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NITROGEN-PHOSPHORUS POLYMERS

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FOREWORD

This report was prepared by the Anorganisch-Chemisches Institut, University of Heidelberg, Heidelberg, Germany under Contract AF 61(052)-682. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors on the Synthesis of Macromolecular Material". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Dr. W. L. Lehn, Project Engineer.

This report covers work conducted from July 1966 through October 1968. The manuscript was released by the author in March 1969 for publication as a technical report.

This technical report has been reviewed and is approved.

William E. Gibbs
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ABSTRACT

The structure of phosphorus pentachloride has been investigated and reviewed. The two general types of reactions of phosphorus pentachloride, the formation of adducts and substitution reactions are discussed. The reactions of phosphorus pentachloride with ammonia derivatives of the structure $R-NH_2$, ammonia and its salts, hydroxylamine and its salts, hydrazine and its derivatives, phosphoryl amide and thiophosphoryl amide, and monomethyl ammonium chloride are described.

TABLE OF CONTENTS

SECTION I

INTRODUCTION

The purpose of the work covered by this report was the preparation of new and novel phosphorus nitride derivatives as potential monomers and intermediates for inorganic and semi-inorganic polymers. The work is divided into two sections: Section II covers the structure of phosphorus pentachloride, one of the major intermediates for the preparation of phosphorus nitride compounds; and Section III covers the reactions of phosphorus pentachloride with ammonia derivatives of the structure $R-NH_2$, ammonia and its salts, hydroxylamine and its salts, hydrazine and its derivatives, phosphoryl amide and thiophosphoryl amide, and monomethyl ammonium chloride.

SECTION II

THE STRUCTURE OF PHOSPHORUS PENTACHLORIDE

Phosphorus pentachloride, PCl_5, was discovered in 1810 by Davy, and its composition was elucidated six years later by Dulong.

Pure phosphorus pentachloride, which is obtained by reaction of chlorine and phosphorus trichloride, is a colorless crystalline substance at room temperature. In a sealed tube it melts at 160°C, while under atmospheric pressure it sublimates before the melting point is attained. In the gaseous state molecules with a composition of PCl_5 are present. The five chlorine atoms form a trigonal bipyramid (Reference 19) at the center of which is located the phosphorus atom (Figure 1). The P-Cl bond lengths are 2.19 Å and 2.04 Å.

In the solid state the ionic species PCl_4^+ and PCl_6^- are prevalent (Reference 21). Whereas PCl_4^+ has its phosphorus atom tetrahedrally surrounded by the four chlorines with a P-Cl bond length of 1.98 Å, the PCl_6^- ion possesses octahedral symmetry and a P-Cl internuclear distance of 2.07 Å.

The Raman spectrum (Reference 49) of PCl_5 in the liquid state could be interpreted on the assumption of a trigonal-bipyramidal structure. Consequently pure, liquid PCl_5 is a non-conductor. Also PCl_5 may exist in this form in solutions. In the case of CS_2, for example, ^{31}P nuclear magnetic resonance shows a chemical shift of $+80 \cdot 10^{-6}$ (Reference 27).

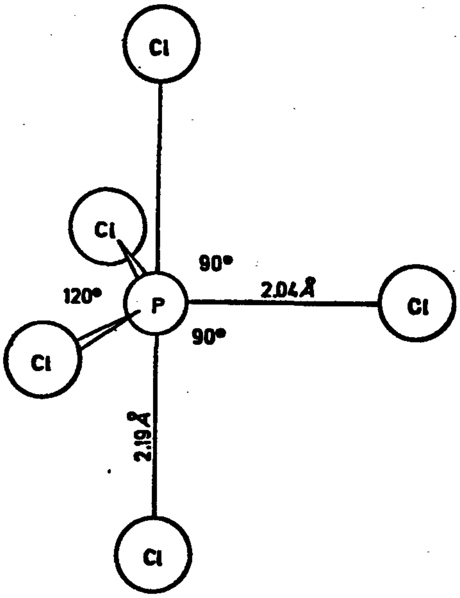

FIGURE 1

It has frequently been maintained (Reference 47) that PCl_5 exists in an ionic form when dissolved in polar solvents. For example such a conclusion was arrived at on the basis of conductivity and transport measurements on solutions of PCl_5 in acetonitrile (Reference 47). The nuclear magnetic resonance spectrum of PCl_5 nevertheless always shows the chemical shift of pentavalent phosphorus, namely $+80 \cdot 10^{-6}$, even in $OPCl_3$ solutions, as well as in solvents such as PCl_3, nitrobenzene, methylene chloride, and other chlorinated hydrocarbons*. When PCl_5 is dissolved in acetonitrile (occasionally described as a good solvent for PCl_5), a chemical reaction could be observed - even at room temperature (Reference 24).

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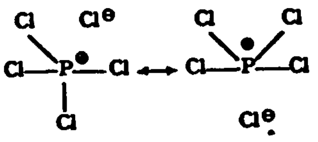
* D. S. Payne (Reference 47) noticed that such solutions conduct electricity, and therefore postulated the presence of PCl_4^+ and PCl_6^- in these systems.

Thus one can draw the conclusion that PCl_5 exists primarily as a molecular species in the gaseous, liquid, and dissolved states, while the ionic forms $[PCl_4]^+$ and $[PCl_6]^-$ predominate in the solid state.

For a long time the nature of the chemical bonds in PCl_5 presented a theoretical enigma. Pauling (Reference 46) conjectured that the 3s and 3p orbitals alone were involved in chemical bonding. With these four orbitals only four covalent bonds could be formed. In the case of PCl_5 it was thus necessary to postulate that electrovalent as well as covalent forces were involved in maintaining the structure of the PCl_5 molecule. Pauling distributed the negative charge over all five chlorine atoms. The compound was envisioned as a resonance hybrid, in which each P-Cl bond was one fifth ionic and four fifths covalent in character.



In addition to the above representation another was frequently employed, namely that the d orbitals of phosphorus were involved in the formation of the sigma bonding hybrid orbitals. To this end the following electronic configuration is required:

$$3\,s^2\;3\,p^3 \rightarrow 3\,s\;3\,p^3\;3\,d$$

The energy for the promotion of the electron is rather high (Reference 35) (about 17 ev); some of the energy is regained, however, by the hybridization of the s and p orbitals with the d_{z^2} orbital (Reference 38). Craig and Magnusson (Reference 22), furthermore, have suggested that the d orbitals, although too diffuse for sigma bonding in the free atom, are strongly polarized and reduced in size - depending on the electronegativity of the ligand - and thus become available for the formation of sigma bonding hybrid orbitals (Reference 35).

From the point of view of valence-bond theory the structure of PCl_5 can be described as a resonance hybrid, the extremes of which are $PCl_4^+Cl^-$ and PCl_5; this means to say that PCl_5 has covalent bonds with considerable electrovalent character. The d-orbitals play a role in the hybridization of the phosphorus, and the hybrid bonds are relatively polar.

SECTION III

REACTIONS OF PHOSPHORUS PENTACHLORIDE

On considering the chemistry of phosphorus pentachloride, one can basically distinguish two general types of reactions: the first of these is the formation of adducts, while the second consists of substitutions in which Cl is partially or entirely replaced by other functional groups or atoms.

