, and diethylamine hydrochloride was obtained.

Extraction of this product with benzene left a residue which was identified as diethylamine hydrochloride, while the benzene fraction yielded diphenylphosphinic acid. There was no evidence from the infra-red spectrum for the presence of a P-H bond in this mixture. For comparison, the hydrolysis of diphenylchlorophosphine was carried out, the only product being diphenylphosphinic acid, diphenylphosphine being absent. This is not what would be expected on the basis of the equation often quoted (8) for this type of hydrolysis using alkali

$$2Ph_2PCl + 2H_2O \longrightarrow Ph_2PH + Ph_2PO_2H + 2HCl.$$

It would thus appear that aerial hydrolysis of diphenylchlorophosphine goes according to the equation:-

$$Ph_2PCl + H_2O \xrightarrow{[O]} Ph_2PO_2H + HCl.$$

The net reaction for the hydrolysis of N:N-diethylaminodiphenyl:phosphine can be expressed as:-

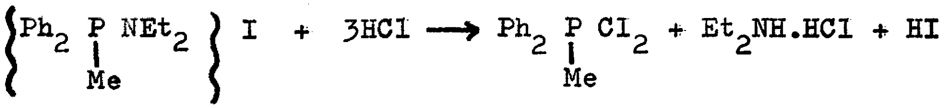
$$Ph_2PNEt_2 \xrightarrow[\text{in air}]{\text{Aqueous HCl.}} Ph_2PO_2H + Et_2NH.HCl.$$

The compound N:N-diethylaminodiphenylphosphine oxide has been reported in the literature and was prepared by Michaelis by the reaction of N:N-diethylaminooxychlorophosphine with bromobenzene, in the presence of sodium. An attempted oxidation of N:N-diethylaminodiphenylphosphine with ethanolic hydrogen peroxide yielded only diphenylphosphinic acid, which indicated that there had been cleavage of the phosphorus - nitrogen bond in this reaction rather than oxidation.

The reaction with methyl iodide.

When methyl iodide was added to N:N-diethylaminodiphenylphosphine in the absence of solvent, there was a reaction of some vigour, and it was more convenient to prepare the adduct in ether solution. Even in the presence of a large excess of methyl iodide, onlya 1:1 adduct could be obtained. This is in accord with the work of Issleib and Seidel (10) on the diphosphines and with that of Burg and Slota on the aminophosphine (9). The location of the methyl group in the adduct is of interest in relation to the relative basicity of the P and N atoms. Burg and Slota resolved this problem for N:N-dimethylaminodimethylphosphine methiodide by preparing its mercuric iodide adduct, hydrolysing this with alkali, and showing that only dimethylamine was produced, thus indicating the presence of the methyl group on the phosphorus.

The position of the methyl group in N:N-diethylaminodiphenylphosphine can be determined in a similar fashion by the action of dry hydrogen chloride on the phosphorus - nitrogen bond to produce halophosphine and the corresponding amine hydrochloride. The action of hydrogen chloride on the aminophosphine methiodide gave a benzene insoluble residue which was shown by analysis and infra-red spectroscopy, to be diethylamine hydrochloride, no diethylmethylamine hydrochloride being present. It follows that the methyl group must be attached to the phosphorus and the reaction of the methiodide with hydrogen chloride goes according to the equation:-



$$\left\{ Ph_2\underset{Me}{\overset{}{P}}NEt_2 \right\} I + 3HCl \longrightarrow Ph_2\underset{Me}{P}Cl_2 + Et_2NH.HCl + HI$$

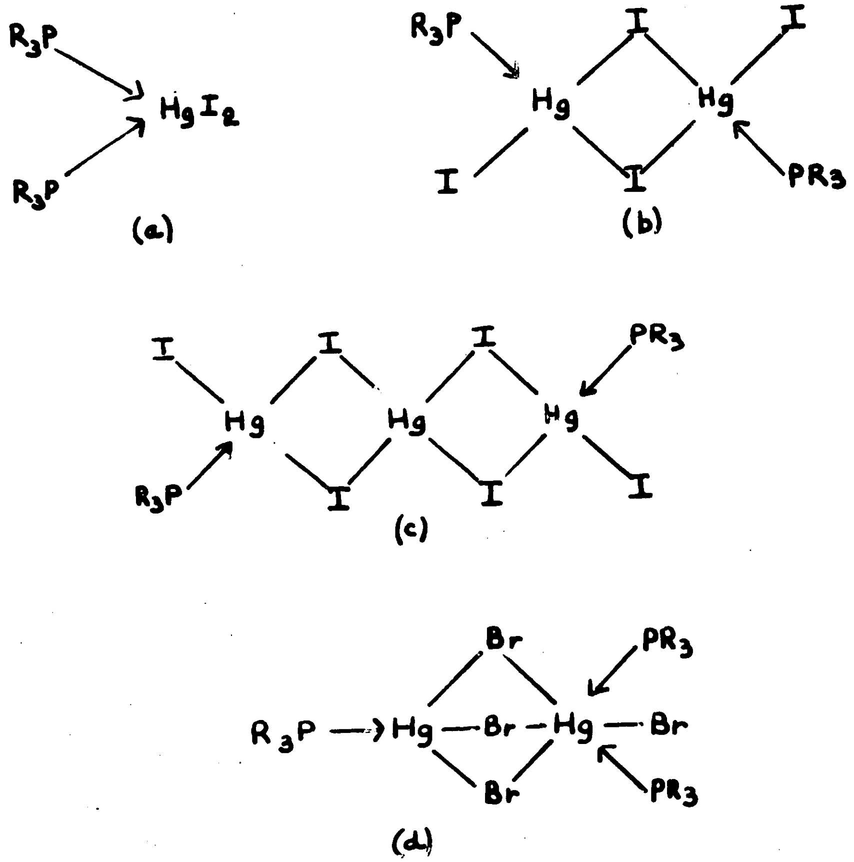
In N:N Diethylaminodiphenylphosphine the phosphorus is thus more basic than the nitrogen, and acts as the only basic atom, the compound being capable of forming only a 1:1 adduct with methyl iodide. The argument depends on the assumption that there is no possibility of acid catalyzed migration of the methyl group prior to cleavage of the phosphorus to nitrogen bond. There is no indication in the literature that any such migration takes place and, based on present knowledge, the premise for the above argument seems reasonable.

Quaternary phosphonium salts generally decompose on pyrolysis with the formation of a tertiary phosphine and an organic halide. Ingold and his colleagues have shown (25) that the order of cleavage is such that in the case of N:N diethylaminodiphenylphosphine methiodide we would expect methyl iodide to be evolved and the aminophosphine to be reformed. However, on heating in vacuo, to 200° the methiodide yielded no volatiles, and a water-soluble, oily residue remained. The mode of decay of the quaternary aminophosphine methiodide is therefore different from that of simple phosphine salts.

The reaction with mercuric iodide.

The tertiary phosphines, in contrast to the tertiary amines, have strong donor properties with certain acceptors, particularly those in which the back donation of electrons from filled shells to the vacant d orbitals is possible. In particular, the phosphines form complexes readily with mercury (II) and a large number of mercuric iodide - phosphine complexes are known. These compounds can be prepared either by mixing the correct

Fig. iv.



Mercuric iodide adducts of phosphines.

stoicheiometric quantities of phosphine and mercuric iodide, or by adding the correct quantity of mercuric iodide or phosphine to another adduct. The adducts are generally crystalline, readily soluble in organic solvents and, as such, are readily purified.

A detailed study of the adducts formed by tertiary phosphines and mercuric iodide was carried out by Evans, Mann, Peiser and Purdie (25). Four series of adducts were investigated, viz:-

Name	Class	Formula
Dihalogenobisphosphinemercury	A	$(R_3P)_2.HgI_2$
Dihalogenobisphosphine-u-dihalogenodimercury	B	$(R_3P)_2(HgI_2)_2$
Bisphosphinetrismercuric halide	C	$(R_3P)_2(HgI_2)_3$
Tetrahalogenotrisphosphinedimercury	D	$(R_3P)_3(HgI_2)_2$

Stable compounds of class A were shown to be formed by triaryl phosphines, but not, apparently, by trialkyl phosphines. It has been shown that tetrahedral 4-covalency is favoured by mercury in its adducts, and the tetrahedral structure shown in Fig. iva was assigned to this class of adducts.

The compounds in class B, those of empirical formula $R_3P.HgI_2$, were shown to be dimers, having the structure shown in Fig. ivb. In this structure there are two bridging iodine atoms, and the phosphine molecules are trans to one another. This is not a planar structure, the mercury retaining its tetrahedral 4-covalency.

In class C, the compound $(Et_3As)_2.(HgI_2)_3$ was given the possible structure shown in Fig. ivc, on the basis of some preliminary investigations.

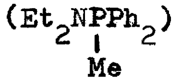
The structure shown in Fig. ivd. was given to compounds of class D, i.e. $(R_3P)_3(HgI_2)_2$.

Whilst there is no reason to doubt the structural assignments made above, it should be noted that of the four structures given, A has been made by analogy with the structure of the corresponding cadmium iodide complex, B by a rigorous X-ray analysis, C on the grounds that the molecule does not possess a centre of symmetry, and D by analogy, once again with the corresponding cadmium compound, whose structure was assigned on a preliminary investigation, which has not been further reported upon. Further confirmation of these structures, particularly the last two (C and D), is long overdue.

The adducts prepared from mercuric iodide and the amino- and bisaminophosphines have been confined to classes A and B. For N:N-diethylaminodiphenylphosphine only the 1:1 adduct was prepared, and as this was insoluble in benzene, nitrobenzene and sulpholane, further investigation of the molecular complexity was difficult without a more time consuming investigation. By analogy with the simple phosphines, this 1:1 complex might be expected to possess the bridged structure of class B above.

The mercuric iodide adducts of the methiodides.

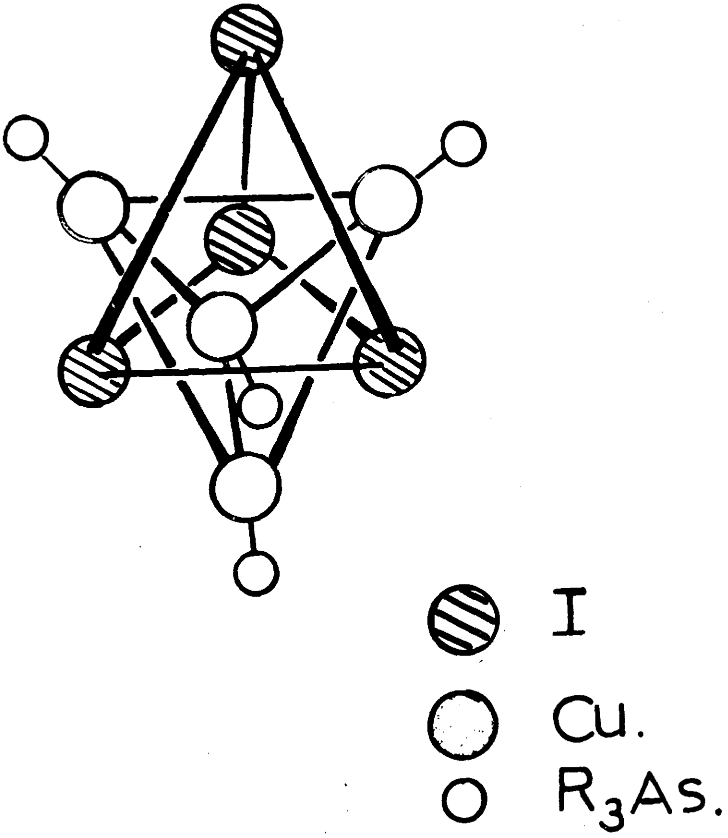
Deacon and West (27) have recently investigated iodomercurate complexes with Group V quaternary iodides and have shown that tetramethylphosphonium iodide forms three types of complexes with mercuric iodide, viz:- tetraiodomercurates $M_2(HgI_4)$, tri-iodomercurates $M(HgI_3)$ and pentaiodomercurates $M(Hg_2I_5)$. These compounds were prepared by mixing stoicheiometric quantities of the reactants, either in acetone or aqueous potassium iodide solution, the latter method being particularly suitable for the tri- or tetraiodomercurates.

The preparations both for N:N-diethylamino:diphenylphosphine and for the bisaminophosphines (Chapter II) have involved the addition of an excess of mercuric iodide, dissolved in ethanol, to an alcoholic solution of the quaternary phosphonium iodide. In this way the compound N:N-diethylaminomethyldiphenylphosphonium tri-iodomercurate,  $(\mathrm{Et_2N}\underset{\substack{|\\ \mathrm{Me}}}{\mathrm{P}}\mathrm{Ph_2})\ \mathrm{HgI_3}$, a greenish crystalline solid was prepared. No evidence for a tetraiodomercurate was obtained.

The reaction with cuprous iodide.

Copper (I) phosphine and arsine complexes have been the subject of study by several workers (28), (29), in particular by Coates and his colleagues (30).

Fig. v.



Tetrameric cuprous iodide adduct of phosphines.

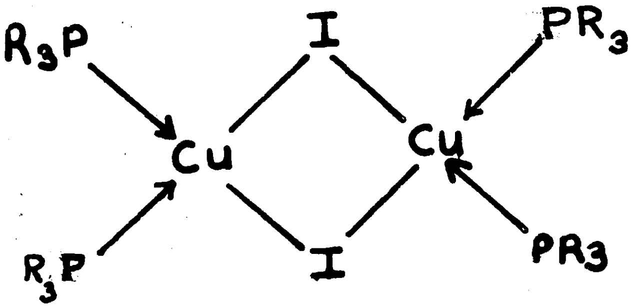
and by Chiswell and Livingstone (31). These adducts are also similar to those recently reported between phosphites and cuprous halides (32).

Two types of adducts are reported between phosphines and cuprous iodide; the 1:1 adduct and the 2:1 adduct. The 1:1 adduct would appear to give the copper a co-ordination number of 2. Mann and his co-workers carried out a detailed X-ray analysis of the corresponding arsine compound, with which the phosphine compound is strictly isomorphous, obtaining the tetrameric structure shown in Fig. v. The tetrameric natures of the arsine and the phosphine complexes has been confirmed by cryoscopic molecular weight determinations.

The 2:1 adduct has not received as much attention, from a structural point of view as has the 1:1 adduct. However, Arbuzov reports (29) the preparation of a compound of empirical formula $(PEt_3)_2.CuI$, which on warming lost triethylphosphine to yield the 1:1 compound. Mann and his colleagues concluded (28) that this compound has the bridged structure shown in Fig. vi.

Coates and his co-workers (30) prepared further 2:1 phosphine - cuprous iodide adducts. In the case of the 2:1 silver iodide complexes these workers showed that the molecular weight in boiling benzene solution corresponded to a monomeric form. The suggestion by Mann and his colleagues that the copper (I) 2:1 adducts are 4-co-ordinated bridged structures is subject to doubt. This doubt is supported by recent work on the phosphites (32) in which the molecular weights of several bis-phosphite

Fig.vi.



Mann's proposed structure for
2:1 cuprous iodide adduct of phosphines.

cuprous halides have been shown to be in keeping with that for monomeric adducts.

For N:N-diethylaminodiphenylphosphine only the 1:1 adduct with cuprous iodide has been prepared. This was formed by adding the correct stoicheiometric weight of aminophosphine dissolved in ethanol to an aqueous potassium iodide solution of cuprous iodide. The adduct, which precipitated immediately, was recrystallised from ethanol and was readily soluble in benzene, in which it was shown by cryoscopic molecular weight determinations to be approximately tetrameric. The molecular weight of 1620, compared to a theoretical value of 1788 for the tetramer, may indicate that there is some dissociation.

SUMMARY.

N:N-diethylaminodiphenylphosphine and the following derivatives have been prepared:-

Compound	m.p.
$Ph_2PNEt_2.MeI$.	112 - 115°
$Ph_2PNEt_2.MeI.HgI_2$	116 - 118°
$Ph_2PNEt_2.HgI_2$.	188 - 190°
$(Ph_2PNEt_2.CuI)_4$.	225 - 227°

N:N-diethylaminodiphenylphosphine, unlike similar compounds reported by Sisler and Smith (11), appears to be stable to air. A study of its adducts and its other addition compounds shows that this compound behave primarily as a tertiary phosphine, which is in accord with our own ideas of the phosphorus (III) - nitrogen bond discussed earlier, and with the results obtained by Burg and Slota (9) for N:N-dimethylaminodimethylphosphine.

It is reasonable to assume that the reactions of this aminophosphine could be extended to the general reactions of phosphines. Thus it is to be expected that it would readily form adducts with halogens, with sulphur, and would be oxidised, using, for example, manganese dioxide, to the corresponding oxide.

The infra-red spectrum of N:N-diethylaminodiphenylphosphine is as follows:-

3030s, 2928s, 2835s, 1950w, 1875w, 1805w, 1755w,
1720w, 1660w, 1586m, 1474s, 1460s, 1432s, 1372s,
1342m, 1328m-sh, 1306m-sh, 1292m, 1180s, 1088s, 1070s,
1026s, 1000m, 920s, 848w, 788m-s, 743s, 724m,
698s, cm.$^{-1}$

A discussion of the infra-red spectra of aminophosphines will be given later in Chapter II.

CHAPTER II.

THE PREPARATION AND PROPERTIES OF BISN:N-DIALKYLAMINOPHENYLPHOSPHINES

INTRODUCTION.

There is no report in the literature of the preparation of any bis N:N-dialkylaminophenylphosphines* and a natural development of the study of the simple tervalent phosphorus - nitrogen system is an investigation of the N - P - N system.

Such compounds can be readily prepared by the reaction of phenydichlorophosphine and a secondary amine and can be studied by the methods used for the monoaminophosphine.

In the N - P - N system there is a possibility that the basicity of the phosphorus, compared to its basicity in the monoaminophosphines, will be noticeably different. There is also the possibility that the nitrogen atom may not be equally affected by the proximity of the phosphorus atom and that, as a result, two distinct nitrogen atoms may be distinguished.

This chapter reports the preparation of a series of aliphatic bisaminophosphines, their properties, and a discussion of the adducts which they form with methyl iodide, mercuric iodide and, for bis N:N-diethylaminophenylphosphine, with cuprous iodide.

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* Since the completion of the text of this thesis, the compound bisdimethylaminophenylphosphine has been reported by Evleth et al., J. Org. Chem., 1962, 27, 2192. The details of its properties are in close agreement with those reported here.

RESULTS AND DISCUSSION.

The preparation of bis N:N-dialkylaminophenylphosphines.

The symmetrical bis N:N-dialkylaminophenylphosphines were prepared by adding phenyldichlorophosphine to an excess of the appropriate amine, both in either anhydrous benzene or anhydrous ether, under dry nitrogen. The precipitation of the hydrochloride starts immediately on the addition of the halophosphine, however the reactants were stirred for several hours to produce an easily filterable precipitate. Filtration, followed by removal of solvent gave a crude product whose infra-red spectrum indicated the absence of amine hydrochloride. Further precipitation of amine hydrochloride, however, often took place after the initial bulk of hydrochloride had been separated. Even after double fractional distillation up a 14" Fenske column, samples continued to yield traces of amine hydrochloride.

It has proved impossible to eliminate this feature of the preparation. Even in the most favourable cases, when considerable care was taken to avoid the ingress of moisture or oxygen in the course of the preparation, isolation, and subsequent purification, the bisaminophosphines, although clear when freshly distilled, developed a cloudiness on standing. It was found that samples of high purity could be obtained by shaking a benzene solution of the compound with water for several hours, separating the benzene layer, and, after drying with calcium hydride and removal of the benzene, distilling the purified product in vacuo.

A similar observation of the retention of chloride has been made by other workers studying the reaction of phosphonitrilic chloride and amines (33) and the basicity of aminophosphonitriles (34). The apparent solubility of the amine hydrochloride in benzene and ether may well be due to an interaction between the bisaminophosphine and amine, giving an intermediate, possibly of the form $((R_2N)_2PhP \longleftarrow NR_2H).HCl$, which breaks down finally and completely only on heating. Another possibility is that the basicity of the bisaminophosphine is sufficiently great to allow some of the hydrogen chloride to be retained in the form of a phosphonium hydrochloride, $((R_2N)_2PhPH)Cl$, which on distillation suffers cleavage of the phosphorus to nitrogen bond to yield the amine hydrochloride and a compound containing a phosphorus to phosphorus bond. Evidence for the production of such polyphosphines will be discussed subsequently in this thesis. A possible reaction scheme for the above breakdown is:-

$$2((R_2N)_2PhPH)Cl \xrightarrow{2H} (R_2NPhP)_2 + 2R_2NH_2Cl.$$

In the reactions of phenyldichlorophosphine and secondary amines it is possible to isolate the intermediate aminophenylchlorophosphines, and to use these compounds in the synthesis of the unsymmetrical bisaminophenylphosphines. The replacement of the second chlorine atom is thus much slower than that of the first. For example N:N-diethylaminophenylchlorophosphine was prepared by reacting phenyldichlorophosphine with the correct quantity of diethylamine, and from this, unsymmetrical compounds synthesised. The compound $PhPCl(NEt_2)$ is reported in the literature (15).