A. Formation of Adducts

In the formation of adducts penta-coordinated phosphorus, as in PCl_5, is converted to a tetra- or hexa-coordinated form. A compound such as $PCl_5 \cdot AlCl_3$, which melts at 343°C, very probably consists of the structures (Reference 55) $[PCl_4]^+[AlCl_4]^-$. Analogous ionic compounds almost certainly exist in the adducts formed between PCl_5 and antimony pentachloride, boron trichloride, or titanium tetrachloride. The ^{31}P-nuclear magnetic resonance spectrum of $[PCl_4][SbCl_6]$ revealed a chemical shift of $-86 \cdot 10^{-6}$, consistent with the relatively unshielded P-atom of the PCl_4^+ ion. In the case of $[PCl_4][BCl_4]$ the chemical shift was $-76.8 \cdot 10^{-6}$. For $PCl_5 \cdot TiCl_4$ (Reference 50) the structural formula $[PCl_4][TiCl_5]$ could be inferred from conductivity measurements of Gutmann (Reference 31). The compound of 2 $PCl_5 \cdot TiCl_4$ dissolved in nitromethane, had a chemical shift of $9.3 \cdot 10^{-6}$ in the ^{31}P-nuclear magnetic resonance spectrum. Although this suggests tetra-coordinated phosphorus, the presence of free PCl_4^+ cations is rendered unlikely. Finally PCl_6J, a yellow crystalline substance, has a structural formula of $[PCl_4]^+[Cl\text{-}J\text{-}Cl]^-$ in the solid state (Reference 58).

Adduct formation with concomitant conversion of pentavalent phosphorus into hexavalent phosphorus is observed in the reaction of PCl_5 with pyridine. The resulting $PCl_5 \cdot C_5H_5N$ is a crystalline substance with a ^{31}P-chemical shift of $+234 \cdot 10^{-6}$. The NMR spectrum shows a highly shielded phosphorus atom, suggesting a hexavalent structure. Further evidence is provided by the chemical shift of PCl_6^- in hexachlorophosphates (Reference 27), namely $+300 \cdot 10^{-6}$, in contrast to PCl_5, which, as already mentioned above, has a chemical shift of $+80 \cdot 10^{-6}$ either in the liquid state or in solution.

B. Substitution Reactions

The chlorine atoms of phosphorus pentachloride can be displaced. When substitution of chlorine is attempted using oxygen, tetra-coordinated phosphorus is always formed. Matters are different, however, when chlorine is replaced by ligands other than oxygen.

In the pages that follow only the reactions of phosphorus pentachloride with nitrogen containing compounds will be considered, and the valence states arising in the substitution of the Cl atoms by nitrogen containing functional groups will be detailed.

1. Reactions with Ammonia Derivatives of the Structure $R-NH_2$

The reaction of PCl_5 with derivatives of ammonia such as acid amides is very simple. Phosphorus pentachloride reacts with acid amides in such a fashion that the two hydrogen atoms of the amide are replaced by a PCl_3 group. For example, when the monoamide of sulfuric acid is allowed to react with PCl_3, then product $Cl_3P{=}N-SO_2Cl$ is easily obtained, and the same compound is formed when amidosulfuric acid chloride is reacted with PCl_3 directly:

$$H_2N-SO_3H + 2\ PCl_5 \rightarrow Cl_3P{=}N-SO_2Cl + 3\ HCl + OPCl_3$$

$$H_2N-SO_2Cl + PCl_5 \rightarrow Cl_3P{=}N-SO_2Cl + 2\ HCl$$

Using sulfuryl amide, one analogously obtains $Cl_3P{=}N-SO_2-N{=}PCl_3$ (m.p. 41-42°C)

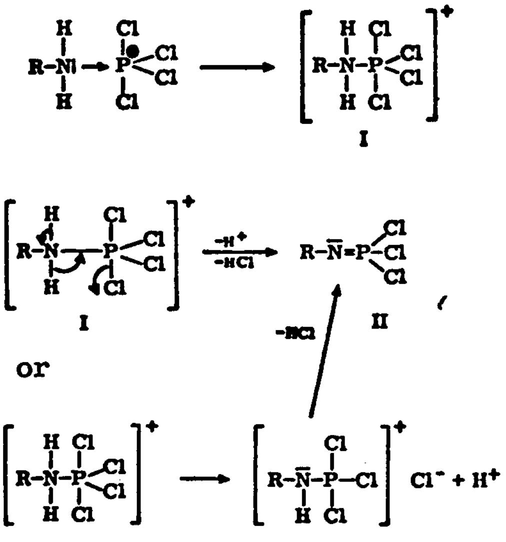
$H_2N-SO_2-NH_2 + 2\ PCl_5 \rightarrow Cl_3P{=}N-SO_2-N{=}PCl_3 + 4\ HCl$ (References 3, 25, 39, and 44).

We conjecture that this reaction, which we called the "Kirsanov-reaction" (Reference 6), proceeds according to a scheme in which the acid amide, acting as a Lewis base, attacks the PCl_5, that is to say the PCl_4^+ cation, with the formation of adduct I. Substance I then deprotonates and with release of HCl forms compound II.

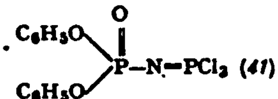
This type of reaction of PCl_5 is not limited to the amides of sulfuric acid: for example, it occurs in an analogous fashion with amides of phosphoric acid.

In the case of the monoamide of phosphoric acid one observes

$$O{=}P(OH)_2NH_2 + 3\,PCl_5 \rightarrow Cl_3P{=}N{-}P(O)Cl_2 + 4\,HCl + 2\,OPCl_3$$

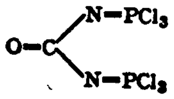


the replacement of both amide hydrogens by the PCl_3 moiety and, in addition the replacement of the OH group by Cl (Reference 13). The diphenyl ester of ortho-phosphoric acid amide reacts with PCl_5 to give compound III.

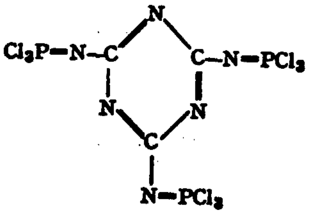


III

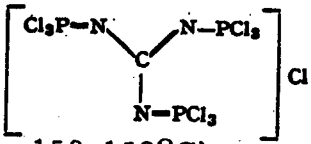
The amide of carbonic acid also reacts with PCl_5 in a similar manner. Employing urea compound IV is obtained among other products, while melamine reacts to give V and guanidine yields the resonance stabilized salt VI:



IV (*14c*)

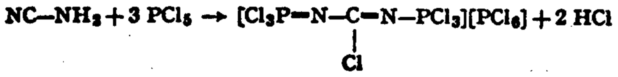


V (m.p. 185-191°C) (29)



VI (m.p. 150-152°C)

When cyanamide was allowed to react with PCl_5 a more complicated process was observed, namely:



$$NC{-}NH_2 + 3\,PCl_5 \rightarrow [Cl_3P{=}N{-}\underset{\overset{|}{Cl}}{C}{=}N{-}PCl_3][PCl_6] + 2\,HCl$$

VII (m.p. 167-169°C)

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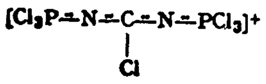
* A salt of the type $[Cl_3P{=}N{=}\underset{\overset{|}{R}}{C}{=}N{=}PCl_3]SbCl_6$ was first described by A. Schmidpeter, K. Düll, and R. Böhm, Angew. Chem. 76, 605 (1964).

As with guanidine, a salt is obtained in this reaction which is stabilized by resonance; that is, the double bonds may be delocalized as indicated in VIIa. The results of the ^{31}P-nuclear magnetic resonance of VII provide support for such a contention in that chemical shifts of $-38.5 \cdot 10^{-6}$ and $+297.5 \cdot 10^{-6}$ are observed.



VIIa

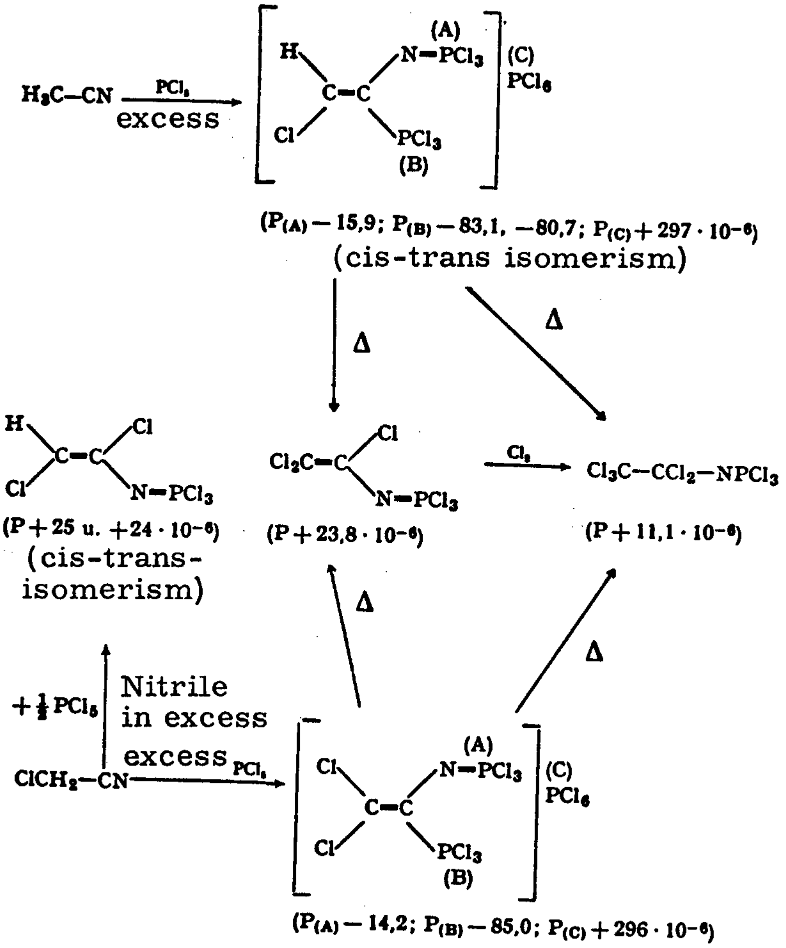
$$[\mathrm{Cl_3P{=}N{=}}\underset{\substack{| \\ \mathrm{Cl}}}{\mathrm{C}}\mathrm{{=}N{=}PCl_3}]^+$$

Compound VII is also a product of the reaction between urea and PCl_5 (Reference 36).

The very formation of VII demonstrates that even in cyanamide a PCl_3 group replaces the two amide hydrogens. In addition, however, the nitrile group reacts with PCl_5, an attack on the C-N triple bond, ultimately leading to the chlorination of the carbon atom and the formation of a second $Cl_3P{=}N$ moiety.

Nitriles, such as acetonitrile, show an analogous reactivity towards PCl_5. Products for the cases of acetonitrile and chloroacetonitrile are indicated below (Reference 24). The chemical shifts of ^{31}P accompany the structural formulas (Reference 17), demonstrating the formation of P-C bonds in addition to P-N bonds.

The course of these reactions is considerably more complicated when ammonia derivatives of the type RNH_2, are involved in which R is an alkyl or an aryl group, in other words when an amine is employed instead of an acid amide.



In the case of the amines it depends on the nature of the R substituent whether a monomeric compound of the type R-N=PCl_3 or a dimer of the structure $(R\text{-}NPCl_3)_2$ is obtained. If R is CH_3 or C_4H_9, that is to say, if primary alkyl amines are used, dimers are formed. Dimers are also produced when aniline is employed. O-nitro aniline, however, yields a monomeric product.

The relations are summarized in Table I (Reference 24):

TABLE I

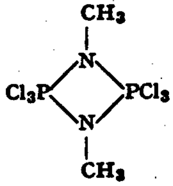
REACTIONS OF PHOSPHORUS PENTACHLORIDE WITH AMMONIA DERIVATIVES

AMINE	DIMER IN BENZENE	MONOMER IN BENZENE	K_B OF THE AMINE AT 25°C IN H_2O
$C_6H_5NH_2$	by cooling or heating	-	$4.6 \cdot 10^{-10}$
$p\text{-}Cl\text{-}C_6H_4NH_2$	by cooling or heating	-	$1.5 \cdot 10^{-10}$
$o\text{-}CH_3C_6H_4NH_2$	only by cooling	at boiling temperature	$2.5 \cdot 10^{-10}$
$o\text{-}ClC_6H_4NH_2$	only by cooling	at boiling temperature	$3.7 \cdot 10^{-12}$
$o\text{-}NO_2C_6H_4NH_2$	-	in cold or at boiling temperature	$1.0 \cdot 10^{-14}$

Kirsanov (Reference 24) noted that monomers were obtained primarily when weak bases were reacted with PCl_5, whereas dimers could be synthesized from the strong bases, such as aliphatic amines ($K_B > 10^{-12}$).

The compound yielded by the reaction of PCl_5 with monomethyl amine, having the formula $(Cl_3PN\text{-}CH_3)_2$, has been examined most thoroughly of all the substances in the dimer category (Reference 24). The phosphorus atoms are all chemically equivalent in this compound, since the ^{31}P-nuclear magnetic resonance spectrum of the material in bromoform solution has a single peak with a chemical shift of $+78.2 \cdot 10^{-6}$ (relative to a standard of 85% phosphoric acid). This markedly positive chemical shift indicates that the phosphorus is pentavalent, the comparable chemical shift of PCl_5 being $+80 \cdot 10^{-6}$.

Consequently the assignment of this compound of structural formula VIII was reasonable. Also the proton magnetic resonance spectrum, investigated by Trippett (Reference 51), was in agreement with this structure. The crystallography of VIII was examined by Hess and Forst (Reference 34); the data of these authors are presented in Figures 2 and 3.



VIII

Thus it was found that substitution reactions could be performed on phosphorus pentachloride, which yielded not only tetra-coordinated products but also penta-coordinated substances. Compound VIII melts at 178°C, showing that penta-coordinated phosphorus and this four membered ring possess a great deal of thermal stability. Nevertheless this material can readily undergo chemical reaction to form different compounds in which the phosphorus is tetra-coordinated.