The properties of the bisaminophenylphosphines.

The compounds shown in the table have been isolated.

Compound.	B.p.
PhP $(NMe_2)_2$	61°/0.1 mm.
PhP $(NMe_2)(NEt_2)$	72.5°/0.1-0.2 mm.
PhP $(NEt_2)_2$	91.5°/0.1 mm.
PhP $(NEt_2)(NPr^n_2)$	100°/0.05 mm.
PhP $(NPr^n_2)_2$	122°/0.1 mm.

All are liquids, readily soluble in benzene, toluene, petroleum ether, ether, methanol and ethanol, but insoluble in water. They show no tendency to aerial oxidation, to hydrolysis or to polymerisation. As in the monodialkyl:aminodiphenylphosphine, the phosphorus to nitrogen bond is readily cleaved by the action of anhydrous hydrogen chloride. Thus bis N:N-diethylaminophenylphosphine gave a quantitative yield of diethylamine hydrochloride on treat:ment with an excess of dry hydrogen chloride in a vacuum system. The action of aqueous hydrochloric acid was to effect hydrolysis of the phosphorus to nitrogen bond, all the products being soluble, particularly on warming. No obvious reaction occurred with dilute aqueous sodium hydroxide, the liquids remaining immiscible, even on warming.

Reaction with carbon tetrachloride.

Like N:N-diethylaminodiphenylphosphine, the bis N:N-dialkylaminophenylphosphines react exothermally with carbon tetrachloride to yield a brown oil. Infra-red and nuclear magnetic resonance spectra of one of these oils have been obtained by Mr. R. Wallace of this department, but their examination has not yielded any clue as to its identity.

The reaction with methyl iodide.

By addition of methyl iodide to an ethereal solution of the bisaminophosphines, methyl iodide adducts are readily formed. They do not appear to deviate from a 1:1 formulation even when a large excess of methyl iodide is employed. The table lists the methiodides isolated.

Compound	State
$PhP\ (NMe_2)_2.MeI$	Solid.
$PhP\ (NMe_2)(NEt_2).MeI.$	Hygroscopic oil.
$PhP\ (NEt_2)_2.MeI.$	Oil.
$PhP\ (NEt_2)(NPr^n_2).MeI.$	Waxy solid.
$PhP\ (NPr^n_2)_2.MeI.$	Solid.

Three of the compounds are typically quaternary salts, being solids, two of these are quite definitely crystalline. Other two have been obtained as liquids, which have not been crystallised, despite considerable efforts to do so. (A similar liquid methiodide has been prepared from 1:phenyl-cyclotetramethylene-:phosphine (35)). All are soluble in water. Bis N:N-diethylaminophenylphosphine methiodide in methyl cyanide is a 1:1 electrolyte in which free iodide ion is present. The molecular weight in aqueous solution is roughly half of the formula weight. Despite the physical state of the bis-diethylamino- and diethylaminodimethylamino- adducts, their behaviour is entirely in accord with quaternary salts. It is, of course, possible that these two represent some quinquecovalent form of the phosphorus which readily breaks down in suitable media:-

$$R_4PI \longrightarrow R_4P^+ + I^-$$

An aqueous solution of 0.6m. mole of the methiodide of the bisdiethylamino- compound had a pH of 3.9 and on addition of 0.05m. mole of sodium hydroxide there was a rapid rise in pH to 9.6. Thus, there is no reaction between the sodium hydroxide and the methyl iodide adduct. The dissolution of this liquid methiodide in water must therefore involve simple ionisation.

Recently Nyholm and his colleagues (36) have shown that it is possible to titrate, conductimetrically, di-(3-dimethylarsinylpropyl)methylarsine, $MeAs(CH_2CH_2CH_2AsMe_2)_2$, triarsine, with methyl iodide. Similar conductimetric titrations of the bisaminophosphines with methyl iodide in absolute ethanol, nitrobenzene, and acetonitrile showed a rise in conductivity, which was, however, too slow to render this a reasonable titrimetric method for the stoicheiometric study of these compounds.

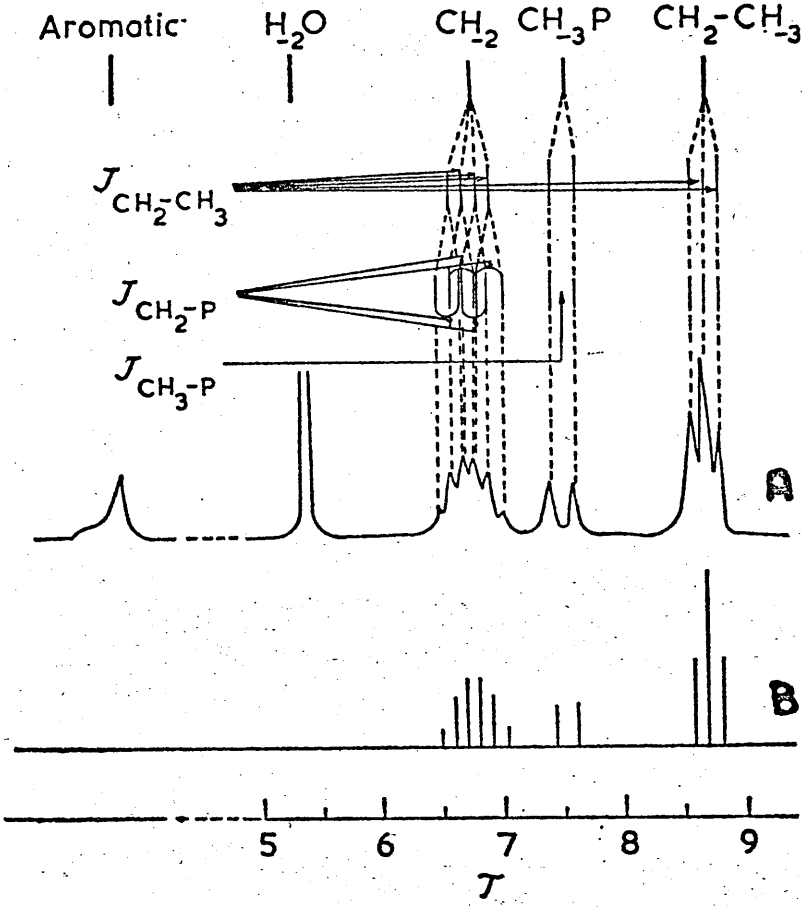
The rate of reaction of bisdiethylaminophenyl:phosphine with methyl iodide was investigated by measuring the variation in conductance with time of a 1:1 molar mixture of the bisaminophosphine and methyl iodide. The results are shown in the table below:-

Time (mins)	Conductivity (Micromhos).	(a - x)	$\log \frac{a}{a - x}$
5	0.40×10^{2}	2.78	0.0580
10	0.79	2.39	0.1239
15	1.13	2.05	0.1903
20	1.40	1.78	0.2504
50	2.49	0.69	0.6637
60	2.66	0.52	0.7868
100	3.06	0.12	1.4065
200	3.18	0	
∞	3.18	0	

a = Initial concentration of reactants

x = Concentration of products.

The plot of time against $\log \frac{a}{a - x}$ was a straight line, and is thus first order with $k = 3.27 \times 10^{-2}$ sec.$^{-1}$ and half-life of 21 minutes at room temperature. The rate determining step in this reaction must be the ionisation of



Proton magnetic resonance spectrum of the 1 : 1 methyl iodide adduct formed by bisdiethylaminophenylphosphine, observed at 60 Mc./sec. The magnetic field increases from left to right. τ values were obtained by measuring the chemical shifts relative to $(CH_3)_3C{\cdot}OH$ (τ 8·74), used as an internal standard.

Fig. vii.

the adduct, and not the reaction of the methyl iodide with the bisaminophosphine. This slow ionisation process is also observed in the ionisation of other complex halogenophosphorus and arsenic compounds.

It has been shown earlier that in N:N-diethylaminodiphenylphosphine methiodide, the methyl group is attached to the phosphorus. The proton magnetic resonance spectrum of an aqueous solution of the corresponding bisdiethylaminophenylphosphine adduct has been used to show that this is also true in the compounds in which two nitrogen atoms are present in addition to the phosphorus. The resulting spectrum is only interpretated satisfactorily in terms of a methyl-phosphorus group being present. The spectrum was recorded and interpreted by Dr. A. L. Porte, to whom I am indebted for some of the following.

The proton magnetic resonance spectrum of an aqueous solution of 1:1 methyl iodide adduct formed by bisdiethylaminophenylphosphine.

The spectrum was recorded using an A.E.I. R.S.2 spectrometer, operating at 60 Mc/s., from a 1M solution of the adduct in water, and it is shown in part A of Fig. vii. In addition to the peaks arising from the aromatic protons and the solvent, the spectrum consists of a multiplet of six peaks, a doublet, and a triplet. The multiplet arises from the methylene protons. It consists of two superimposed quartets, which result from the coupling of the methylene proton spins with those of the neighbouring methyl group protons and the phosphorus nucleus. The methylene protons are all chemically equivalent. The triplet arises from coupling of the methyl group protons with those of the neighbouring methylene group. The doublet arises from the remaining methyl group. The line spectrum on part B of Fig. vii is calculated, using first-order splitting rules, from the τ values and coupling constants listed in the table, and when it is compared with the observed spectrum, A, it immediately follows that the methyl group is attached to the phosphorus atom and not to a nitrogen atom. The adduct is $\{Ph\cdot P(Me)(N(Et)_2)_2\}^+I^-$.

Group	Aromatics	$\underline{-CH_2-}$	$\underline{CH_3}-P$	$-CH_2-\underline{CH_3}$
τ	2.0	6.73	7.56	8.84

Coupling constants (c.p.s.) $J_{CH_2-CH_3} = 6.7$; $J_{CH_2-P} = 11.3$; $J_{CH_3-P} = 12.6$

Both the chemical and the n.m.r. investigations show that a very significant feature of the N - P - N system, as with the P - N system, is the apparent complete lack of basic character on the part of the nitrogen. This basic character depends on the pi electron density on the nitrogen atom and it follows from our results that the process of $p\pi - d\pi$ bonding between the filled p orbital of the nitrogen and the vacant d orbitals of the phosphorus serves to remove all donor characteristics from the nitrogen, and to reinforce those of the phosphorus. The full effect of this transfer of π-electron density to the phosphorus, $P \leftarrow N$, should emerge from studies of the wide range of complexes formed by these compounds.

The main contribution to coupling constants arises from nuclear and electron spin interactions within sigma electronic frameworks and, because of this, coupling constants are normally rapidly attenuated as bonds are interposed between the nuclei concerned. However, J_{CH_2-P} and J_{CH_3-P} are of the same order of magnitude and so coupling must be enhanced through the P - N - C - H sigma framework. The coupling between the phosphorus nucleus and a methylene proton depends on the s electron density of the two nuclei and on the interactions between these s electrons and the other electrons in the sigma framework. The value of J_{CH_2-P} indicates that polarization of the electrons in the sigma framework is in the sense $P \overset{\rightarrow}{-} N \overset{\leftarrow}{-} C$ so that the interactions between these electrons, and hence also the coupling of the phosphorus nuclear spin to the spins of the methylene protons, are enhanced. The polarization of the electron density in the phosphorus to nitrogen bond in the adduct is opposite in sense to that between the same two atoms in the phosphine.

Mercuric iodide adducts.

The bisaminophenylphosphines readily form mercuric iodide adducts by mixing alcoholic solutions of the phosphines and mercuric iodide. Examples of both 1:1 and 2:1 adducts have been prepared and these are listed in the table; all are colourless crystalline solids, sparingly soluble in water, but soluble in hot alcohol.

1:1 Compounds $(PhP(NR_2)_2.).HgI_2$.

R.	Me.	Et.	Pr^n.
M.p.	192-196°	176-178°	134-136°

2:1 Compounds $(PhP(NR_2)(NR^1_2))_2.HgI_2$.

R.	Me.	Me.	Et.	Et.	Pr^n.
R^1.	Me.	Et.	Et.	Pr^n.	Pr^n.
M.p.	86-88°	159-161°	142-143°	102-108°	126-127°

For each of the bisaminophenylphosphines a 2:1 complex has been prepared, and they might be expected to be either of the form $(R-Hg-R)^{2+}(I^-)_2$ or an appropriate tetrahedral covalent form. The high solubility of these complexes in benzene and the low solubility in hydroxylic solvents, together with their monomeric nature in benzene, is more in accord with the idea of tetrahedral complexes (Class A). The 1:1 adducts were different in their properties and probably have the bridge structure (Class B) described previously. The methyl and ethyl compounds were not readily soluble in organic solvents other than alcohols. It was only possible to obtain the molecular weight of the ethyl derivative by using sulpholane (dielectric constant 44 at 30°, cryoscopic constant 696) as solvent. The value obtained, 1080, is considerably in excess of that required for the monomer ($PhP(NEt_2)_2.HgI_2$ requires M = 706). In the case of the n-propyl derivative, the solubility in benzene was sufficiently great for the molecular weight to be determined cryoscopically. Again, the value, 1370± 50, is considerably in excess of that required for the monomer.

($PhP(NPr_2).HgI_2$ requires M = 762). The deviation from the exact values for the dimers is indicative of dissociation, which may be ionic in sulpholane, and non-ionic in benzene. The nature of mercury II complexes in general supports the monodentate function of these bisaminophosphines, suggesting that the ligand atom is phosphorus.

The mercuric iodide adducts of the methiodides were readily formed in alcoholic solution as pale green crystalline solids. The compounds isolated are shown in the table, all except one being of the form $R^+ HgI_3^-$.

Compound.	M. p.
$PhP (NMe_2)_2. MeI.HgI_2$	132 - 134°
$PhP (NMe_2) (NEt_2). MeI.HgI_2$.	90 - 92°
$(PhP (NEt_2)_2.MeI)_2. HgI_2$.	79 - 81°
$PhP (NEt_2)(NPr^n_2). MeI.HgI_2$.	82 - 84°
$PhP (NPr^n)_2. MeI. HgI_2$.	59 - 61°

The exception, $(PhP(NEt_2)_2MeI)_2. HgI_2$, may be formulated as $(R^+)_2.HgI_4^{2-}$. In this case, despite several attempts, the 1:1 compound has not been prepared. Support for the formulation of this 2:1 complex as a compound containing the HgI_4^{2-} ion was forthcoming from cryoscopic molecular weight determinations in sulpholane, which gave a value of about one third of the calculated value, in keeping with the idea of three ions being present.

The stability constants for the ions formed by mercury and iodine have been determined in acetonitrile (37) as shown:-

$$HgI_2 + I^- \longrightarrow (HgI_3)^- \qquad K = 9 \times 10^5.$$

$$HgI_3^- + I^- \longrightarrow (HgI_4)^{2-} \qquad K = 40.$$

$$HgI_3^- + HgI_2 \longrightarrow (Hg_2I_5)^- \qquad K = 10.$$

Clearly the HgI_3^- ion is by far the most stable of the complex ions and we would expect the 1:1 adducts to form most readily. The 2:1 adduct reported above may result because of some peculiarly high stability of the HgI_4^{2-} ion in the presence of the particular phosphonium ion involved in this adduct. A more likely reason is that this particular adduct is much less soluble than the other adducts, a feature probably arising from the lattice energy of the solid and arising from favourable packing of the tetrahedral HgI_4^{2-} ion with the $(PhP(NEt_2)_2.Me)+$ cation.

The interaction of the mercuric iodide adducts and alcohol.

It was observed while attempting to recrystallize the mercuric iodide adducts of the bisaminophosphines in alcohol that mercury was produced, particularly on prolonged heating. For example, a sample of $(PhP(NEt_2)_2)_2.HgI_2$ refluxed for 5 hrs. in ethanol produced a globule of mercury corresponding to almost 100% of the mercury originally present in the adduct. Evaporation of the ethanol subsequent to the removal of the mercury yielded a residue whose infra-red spectrum indicated the presence of hydroxyl, phenyl and aliphatic C - H. A possible scheme for the breakdown is:-

$$(PhP(NEt_2)_2)_2.HgI_2 \xrightarrow[\text{in air}]{EtOH} PhP(NEt_2)_2 + (PhP(OH)(NEt_2)_2)I + Hg^o$$

It was found that if the mercuric iodide adducts were refluxed in benzene for a similar period of time, the amount of mercury produced was very small. However, it was observed that a benzene solution of $PhP(NPr_2)_2.HgI_2$ slowly yielded mercuric iodide on standing at room temperature for a considerable time.

Mann and his colleagues (26) mention a similar reduction of mercuric in their work on the phosphine adducts, already referred to, but in this instance the reduction occurs only to the mercurous state. Thus the 1:1 adduct between triethylphosphine and mercuric bromide yielded mercurous bromide when it was recrystallised from alcohol: the exact nature of this reaction was not investigated. Similarly, they observed a slight precipitate of mercurous chloride when tri-n-butylphosphine and mercuric chloride were mixed in alcohol in the ratio 2:3, and also when the resulting adduct was heated above its melting point, or when vigorously boiled with alcohol.

A similar reduction of Hg(II) compounds to Hg^o by monoethanolamine or diethanolamine is reported (38). It can in fact be employed as an analytical method for mercury analysis, and has been successfully used in this work.

The elimination of mercury can be interpreted in terms of the relatively high stability of mercury metal. The effect is certainly not general amongst all the mercury (II) complexes, although one might speculate as to the number of occasions on which the formation of a small precipitate of mercury (I) salt or even mercury metal has been ignored by other workers. Mann's observation is in the highest tradition of scientific accuracy, and it was satisfying to find the observation of this type of reaction confirmed by this previous piece of work. Recent work on $(CF_3)_3P\text{-}HgI_2$ complexes has certainly not indicated any tendency for such a reaction, even though these complexes are not particularly stable. The fact that the reaction occurs more readily in ethanol than in benzene is indicative of the general mechanism by which the complex breaks down to give a quaternary salt,

$$R_3P.HgX_2 \longrightarrow (R_3PX.)^+ X^- + Hg^o.$$

a reaction which is likely to be favoured by an ionic solvent. Clearly the occurrence of this type of reaction would depend on the strength of the phosphorus - mercury bond and also upon the stability of the resulting phosphonium ion.

The reaction of bis N:N-diethylaminophenylphosphine with cuprous iodide.

The reaction of bis N:N-diethylaminophenylphosphine with cuprous iodide in the ratio 2:1 gave a solid which analysed approximately to the composition $(PhP(NEt_2)_2)_2.CuI$. This compound was subsequently investigated by Mr. A. Lane of this department, who showed that it was a non-conductor and monomeric in benzene. It is therefore an example of 3-coordinated copper and is analogous to the 2:1 phosphine - silver iodide monomeric adduct described by Coates and his co-workers (30). It would appear to be the first authenticated example of a monomeric 3-coordinated copper (I) complex and its further investigation is clearly a matter of importance.

A 1:1 complex has also been prepared and it is tetrameric, as are other such phosphine adducts.

INFRA-RED SPECTRA. *

The infra-red spectra are as shown in the figures, and were measured on a Unicam S.P. 100. Mark II (primary grating monochromater) with evacuated optics.

The values for the absorptions are as follows:-

PhP $(NMe_2)_2$.

3070w, 3058w, 2982w-m, 2970w-m, 2905sh, 2897s,
2858s, 2828s, 2809w, 2789s-m, 1589w, 1479m,
1465w-m, 1455w-m, 1446w-m, 1435m, 1407w, 1298w,
1262m, 1210w-m, 1185s, 1139w, 1117w, 1093m,
1058m, 1028w, 971s, 958s, 749s, 738w,
705s, 692m, 672s, cm^{-1}.

PhP $(NMe_2)(NEt_2)$.

3070w, 3058w, 2968m-s, 2929m, 2910m, 2878m-s,
2861m-s, 2828m, 2787m, 1692w, 1588w, 1478m,
1462w-m, 1432m, 1405w, 1375m, 1341w, 1288w,
1261w-m, 1217w-m, 1188s, 1139w, 1114w, 1093w-m,
1069w, 1058w-m, 1018m, 1005w, 966s, 920m,
798w-m, 782w, 748m, 732w-m, 704s, 692m,
670s, cm^{-1}.