To this end compound VIII was reacted with sulfur dioxide (Reference 11). Substance IX could be isolated with an excellent yield. IX is a crystalline, colorless material which is sensitive to moisture. In benzene solution only one ^{31}P-nuclear magnetic resonance signal is detected, having a chemical shift of $+5.3 \cdot 10^{-6}$. This indicates that compound IX has its phosphorus in a tetra-coordinated state, as shown below (Reference 30):

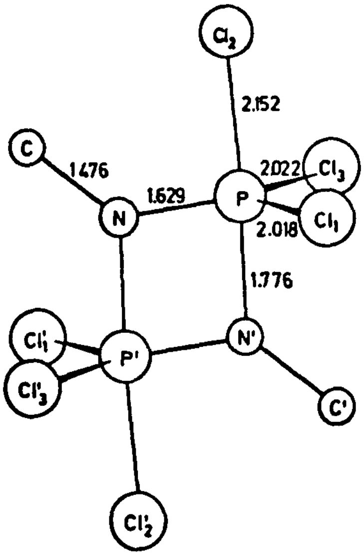


Fig. 2

Bond lengths of VIII

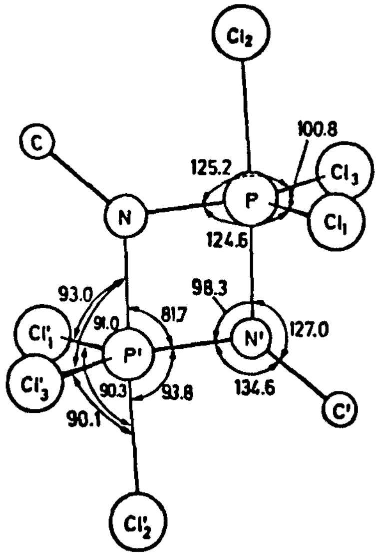
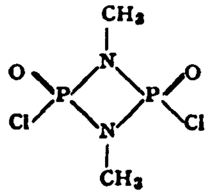


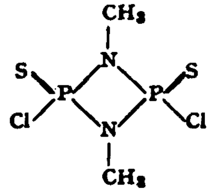
Fig. 3

Bond angles of VIII



IX

(m.p. 101-103°C)



X

(m.p. 120-122°C)

The sulfur containing compound X, analogous to IX was also synthesized (Reference 11). Crystallographic examination of this substance (Reference 56) revealed a planar four membered ring system. The bond lengths of this ring are remarkably uniform in contrast to compound VIII. The phosphorus is sp^3 hybridized, while the nitrogen is sp^2.

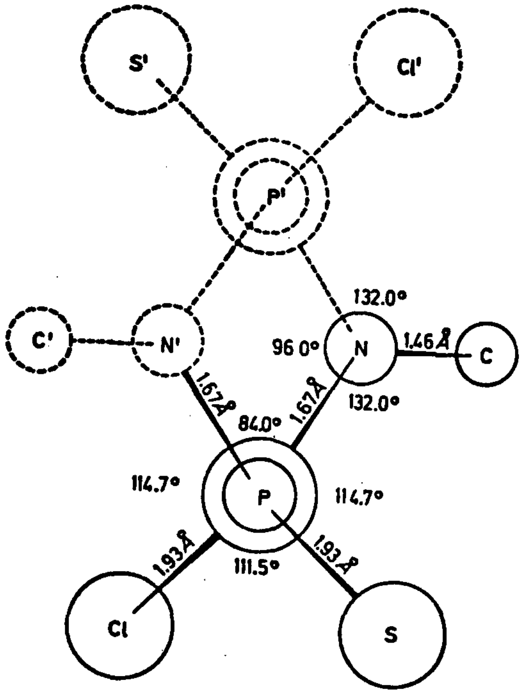
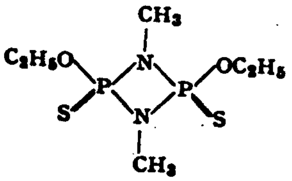


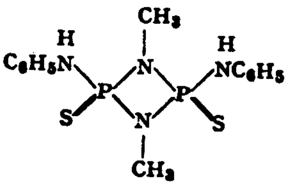
Fig. 4
Bond lengths and bond angles of compound X.

The chlorine atoms of X may be substituted without opening the four membered ring. Alcoholysis leads to the formation of XI, treatment with aniline yields XII, and reaction with diethyl amine gives compound XIII (Reference 48).



XI

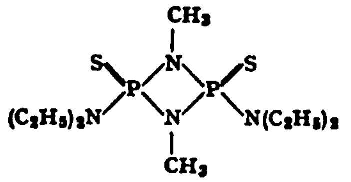
(m.p. 103°C)



XII

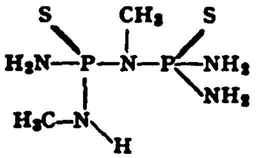
(m.p. 146°C)

When X is subjected to an excess of ammonia, the ring is opened and XIV is obtained (References 48, 60).



XIII

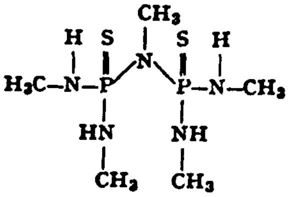
(m.p. 168°C)



XIV

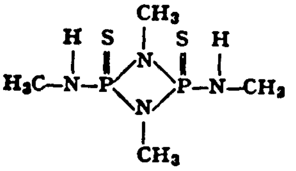
(m.p. 91°C)

Treatment with monoethyl amine also results in ring opening. The cyclic system is reformed, however, when the amide with structure XV is heated in a vacuum (Reference 11):



XV

(m.p. 92°C)

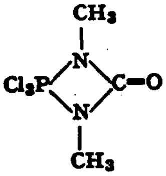


XVa

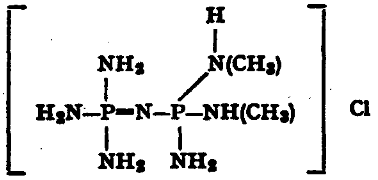
(m.p. 224°C)

Thus such four membered ring systems containing phosphorus are stable; indeed the phosphorus may be either tetra- or penta-coordinated. Compound VIII is an example of the latter case. Another structure of this kind is that depicted in formula XVI, being a product of the reaction of dimethyl urea and PCl_5 (Reference 52).

When we attempted to substitute the chlorine atoms in these systems however, it readily became evident that the four membered ring system did not remain intact. Compound XVII is formed by the treatment of VIII with ammonia*, in other words, a phosphorus nitrilic salt is formed, which has a linear structure and a phosphorus atom which is tetracoordinated.

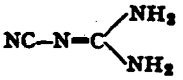


XVI
b.p. 78-79°C/1.5 torr



XVII

Furthermore in the reaction of PCl_5 with dicyandiamide the formation of ring systems containing phosphorus and nitrogen was noticed. When the above compounds are allowed to react in a 2:1 mole ratio, respectively, a substance with the composition $C_2N_4P_2Cl_6$ can be isolated. The ^{31}P-nuclear magnetic resonance spectrum consists of two doublets with chemical shifts of $-23\cdot10^{-6}$ and $-58\cdot10^{-6}$. The coupling constant is 40 hz. We propose the following interpretation (Reference 36):



reacts with PCl_5 initially to form the unstable intermediate XVIII. The four membered ring system of XVIII is opened by the action of PCl_5

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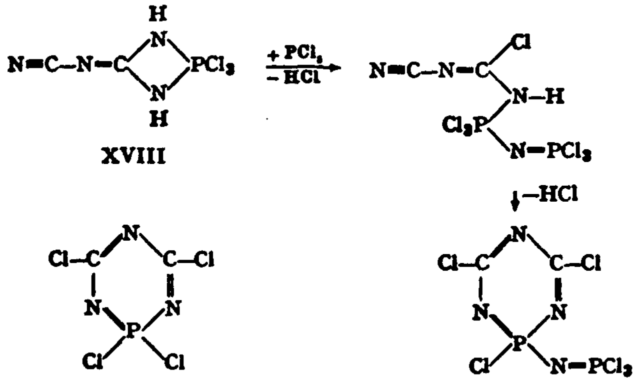
*V. Gutmann et al. (Reference 32) suggested a symmetrical structure for XVIIa; the x-ray structure determined on the iodide by M. Ziegler (Reference 48) demonstrated the validity of XVII as written above.

or perhaps by a protonation. A substance is formed which releases HCl in the process of cyclizing, yielding the stable product XIX.

Sodium dicyanimide and PCl_5 react yielding a crystalline material, depicted in XIXa; this is consistent with the behavior of nitriles discussed above. XIXa has a ^{31}P chemical shift of $-55 \cdot 10^{-6}$.

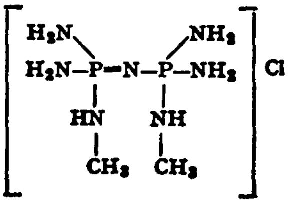


XVIII

XIXa

XIX

(m.p. 141-143°C) (m.p. 109-111°C)

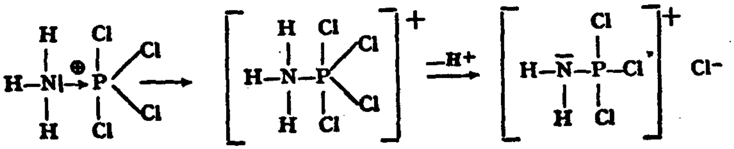


XVIIa

In summary, therefore, it is proper to say that derivatives of ammonia with the structure $R\text{-}NH_2$ - acid amides and amines - react in a manner consistent both with the formation of an adduct between the nitrogen containing donor molecule and a PCl_4^+ species (I) and with an imine hydrochloride intermediate (Ia). The products of such reactions are either monomers with the formula, $R\text{-}N{=}PCl_3$, or dimers with the general formula $(R\text{-}NPCl_2)$, the latter consisting of four membered ring systems containing two nitrogen and two phosphorus atoms, in which the phosphorus has a coordination number of five. Compounds having pentacoordinated phosphorus are easily converted to substances with tetracoordinated phosphorus.

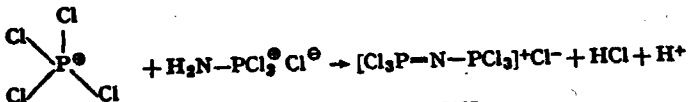
2. Reactions with Ammonia and its Salts

The same general reaction schemes outlined above are followed in the reaction of ammonia and its salts with PCl_5. Again we envision a donor-acceptor reaction involving the nucleophilic NH_3 species and the electrophilic PCl_4^+ cation (Reference 9):



XX XXI

The imine hydrochloride[*] XXI is formed via the adduct XX; compound XXI can react further as a nucleophilic reagent with another mole of PCl_5:



XXII

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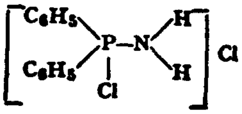
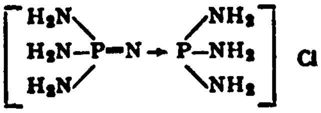
[*] With reference to the reactions written above, it should be remarked that we consider XXI a likely intermediate, despite the fact that it could not be isolated. By reaction of diphenyl phosphinic acid amide $(C_6H_5)_2P(O)NH_2$ with PCl_5 we obtained (Reference 7) the diphenylated derivative of XXI, which released HCl upon heating and yielded compounds with the formulas $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$.



Thus the cation $[Cl_3P{=}N{-}PCl_3]^+$ is formed, which in excess PCl_5 is isolated as the salt, $[Cl_3P{=}N{-}PCl_3]PCl_6$. It has a melting point of 310-315°C with decomposition, and is the first isolable intermediate in the reaction of NH_4Cl and excess PCl_5 in inert solvents (Reference 12). When liquid ammonia is employed directly as a solvent for PCl_5, the reaction proceeds in an entirely analogous fashion except that XXII is converted relatively easily to XXIII by exhaustive amminolysis (Reference 14).

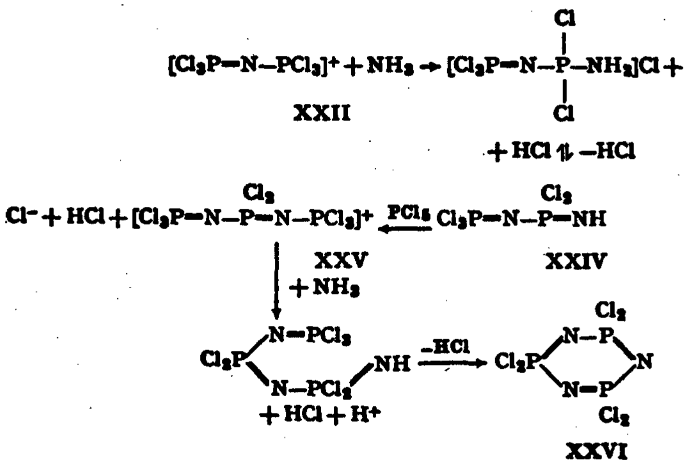


XXIII

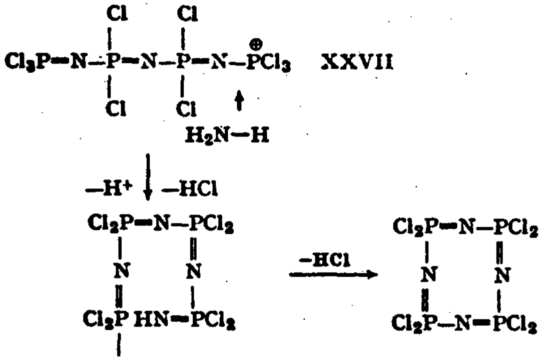
Other reactions may, however, occur in addition to the complete replacement of the chlorine atoms by amino groups. When NH_3 is not in excess, the nucleophilic attack of NH_3 leads predominantly to the formation of XXIV, which can react with additional PCl_5 to yield XXV (Reference 9). Thus a process resulting in chain lengthening takes place, producing a cation with the structure

$$[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_3]^+$$

which is isolated from the reaction mixture along with the hexachloro phosphate anion (Reference 8). Upon reacting with further NH_3 this cation is converted to trimeric phosphorus nitrilic chloride, XXVI, which is also the major product of the reaction of PCl_5 and ammonium chloride in inert organic solvents.