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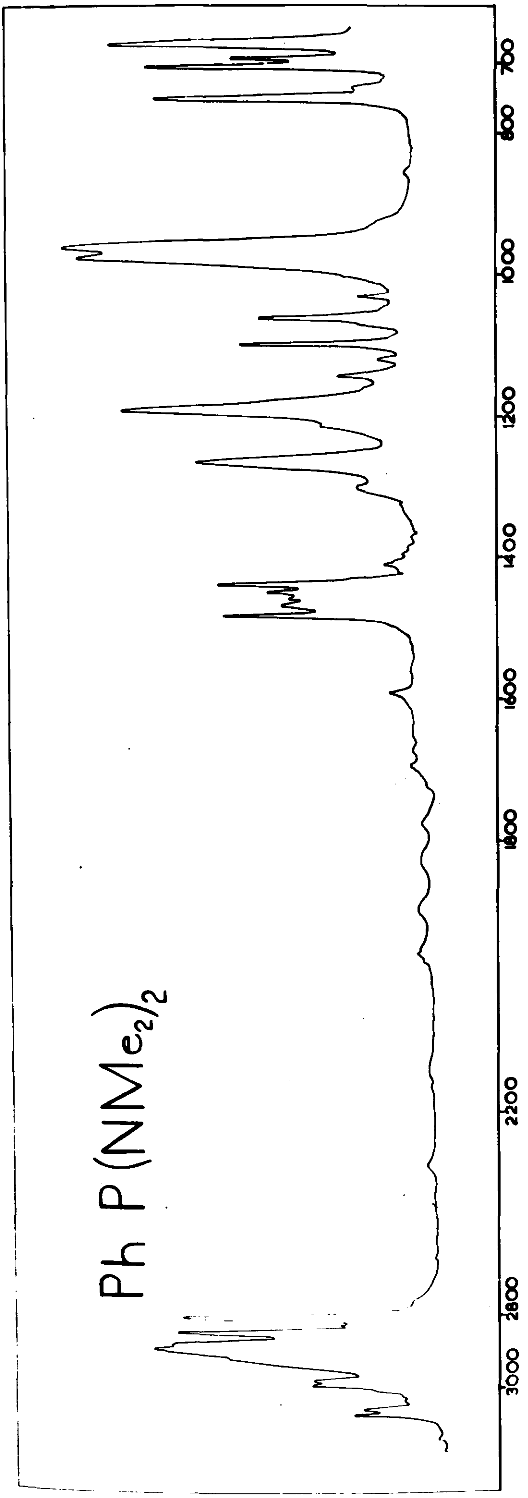
* The thanks of the author are due to Dr. L. C. Thomas, Chemical Defence Experimental Establishment, Porton Down, for a discussion of these spectra.

Fig viii. - Absorption spectra.



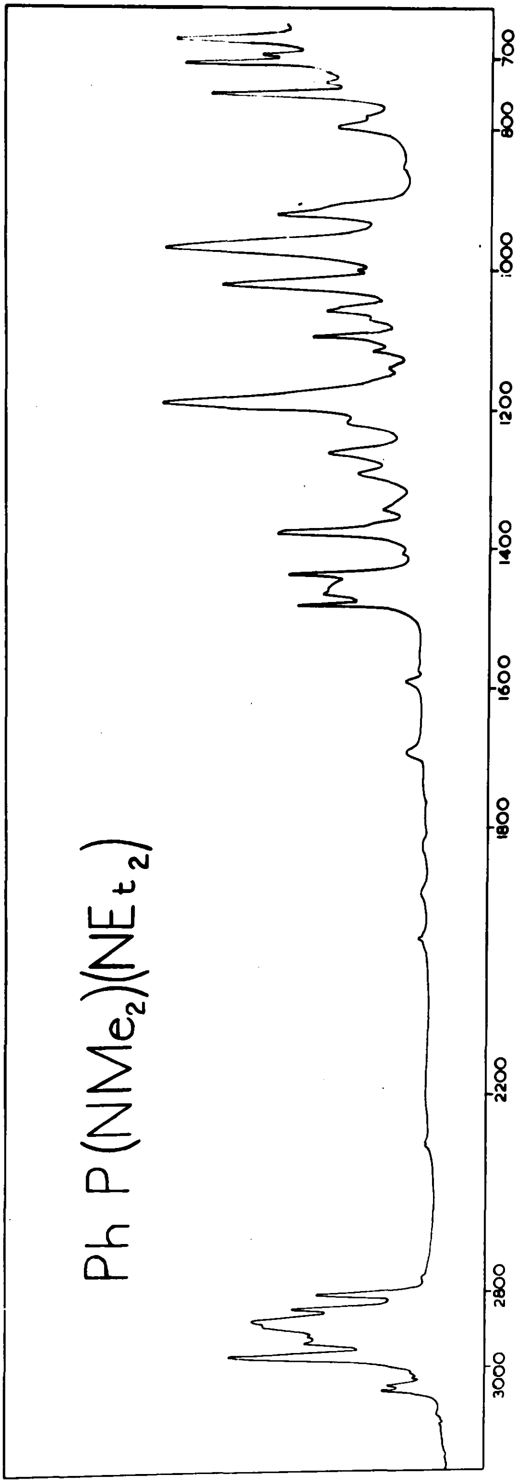


Fig. ix. - Absorption spectra.

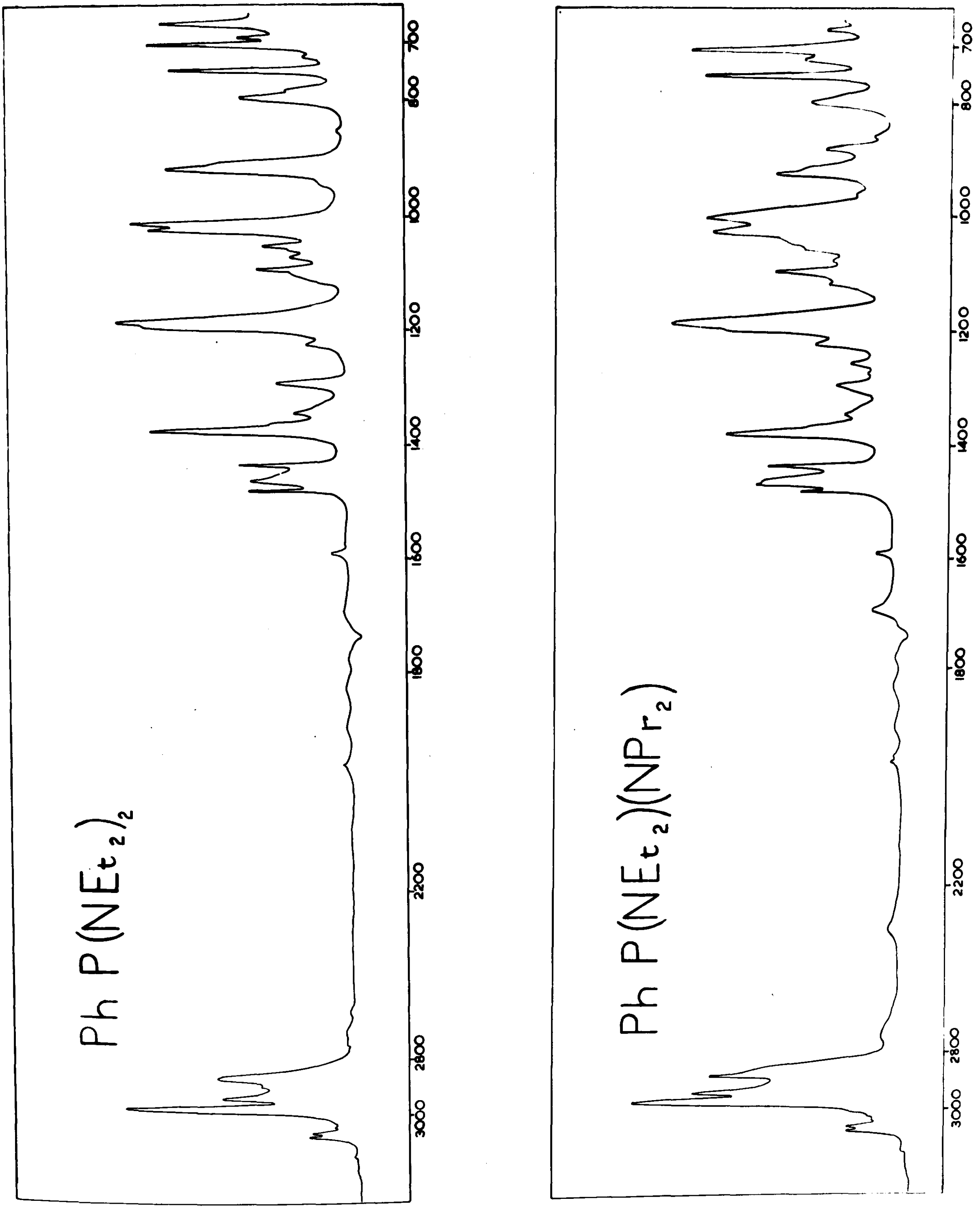
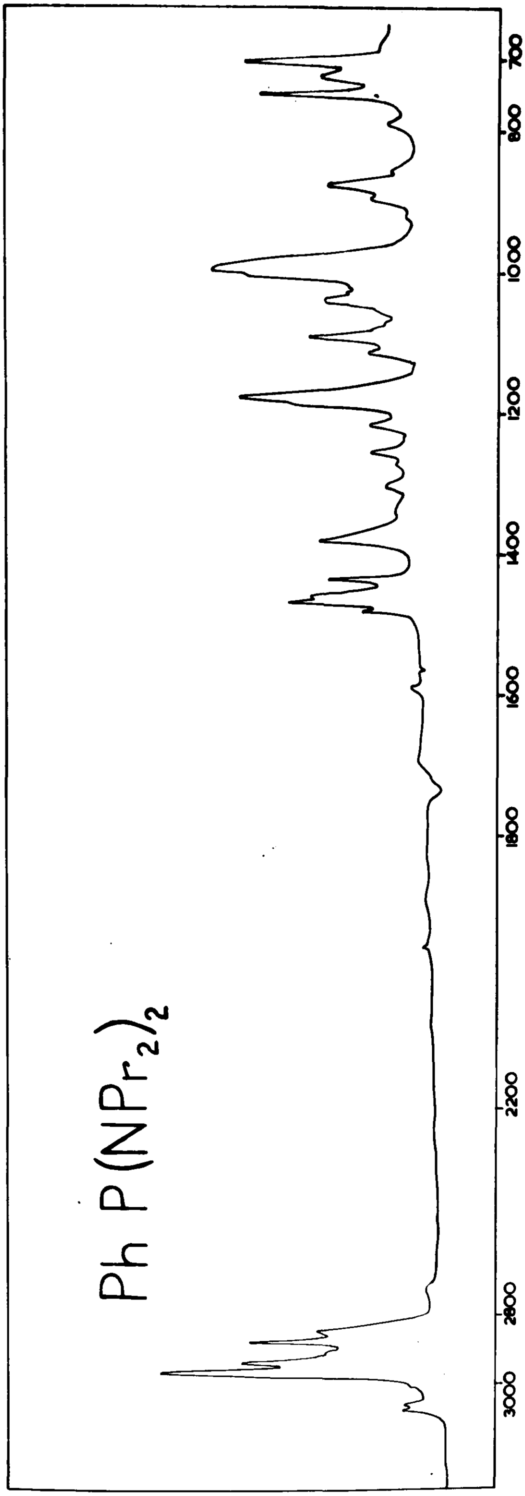


Fig. x. - Absorption spectra.



PhP $(NEt_2)_2$.

3071w, 3058w, 2968s, 2930-, 2888w-m, 2858m,
1588w, 1478w-m, 1462w-m, 1433w-m, 1373s, 1360w sh,
1342w, 1290w, 1222w, 1191s sh, 1194s, 1092w-m,
1071w, 1052w-m, 1024s, 1012s, 918s, 795m,
782w sh, 745m, 724w, 702s, 690m, 668s. cm.$^{-1}$

PhP $(NEt_2)(NPr_2)$.

3072w, 3058w, 2962s, 2932m-s, 2871m-s, 1690w,
1589w, 1478m, 1466m, 1433m, 1376m, 1342w,
1292w, 1272w, 1254w, 1223w-m, 1192m sh, 1180s,
1114w, 1091m, 1073w, 1052w-m, 1038w-m sh, 1020m,
997m, 954w, 920m, 878w-m, 854w, 795w-m,
747s, 718w-m, 703s, 668w-m. cm.$^{-1}$

PhP $(NPr_2)_2$.

3071w, 3058w, 2960s, 2930m-s, 2870m-s, 2840m,
1588w, 1479w, 1466m, 1458w-m, 1433w-m, 1378w-m,
1303w, 1270w, 1252w, 1214w, 1174m-s, 1112w,
1088w-m, 1076wsh, 1068w, 1037w-m, 1028w, 1002m-s sh,
993s 920w, 892w, 874w-m, 856w, 789w,
746m-s, 721w-m, 700m-s. cm.$^{-1}$

In quinquevalent P - NR_2 compounds the following assigments have been made by other workers:-

(a) $PNMe_2$.

2780 - 2860 w
1290 - 1320 m
1155 - 1185 w-m
1060 - 1075 w-m. cm.$^{-1}$
975 - 1010 s

with a linear relationship between the band near 1000 $cm.^{-1}$ and summed electronegativity of the phosphorus substituents.

(b) $PNEt_2$.	1190 - 1215	m
	1160 - 1175	m
	1095 - 1110	w-m
	1055 - 1065	m
	1015 - 1030	s
	930 - 960	s
	915 - 935	m. $cm.^{-1}$

The 950 $cm.^{-1}$ band also varies linearly with the summed electronegativity of the phosphorus substituents.

The spectra of the compounds reported in this chapter absorb near or below the lower limit of these ranges, which fits into the general pattern. A medium to strong band appearing at 2820 $cm.^{-1}$ is characteristic of N-methyl compounds in which the lone pair of electrons on the nitrogen atom is not involved in conjugation (39). The appearance of this band in the dimethylamino compounds is of interest in the light of the lack of basic character of the nitrogen. It appears that the $d\pi$ -$p\pi$ bonding does not affect the characteristic N-methyl absorption bond at 2820 $cm.^{-1}$ since it is also present in the spectrum of the compound $CH_3N(SiH_2CH_3)_2$, which is also a non-donor molecule due, presumably, to $d\pi$ -$p\pi$bonding (40). The presence of this 2820 $cm.^{-1}$ band in methylaminophosphines has also been observed by Harris (41).

The amino- and bisaminophosphines absorb around 1435 $cm.^{-1}$ which is on the lower limit of the accepted assignment for P-Ph; however, the band shape is in general agreement with the corresponding absorption bands in other P-Ph compounds. There is reason to think that this absorption is not a P - C absorption, but rather arises from a phenyl group vibration; a similar band assigned to phenyl occurs in Si - Ph compounds.

The absorption bands associated with the P - N bond are by no means clear. For the P (V) - N compounds, a fairly large number of spectra has now been examined and there are widely differing views as to the assignments. The original assigment at 700 $cm.^{-1}$ is not now favoured, a value of 1000 $cm.^{-1}$ being more probable. There is more certainty of the frequencies associated with the phosphonitrilic ring. The only available spectra of P (III) - N compounds are those of Sisler and Smith, and these are too few and too limited to be of great use. As a result of examination of our spectra it was thought that a band at 1180 $cm.^{-1}$ might be assigned to the P - N bond. However, it would appear that this is unlikely to be correct, being more probably a C - N stretching vibration.

In conclusion, the spectra of these and those of other compounds reported in this thesis are not, at the moment capable of interpretation. Even the assigment of the obvious groups such as P - Ph is still open to further investigation. The only purpose these spectra serve at present is one of identification and as something of a criterion of purity. The spectra of the mixed compounds also serve to show the chemical individuality of these compounds.

SUMMARY.

The bisdialkylaminophenylphosphines are similar to N:N-diethylaminodiphenylphosphine described in Chapter I, and to the other aminophosphines reported in the literature. The general pattern of behaviour is in accord with the idea that the nitrogen atoms forms $p\pi - d\pi$ bonds with the phosphorus and hence lose their basic character, whilst the phosphorus retains its phosphine character, perhaps somewhat enhanced. They are thus to be classed as tertiary phosphines and might be considered as being closely similar to the compounds in which the nitrogen is replaced by CH.

cf. $(Me_2N)_2PPh$. and Pr^i_2 PPh.

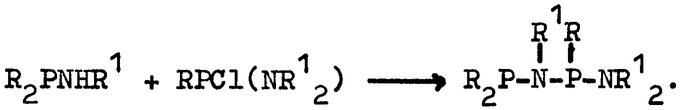
Like N:N-diethylaminodiphenylphosphine, the bisdialkylaminophenylphosphines are stable to air. They readily form 1:1 adducts with methyl iodide in which the methyl group has been shown in one case to be attached definitely to the phosphorus atom. With mercuric iodide and cuprous iodide they form crystalline adducts closely similar to those of the phosphines. With bisdiethylaminophenylphosphine a 2:1 cuprous iodide adduct, which may be 3-coordinated is formed. The phosphorus - nitrogen bond is attacked by gaseous hydrogen chloride, leading to amine hydrochloride and chlorophosphine. Aqueous hydrogen chloride hydrolyses the phosphorus - nitrogen bond, but aqueous sodium hydroxide has no effect.

CHAPTER III.

THE REACTION OF DIPHENYLCHLOROPHOSPHINE WITH PRIMARY AMINES.

INTRODUCTION.

The reaction of secondary halophosphines with primary amines is of importance in any complete study of aminophosphines. The products reported in the literature from reactions of this type are of the general formula R_2PNHR and, apart from their significance as compounds containing a phosphorus (III) - nitrogen bond, they are of importance in that, by reaction with a suitable halophosphine, they offer a route to more complex phosphorus (III) - nitrogen skeletons - e.g.

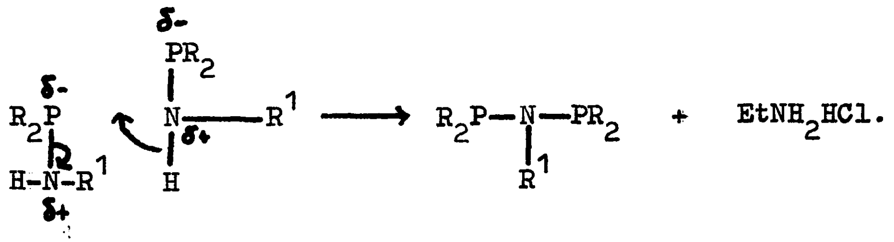


$$R_2PNHR^1 + RPCl(NR^1_2) \longrightarrow R_2P\text{-}\overset{R^1}{\overset{|}{N}}\text{-}\overset{R}{\overset{|}{P}}\text{-}NR^1_2.$$

Sisler and Smith (11) investigated the reaction of diphenylchlorophosphine with t - butylamine and 2:6-dimethylaniline, the yield of product for the former reaction being 65%, for the latter, 46%. These low yields may indicate the extent to which substitution has proceeded beyond the required -P-NH compound. However, the fact that compounds of the type R_2PNHR can be isolated shows that there is a difference between the reactivity of the amino group in the phosphinoamine and that in a primary amine.

This observation has also been made by Harris (12) in his study of the reactions of halogenotrifluoromethylphosphines with ammonia, and methylamine; even in the presence of a large excess of phosphine, only one amino hydrogen atom was replaced.

It would appear that in compounds of the type R_2PNHR, the electron density on the nitrogen is reduced to such an extent as to inhibit the reactions of the NH group with a halophosphine, which is generally assumed to involve attack of the phosphorus atom by the unbonded electrons on the nitrogen atom. However, as has already been mentioned, the reaction of phosphorus trichloride and methylamine, (Holmes (18)), in the presence of an excess of amine results in a condensed product, as does the reaction of phosphorus trichloride and aniline, (Grimmel (18)). Both these reactions must involve the formation of intermediates of the type $P(NHR)_3$, and under certain conditions condensations must take place. Assuming that there is polarisation of the phosphorus - nitrogen bond, a possible mechanism for such condensations is:-



The stability of M - NH_2 and M - NHR relative to M - NH - M and M - NR - M has not been investigated to any great extent. In carbon and nitrogen chemistry there appears to be little tendency for condensation by intermolecular elimination of ammonia or primary amine from compounds containing amino or monoalkylamino groups. However, silicon and sulphur both show this tendency. Sulphur - nitrogen ring compounds can be readily built up from sulphur chloride and ammonia, or primary amines, but there is only limited information available on the effect of different conditions and amines. The study of intermolecular condensation with monoalkylaminosilanes has been more extensive and the results are relevant to the chemistry of the analogous phosphorus compounds.