Compound XXVI is not the only product, however, because the process of chain lengthening, initiated by the attack on XXII, does not terminate at species XXV, but instead may continue - by reaction with further NH_3 and PCl_5 - in an analogous fashion to form the cation $[Cl_3P{=}N{-}PCl_2{=}N{-}PCl_2{=}N{-}PCl_3]^+$ (XXVII). When NH_3 reacts with this cation, tetrameric phosphorus nitrilic chloride is formed (XVIII). Nevertheless the predominant reaction is the formation of the trimer XXVI. A further side reaction is therefore also the polymerization to phosphorus nitrilic chlorides with the formula $[NPCl_2]_x$ (Reference 9).



XXVIII

The reactions of PCl_5 with ammonia are characterized by the formation of ions containing the groups $[Cl_3P\text{-}N{=}]^+$ etc. Furthermore, polymers are synthesized which are frequently cyclic in structure, being phosphorus nitrilic chlorides having a unit grouping of $-PCl_2{=}N-$.

The formation of the phosphoric nitrilic salts is thus fully elucidated. The ^{31}P-nuclear magnetic resonance spectrum of the first isolable intermediate in the reaction of PCl_5 and NH_4Cl is presented in Figure 5. It is apparent that the salt contains both tetra-coordinated and hexa-coordinated phosphorus. Both phosphorus atoms in the cation are chemically equivalent (References 6, 26).

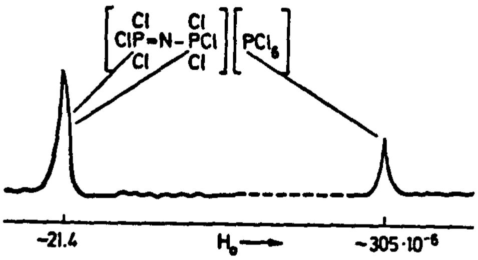
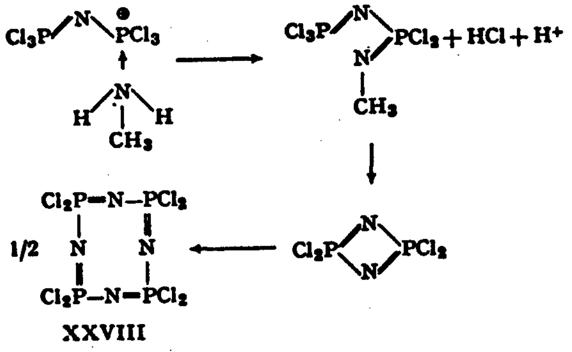


Fig. 5: The Nuclear magnetic resonance spectrum of P_3NCl_{12}.

The cation has a non-linear structure with a bond angle of 140° around the nitrogen (Reference 2). An ammonium salt having a cation of the linear structure $[Cl_3P{=}N{=}PCl_3]^+$ is thus ruled out, since, with two P-N double bonds, an angle of 180° would be predicted. The double bond character of the P-N bonds is only 60%.

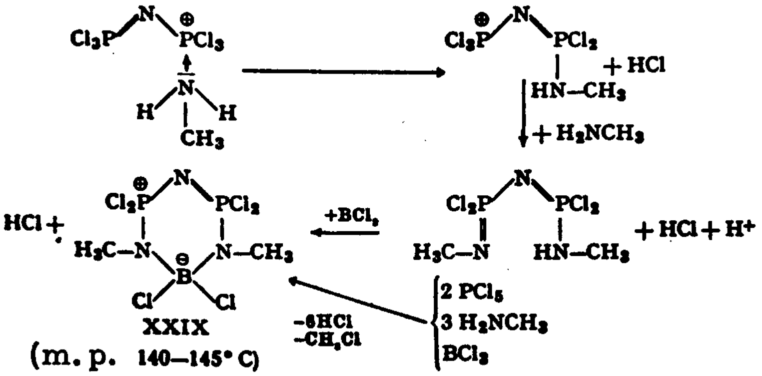
The reaction of the $[Cl_3P{=}N\text{-}PCl_3]^+$ cation with primary amines and the salts of such amines is also of particular interest. For example, when the chloride $[Cl_3P{=}N\text{-}PCl_3]Cl$ reacts with methyl ammonium chloride in an inert solvent at 120°C, CH_3Cl is released and $[NPCl_2]_4$ is produced in good yield (Reference 28). This is presented in reaction pathway (1):



Reaction pathway (1).

Again the initiating step is the nucleophilic attack of the amine on the cationic species of phosphorus with a coordination number of four.

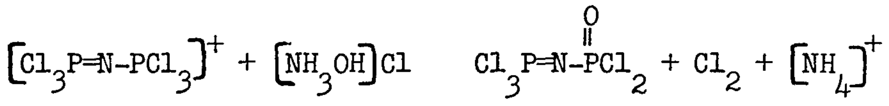
With respect to the formation of the phosphorus nitrilic salts discussed above, nothing has been mentioned about the feasibility of attacking both phosphorus atoms of the $[Cl_3P{=}N{-}PCl_3]^+$ cation with amine, since both phosphorus atoms share an equal amount of the positive charge. Indeed such an attack on both phosphorus atoms is possible when the product is stabilized by a reaction involving ring closure (Reference 45). Employing $[Cl_3P{=}N{-}PCl_3]Cl$ and methyl ammonium chloride in the presence of BCl_3 one obtains the products listed under "reaction pathway 2", inert solvents being utilized throughout.



Reaction pathway (2).

3. Reactions with Hydroxylamine and its Salts

The reaction of PCl_5 with hydroxylammonium salts was first described by Kahler (Reference 37). He found that a compound with the formula P_2NOCl_5 and chlorine were formed in addition to $OPCl_3$ and NH_4Cl. P_2NOCl_5 could also be prepared from amides of phosphoric acid and PCl_5 (as described above) (Reference 13), as well as from PCl_3 and N_2O_4* (Reference 4). Compound XXX is formed in these reactions. It is not, however, the very first isolable intermediate. Indeed hydroxylamine reacts with PCl_5 in such a way as to result in the replacement of the two protons bound to the nitrogen by a PCl_3 group (Reference 5). The hydroxyl group is furthermore replaced by a Cl atom. Thus the intermediate is probably $Cl_3P{=}N{-}Cl$. This may react further with PCl_5 to form $[Cl_3P{=}N{-}PCl_3]^+$ with the simultaneous release of chlorine. When an excess of hydroxyl-ammonium salt is employed, this may react further with the phosphorus nitrilic cation:



$$[Cl_3P{=}N{-}PCl_3]^+ + [NH_3OH]Cl \qquad Cl_3P{=}N{-}\overset{O}{\overset{\|}{P}}Cl_2 + Cl_2 + [NH_4]^+$$

XXX

(m.p. 35°C)

Hydroxylamine and its salts thus react with PCl_5 in a pattern entirely in analogy to ammonia and the salts thereof; ions with the functional grouping $[Cl_3P{-}N{=}]^+$ are initially formed via a "Kirsanov-reaction".

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* The supposition, still prevalent in the literature (Gmelin, Vol. 16, part C (1965) p 457/8), that $P_4O_4Cl_{10}$ is formed in this reaction, is incorrect. $P_4O_4Cl_{10}$ does not exist (Reference 4).

4. Reactions with Hydrazine and its Derivatives

Since all compounds having the NH_2 group seemed to react with PCl_5 via a reaction resulting in the replacement of the amino protons by a PCl_3 moiety, it appeared significant to investigate whether hydrazine might undergo similar transformations.

When hydrazinium sulfate or hydrazinium monochloride is subjected to PCl_5 in an inert solvent (such as tetrachloroethane), a redox reaction takes place:

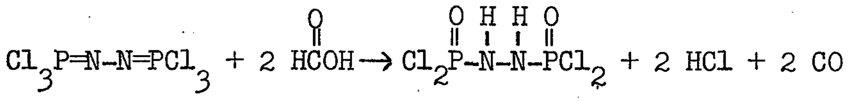
$$2\ PCl_5 + N_2H_4 = 2\ PCl_3 + N_2 + 4\ HCl$$

This reaction is to be expected, since PCl_5 is an oxidation agent, and the reducing action of N_2H_4 is well established. One might predict, however, that a "Kirsanov-reaction" would predominate, when the formation of ionic species is favored by a solvent having an extremely high dielectric constant. We utilized phosphorus oxychloride, which has a dielectric constant of 13.3 at 22°C. The existence of ionic reactions in this solvent is established (Reference 1). Hydrazinium monochloride and PCl_5 (in a mole ratio of 1:2) are converted to XXXI in phosphorus oxytrichloride at 100°C without evolution of N_2 (Reference 15):

$$N_2H_4 + 2\ PCl_5 \rightarrow Cl_3P{=}N{-}N{=}PCl_3 + 4\ HCl$$

XXXI

XXXI is thermally stable up to 134°C. In anhydrous formic acid it can be converted into hydrazido-N,N'-bis-phosphoryl dichloride, which decomposes above 30°C (Reference 15):



$$Cl_3P{=}N{-}N{=}PCl_3 + 2\ H\overset{\overset{\displaystyle O}{\|}}{C}OH \rightarrow Cl_2\overset{\overset{\displaystyle O}{\|}}{P}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{P}Cl_2 + 2\ HCl + 2\ CO$$

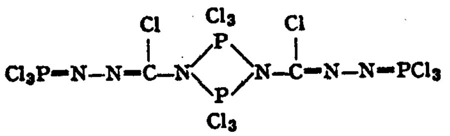
The above reaction provides strong confirmation for the assignment of structure XXXI, since Kirsanov et al. (References 40, 41) demonstrated that $-N{=}PCl_3-$ groups could easily be transformed into $-NH-P(O)Cl_2-$ functions by formic acid (Reference 33):

$$\begin{array}{llll}
(C_6H_5O)_2P(O)-N{=}PCl_3 & + HCOOH \rightarrow & (C_6H_5O)_2P(O)-NH-P(O)Cl_2 & + HCl + CO \\
CCl_3-CO-N{=}PCl_3 & + HCOOH \rightarrow & CCl_3-CO-NH-P(O)Cl_2 & + HCl + CO \\
C_6H_5-SO_2-N{=}PCl_3 & + HCOOH \rightarrow & C_6H_5-SO_2-NH-P(O)Cl_2 & + HCl + CO
\end{array}$$

The fact that PCl_5 was found to react with hydrazine in the sense of the "Kirsanov reaction", was further validated when a derivative of hydrazine, namely the semicarbazide, was reacted with PCl_5 (Reference 16). As before phosphorus oxytrichloride was the solvent of choice.

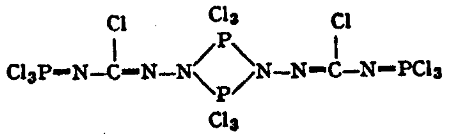
When a 1:3 mole ratio of $H_2N-CO-NH-NH_2:PCl_5$ is employed, a crystalline substance (A) with the composition $(CCl_8N_3O_2P_3)_x$ is obtained. When the reaction mixture is allowed to stand and is slowly heated to 60°C, A is transformed into $[Cl_7P_2N(N-N)C]_2$ (B).

The structure of substance (B), which is crystalline and lends itself to an ebullioscopic determination of its molecular weight, was readily elucidated. The ^{31}P-nuclear magnetic resonance spectrum revealed two distinct types of phosphorus, a heavily shielded nucleus with a chemical shift of $+78.8 \cdot 10^{-6}$, and a second nucleus with a chemical shift of $-15.2 \cdot 10^{-6}$. Half of the phosphorus in this compound thus has a coordination number of five, while the other half has a coordination number of four. The infra-red spectrum shows bands characteristic of the N-N band (920 cm^{-1}) as well as the C-Cl band at 795 cm^{-1}. Structure XXXII is consistent with this data.



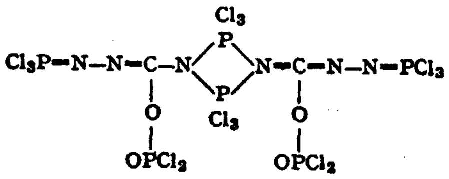
XXXIIa

or



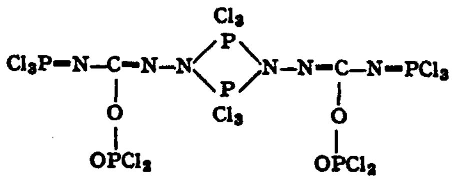
XXXIIb

The material with the composition A differs from XXXII only in the sense that two chlorine atoms of XXXII are replaced by $Cl_2(O)P\text{-}O\text{-}$ functions. The spectroscopic data are consistent with the assignment of structural formula XXXIII to compound A.



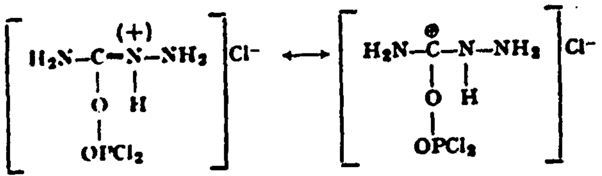
XXXIIIa

or

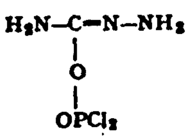


XXXIIIb

Semicarbazide, $H_2N\text{-}CO\text{-}NH\text{-}NH_2$, tends to react with $POCl_3$ according to the Vilsmeier reaction (Reference 53), involving the formation of a stable acid amide $POCl_3$ adduct in a single-step reaction (Reference 18). With semicarbazide as the starting compound such an adduct might be envisioned as the hypothetical intermediate XXXIV. XXXIV is readily converted into XXXV with the release of HCl. Thereafter XXXV may react with PCl_5 in a Kirsanov reaction, forming A.



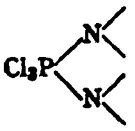
XXXIV



XXXV

These organic $OPCl_3$ adducts react with PCl_5, forming amide chlorides. Thus it seems reasonable that product A undergoes such a transformation in a $POCl_3$ solution when PCl_5 is present. Indeed the $-O-P(O)Cl_2$ group attached to the carbon atom is replaced by chlorine upon heating to 60°C.