Dimethyldichlorosilane reacts with primary amines to give in addition to the NHR compounds silazanes containing the SiNRSi group. The extent of the condensation appears very dependent on the nature of the group R. With methylamine, the condensation proceeds largely to completion and the NHMe compound is isolated in small yield, while with ethylamine the tendency to condensation is less marked (42).

The stability of the -NHR group is likely to be very dependent on the ease of elimination of the amine, and this will certainly be more difficult with bulky substituent groups such as tert-butyl. It is likely that the reaction of a secondary phosphine with a primary amine will produce condensed products, but that in some cases it will be possible to isolate products in which only one of the amino - hydrogen atoms in the amine will have been replaced.

This chapter reports the reaction of diphenylchlorophosphine with methylamine and discusses some of the properties of the products obtained.

RESULTS AND DISCUSSIONS.

The reaction of diphenylchlorophosphine with ethylamine in benzene.

Sisler and Smith reported (11) the preparation of N - tert - butylaminodiphenylphosphine in benzene by addition of diphenylchlorophosphine to t - butylamine at 0 - 5° and the reaction of diphenylchlorophosphine and ethylamine was carried out under similar conditions, but under dry nitrogen. The product was a yellowish oil which on distillation up to 190° at 0.1 mm. gave a colourless liquid, which on a second distillation yielded a liquid which could be solidified in an acetone/solid carbon dioxide bath and which melted at around room temperature. This liquid, which showed a characteristic amino absorption frequency at 3280 $cm.^{-1}$ in its infra-red spectrum, was identified as N - ethylaminodiphenylphosphine and was found to yield only a 1:1 methiodide in the presence of excess methyl iodide.

At temperatures greater than 190°/0.1 mm. a high boiling distillate whose isolation was accompanied by severe bumping, which interfered with the distillation was obtained. As a result, only part of this product was isolated. The distillate was a viscous oil, which partially solidified on standing. Dissolution in hot rectified spirit gave, on cooling, a white crystalline solid, which was identified, by molecular weight determinations and analysis, as ethylbis(diphenylphosphino)amine, $(Ph_2P)_2NEt$, its infra-red spectrum showing no absorption corresponding to an amino group.

The low-boiling N - ethylaminodiphenylphosphine constituted 10% of the crude reaction product, whilst the ethylbis(diphenylphosphino)amine which was obtained represented at least 40% of the product.

The reaction of diphenylchlorophosphine with ethylamine using ethylamine as solvent.

To investigate the yields of products obtained in the presence of a large excess of amine, the reaction was carried out in anhydrous ethylamine, the amine being evaporated and the crude phosphorus - nitrogen product isolated using ether. Distillation in vacuo showed that the crude product had retained a large amount of highly volatile material which was probably ethylamine, and which was evolved during distillation but did not condense in the distillation unit. The phosphorus - nitrogen products indicated that 50% of the diphenylchlorophosphine had formed N-ethylaminodiphenylphosphine, the remainder, presumably, having formed the less volatile ethylbis(diphenylphosphino)amine, which was isolated from the distillation residue by crystallisation from aqueous alcohol.

From the above experiments it is obvious that the reaction of ethylamine with diphenylchlorophosphine is not as simple as the reactions reported by Sisler and Smith. Under the conditions which they used, it has been found that only 10% of the halophosphine yielded

N-ethylaminodiphenylphosphine, and that even in the presence of a large excess of amine, the yield of this compound only constituted 50% of the product. It is of course possible that products involving the P - N - P skeleton were obtained as by-products in Sisler and Smith's work, but possibly in low yield, and as unisolated distillation residues.

The reaction between diphenylchlorophosphine and ethylamine, both in benzene and in ethylamine, thus gave two products, the initial reaction being the formation of N-ethylaminodiphenylphosphine, according to the equation:-

$$Ph_2PCl + 2EtNH_2 \longrightarrow Ph_2PNHEt + EtNH_2.HCl.$$

The yield of NH compound is appreciably increased by using a large excess of amine. The other product ethylbis(diphenylphosphino)amine is produced even in the presence of excess amine, i.e. under conditions in which the production of the monosubstituted amino compound is favoured. It would therefore appear that this reaction is similar to those mentioned earlier, in which condensed products are obtained from phosphorus trichloride and methylamine or aniline in the presence of excess amine.

The formation of ethylbis(diphenylphosphino)amine could take place in two ways. The first, and perhaps most obvious one is by reaction of diphenylchlorophosphine with ethylaminodiphenylphosphine:-

$$Ph_2PCl + Ph_2PNHEt \longrightarrow (Ph_2P)_2NEt. + HCl.$$

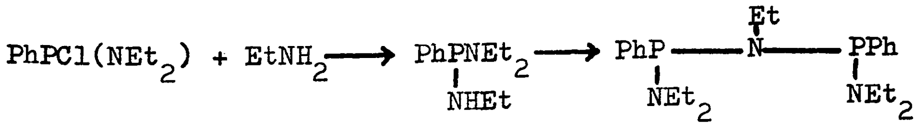
This reaction would be favoured by a low concentration of amine, so that an appreciable concentration of chlorophosphine could be built up, sufficient to react with the ethylaminodi:phenylphosphine. It might be expected to occur if amine were added to chlorophosphine rather than chlorophosphine to amine as was in fact done.

The alternative route involves the type of condensation reaction discussed in the introduction to this chapter, namely:-

$$2Ph_2PNHEt \longrightarrow (Ph_2P)_2NEt + EtNH_2.$$

That this is the route actually involved is strongly supported by the fact that ethylamine is eliminated in the course of the isolation of the monoalkylaminophosphine from the reaction in ethylamine, and this would also account for the severe bumping reported in the course of the distill:ation of the products from the benzene solution. Appreciable quantities of ethylamine were always found to be present in the traps after the vacuum distillation of the products from these reactions.

The facility with which the formation of the P - N - P skeleton takes place opens up tremendous poss:ibilities in the field of synthetic tervalent phosphorus - nitrogen chemistry. As an example, the reaction of diethylaminochlorophenylphosphine with ethylamine would lead to a five-membered P - N skeleton by the following scheme:-



$$PhPCl(NEt_2) + EtNH_2 \longrightarrow \underset{NHEt}{\underset{|}{PhPNEt_2}} \longrightarrow \underset{NEt_2}{\underset{|}{PhP}} — \overset{Et}{\overset{|}{N}} — \underset{NEt_2}{\underset{|}{PPh}}$$

Further, the elimination of amine from $RP(NHR^1)_2$ would lead to polymeric or cyclic tervalent phosphorus compounds, and by suitable admixture of di- and tri- functional phosphorus compounds (e.g. $PhPCl_2$ and PCl_3) materials with varying degrees of cross-linking could be produced.

The reaction of diphenylchlorophosphine and ethylamine using ethylamine as solvent, without the exclusion of oxygen and moisture.

Addition of diphenylchlorophosphine to ethylamine without taking any precautions to exclude moist air, resulted, after isolation of the crude product by the method described, in an oil. Some of this oil was solidified, after some difficulty, to give a white solid which softened at 155° and melted in the range 164 - 166°. There was no nitrogen in the compound and a complete analysis of the product showed that it was a mixture of 72% tetraphenyldiphosphine and 28% tetraphenyldiphosphine dioxide. The dioxide presumably arose from aerial oxidation of the diphosphine.

Tetraphenyldiphosphine is the product of the reaction of diphenylphosphine and diphenylchlorophosphine and the diphenylphosphine must have arisen in the above reaction from hydrolysis of the chlorocompound. A possible method of production is by the equation already quoted for the alkaline hydrolysis of diphenylchlorophosphine,

$$2Ph_2PCl + 2H_2O \longrightarrow Ph_2PH + Ph_2PO_2H + 2HCl.$$

since, due to the hygroscopic nature of ethylamine, it is very likely that large quantities of water are present from the atmosphere.

The reaction between diphenylchlorophosphine and methylamine, using alcoholic methylamine.

Methylamine can be obtained commercially as a 33% alcoholic solution. There does not appear to be any information in the literature on the relative reactivity of a phosphorus - halogen group with alcohols and amines. This is not surprising since such a comparison would require a knowledge of the formation of phosphorus (III) - nitrogen which up to the present work has not been available. The reaction of diphenylchlorophosphine and this amine solution was carried out in the hope that a phosphorus - nitrogen compound would be produced in reasonable yield, i.e. phosphorus - nitrogen bond formation would occur in preference to or simultaneously with phosphorus - oxygen bond formation. However, it was found that both under normal atmospheric conditions and under dry nitrogen no such product resulted, but the results are of interest in view of the previous experiment.

The diphenylchlorophosphine was added to the ethanol/methylamine solution at 0°, benzene being used as solvent for both reagents. A precipitate of amine hydrochloride formed immediately. The reactants were stirred for about an hour before the hydrochloride was removed by filtration. The crude product, which was a suspension of a white solid in a liquid, was obtained after removal of benzene. The solid appeared during evaporation of the solvent and, after keeping the crude products at 4° for a few days this material, which was insoluble in ether, was filtered off. It had an infra-red spectrum identical with that of the solid from the previous experiment shown to be a mixture of tetraphenyldiphosphine dioxide and tetraphenyldiphosphine. The liquid product was shown by analysis to contain no nitrogen and distillation gave a liquid, b.p 120°/0.1 mm., whose infra-red spectrum indicated that it was an ester. The cuprous iodide adduct of this compound had m.p. 186°C. This liquid is thus the ethyl ester of diphenylphosphinous acid, Ph_2POEt, whose cuprous iodide adduct has m.p. 190 - 191°.

From the above reaction, it is clear that alcoholic solutions of amine are unsuitable for the synthesis of phosphorus (III) - nitrogen compounds. There are two possible conclusions which can be arrived at. The first is that the formation of the phosphorus (III) - nitrogen bond takes place, and then the resulting methyl:aminodiphenylphosphine reacts with alcohol, to produce an ester. The second possibility is that the formation of the ester takes place immediately, and that methylamine does not take part in the reaction, other than as a base for the removal of hydrogen chloride. The latter possibility would appear to be the more likely since such reactions are in fact used in the synthesis of phosphites, e.g. Reaction of phosphorus trichloride with alcohol in the presence of base yields tertiary esters of phosphorous acid:-

$$PCl_3 + 3ROH + 3B \longrightarrow P(OR)_3 + 3B.HCl.$$

Similarly, the reaction of a monohalophosphine with alcohol, in the presence of base, yields esters of phosphinous acid.

$$Ph_2PCl + EtOH \longrightarrow Ph_2POEt.$$

<u>The reaction of diphenylchlorophosphine and methylamine using methylamine as solvent.</u>

Dry methylamine prepared by the action of base on methylamine hydrochloride, followed by suitable drying processes was used as solvent. The reaction was carried out at -50°, by adding the diphenylchlorophosphine to the amine, the resulting methylamine hydrochloride being soluble in the amine solvent. The excess of amine was removed and ether extraction of the residue yielded the crude phosphorus - nitrogen products, which on distillation gave a fraction boiling in the range $104 - 108^{\circ}/0.2$ mm., which constituted 25% of the crude products. (Found: N, 4.3; Ph_2PNHMe require: N, 6.5%). Redistillation did not produce any change in the nitrogen value.

The infra-red spectrum of the above distillate showed the presence of amino, aliphatic and phenyl groups, indicative of the presence of N-methylaminodiphenylphosphine in the distillate. This was confirmed by the fact that an ethereal solution of the liquid, treated with methyl iodide, yielded a white crystalline solid, whose nitrogen value corresponded to that expected for N-methylaminodiphenylphosphine methiodide.

A vapour-phase chromatograph of the distillate on an Apiezon column indicated the presence of three constituents. The liquid was obviously a mixture, which could not be separated by ordinary distillation, and it was not investigated further. It is possible that this liquid contained products of the type N:N-diethylaminodiphenylphosphine, arising from dimethylamine, which is often present as an impurity in methylamine.

The residue from the distillation of the crude product was dissolved in hot aqueous alcohol, and on cooling methylbis(diphenylphosphino)amine separated as white crystals, m.p. 112 - 114°.

This reaction was repeated and in the course of the removal of ether the products were heated for considerably longer on the steam bath, in order to ensure the removal of volatiles. It appeared that heating encouraged the formation of the condensed product, since there was continuous bubbling, presumably due to the evolution of amine. Distillation of the crude product did not appear to give any N-methylaminodiphenylphosphine but gave a high-boiling fraction, from which solid separated on standing and which gave, from hot aqueous alcohol, methylbis(diphenylphosphino)amine in 50% yield.

Thus, like ethylamine, methylamine with diphenylchlorophosphine yields a condensed product, in addition to monoalkylaminodiphenylphosphine. The difficulty experienced in the isolation of methylaminodiphenylphosphine is probably due to the presence of impurities whose boiling points are close to that of the aminophosphine. In addition, the yield of ethylbis(diphenylphosphino)amine is lower than that of the methyl analogue. These facts, together with the results of Sisler and Smith, demonstrate that the tendency to condensation is

$$\mathrm{Me} > \mathrm{Et} > \mathrm{Bu}^t.$$

It would be of interest to study the reaction of diphenylchlorophosphine and propylamine in order to check this series.

The properties of the N-alkylaminodiphenylphosphines.

Only N-ethylaminodiphenylphosphine was isolated in a pure form. It was a colourless liquid and its properties were not investigated beyond the formation of a 1:1 methyl iodide adduct, since Sisler and Smith prepared and reported upon similar compounds. A complete understanding of the mode of formation of the alkyl(bisdiphenylphosphino)amines would require an investigation of the properties of the alkylaminodiphenylphosphines, and in particular, the effect on them of heat. Such an investigation is not easy, due to the difficulty of obtaining the N-alkylaminophosphines in a sufficiently high yield and degree of purity.

The properties of the alkylbis(diphenylphosphino)amines.

Both the methyl and ethyl derivatives are white crystalline solids, soluble in benzene, chloroform, ether and hot alcohols, but insoluble in hot and cold water and dilute sodium hydroxide. Like the other aminophosphines studied, they are stable to aerial oxidation. They are odourless and can be conveniently handled. On addition of carbon tetrachloride to the solids, there is no apparent reaction, a colourless solution resulting.

Treatment of a sample of the compounds with warm dilute hydrochloric acid results in cleavage of the phosphorus to nitrogen bonds, with the production of diphenylphosphinic acid.

Reaction with alkyl iodides.

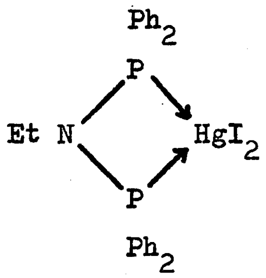
The methyl compound on reaction with excess methyl iodide gave an oil after removal of solvent and excess reagent. From the weight changes, it was inferred that this was the 1:1 adduct.

Addition of ethyl iodide directly to the ethyl compound, followed by removal of excess ethyl iodide, yielded a white solid, which was shown by analysis, and the weight change involved in the reaction, to be ethylbis(diphenylphosphino)amine ethiodide, again a 1:1 adduct.

Therefore, towards the alkyl halides, the compounds investigated act as monobases. This must be due to a similar mechanism to that which inhibits the formation of 2:1 adducts between methyl iodide and unsaturated diamines in which the nitrogen atoms are only separated by a methylene bridge. Reduction in the basicity of the neighbouring potential base is due to the positive charge on the quaternised phosphorus atom, this effect being transmitted through the sigma bonds.

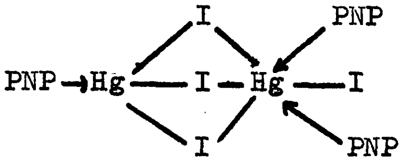
The reaction with mercuric iodide.

With the ethyl compound, a 1:1 adduct was readily prepared. Although initially the cryoscopic molecular weight in nitrobenzene indicated that the adduct was monomeric, the subsequent drift in freezing point suggested a breakdown in solution. This monomeric compound must correspond to ethyl(bisdiphenylphosphino)amine acting either as a bidentate ligand with 4-coordinate mercury, or as a monodentate ligand with 3-coordinate mercury. Since structures containing 3-coordinate mercury are not yet reported, the adduct is probably one in which mercury has the common tetrahedral configuration, and the ligand is bidentate, thus:-



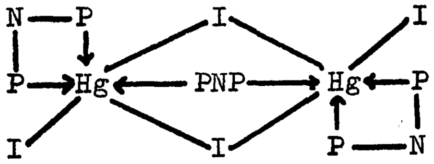
Attempts to prepare the 2:1 adduct between the ethyl compound and mercuric iodide resulted in the isolation of a product which was found, by iodine analysis, to be almost entirely the 1:1 adduct. Admixture of the corresponding methyl compound with mercuric iodide in the ratio 2:1 gave a solid which on crystallisation to constant melting point was found, by analysis, to be the 3:2 compound. Ebullioscopic molecular weight determinations in benzene gave $M = 1317 \pm 100$ and 1355 ± 100 and the 3:2 adduct requires $M = 2105$. It would thus appear that in boiling benzene, there is partial dissociation of the adduct, possibly to yield 1:1 adduct and free methylbis(diphenylphosphino)amine.

On the assumption that the bis(diphenylphosphino)-amine acts as a bidentate ligand, it is very difficult to assign a structure to this 3:2 adduct. However, it can be argued that the compound may be capable of acting as a monodentate ligand under certain circumstances. Using this hypothesis, and on the basis of Mann's suggestion for the structure of the 3:2 adduct one possibility is:-



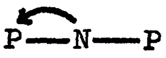
PNP = $(Ph_2P)_2NMe$.

Another possibility is that in which both the mercury atoms are 6-coordinate, giving a similar compound, in which the diphosphinoamine acts as a bidentate ligand:-



Attempts to prepare the ethyl analogue of the 3:2 compound resulted in substances of indefinite composition, but close to the 1:1 adduct. Whilst the ethyl compound yielded the 1:1 adduct even in the presence of an excess of diphosphinoamine, the methyl compound gave the 3:2 adduct.

In view of the unusual form of the 3:2 complex, the specificity of the methyl analogue is perhaps significant. It is difficult to appreciate how the substituent on the nitrogen atom would so influence the diphosphinoamine as to make it act as a monodentate ligand, although this could be a consequence of the dπ -pπ bonding being confined to only one of the phosphorus atoms, thus,



instead of

The alternative formulation of the 3:2 compound would involve a bidentate diphosphinoamine unit, and here again, the differing effects of the methyl and ethyl substituents are difficult to accept.

The reaction with nickel chloride.

Reaction of the methyl compound with nickel chloride, in the ratio 2:1 yielded a red solid, which was soluble in nitrobenzene, acetone and acetonitrile, but only sparingly soluble in ethanol and benzene. This compound was subsequently studied by Mr. J. Dunlop of this department who showed it to be the 1:1 adduct whilst ebullioscopic determinations of the molecular weight in chloroform indicated that it was monomeric. This is in agreement with the idea that the alkylbis(diphenylphosphino)amines act as bidentate ligands, a hypothesis which is confirmed by the work of Lane on the adducts of these compounds with other transition metals.

The Oxidation with 'activated' manganese dioxide.

Sisler and Smith (11) have recently reported the preparation of N-alkylaminodiphenylphosphine oxides by the action of activated manganese dioxide on the phosphine. By refluxing a benzene solution of methyl:bis(diphenylphosphino)amine with a six-fold excess of activated manganese dioxide, followed by removal of excess manganese dioxide and solvent, a crude product was obtained from which methylbis(diphenylphosphino)amine dioxide was isolated by crystallisation.

Comparison of the infra-red spectrum of the dioxide with that of the starting material showed the appearance of a peak at 1200 $cm.^{-1}$, which is in the expected region of absorption for a phosphoryl group.

The reaction with sulphur.

Reaction of ethylbis(diphenylphosphino)amine with two moles of sulphur in benzene at room temperature gave ethylbis(diphenylphosphino)amine disulphide. The infra-red spectrum of this compound showed a peak at 710 $cm.^{-1}$, corresponding to Sisler and Smith's assignment of the thiophosphoryl absorption frequency.

These experiments show that in the alkylbis(diphenylphosphino)amines both the phosphorus atoms are readily oxidised to the P (V) state. It will be interesting to investigate the ligand properties of these compounds, particularly compared to triphenylphosphine oxide.

SUMMARY.

The compounds N-ethylaminodiphenylphosphine, methylbis(diphenylphosphino)amine and ethylbis(diphenylphosphino)amine have been prepared, and the conditions for the formation of P - N - P bridges discussed and investigated. The ligand properties of the diphenylphosphinoamines have been investigated in the case of Hg (II) and in a preliminary fashion with Ni (II). The bis(diphenylphosphino)amines have also been shown to form monomethiodides, disulphides and dioxides.

CHAPTER IV.

THE REACTION OF PHENYLDICHLOROPHOSPHINE WITH ETHYLAMINE.

INTRODUCTION.

Heterocyclic ring compounds containing phosphorus are known (35) but rings containing phosphorus with other atoms are so far little known except in the case of the cyclic polyphosphates and phosphonitriles. Of special interest are compounds with rings involving tervalent phosphorus (i.e. essentially phosphines). This type of system has not been investigated although Michaelis (45) and later workers (17), (43) have examined the dimeric product from the reaction of phosphorus trichloride and aniline, in which the existence of a 4-membered phosphorus - nitrogen ring is likely. Ring compounds which contain phosphorus (III) adjacent to another potential donor atom such as nitrogen are of considerable interest, especially in respect of their likely participation in donor - acceptor reactions and formation of complexes with metal ions. Such a ring system would be found in the cyclic polymer $(\text{-RP-NR-})_n$ and it was the aim of this section of the work to attempt to prepare ring compounds of this general formula.

The four-membered ring system was the starting point of these investigations, since it offers interesting possibilities in respect of the phosphorus (III) chemistry and stereochemistry involved. The general features of such a 4-membered ring are difficult to predict, especially on the basis of phosphorus (III) and Nitrogen (III) with the generally accepted sp^2 and p^3 directional properties. Allowing for such a 4-membered ring to be formed, several isomers would certainly be expected, arising from non-planarity of the ring.

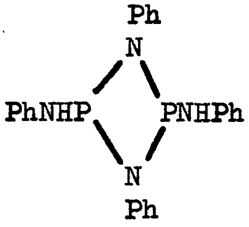
Exploratory experiments were undertaken with phenyldichlorophosphine and aniline, but did not lead to any break-through, and as a result attention was transferred to a simpler system.

The general lack of published information on tervalent phosphorus - nitrogen compounds has given rise to much detailed exploration in order to arrive at suitable techniques and reaction conditions for the formation and study of this type of compound. Attention has, of necessity been restricted to a few reactions only, and in this chapter, which represents the culmination of this investigation of aminophosphines, only one reaction has been studied, namely that of phenyldichlorophosphine and ethylamine, which it was expected would lead to the cyclic system $(\text{-PhP-NEt-})_n$.

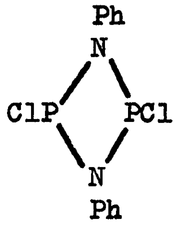
Much of the general background to this chapter has already been covered in previous discussions dealing with the formation of the P - N, N - P - N and P - N - P skeletons. However, the existence of compounds established as containing, or thought to contain, phosphorus (III) - nitrogen rings makes it relevant to survey them together now, and to bring out some new points.

Unfortunately, the simplest reactants give rise to the most complicated structures. For example, the reaction of phosphorus trichloride and ammonia, has recently been shown (44) to yield a series of products including the apparently simple compound phosphorus nitride, of which very little is known. The same authors showed that monochlorophosphines yield products of the type R_2PNH_2.

The products from the reaction of aniline and phosphorus trichloride demonstrate how limited the compounds from this type of reaction can be, despite the diversity of the possible routes by which they can be obtained. Michaelis prepared the compound (A) by the reaction of aniline on (B). It might be expected that



(A)



(B)

(B) is a precursor of (A), which is the product of the reaction of aniline and phosphorus trichloride in the correct stoicheiometric ratio. The mode of formation of the chloro ring compound (B) is of passing interest. It would appear that aniline and excess phosphorus trichloride might initially yield a mixture of $PhNH.PCl_2$ and $PhN(PCl_2)_2$. The former would yield (B) by direct elimination of hydrogen chloride from two molecules, whilst the latter would involve the elimination of phosphorus trichloride in the formation of the four-membered ring compound.

$$2PhNHPCl_2 \longrightarrow (PhNPCl)_2 + 2HCl.$$

$$2PhN(PCl_2)_2 \longrightarrow (PhNPCl)_2 + 2PCl_3.$$

When, as in the synthesis of (A) by Michaelis and Schroeter (45), the phosphorus trichloride is added to the aniline in stoicheiometric amounts, there is initially a large excess of aniline and, in view of the speed of the amino-halophosphine reaction, the initial product would certainly be P $(NHPh)_3$, according to the equation:-

$$PCl_3 + 6PhNH_2 \longrightarrow P(NHPh)_3 + 3PhNH_2HCl.$$

However, the excess of aniline would rapidly disappear as the addition of phosphorus trichloride was continued, and conditions would arise in which the reverse situation would hold, i.e. a nominal excess of phosphorus trichloride, along with a mixture containing $P(NHPh)_3$ and aniline hydro:chloride. The product would arise from interaction of this mixture, via intermediates of the type $ClP(NHPh)_2$, and possibly even the chloro compound (B).

Likewise, in the case of the formation of $P_4N_6Me_6$ the addition of phosphorus trichloride to a large excess of methylamine must involve numerous intermediates of the type $P(HNMe)_3$, which lead by condensation, by elimination of methylamine, to the final product. The compound from the phosphorus trichloride reaction with methylamine is more condensed than that obtained with aniline, which once again illustrates the greater tendency for methyl:amino compounds to form condensed products by the elimination of amine.

On the basis of the above discussion, we would expect the reaction of phenyldichlorophosphine and an excess of ethylamine to produce a product of empirical formula PhPNEt, which is most likely to be a ring compound. This chapter describes the results of such a reaction in which this aspect is investigated.

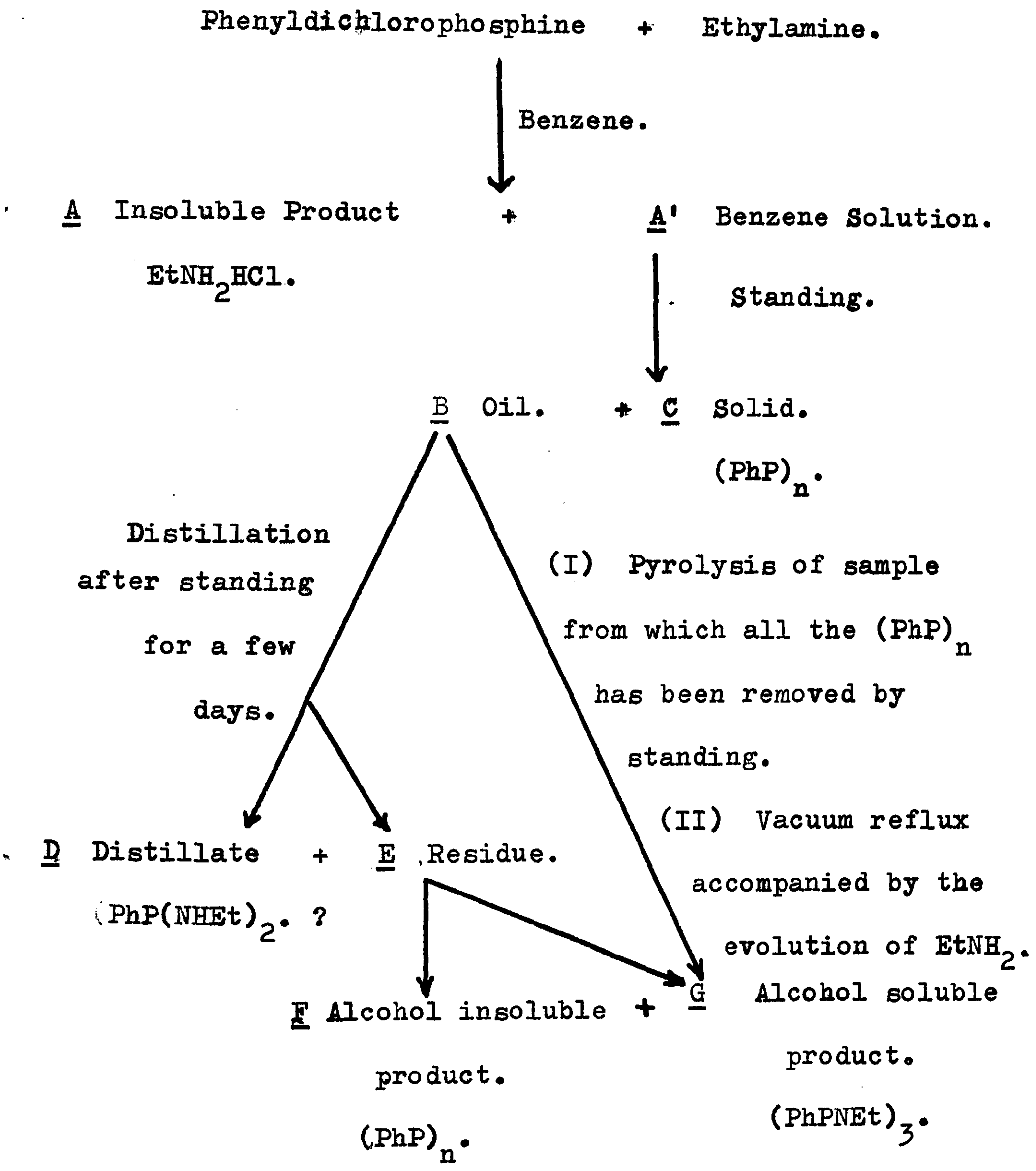
RESULTS AND DISCUSSIONS.

The reaction of phenyldichlorophosphine and ethylamine in benzene.

In the first instance, this reaction was carried out without the exclusion of moisture or oxygen, the halophosphine being added to an excess of amine dissolved in sodium dried benzene. Isolation of the benzene soluble product, by solvent evaporation after removal of the precipitated ethylamine hydrochloride, yielded a yellow oil. This oil, on heating to 180 - 190° in vacuo evolved ethylamine and at the same time its nitrogen content fell from an initial value of 6.19% to a final one of 3.07%.

The resulting material dissolved completely in cold water to give an acid solution. Its infra-red spectrum and titration with sodium hydroxide indicated the presence of phenylphosphonous acid, $PhPO_2H_2$ (70%), and it is assumed that the nitrogen is due to cyclo-N-ethylaminophenylphosphine, (30%). Such a mixture would be water soluble, since in acid solution the phosphorus (III) - nitrogen bond would be broken to yield water soluble products.

The above reaction products are surprising, particularly the high yield of acid. It is concluded that extensive hydrolysis of the halophosphine took place, presumably due to absorption of moisture from the atmosphere by the ethylamine, and that it is essential to eliminate



FLOW-SHEET FOR THE REACTION OF PHENYLDICHLOROPHOSPHINE AND ETHYLAMINE.

moisture and oxygen in this reaction.

The reaction was repeated in an atmosphere of dry nitrogen, to remove complications due to hydrolysis by atmospheric humidity. The products obtained can be conveniently divided into seven groups, and these are related to one another as shown in the flow sheet.

A. A white substance precipitated immediately on the addition of the halophosphine to the amine. This solid was separated from the benzene solution A' by filtration.

B. An oil obtained by evaporation of the benzene.

C. A white solid which crystallised during evaporation of the benzene and when the oil (B) was allowed to stand.

D. Volatile products obtained when an attempt was made to distil the oil (B) immediately after its isolation.

E. An involatile residue from the above distillation.

F. An alcohol insoluble solid obtained by the extraction of the residue E with ethanol.

G. An alcohol soluble, viscous brown oil obtained by the extraction of the residue E.

Identification of the benzene insoluble product (A).

A sample of this material was shown, after repeated washing with benzene, by its infra-red spectrum to be ethylamine hydrochloride, there being no suggestion of the presence of any benzene insoluble aromatic compound.

Investigation of the benzene soluble oil B.

Evaporation of benzene from the solution A' yielded a brown liquid and an alcohol insoluble white solid, which appeared in the course of the removal of the solvent. The white solid C was also observed to crystallize from the oil when it was allowed to stand for several weeks. This white solid was polyphenylcyclopolyphosphine, $(PhP)_n$, and is discussed later (Chapter V). It was possible to obtain a solid-free sample of liquid by decantation or by filtration. This liquid had a nitrogen content and molecular weight corresponding to a mixture of bis(ethylamino)phenylphosphine and cyclo-N-ethylaminophenylphosphine. The oil was completely soluble in alcohol, confirming the absence of any polyphenylcyclopolyphosphine.

The separation of this oil into its components might be achieved by the following methods

(a) Removal of the bis(ethylamino)phenylphosphine by hydrolysis under conditions in which the cyclic compound is stable.

All the simple aminophosphines so far investigated have been shown to be stable to alkali and this application would depend on the instability of bis(ethylamino)phenylphosphine relative to the cyclic compound.

(b) Complex formation in which only one of the constituents is involved.

It would be expected that the bis(ethylamino)-phenylphosphine would readily form a quaternary salt, on the basis of the ease with which ethylaminodiphenylphosphine methiodide is prepared. The cyclic compound might be expected to give a quaternary salt only with difficulty, if at all, and the use of suitable solvents might effect separation. A similar argument might be applied to the reactions with mercuric iodide.

(c) Chromatography.

(d) Distillation.

(e) The most attractive method for isolation of the cyclic compound would involve the completion of the formation of the P - N - P bonds by the elimination of ethylamine from bis(ethylamino)phenylphosphine, this reaction proceeding under the action of heat.

The separation of the cyclic phosphorus (III) - nitrogen compound.

(a) Hydrolysis.

The oil was partially soluble in hot aqueous sodium hydroxide with the evolution of ethylamine and it seemed likely that this represented the hydrolysis of bis(ethylamino)phenylphosphine, leaving the cyclic compound as an insoluble. When an ethereal solution of the oil was shaken overnight with dilute sodium hydroxide solution and the ethereal solution subsequently washed with water and dried over calcium hydride, filtered and evaporated, an oily residue was obtained. The infra-red spectrum of this oil was closely similar to that of the starting material, i.e. the oil B, except that there was a noticeable intensification of absorption at 850 $cm.^{-1}$ The amino absorption was, however, still present, and it was clear that the separation had not been effective.

The oil reacted exothermally with dilute hydrochloric acid, and on heating dissolved completely. The products were assumed to be phenylphosphonous acid and ethylamine hydrochloride.

(b) Complex formation.

Reaction of the oil with ethanolic mercuric iodide gave a green coloured precipitate, which was too finely grained to be filtered, whilst with alcoholic nickel chloride it yielded a red solution, indicating the formation of some nickel adduct, but no precipitation occurred. Neither of these addition reactions was investigated further.

(d) and (e) Distillation and pyrolysis.

In the first instance, an attempt was made to distil the liquid product B. A colourless liquid was obtained. Its infra-red spectrum was similar to that of the brown oil B, but there was a distinct sharpening of the peak at about 3,300 $cm.^{-1}$ (the amino frequency), and a peak at

850 $cm.^{-1}$, present in the undistilled liquid B, was absent.

On heating with concentrated aqueous sodium hydroxide, some of the distillate D reacted with the evolution of amine, but the bulk of it was insoluble, even on heating. The liquid reacted exothermally with dilute hydrochloric acid, and on gentle warming a homogeneous liquid resulted.

By analogy with the results of the study of the reaction of diphenylchlorophosphine and ethylamine, it was anticipated that the products from phenyldichloro:phosphine and ethylamine would be condensed phosphorus (III)-nitrogen compounds and bis(ethylamino)phenylphosphine, $PhP(NHEt)_2$, and that this latter would be volatile and appear as a distillate. The infra-red spectra supported this, but the nitrogen analysis was poor and indicated the presence of substantial amounts of impurities which were either nitrogen free or of very low nitrogen content. Molecular weight determinations indicated that the impurity had a molecular weight close to that of bis(ethylamino)-:phenylphosphine. (Found: M, 183; N, 8.85%. $C_{10}H_{17}N_2P$ requires: M, 196; N, 14.28%). Occasional unexpected results for nitrogen analysis have been obtained, and this might explain the great difference here.

In an attempt to confirm the presence of bis(ethylamino)phenylphosphine a methiodide adduct was prepared. This corresponded to approximately 1 mole of the liquid D reacting with 0.81 mole of methyl iodide. The resulting solid, which was obtained by removal of excess reagent and solvent by pumping, had a nitrogen content of 7.5%, instead of the expected 5.4% on the basis of the 8.85% nitrogen in the starting material. The nitrogen content of the methiodide is close to, but not exactly that required for, bis(ethylamino)phenylphosphine methiodide.

A sample of the distillate D was heated in vacuo to 120°. Ethylamine, which was removed by pumping, was evolved. The temperature was slowly raised to 190° and this temperature maintained overnight, at the end of which time the evolution of gas had ceased. The residue was a very viscous liquid containing a trace of white solid, which was shown to be polyphenylcyclopolyphosphine. The brown liquid was not investigated, although it might reasonably be expected to contain a condensed phosphorus - nitrogen product.

Investigation of the residue E from the attempted distillation of B.

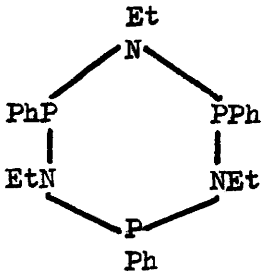
The residue E from the above distillation of B was a brown liquid, of molecular weight 469 (cryoscopic in benzene). Extraction of this with ethanol gave an alcohol insoluble residue, which was identified as polyphenylcyclopolyphosphine. This solid constituted 20% of E. The alcohol soluble portion yielded the product G, a brown viscous material which was considered to be identical with material obtained by a more direct route from the oil B, to be referred to in a subsequent paragraph. The distillation of B was carried out on a sample which had not been left standing for a sufficiently long time to allow complete crystallisation of the polyphosphine. Hence, the presence of the polyphosphine in the residue E was not a result of the distillation process, but was already present in B before heating.

A sample of the oil B was heated in an evacuated Carius tube for 10 days at 220°, to convert the bis(ethylamino)phenylphosphine to a condensed product. On opening the tube it was found that an excess pressure had built up, and the smell of ethylamine was detected. The residue was a colourless viscous oil, and there were present traces of what appeared to be carbon and red phosphorus. A molecular weight determination on a small sample of the oil, and nitrogen analysis, indicated that this was cyclotri-N-ethylaminophenylphosphine, $(PhPNEt)_3$.

The condensation should be more effective under conditions in which the ethylamine is removed from the reactants as it is formed. A sample of B was heated at 200° under vacuum until no more volatile material was given off. The volatile was shown, by its gas-phase infra-red spectrum, to consist entirely of ethylamine. Extraction of the involatile residue with ethanol gave a very low yield of insoluble polyphenylcyclopolyphosphine, which was identified by its infra-red spectrum. The ethanol extract, on removal of solvent, gave a brown viscous liquid whose molecular weight and nitrogen analysis corresponded to cyclotri-N-ethylaminophenylphosphine, and represented approximately 70% of the oil B.

The properties of Cyclotri-N-ethylaminophenylphosphine.

Condensed phosphorus (III) - nitrogen products have thus been obtained from the three pyrolysis - distillation experiments. The analysis and molecular weight correspond to a trimeric cyclic unit, i.e.



The compound has not yet been distilled and is certainly not readily volatile. It is a dark brown very viscous liquid, which on attempted crystallisation from organic solvents only yielded an oil. It was soluble in alcohols and benzene. With dilute hydrochloric acid there was a reaction to produce soluble products, presumably as a result of cleavage of the phosphorus to nitrogen bond. It did not appear to react with hot dilute alkali. The addition of alcoholic nickel chloride to an alcoholic solution of the cyclo-aminophosphine produced only a light brown coloration; no solid complex was formed.

One mole of cyclotri-N-ethylaminophenyl-:phosphine reacted with one mole of ethyl iodide to yield a brown viscous substance, which was insoluble in water, but with dilute nitric acid gave a solution in which there were free iodide ions (confirmed by silver nitrate). This is similar to the reaction of tri-N-methylimide, $P_4N_6Me_6$, with methyl iodide as described by Holmes (18). The formation of this 1:1 complex is difficult to understand on the basis of there being trivalent phosphorus atoms in a ring. Further comment must await the preparation of other, and more highly purified trimeric aminophosphines and the crystallisation of a quaternary iodide.

The investigation of the solid C.

The solid C which crystallised from the oil B was removed by filtration. Its infra-red spectrum indicated the presence of only a phenyl group, there being no other significant bands present. The substance was insoluble in ether, methanol and ethanol, but soluble in benzene and had the typically phosphine smell. Elements analysis suggested the composition $(PhP)_n$ and this was confirmed by the infra-red spectrum described above when compared with the published spectrum of tetraphenylcyclo-:tetraphosphine.

It was sometimes found during filtration of the solid from alcohol, that it fumed, even under dry nitrogen, and became a sticky mass. In general, however, the solid could be readily filtered off in small quantities. This effect has been observed by other workers (46) who explained it as being an oxidative effect, induced by traces of solvent.

Molecular weight determinations carried out in benzene under normal atmospheric conditions gave values which varied between 800 and 700. The value obtained appeared to depend on the time required for dissolution, and the value resulting from one determination fell from 694 to 670 in 30 minutes and is indicative of the fact that there is some breakdown taking place under these conditions, presumably arising from the effect of oxygen. However, despite this variation in value, the molecular weight must be greater than that of tetraphenylcyclotetraphosphine. The polyphosphines will be discussed further in Chapter V.

The reaction of phenyldichlorophosphine and ethylamine in ethylamine as solvent.

In an attempt to study the formation of the cyclic compound once again, a second preparation was carried out with certain changes in the conditions. The solvent was replaced by ethylamine and the temperature was lowered to -60°C. It was hoped by these means to control the formation of the P - N - P linkages and to obtain higher yields of cyclic material, perhaps of differing ring size or stereochemistry.

The excess ethylamine was removed by heating in a stream of nitrogen, and finally by pumping. The reaction products were extracted with benzene and the insoluble ethylamine hydrochloride was filtered off. Removal of benzene from the filtrate yielded a yellow waxy solid which was pumped at 80° for 3 hours and, which, on heating to 160° under vacuum showed no tendency to distil, although continuous bubbling occurred. This was presumably ethylamine being liberated as this was detected in the sludge trap of the rotary pump.

On cooling, the product was found to contain chloride (ca. 4%) and on dissolving in benzene, followed by addition of triethylamine it gave a precipitate of triethylamine hydrochloride. Infra-red spectroscopy indicated that the chloride in the crude product was not due to ethylamine hydrochloride. It is possible that it is present in the form of a hydrochloride of a phosphorus - nitrogen compound, similar to the hydrochlorides reported for the amino derivatives of the phosphonitriles (34). The triethylamine hydrochloride was filtered off and on removal of solvent from the filtrate and after prolonged pumping, a solid residue was obtained. Extraction of this waxy material, with ethanol gave a yield of polyphenylpolyphosphine which represented 31% of the phenyldichlorophosphine added initially and 26% of the total product. The alcohol soluble material had an infra-red spectrum which was very similar to the crude product <u>B</u>, obtained from the reaction of phenyldichlorophosphine and ethylamine in benzene, except that there was an intensification of the absorption in the hydroxide region (2,500 - 3,300 $cm.^{-1}$) and a corresponding weak broad band at 1500 - 1700 $cm.^{-1}$, suggesting the presence of water. Unfortunately, the product was lost due to the ingress of a large quantity of water during pumping with a water-pump.

The unexpected outcome of this reaction is the large amount of polyphenylpolyphosphine produced. Since the reaction was carried out under anhydrous conditions, it is very difficult to explain this high yield. It is of significance that this experiment has shown conclusively the ability of the phosphorus III - nitrogen compound, to retain chloride in the form of a hydrochloride. It is possible that this hydrogen chloride is involved in the formation of the polyphosphine. This aspect will be discussed in Chapter V.

SUMMARY.

The reaction of phenyldichlorophosphine and ethylamine has been studied in a preliminary fashion. The products have been shown to consist of an amino compound, probably bisethylaminophenylphosphine and a polymeric phosphorus - nitrogen product, which appears to be trimeric cyclo-N-ethylaminophenylphosphine. Polyphenylpolyphosphine has been obtained as a by-product in surprisingly large yield. Cyclotri-N-ethylaminophenylphosphine has little tendency to form crystalline adducts with mercuric iodide or with nickel chloride. A 1:1 ethiodide is formed, the structure of which is open to speculation.

NOTE:

Whilst the cyclic type of P - N compound was the main objective of the work described in the fore-going chapter, the problem which tended to dominate the thinking during the experimental work was the formation and removal of polyphosphine. To some extent the original objective was lost sight of in the face of this interesting development of phosphorus chemistry and this explains the approach which has been used.

CHAPTER V.

THE FORMATION OF DIPHOSPHINES AND CYCLOPHOSPHINES.

INTRODUCTION.

The formation of compounds containing phosphorus to phosphorus bonds is an interesting feature of several of the reactions which have been studied during this work. Two such compounds have been identified as products viz. tetraphenyldiphosphine and a polyphenylcyclopolyphosphine.

Kosolapoff (8) and Van Wazer (16), in their authoritative books on phosphorus chemistry make little comment on the diphosphines and the cyclophosphines. However, since the publication of these books there has been a considerable interest in such compounds, and they are discussed in several recent publications.

Tetraphenyldiphosphine was recently reported by Kuchen and Buchwald (46), (47), who prepared it by the elimination of hydrogen chloride between diphenylchlorophosphine and diphenylphosphine. This preparation has since been repeated by several workers and is variously mentioned in the literature. Niebergall (48) also reported the preparation of the compound by the desulphuration of $(Ph_2PS)_2$ using iron or copper metal.

Phosphorus ring compounds are much less frequently reported than the diphosphines. The earliest cyclic phosphine polymer seems to have been the so-called "phosphobenzol" of Kohler and Michaelis (49), who formulated it as a dimer, $(PhP)_2$, Reesor and Wright claimed (50) that the compound can exist in dimeric, tetrameric and polymeric forms. This compound has also been investigated by Kuchen and Buchwald (46) who showed it to be tetraphenylcyclotetraphosphine, $(PhP)_4$; they also prepared its sulphur addition compound $(PhPS)_4$, but report no higher analogue (51).

Burg and his colleagues (19) have prepared the trifluoromethyl compound, $(CF_3P)_n$, which is most stable as the tetramer and pentamer, although higher compounds can be obtained by suitable techniques. The structure of the tetramer and pentamer have been investigated and the rings have been shown to be puckered.

The corresponding methyl derivative, $(MeP)_n$, appears to have been prepared by the decomposition of the compound MePH CH_2PHMe, to form dimethylphosphine and apparently polymethylcyclopolyphosphine (53). It is also reported, by Kulakova, Zinoviev and Soborovskii (54), to be formed as the pentamer along with methyltetrafluorophosphorane from methyldifluorophosphine.

There have been other methods of forming phosphorus to phosphorus bonds reported in the literature. For example, tetrakistrifluoromethyldiphosphine can be prepared by the reaction of bistrifluoromethyliodophosphine and mercury (55), whilst tetraiododiphosphine is formed by the action of iodine on white phosphorus.

DISCUSSION.

In the present work, tetraphenyldiphosphine resulted in high yield from reactions between diphenylchlorophosphine and ethylamine or methylamine in which no precaution was taken to eliminate possible effects of humid air.

As already suggested, it is very likely that the tetraphenyldiphosphine arises from diphenylphosphine, which results from the alkaline hydrolysis of diphenylchlorophosphine:-

$$2Ph_2PCl + 2H_2O \longrightarrow Ph_2PH + Ph_2PO_2H + HCl.$$

There are three possible methods by which diphenylphosphine might be expected to form tetraphenyldiphosphine. The first involves reaction of diphenylchlorophosphine with diphenylphosphine, with the elimination of hydrogen chloride, The net reaction for this is:-

$$3Ph_2PCl + 2H_2O \longrightarrow (Ph_2P)_2 + Ph_2PO_2H + 3HCl.$$

By this reaction 3 moles of diphenylchlorophosphine would yield 1 mole of tetraphenyldiphosphine and would require the uptake of 2 moles of water. The second possibility is that of the action of oxygen on diphenylphosphine:-

$$2Ph_2PH + \tfrac{1}{2}O_2 \longrightarrow (Ph_2P)_2 + H_2O.$$

The net reaction for this is:-

$$4Ph_2PCl + 3H_2O \longrightarrow (Ph_2P)_2 + 2Ph_2PO_2H + 4.HCl.$$

The last possibility is that diphenylphosphine reacts with ethylaminodiphenylphosphine, with the elimination of amine:-

$$Ph_2PH + Ph_2PNHR \longrightarrow (Ph_2P)_2 + RNH_2.$$

This latter reaction is most unlikely. The aminophosphine has been shown to be stable to oxygen and hydrolysis and would not be expected to react in this way.

In marked contrast, the formation of the phenylcyclophosphines occurred in reactions in which stringent precautions had been taken to exclude air and moisture. Thus polyphenylcyclopolyphosphine was obtained as a solid in the crude reaction products of phenyldichlorophosphine and ethylamine, and in very low yield on vacuum reflux of crude bis(ethylamino)phenylphosphine.

It was found that vacuum reflux of a crude mixture of bis(ethylamino)phenylphosphine and cyclo-tri-N-ethylaminophenylphosphine, from which all of the phenylcyclophosphine had apparently crystallised, produced only a small quantity of phenylcyclophosphine, whilst a similar sample, heated in an evacuated tube at 220° for 10 days, yielded no cyclic phosphine. Thus, polyphenylcyclopolyphosphine does not result from the action of heat on the crude phosphorus - nitrogen compounds.

The cyclophosphine was insoluble in alcohol and could be separated from the other reaction products by careful filtration of an alcohol extract, followed by pumping to remove the last traces of solvent. If allowed to stand for any length of time when moist with solvent, the phosphine showed obvious signs of oxidation. The white solid melted in the range 146 - 150° and analysed closely to the composition $(C_6H_5P)_n$. Initially complete dissolution in benzene occurred, but on standing the solution developed a cloudiness and a solid was deposited. In a series of experiments, values of the molecular weight were obtained which fitted in with values of n in the formula from 7.4 to 6.3. As described above, the solutions became cloudy on standing and solid appeared, but there was no great change in the depression of freezing point as a result of this change.

When the molecular weight of a corresponding sample of polyphenylcyclopolyphosphine, produced in a reaction with propylamine rather than ethylamine, was examined under carefully controlled conditions in which oxygen was excluded, no cloudiness was apparent, and the molecular weight was consistent with a value of n of 4.9.

The values of n suggest that rings with more than 4 phosphorus atoms occur in the product, which would appear to be a mixture. The detailed work on the phosphorus rings so far carried out shows that 4- and to some extent 5- membered rings are the most readily accessible and their molecular dimensions are now well known (52). The system examined here would appear to include rings of greater size, which is not unlikely in view of the puckered nature of the 4- and 5- membered rings, which could readily expand to 6, 7, 8, etc., without undue strain. This lends support to the conclusion of Reesor and Wright (50) that the compound can exist in a more condensed state than the tetramer.

It is difficult to explain in terms of

definite reactions the formation of this cyclophosphine in the experiments reported. Having in mind the fact that the reaction of a substituted phosphine and a substituted halophosphine has been used to give compounds containing phosphorus - phosphorus bonds, it is easy to assume that the cyclophosphine results from such an interaction.

The high conversion (30% approx.) of the phenyldichlorophosphine initially present to the ring compound would require the formation of a large quantity of phenylphosphine. The hydrogen required could come from two possible sources:-

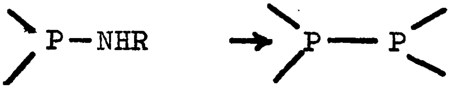
(1) By the ingress of moisture to the reaction mixture.

(2) By abstraction of hydrogen from either the phenyl or ethyl groups present in the cycloaminophosphine, $(PhPNEt)_3$, or from the bis(ethylamino)-phenylphosphine.

If water is required in more than catalytic quantities, the first of the above possibilities can be eliminated, since the reaction was carried out under anhydrous conditions. There was no apparent increase in the yield of cyclophosphine when the experiment was conducted without taking precautions to eliminate oxygen or moisture.

The second possibility is unlikely, since the production of cyclophosphine would have taken place, to a slight extent at least, in the reaction of phenyldichlorophosphine and secondary amines, and in these reactions there was no indication of such a by-product.

Failing any obvious route to the phenylphosphine required for phosphorus - phosphorus bond formation by the elimination of hydrogen chloride on reaction with halophosphine, other possibilities must be set down:-

(1) 2  $+ RNH = NHR$

(2) $2\ P{-}NHCH_2CH_3 \rightarrow P{-}P + CH_2{=}CH.NH_2$

(3) $PNHR + ClP \rightarrow P{-}P + RNHCl.$

(4) $PH + ClP \rightarrow P{-}P + HCl.$

(5) $PCl + ClP \rightarrow P{-}P + Cl_2.$

(6) $2\ PCl + R_3P \rightarrow P{-}P + R_3PCl_2.$

(7) $2\ PNHR + R_2PCl \rightarrow P{-}P + R_2\underset{Cl}{P}(NHR)_2.$

(8) $3\ P{-}X \rightarrow P{-}P + PX_3.$

The experimental evidence available does not assist in any way in deciding which, if any of these routes is in fact the preferred one.

EXPERIMENTAL.

EXPERIMENTAL.

Phenyldichlorophosphine and diphenylchlorophosphine were obtained commercially and were used without purification. Where necessary, amines were dried over potassium hydroxide or calcium hydride. Sodium dried solvents were generally used and preparations of the aminophosphines were carried out under an atmosphere of dry nitrogen.

Considerable difficulty was experienced in obtaining concordant and acceptable analytical figures for carbon and hydrogen, these analyses being carried out by Bernhardt of Mulheim (Ruhr), Germany. Generally, nitrogen analyses, carried out in this department, were very satisfactory. The Lassaigne nitrogen test was negative for the aminophosphines, and the confirmation of the presence of this element depended on analysis. Confirmation of the compounds listed had in some case to depend on the satisfactory analysis of derivatives, rather than the original material. Extensive use of infra-red spectra showed the purity of the material employed at all stages of the preparations. In particular, the absence of a frequency which could be assigned to $P = O$ was of significance in assessing the possible presence of phosphine oxides as impurities.

CHAPTER I.

Preparation of diethylaminodiphenylphosphine.

A solution of diethylamine (7.3 g., 0.1 mole) in sodium dried benzene (20 ml.) was added dropwise with stirring to diphenylchlorophosphine (8.3 g., 0.038 mole) dissolved in benzene (20 ml.) Entry of air to the reaction mixture was prevented by the use of a flow of dry nitrogen. The reactants were stirred for approximately 15 minutes and then the precipitated diethylamine hydrochloride was filtered off and washed with benzene, and the combined filtrate and washings freed from benzene. During removal of the benzene a solid appeared; there seemed to be a considerable quantity but on heating a solution was formed which on fractional distillation yielded a colourless liquid, b.p. 126°/0.1 mm. (2 g. 38%). (Found: C, 74.0; H, 7.6; N, 5.7; P, 11.7. $C_{16}H_{20}NP$ requires: C, 74.6; H, 7.8; N, 5.5; P, 12.1%.)

Stability of diethylaminodiphenylphosphine to aerial oxidation.

A weighed sample of the liquid was exposed to the air and reweighed after several time intervals.

Wt. of solid (g)	Time (mins.)
0.2090	0
0.2098	15
0.2098	30
0.2099	45
0.2099	60

From the constancy in the weight of the sample, it is inferred that for periods up to 1 hour the liquid is stable to air.

The action of dilute hydrochloric acid on diethylaminodi:phenylphosphine.

The phosphine (209 mgms.) was mixed with dilute hydrochloric acid (5 ml.). Initially a white oil remained as an insoluble phase, but on heating this dissolved. The excess hydrochloric acid was boiled off and the residual solid pumped overnight. The weight of the product was 268 mgms., representing a weight gain of 29%. Extraction of this residue with benzene left an insoluble which was identified by its infra-red spectrum as diethylamine hydrochloride, whilst evaporation of the benzene yielded a residue, whose infra-red spectrum was identical to that of a known sample of diphenylphosphinic acid, Ph_2PO_2H.

Reaction of diethylaminodiphenylphosphine with hydrogen peroxide.

Hydrogen peroxide (5 ml. of 100 volume) was added to the phosphine (0.4 g.) dissolved in ethanol (25 ml.). Removal of solvent yielded a product whose infra-red spectrum indicated that there had been breakdown of the compound. Extraction with sodium hydroxide, followed by acidification, yielded a crude product whose infra-red spectrum was identical with that of a known sample of diphenylphosphinic acid.

Preparation of diethylaminodiphenylphosphine methiodide.

The reaction of diethylaminodiphenylphosphine (0.133 g., 0.52 m. mole) and excess methyl iodide was markedly exothermic and gave a white solid of m.p. 122 - 124°. (Found: I, 31.9; N, 3.2. $C_{17}H_{23}INP$ requires: I, 31.8; N, 3.5%). The yield was theoretical for the 1:1 addition compound.

Action of dry hydrogen chloride on diethylaminodiphenylphosphine methiodide.

A sample of the methiodide dissolved in methanol was treated with dry gaseous hydrogen chloride and yielded, on removal of the alcohol, a residue which appeared to be a mixture of a solid and a liquid. This residue contained a benzene insoluble product which was identified, by its infra-red spectrum and analysis, as diethylamine hydrochloride. (Found: C, 43.3; H, 10.6; N, 12.3. $C_4H_{12}NCl$ requires: C, 43.8; H, 10.9; N, 12.7%).

Attempted pyrolysis of diethylaminodiphenylphosphine methiodide.

The methiodide was heated slowly to 200° in a vacuum system. The solid melted in the range 130 - 140°. There was no apparent change in the solid and no volatile was given off. The product was a dark coloured, water-soluble material. Thus at temperatures up to 200° the methiodide does not yield any volatile product.

Preparation of the mercuric iodide complex of diethylamino:diphenylphosphine.

Diethylaminodiphenylphosphine (0.227 g., 0.88 m. mole) with an excess of mercuric iodide gave a yellow coloured product. This solid, recrystallised from methanol, melted at 188 - 190°. It was insoluble in benzene and corresponded to the 1:1 adduct. (Found: C, 26.75; H, 2.8; N, 2.3. $C_{16}H_{20}HgI_2NP$ requires: C, 27.0; H, 2.8; N, 2.0%).

Preparation of the mercuric iodide complex of diethylamino:diphenylphosphine methiodide.

Diethylaminodiphenylphosphine (0.473 g., 1.8 m. moles) was converted to the methiodide and then allowed to react with an excess of mercuric iodide in methanol. Ether was added and after cooling in a refrigerator for some days this yielded a greenish crystalline solid, m.p. 116 - 118°. (Found: C, 24.0; H, 2.8; N, 1.7%. $C_{17}H_{23}HgI_3NP$ requires: C, 23.9; H, 2.7; N, 1.6%).

Preparation of the cuprous iodide complex of diethylamino:diphenylphosphine.

Cuprous iodide (approx. 2 g.) was

dissolved in saturated potassium iodide solution (30 ml.). The phosphine (0.474 g., 1.8 m. moles) in alcohol (10 ml.) was added. A complex (0.638 g.) was precipitated immediately. This solid, recrystallised from ethanol, had m.p. 225 - 227° and was freely soluble in benzene. (Found: C, 43.2; H, 4.4; N, 2.9%; M (cryoscopic in benzene), 1620. $C_{16}H_{20}CuINP$ requires; C, 43.0; H, 4.5; N, 3.1%; $(Ph_2PNEt_2.CuI)_4$. requires M, 1788).

CHAPTER II.

The detailed preparations of bisdimethyl:aminophenylphosphine and its derivatives are quoted as examples of the methods employed.

The preparation of bisdimethylaminophenylphosphine.

Dimethylamine (58 g., 1.3 moles) in dry benzene (100 ml.) was added dropwise, with stirring, to the phenyldichlorophosphine (40 g., 0.21 mole) in benzene (300 ml.) at 0°. Entry of air to the mixture was prevented by the use of a nitrogen stream. The mixture was stirred for about a day to ensure an easily filterable precipitate. The hydrochloride was separated by filtration under nitrogen and washed with dry benzene and the washings were combined with the filtrate. The benzene was removed by distillation, giving a product (39.6 g., 90%) which was distilled through a 14" Fenske column. A fraction (26.2 g.), b.p. 59.0 - 59.5°/0.2 mm. (Found: N, 13.8%) was purified by redissolving it in benzene, washing it with several portions of cold water to remove traces of the amine hydrochloride complex, drying (CaH_2) and distillation; this product had b.p. 61.0°/0.1 mm. (Found: N, 14.3. $C_{10}H_{17}N_2P$ requires N, 14.3%).

Bisdimethylaminophenylphosphine Methiodide.

Bisdimethylaminophenylphosphine (0.439 g.) was treated in ether with an excess of methyl iodide.

Evaporation under a vacuum gave a white solid (0.743 g., 98%) (Found: N, 8.3. $C_{11}H_{20}IN_2P$ requires N, 8.3%). The methiodide was water soluble, giving an immediate precipitate with aqueous silver nitrate solution.

Mercuric Iodide Complexes of Bisdimethylaminophenyl:phosphine.

(a) 1:1 Complex. Bisdimethylaminophenyl:phosphine (0.502 g., 2.56 mmoles) in methanol was added to mercuric iodide (1.140 g., 2.52 mmoles) in methanol. The fine white complex (1.506 g.) which separated was filtered off and washed with ether. Recrystallisation from acetone gave pale yellow crystals, m.p. 192 - 196° (Found: I, 39.2. $C_{10}H_{17}HgI_2N_2P$ requires I, 39.1%).

(b) 2:1 Complex. Bisdimethylaminophenyl:phosphine (0.305 g.) in a few ml. of methanol was mixed with a solution of mercuric iodide in methanol. A white crystalline precipitate appeared at once. This complex recrystallised from ethanol as needles, m.p. 86 - 88° (0.610 g., 92%) (Found: C, 27.2; H, 4.1; I, 29.35; N, 6.0. $C_{20}H_{34}HgI_2N_4P_2$ requires C, 28.4; H, 4.0; I, 29.9; N, 6.6%).

Mercuric Iodide Complex of Bisdimethylaminophenylphosphine Methiodide.

Direct addition of a methanolic solution of the methiodide to an excess of mercuric iodide, diss:olved in methanol, gave greenish crystals of the adduct, m.p. 132 - 134° (Found: C, 16.7; H, 2.2; Hg, 24.9; N, 4.3 $C_{11}H_{20}HgI_3N_2P$ requires C, 16.7; H, 2.5; Hg, 25.2; N, 3.5%). Alternatively the methanolic solution of mercuric iodide is added to an ethereal solution of the phosphine and methyl iodide.

Bisdiethylaminophenylphosphine.

Reaction of diethylamine (174 g., 2.38 moles) and phenyldichlorophosphine (103 g., 0,57 mole) was carried out as described for dimethylamine, except that ether was employed as solvent. 100 G. (70%) of a fraction, b.p. 80°/0.025 mm., was obtained (Found: N, 10.6%). This was washed with water as described above, giving a liquid phosphine, b.p. 91.5°/0.1 mm. (Found: C, 66.3; H, 9.9; N, 11.1%; M. 257 (cryoscopic in benzene), 245 (ebullioscopic in benzene). $C_{14}H_{25}N_2P$ requires C, 66.6; H, 10.0; N, 11.1%; M, 252).

Bisdiethylaminophenylphosphine Methiodide.

This reaction was carried out as described in the case of the dimethylamino-compound; the product was, however, a viscous liquid (yield 100% for a 1:1 complex) (Found: I, 31.6; N, 6.9. $C_{15}H_{28}IN_2P$ requires I, 32.2; N, 7.1%). The liquid methiodide was stable up to 250°; above this temperature decomposition occurred. The liquid was water-soluble, the solution being acid and containing free iodide ions. The molecular weight (cryoscopic in water) was 206 (M, calc. 394). The conductance Λ_m in dry acetonitrile was 112.1 ohm.$^{-1}$ cm.^{2} mole^{-1}.

Mercuric Iodide Complexes of Bisdiethylaminophenylphosphine.

(a) 1:1 Complex. The phosphine (1.29 g.) was treated in methanol with an excess of a saturated solution of mercuric iodide in methanol. The white complex (2.70 g.) that separated, recrystallised from ethanol, then having m.p. 176 - 178° (75%). It was sparingly soluble in benzene but readily soluble in sulpholane (Found: C, 24.4; H, 3.7; N, 4.6% M (cryoscopic in sulpholane), 1080. $C_{14}H_{25}HgI_2N_2P$ requires C, 23.8; H, 3.4; N, 4.0%; M, 706).

(b) 2:1 Complex. An excess of a methanol solution of the phosphine was added to a solution of mercuric iodide in methanol. A white crystalline complex, m.p. 142 - 143°, was obtained (Found: C, 35.4; H, 5.2; I, 26.5; N, 6.0%; M (cryoscopic in benzene), 970. $C_{28}H_{50}HgI_2N_4P_2$ requires C, 35.1; H, 5.2; I, 26.5; N, 5.9%; M, 958).

Mercuric Iodide Complex of Bisdiethylaminophenylphosphine Methiodide.

The methiodide (1.970 g.) yielded a greenish crystalline complex (2.043 g.) when mixed with an alcoholic solution of mercuric iodide and left overnight; this had m.p. 79 - 81° (Found: C, 29.0; H, 4.4; N, 4.6%; M (cryoscopic in $C_4H_8O_2S$), 406. $C_{30}H_{56}HgI_4N_4P_2$

requires C, 29.0; H, 4.4; N, 4.5%; M = 1244).

Bisdipropylaminophenylphosphine.

Phenyldichlorophosphine (40 g., 0.22 mole) was treated with di-n-propylamine (100 g., 1 mole). A product (54%), b.p. 140°/0.2 mm., was obtained (N, 9.4%) that was washed with water as described above, to give a liquid, b.p. 122°/0.1 mm. (Found: N, 9.1. $C_{18}H_{33}N_2P$ requires N, 9.1%).

With an excess of methyl iodide this gave a methiodide, m.p. 111 - 114° (Found: N, 6.15. $C_{19}H_{36}IN_2P$ requires N, 6.2%).

Mercuric Iodide Complexes of Bisdipropylaminophenylphosphine.

(a) 1:1 Complex. The aminophosphine (0.498 g., 1.61 mmoles) in methanol was added to a methanolic solution of mercuric iodide (0.720 g. 1.59 mmoles); the complex (0.858 g.) had m.p. 134 - 136° (Found: I, 33.7%; M (cryoscopic in benzene), 1370 ± 50. $C_{18}H_{33}HgI_2N_2P$ requires I, 33.3%; M, 762).

(b) 2:1 Complex. The aminophosphine (2.2 g., 7.15 mmoles) reacted with mercuric iodide (1.5 g., 3.3 mmoles) to give a white solid complex, m.p. 126 - 127° (Found: I, 23.8; N, 4.9. $C_{36}H_{66}HgI_2N_4P_2$ requires I, 23.8; N, 5.2%).

Mercuric Iodide Complex of Bisdipropylaminophenylphosphine Methiodide.

This aminophosphine (1.45 g., 4.71 mmoles) was converted into the methiodide which was treated in methanolic solution with mercuric iodide (2.15 g., 4.74 mmoles) in methanol. A crystalline complex separated slowly and after a week 1.7 g. were available; it had m.p. 59 - 61° (Found: C, 24.3; H, 4.2; Hg, 21.7; N, 2.9. $C_{19}H_{36}HgI_3N_2P$ requires C, 25.2; H, 4.0; Hg, 22.1; N, 3.1%).

Chlorodiethylaminophenylphosphine.

To phenyldichlorophosphine (100 g., 0.56 mole) in benzene (800 ml.) was added diethylamine (87 g., 1.19 moles) in benzene (100 ml.). The product $PhP(NEt_2)Cl$(57 g., 48%), had b.p. 82 - 84°/0.05 mm.

Diethylaminodimethylaminophenylphosphine.

The preceding compound (19.0 g., 0.088 mole) and an excess of dimethylamine yielded a fraction, b.p. 61 - 62°/0.05 mm., that was washed with water as described above, giving a product, b.p. 72.5°/0.1 mm. (Found: N, 12.4. $C_{12}H_{21}N_2P$ requires N, 12.5%).

With an excess of methyl iodide this afforded a waxy hygroscopic methiodide whose analysis was not possible. The weight increase (0.663 g. from 0.390 g.) is close to that required for a 1:1 adduct.

Mercuric Iodide Complex of Diethylaminodimethylaminophenyl:phosphine.

This phosphine (1.032 g., 4.60 mmoles) with mercuric iodide (1.300 g., 2.80 mmoles) gave a white crystalline complex (1.91 g.), m.p. 159 - 161° (Found: I, 28.1; N, 5.7. $C_{24}H_{42}HgI_2N_4P_2$ requires I, 28.2; N, 6.2%).

Mercuric Iodide Complex of Diethylaminodimethylaminophenyl:phosphine Methiodide.

The phosphine (0.660 g., 2.95 mmoles) was converted into the methiodide and then treated with mercuric iodide, slowly yielding a greenish complex (0.20 g.), m.p. 90 - 92° (Found: C, 18.9; H, 2.85; N, 3.8. $C_{13}H_{24}HgI_2N_2P$ requires C, 19.0; H, 2.9; N, 3.4%).

Diethylaminodiproplylaminophenylphosphine.

The compound $PhClP.NEt_2$ (5.08 g., 0.0236 mole) reacted with n-propylamine (10.0 g., 0.1 mole) gave a product (3.1 g.), b.p. 110 - 114°/0.05 mm. (Found: C, 68.0; H, 10.2; N, 9.95. $C_{16}H_{29}N_2P$ requires C, 68.5; H, 10.4; N, 10.0%).

Diethylaminodipropylaminophenylphosphine Methiodide.

The phosphine (0.181 g., 0.645 mmole) gave an oily methiodide (0.275 g.) which solidified slowly and then had m.p. 107° (Found: N, 6.6; $C_{17}H_{32}IN_2P$

requires N, 6.6%).

Mercuric Iodide Complex of Diethylaminodipropylaminophenylphosphine.

The phosphine (0.404 g., 1.44 mmoles) with mercuric iodide gave, with some difficulty, a complex (0.289 g., 40%), m.p. 102 - 108° (Found: C, 37.8; H, 5.8; N, 5.3. $C_{32}H_{58}N_4P_2HgI_2$ requires C, 37.8; H, 5.7; N, 5.5%).

Mercuric Iodide Complex of Diethylaminodipropylaminophenylphosphine Methiodide.

The methiodide of this phosphine (0.623 g., 2.6 mmoles) with mercuric iodide in methanol gave, on addition of ether and storage in a refrigerator for some days, a greenish complex, m.p. 82 - 84° (Found: C, 22.9; H, 3.9; N, 3.1. $C_{17}H_{32}HgI_3N_2P$ requires C, 23.3; H, 3.7; N, 3.2%).

Reaction of Gaseous Hydrogen Chloride with Bisdiethylaminophenylphosphine.

Dry hydrogen chloride was caused to react with the phosphine (1.965 g., 7.8 mmoles) in a vacuum-system. This yielded a product (3.124 g.), corresponding to an uptake of 31.2 mmole of acid. The mixture, on extraction with benzene followed by filtration, yielded diethylamine hydrochloride (1.647 g., 15.0 mmoles). The reaction is thus:-

$$Ph.P(NEt_2)_2 + 4HCl \longrightarrow 2Et_2NH_2Cl + Ph.PCl_2.$$

Reaction of Aqueous Hydrochloric Acid and Sodium Hydroxide with Bisdiethylaminophenylphosphine.

The phosphine reacted with cold 2M-hydrochloric acid with evolution of heat. Phenylphosphonous acid, identified by its infra-red spectrum, crystallised from the cloudy solution. The overall hydrolysis can be represented:

$$Ph.P(NEt_2)_2 + 2H_2O \longrightarrow Ph.PHO.OH + 2Et_2NH_2Cl.$$

With 4M-sodium hydroxide, no reaction was observed, even on boiling.

Titration of Bisdiethylaminophenylphosphine Methiodide with Sodium Hydroxide.

Freshly prepared methiodide (0.242 g., 0.606 mmole) was dissolved in water; the pH of this solution was 3.9. An addition of 0.5 ml. of 0.1 M NaOH (0.05 mmole) the pH rose to 9.6.

Conductance Study of the Reaction Between the Dialkylaminophenylphosphines and Methyl Iodide in Acetonitrile.

The adduct of bisdiethylaminophenylphosphine and methyl iodide in acetonitrile is given as a typical example. The phosphine (0.502 g., 1.95 mmole) was dissolved in 250 ml. of acetonitrile. A 25 ml. sample was diluted to 200 ml. in the conductance cell and an equimolar amount of methyl iodide added. The mixture was stirred continuously and the change in conductance of the solution studied with respect to time. The results are as shown on page 33, the reaction being first order.

The Interaction of the Mercuric Iodide Adducts with Alcohol.

The 2:1 adduct of bisdiethylaminophenyl:phosphine and mercuric iodide (0.170 g., 0.178 mmole), dissolved in ethanol (10 ml.) was refluxed. Within 1 hour a globule of mercury was visible, and after 5 hours the alcohol solution was carefully sucked off, the residual mercury dissolved in 0.5 ml. concentrated nitric acid and estimated by the usual procedure with ammonium thiocyanate. This corresponded to 0.162 mmole representing 91% of the total mercury present in the adduct.

Reaction of Bisdiethylaminophenylphosphine with Cuprous Iodide.

Bisdiethylaminophenylphosphine in ethanol was added to a saturated solution of cuprous iodide in saturated aqueous potassium iodide. The resulting white oil gradually yielded a crystalline solid which was impure bis-(bisdiethylaminophenylphosphine) copper (I) iodide, $(PhP(NEt_2)_2)_2CuI$. (Found: C, 47.5; H, 7.13; N, 7.22. $C_{28}H_{50}CuIN_4P_2$ requires: C, 48.4; H, 7.21; N, 8.06%).

CHAPTER III.

The Reaction of Diphenylchlorophosphine with Ethylamine in Benzene.

Diphenylchlorophosphine (61.5 g., 0.28 mole) was dissolved in dry benzene (200 mL) and added dropwise, with stirring, under an atmosphere of dry nitrogen to a benzene solution of ethylamine (30 g. 0.66 mole in 100 ml.). The precipitated hydrochloride was removed by filtration, washed with benzene, and the resulting crude yellowish liquid isolated by removal of benzene from the filtrate. The yield was 61.6 g. (Theoretical yield for Ph_2PNHEt, 64.2 g. $(Ph_2P)_2NEt$, 57.9 g.). There appeared to be a considerable amount of ethylamine removed on pumping the product after removal of benzene. Distillation of this crude product gave the following fractions:-

	B.p./0.1 mm.	Yield.
I	$< 190^\circ$	6.3 g.
II	$190 - 192^\circ$	12.5 g.
III	$200 - 203^\circ$	12.8 g.

Redistillation of fraction I yielded a colourless liquid, which melted at room temperature. This was Ph_2PNHEt. (Found: N, 6.41. $C_{14}H_{16}NP$ requires N, 6.11%). The distillation of fraction III had to be discontinued on account of uncontrollable bumping; a considerable residue was left. Fractions II and III partially solidified on standing and were subsequently crystallised from aqueous ethanol to yield $(Ph_2P)_2NEt$. (For fraction II; N, 3.81 Calculated for $C_{26}H_{25}NP_2$; N, 3.39%).

Preparation of N-ethylaminodiphenylphosphine Methiodide.

A sample of Ph_2PNHEt was dissolved in ether and to this was added an excess of methyl iodide. An oil was produced initially from which a white solid was obtained. (Found: N, 3.75. $C_{15}H_{19}INP$ requires; N, 3.77%).

The Reaction of Diphenylchlorophosphine and Ethylamine in Ethylamine.

Diphenylchlorophosphine (22.0 g., 0.1 mole) was added dropwise to ethylamine (50 ml.), under an atmosphere of dry nitrogen, at -10°. The reactants were stirred for 2 hours, extracted with sodium dried ether and the insoluble ethylamine hydrochloride filtered off. (Yield, 9.1 g. Theory requires 8.2 g.) Removal of ether from the filtrate gave an oil. (Yield, 28.7 g. Theory for the production of ethylaminodiphenylphosphine requires 22.9 g., for ethylbis(diphenylphosphine)amine, 20.6 g.) This crude material had excess ethylamine present, as was suggested by the occurrence of bumping when it was pumped with the rotary pump. A fractional distillation was carried out:-

Fraction.	B.p./0.1 mm.	Yield.
I	60 - 111°.	1.1 g.
II	Temp. fell to 105°	5.5 g.

Fraction.	B.p./0.1 mm.	Yield.
III	Temp. rose quickly to 120° then gradually fell, steadying at 100°C and eventually falling off.	3.6 g.
IV	Involatile residual oil.	7.8 g.

The total distillation products, including the residue were 18.0 g., which represented a weight loss of 10.7 g. This must have been due to ethylamine. A sample of the residue, which on standing yielded some solid, was crystallised from aqueous alcohol to give white ethylbis(diphenylphosphino)amine, $(Ph_2P)_2PNEt$, m.p. 96 - 98°. (Found: N, 3.46; M (cryoscopic in benzene) = 421. $C_{26}H_{25}NP_2$ requires: N, 3.39; M, 413.).

The Reaction of Diphenylchlorophosphine and Ethylamine in Ethylamine, Without the Exclusion of Oxygen and Moisture.

The above reaction was repeated with 0.28 mole of diphenylchlorophosphine and 100 ml. of ethylamine. Isolation of the product in the manner described resulted in a yellow oil. A sample (8 g.) of this was crystallised with difficulty from alcohol, as a white solid which softened at 155°, melted in the range 164 - 166° and had no nitrogen present. This solid represented only a small fraction of the crude yield. This was a mixture of 78% tetraphenyldiphosphine and 22% tetraphenyldiphosphine dioxide. (Found: C, 73.2;

H, 5.16; P, 15.9%; M (cryoscopic in benzene), 390.
$C_{24}H_{20}P_2$ requires: C, 77.8; H, 5.41; P, 16.7%; M, 370.
$C_{24}H_{20}P_2O_2$ requires: C, 71.6; H, 4.96; P, 15.4%) M; 402).

The Reaction of Diphenylchlorophosphine and Alcoholic Methylamine.

The reaction was carried out (a) under normal atmospheric conditions, and (b) under an atmosphere of dry nitrogen.

(a) Diphenylchlorophosphine (22.0 g., 0.1 mole) in benzene (25 ml.) was added dropwise with stirring to a benzene solution of the amine/alcohol mixture (32 ml. of a 33% alcoholic solution) in benzene (50 ml.). A precipitate of ethylamine hydrochloride formed immediately, and after stirring the reactants for 1 hour, it was filtered off and washed with benzene. Evaporation of the benzene resulted in a colourless liquid and a white solid, which came out of solution during removal of the solvent. This crude product was kept at about 4° for a few days and then the liquid removed by ether extraction followed by filtration of the solid.

This solid (1.6 g.) was subsequently shown, by its infra-red spectrum, to be a mixture of tetraphenyldiphosphine and tetraphenyldiphosphine dioxide. It softened at 155° and yielded a colourless melt by 170°. It was insoluble in dilute hydrochloric acid and dilute sodium hydroxide.

The ether extract on evaporation of solvent gave a yellow liquid (14.1 g.) which was fractionally distilled:-

Fraction.	B.p./0.04 mm.	Yield.
I	< 87°.	0.6 g.
II	88° rising to 100°. Mainly at 98 - 100°.	3.0 g.
III	100° with a rapid rise to 110°, followed by a slow rise, accompanied by much slower distillation to 120°. Distillation was steady at 120°. At this temperature, the distillate was cloudy and appeared to have a little solid present.	5.4 g.

Neither fraction II nor III contained nitrogen.

(b) The reaction was repeated as above under dry nitrogen when a liquid, b.p. 120°/0.1 mm., was obtained. Analysis showed that nitrogen was absent and the infra-red spectrum of the substance indicated that it was an ester, probably ethyl diphenylphosphinite, Ph_2POEt. The cuprous iodide adduct of this compound was prepared. m.p. 185 - 188°. (m.p. of $Ph_2POEt.CuI$, 190 - 191°).

Preparation of Dry Methylamine.

Methylamine (50 ml.) was prepared by the action of sodium hydroxide (100 g., 2.5 m.) on methylamine hydrochloride (85 g., 1.23 M). The reactants were dissolved in water (200 ml.) and boiled. The evolved gas was dried by passage through a quicklime tower. It was then passed through cooled traps to remove any residual water-vapour, condensed into the reaction vessel and cooled to -50°.

The Reaction of Diphenylchlorophosphine with Methylamine in Methylamine as Solvent.

(a) Diphenylchlorophosphine (22.0 g., 0.1 mole) was added to dry methylamine (50 ml.) at -50°, under a dry nitrogen flow. Excess amine was evaporated and the residue extracted with ether. Insoluble methylamine hydrochloride was removed by filtration, and evaporation of ether from the clear solution gave the crude product (20.5 g.) (Ph_2PNHMe requires 21.5 g. $(Ph_2P)_2NMe$ requires 19.9 g.)

This was vacuum distilled and fractions taken:-

Fraction.	B.p./0.2 mm.	Yield.
I	93 - 102°	0.2 g.
II	104 - 118°	4.7 g.

Analysis of fraction II gave N, 4.3. Ph_2PNHMe requires N, 6.51%. Fraction II was redistilled and yielded:-

II a.	104 - 105°	(0.3 g.)	at 0.1 mm.
II b.	115 - 118°	(1.5 g.)	
II c.	120°	(2.2 g.)	

The infra-red spectrum of each fraction was measured. Fraction II c appeared to have the most prominent amino peak and this fraction was analysed for nitrogen. (Found: N, 4.3%). Redistillation of the material did not change the nitrogen value. A vapour phase chromatograph using a 10% Apiezon on cellite column indicated that there were at least three compounds present.

Addition of methyl iodide to an ethereal solution of the fraction II c yielded a white crystalline solid m.p. 108 - 110°. (Found: N, 4.04; $C_{14}H_{17}INP$ requires: N, 3.92%).

The oil residue from the distillation of the crude reaction product was dissolved in hot rectified spirit and on cooling a white solid crystallised, m.p. 112 - 115°. (yield 7 g.). This was $(Ph_2P)_2NMe$. (Found: N, 3.88. $C_{25}H_{23}NP_2$ requires: N, 3.51%).

(b) The above reaction was repeated. In this case, the product was distilled up a notched column and the following fractions were obtained:-

Fraction.	B.p./0.1 mm.	Yield.
I	180 - 206°	Negligible.
II	206 - 218°	6.4 g.
III	218°	3.4 g.

Fractions II and III were combined and these solidified slowly on standing. Crystallisation from rectified spirit gave $(Ph_2P)_2NMe$, m.p. 111 - 115°. (Found: C, 72.88; H, 5.42; N, 3.59%. M (cryoscopic in benzene), 385. $C_{25}H_{23}NP_2$ requires: C, 75.2; H, 5.77; N, 3.51%. M, 399).

The Reactions of Alkylbis(diphenyphosphino)amines.

Reaction with Dilute Hydrochloric Acid.

Ethylbis(diphenylphosphino)amine (0.21 g., 0.51 mmoles) was boiled with dilute hydrochloric acid (10 ml.). The products were insoluble, but on cooling, followed by neutralisation with sodium hydroxide a colourless solution resulted. The acid which was precipitated on acidification of the solution was filtered off, crystallised from aqueous alcohol and identified as diphenylphosphinic acid, Ph_2PO_2H, by its infra-red spectrum.

Reaction with Alkyl Iodides.

Methylbis(diphenylphosphino)amine (0.50 g., 1.25 mmole) dissolved in ether (10 ml.) with excess methyl iodide yielded on removal of excess solvent and methyl iodide, a colourless oil (0.706 g.), which could not be solidified. The weight gain corresponded approximately to the formation of a 1:1 adduct. (Theoretical yield for the formation of $C_{26}H_{26}IN_2P$: 0.678 g.).

The action of excess ethyl iodide on ethylbis(diphenylphosphino)amine (0.196 g., 0.475 mmole) gave a white solid (0.276 g.), m.p. 90 - 91°. (Found: N, 2.50. $C_{28}H_{30}INP_2$ requires: N, 2.46%).

Reaction with Mercuric Iodide.

(a) Reactions of Ethylbis(diphenylphosphino)amine

1:1 adduct prepared by adding the phosphinoamine to mercuric iodide.

The phosphinoamine (0.414 g., 1.00 mmole) in alcohol (25 ml.) was added to mercuric iodide (0.455 g., 1.00 mmole) in alcohol and yielded a white crystalline product (0.77 g.). (Found: I, 29.17. M (cryoscopically in nitrobenzene), 604 falling to 529 after 2 hours. $C_{26}H_{25}HgI_2NP_2$ requires: I, 29.29; M, 867.

1:1 adduct prepared by adding mercuric iodide to the phosphinoamine.

Mercuric iodide (0.840 g., 1.85 mmole) was added to ethylbis(diphenylphosphino)amine in alcohol (25 ml.). This immediately yielded a white solid (1.94 g.) m.p. 195 - 200°. (Found: I, 28.30. $C_{26}H_{25}HgI_2NP_2$ requires: I, 29.29. $C_{52}H_{50}HgI_2N_2P_4$ requires: I, 19.9. $C_{78}H_{75}Hg_2I_4N_3P_6$ requires: I, 23.6%).

1:1 adduct prepared by adding mercuric iodide to ethylbis(diphenylphosphino)amine in the ratio 1:2.

Mercuric iodide (0.406 g., 0.892 mmole) in ethanol (25 ml.) was added to the phosphinoamine (0.739 g., 1.78 mmole) in ethanol (10 ml.). A white precipitate appeared immediately but quickly dissolved on standing at room temperature. Cooling of the solution in an acetone/solid carbon dioxide bath resulted in crystallisation of a white product, which partially dissolved on heating to room temperature. The insoluble product (0.300 g.) was filtered off. The melting point was ca. 128° and the iodine content was 28.0%. These figures suggested that the product was principally the 1:1 adduct.

(b) Reactions of Methylbis(diphenylphosphino)amine.

3:2 adduct.

Mercuric iodide (0.350 g., 0.772 mmole) in ethanol (20 ml.), when added to a warm solution of the phosphinoamine (0.632 g., 1.585 mmole) in ethanol (20 ml.) gave on cooling a white solid. This was crystallised from benzene m.p. 216 - 219°. (Found: N, 2.14; Hg, 20.15; I, 23.76%. M (ebullioscopic in benzene), 1317 ± 100 and 1355 ± 100. $C_{75}H_{69}Hg_2I_4N_3P_6$ requires: N, 2.90; Hg, 19.05; I, 24.14%. M, 2106).

No 2:1 adduct could be prepared.

Reaction of Methylbis(diphenylphosphino)amine with Nickel Chloride.

The phosphinoamine (0.420 g., 1.05 mmole) on addition to nickel chloride hexahydrate (0.190 g., 0.97 mmole) in alcohol (20 ml.) gave rise to a red product (0.4 g.), m.p. 300°. No suitable solvent was found for the recrystallisation of this substance. (Found: N, 2.88; Ni, 11.36; Cl, 13.38%. M (ebullioscopic in chloroform), 550 ± 80 and 470 ± 80. $C_{25}H_{23}Cl_2NiP_2$ requires: N, 2.65; Ni, 11.10; Cl, 13.42%. M, 529).

Oxidation of Methylbis(diphenylphosphino)amine by Means of Activated Manganese Dioxide.

The phosphinoamine (0.692 g., 1.73 mmole) was refluxed in benzene (25 ml.) with manganese dioxide (0.86 g., 10 mmole) for 2 hours and the mixture was then filtered through a cellulose pad. The filtrate was evaporated off and the residue recrystallised from aqueous acetone. A white solid m.p. 220 - 222° was obtained. (Found: C, 69.14; H, 5.47; N, 3.41; P, 14.42; $C_{25}H_{23}NO_2P_2$ requires: C, 69.6; H, 5.34: N, 3.25 P, 14.39 %).

Reaction of Ethylbis(diphenylphosphino)amine with Sulphur.

The aminophosphine (1.504 g., 3 mmole) and sulphur (0.233 g., 7.3 mmole) were refluxed together in benzene (25 ml.) for 1 hour, after which the mixture was filtered. Evaporation of the filtrate produced a white solid which was purified by crystallisation from aqueous acetone. m.p. 169 - 170°. (Found: C, 64.18; H, 5.37; N, 3.44; S, 13.62. $C_{26}H_{25}NP_2S_2$ requires: C, 65.4; H, 5.24; N, 2.84; S, 13.41%).

CHAPTER IV.

The Reaction of Phenyldichlorophosphine and Ethylamine in Benzene.

(a) Under Atmospheric Conditions.

Phenyldichlorophosphine (20.5 g., 0.11 mole) in sodium dried benzene (200 ml.) was added to ethylamine (35 g., 0.78 mole) in benzene (200 ml.). The precipitated ethylamine hydrochloride was filtered off and on removal of solvent a yellow liquid resulted (Yield 20.5 g., N, 6.19%. Theory for $PhP(NHEt)_2$, 22.4 g., N, 14.3%, for $(PhPNEt)_n$, 17.3 g., 9.25%.).

On heating to 190° at 0.1 mm., none of this material distilled, although it continued to bubble and on heating to constant weight under these conditions a very viscous product was obtained (N, 3.07%), whose infra-red spectrum indicated the presence of phenylphosphonic acid.

It was water-soluble, to give an acid solution and 39.8 mgms. of material required 2.28 ml. of 0.1 M sodium hydroxide for neutralisation.

(b) Under Dry Nitrogen.

Ethylamine was dried over calcium hydride for 24 hours and distilled at atmospheric pressure. Phenyldichlorophosphine was distilled and a fraction boiling at 60°/0.05 mm. taken.

Phenyldichlorophosphine (179 g.,) dissolved in benzene (100 ml.) was added dropwise to ethylamine (190 g., 4.2 mole) in benzene (250 ml.) under dry nitrogen. The reaction was very vigorous and the reactants were cooled with ice-water and stirred for 1 hour after the addition of the phosphine. The precipitated hydrochloride A was filtered off under nitrogen and washed with a little sodium dried benzene. Removal of solvent from the filtrate A' gave a brown liquid B. (Yield: 139 g; N, 10.61%; M (cryoscopic in benzene), 313. $PhP(NHEt)_2$ requires: Yield: 196 g.; N, 14.28% $(PhPNEt)_n$ requires: Yield; 151 g., N; 9.24%). On standing overnight, this oil B yielded a white solid C (1.6 g.), some of which had crystallized during removal of the benzene solvent from A'. A sample of the oil was removed at this stage and on vacuum distillation it yielded a colourless liquid, D, b.p. 98 - 105°/0.02 mm. The residue was a brown viscous liquid, which on standing yielded a glass E.

Investigation of the Volatile Product D.

This liquid was obtained on distillation of the crude oil B after it had been allowed to stand for only 1 day. b.p. 98 - 105°/0.04 mm. (Found: N, 8.85; M, 183. $C_{10}H_{17}N_2P$ requires: N, 14.28; M, 196).

Reaction with Methyl Iodide.

The liquid D (0.817 g.) was dissolved in ether (10 ml.) and an excess of methyl iodide added. The solvent and excess methyl iodide were removed by pumping to yield a white solid. (1.330 g.). m.p. 75 - 80°. (Found: N, 7.54. $C_{10}H_{20}IN_2P$ requires: N, 8.34%).

Effect of Heating in Vacuum.

The liquid D, (0.232 g.) was heated under vacuum reflux overnight at 190°. A gas was given off whose rate of evolution became pronounced at 120° and which was readily condensable in liquid air, and was shown by its infra-red spectrum to be pure ethylamine. There was a slight loss of material due to adherence of liquid to the wall of the condenser. The residue (0.184 g.) was a brown viscous liquid, which on extraction with ethanol yielded insoluble (∼ 0.01 g.) polyphenylcyclophosphine which was identified by its infra-red spectrum.

Investigation of the Residue E, From the Attempted Distillation of B.

Since the distillation was carried out on a sample of B which subsequently yielded polyphenylcyclopolyphosphine, this residue E must contain some of this compound. The residue E (1.51 g.) was heated with alcohol, cooled and the insoluble white residue (0.31 g.) was removed by filtration. This insoluble melted in a range around 145° and was shown by its infra-red spectrum to be polyphenylpolycyclophosphine.

The alcohol soluble material, which is presumed to be crude poly(N-ethylaminophenylphosphine) was not investigated.

Investigation of the Benzene Soluble Oil B.

The oil B was allowed to stand for several weeks and at the end of this period a further sample (10 g.) of polyphenylpolycyclophosphine was removed by filtration; the filtrate was a solid free brown liquid. (Found: N, 10.61. $C_{10}H_{17}N_2P$ requires: N, 14.28. $(C_8H_{10}NP)_n$ requires: N, 9.27%).

Pyrolysis.

The oil (0.849 g.) was heated in a sealed evacuated Carius tube at 220° for 10 days. A pressure, which on opening the tube was recognised by smell as being due to ethylamine, had built up. The product was a colourless, extremely viscous liquid, with traces of carbon and red phosphorus present. The liquid was too viscous to allow its weight to be determined; however, a sample was removed for analysis (Found M. (cryoscopically in a 0.2% benzene solution), 507; N, 9.04%. $(C_8H_{10}NP)_3$ requires M, 453; N, 9.27%).

The liquid was completely soluble in alcohol, indicating the absence of any polyphenylpolycyclophosphine.

Effect of Heating in Vacuo Under Reflux.

The oil B (3.172 g.) was heated in vacuo for four days at 200°, the volatiles being passed up a water cooled condenser. A gas, which was identified as ethylamine by its infra-red spectrum, was evolved, and some colourless liquid adhered to the condenser, the weight loss (0.734 g.) being partially due to loss of material in this way. The residue, a brown viscous liquid, was boiled with ethanol (5 ml.) and the insoluble material (0.05 g.) filtered off. This was identified by its infra-red spectrum as polyphenylpolycyclophosphine. The filtrate was a brown solution, and removal of the ethanol yielded a brown viscous residue of crude tri(N-ethylaminophenylphosphine), $(PhPNEt)_3$. (Found: N, 8.77; M, 464. (cryoscopic in benzene). $C_{24}H_{30}N_3P_3$ requires: N, 9.27; M, 453.).

The Reaction with Ethyl Iodide.

The reaction of crude tri(N-ethylamino:phenylphosphine), (0.252 g, 0.555 mmole) with excess ethyl iodide, followed by removal of excess reagent by pumping, gave a brown viscous residue. (0.339 g., 0.556 mmole of $C_{26}H_{35}IN_3P_3$). The product was insoluble in water, but with dilute nitric acid gave a solution which readily gave a precipitate of silver iodide with silver nitrate.

Investigation of the Solid C.

The solid was removed by filtration and washed with ether. m.p. 146 - 150°. (Found: C, 65.47; H, 4.41; P, 29.83. C_6H_5P requires: C, 66.7; H, 4.62; P, 28.7%. Total yield; 11.6g.).

Molecular weight determinations were carried out cryoscopically in benzene, without taking precautions to avoid ingress of moist air. The results were as follows:-

% Concentration of Solution.	M.	
1.15	800	
1.20	562	
1.22	761	
1.62	694	falling to
	670	in 30 mins.

The sample of polyphenylcyclopolyphosphine obtained from a reaction of phenyldichlorophosphine and propylamine had M = 529. (Constant value obtained by cryoscopic determination in benzene, under an atmosphere of dry nitrogen).

The determinations of molecular weight under normal atmospheric conditions were carried out on solutions which became cloudy and yielded solid on standing, while the determination under dry nitrogen was done on a clear solution, which yielded no solid on standing under nitrogen for 30 minutes, and showed no variation in its freezing point during this time.

The Reaction of Phenyldichlorophosphine and Ethylamine in Ethylamine as Solvent.

Phenyldichlorophosphine (39.6 g., 0.22 mole) was added to dry ethylamine (100 ml.) at -60°. The reactants, having been maintained at this temperature for 24 hours, were slowly heated to room temperature over a period of 3 days. Excess ethylamine was evaporated by heating under a flow of dry nitrogen, and eventually by heating at 80° for several hours.

The products were extracted with benzene and the ethylamine hydrochloride filtered off. (29.6 g. Theory requires 35.9 g.). Removal of benzene from the filtrate gave a waxy yellow product, which on heating to 160° under vacuum showed no tendency to sublime, but bubbled continuously.

On cooling, this material was found to give a strong chloride test, both with silver nitrate, and by the Belstein test. (Found: Cl $\sim$ 4% (by Volhard method.)) The infra-red spectrum of this material indicated the absence of ethylamine hydrochloride. (The characteristic absorption bond of ethylamine chloride at 790 $cm.^{-1}$ was absent.)

Excess chloride was removed as triethylamine hydrochloride by the addition of triethylamine to a benzene solution of the crude product, followed by filtration. The removal of benzene from the filtrate gave a chloride free product which, after prolonged pumping at room temperature gave a residue which was almost completely solid. (Yield: 28.3 g. $C_{10}H_{17}N_2P$ requires 33.2 g. $(C_8H_{10}NP)_n$ requires 43.0 g.)

Extraction of this product with ethanol gave an insoluble material (7.5 g.) which was removed by filtration under an atmosphere of dry nitrogen. Even under these conditions, the product fumed and tended to form a sticky mass.

Removal of solvent from the alcohol solution gave an oil whose infra-red spectrum corresponded to the similar product obtained by the reaction of phenyldichlorophosphine and ethylamine. During subsequent pumping of this material a large volume of water came into contact with the product, due to a suck-back of the water pump and the experiment was abandoned.

CONCLUSION.

At the outset of this study there appeared to be no research school investigating the formation and the properties of tervalent phosphorus - nitrogen compounds. Since that time, there has been a considerable increase in the interest which has been shown in such products, the work of Sisler and Smith being of particular interest, if somewhat limited in its scope.

In the present work, the P (III) - N bond has been shown to be readily formed by the conventional reaction of a halophosphine with an amino group. The compounds synthesised have all conformed to the expected behaviour of aminophosphines in that they all undergo fission of the P (III) - N bond with hydrogen chloride, are readily hydrolysed by acid, but are stable to alkali. The effect of $d\pi$ -$p\pi$ bonding is clearly apparent in the lack of basicity of the nitrogen atom and in the donor character of the phosphorus, and these compounds are clearly to be classified as aryl rather than alkyl phosphines. None of the aminophosphines show any tendency to undergo reorganisation reactions.

The monoalkylaminophosphines, Ph_2PNHR, show no substantial differences in their properties from the bisdialkylaminophosphines, $PhP(NR_2)_2$. The main reaction of compounds containing an NH group is that of condensation to produce the P - N - P skeleton, which occurs particularly readily in the case of the methyl analogue.

The cyclic six-membered P (III) - N compound appears to be stable, but lacks the reactivity expected of a simple triphosphine, (P - X - P - X - P). The possibility of delocalisation in this ring system is an exciting feature which it has not been possible to explore in the time available.

Most surprising has been the occurrence amongst the products from reactions involving primary amines of compounds containing phosphorus - phosphorus bonds. The investigation of the mechanism by which these compounds are formed is the part of the work most obviously requiring further attention.

The author is of the opinion that the work reported in this thesis is only an introduction to a large volume of interesting chemistry. The development of this work, however, will require more fundamental investigations, particularly with regard to infra-red spectroscopy and possibly the use of chromatographic methods of separation and identification. Mass-spectrometry is another physical technique which could be of great help, particularly since there are now available several series of compounds, as for example, the bisdialkylaminophosphines, from which characteristic cracking patterns could be established. The availability of a nuclear magnetic resonance spectrometer, particularly with a phosphorus probe, is a great step forward in the study of any branch of phosphorus chemistry and considerable help can be expected from this technique in the future.

Structure determinations, in particular on compounds and complexes involving the P - N - P skeleton would be of the greatest value in understanding more fully the nature of the phosphorus - nitrogen bond. Work is going on at present on the palladium chloride adduct of ethylbis(diphenylphosphino)amine. The preparation of several adducts of N - P - N and P - N - P compounds is being carried out in this department although, up till now, they do not appear to show any unusual properties, the N - P - N compounds behaving as simple phosphines, and the P - N - P behaving as diphosphines.

Development of the investigation of the reactions of phenyldichlorophosphine and primary amines is an interesting and exciting prospect. Many possible reactions spring to mind, that of phenyldichlorophosphine and aniline being, perhaps amongst the most promising. The reactions of phosphorus trichloride with primary amines must receive further attention and will certainly furnish various ring sizes. Thus whilst methylamine and phosphorus trichloride yield a cage structure the product from aniline and the halide is a 4-membered ring compound and clearly other amines will yield compounds with yet other structures.

Whilst it is realised that the phosphonitriles are still in their infancy as industrial materials, the instability of the higher chain polymers to hydrolysis is a great, though it is hoped not insurmountable, barrier to their development. It is possible that ring tervalent phosphorus - nitrogen polymers may be found to have the thermal and hydrolytic stability required of a commercially applicable polymer. Investigation of the thermal stability of these phosphorus - nitrogen compounds must certainly form a part of any complete study.

The demands which are made on science are ever increasing and the compounds which are of academic interest today may be amongst the every-day materials of tomorrow. Hitherto, phosphorus - nitrogen compounds have not found great application; whether or not they may be of use in our understanding or control of life-processes, or in some other sphere can only be answered by the passage of time.

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