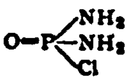
In structures XXXII and XXXIII it is observed that the two alternatives of the "Kirsanov reaction", namely the $Cl_3P{=}N-$ group and the



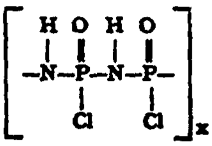
system, may exist simultaneously in the same molecule.

5. Reactions with Phosphoryl Amide and Thiophosphoryl Amide

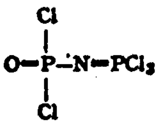
Phosphoryl amide, $OP(NH_2)_3$, reacts rapidly with PCl_5, and HCl is released simultaneously. Initially an NH_2 group is probably replaced by a chlorine atom. Thus the polymer XXXVII is formed via the intermediate step XXXVI.



XXXVI



XXXVII



XXX

If HCl is constantly removed during the course of the reaction by continuous evacuation, then two of the NH_2 functions of $OP(NH_2)_3$ are exchanged for chlorine, while the remaining NH_2 group undergoes a Kirsanov reaction. XXX is the predominant product (Reference 13).

The reaction of PCl_5 with thiophosphoryl triamide is very different from the above. Two products may be obtained in this conversion, one having the formula $P_4N_3Cl_{11}$ and the other having the formula $P_5N_3Cl_{16}$ (References 13, 26). While several alternatives were feasible in the former case, XXXVIII was later demonstrated to be the correct structure. $P_5N_3Cl_{16}$ is the hexachloro phosphate, which is formed by the addition of PCl_5 to the chloride XXXVIII.

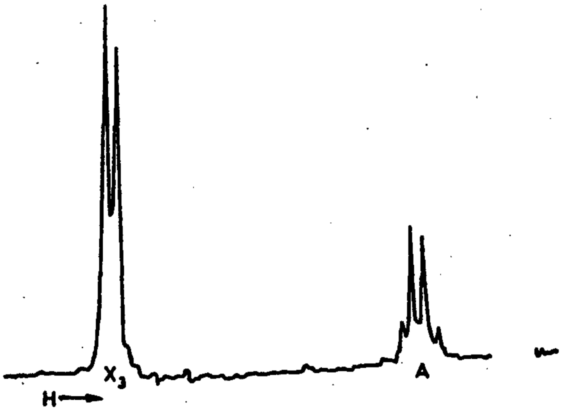
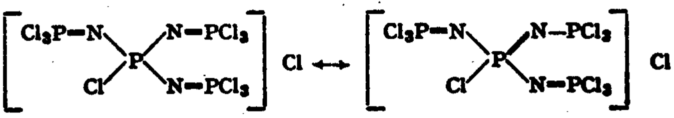
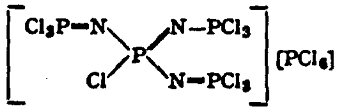


Fig. 6: The ^{31}P-nuclear magnetic resonance spectrum of the compound:

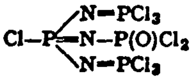


XXXVIII

The proof of structure XXXVIII is provided by the nuclear magnetic resonance data. The spectrum (Figure 6) has a doublet with a chemical shift of $-6.5\cdot10^{-6}$ and a quartet with a chemical shift of $+26.8\cdot10^{-6}$. The intensity ratio of the doublet to the quartet is 3:1, indicating that there is one phosphorus atom coupled with three different chemically equivalent phosphorus atoms. The single phosphorus atom thus gives rise to a quartet, and the chemical shift thereof suggests that the coordination number of this atom is four. The remaining three phosphorus atoms, which are chemically equivalent among themselves, are also tetra-coordinated and are coupled to the single phosphorus atom. XXXVIII is, therefore, the only reasonable structure. It should be noted, of course, that the double bonds between the central P-atom and the three $NPCl_3$ groups are delocalized; in addition each of the bonds between the N and the PCl_3 groups has a considerable degree of double bond character. The two formulas, designated XXXVIII, must therefore be viewed as two out of many limiting structures. With excess PCl_5 XXXVIII is converted into XXXIX, and with SO_2 XXXVIII can be transformed into XL (Reference 26)*.



XXXIX



XL

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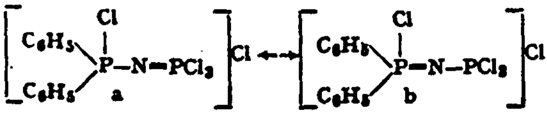
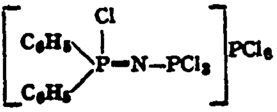
*It should be added that thio-diphenyl phosphinic acid amide reacts in a manner consistent with and analogous to thiophosphoric acid triamide in the presence of PCl_5. Replacement of the sulfur by chlorine and a Kirsanov reaction with an amino group results in the formation of XLI or XLII (Reference 57).

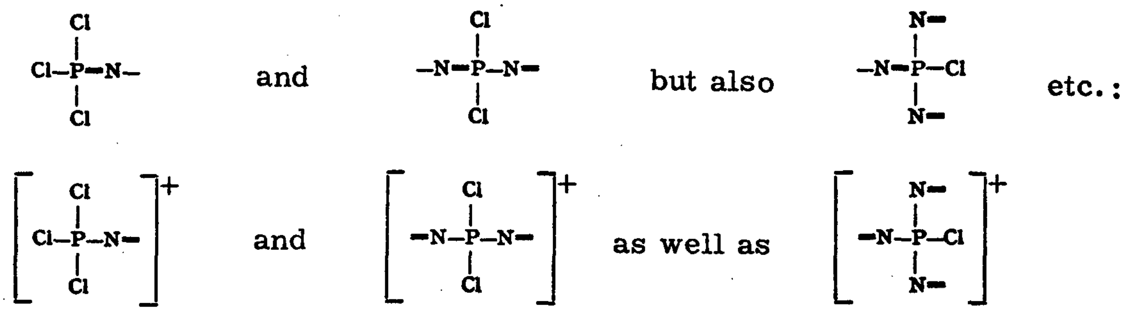


XLI XLI



XLII

Compounds XXXVIII, XXXIX, and XL represent a new category of phosphorus-nitrogen compounds in that they demonstrate the stability of structures which have a single chlorine bound to a tetra-coordinated phosphorus atom along with one, two, or even three nitrogens. Chemically feasible structures thus not only include



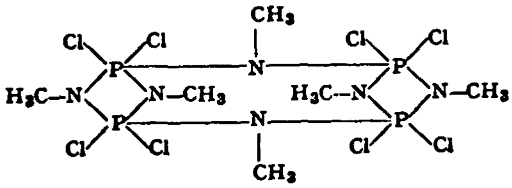
$$\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{-}N{-}} \quad \text{and} \quad \mathrm{{-}N{-}\overset{Cl}{\underset{Cl}{P}}{-}N{-}} \quad \text{but also} \quad \mathrm{{-}N{-}\overset{N-}{\underset{N-}{P}}{-}Cl} \quad \text{etc.:}$$

$$\left[\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{P}}{-}N{-}}\right]^+ \quad \text{and} \quad \left[\mathrm{{-}N{-}\overset{Cl}{\underset{Cl}{P}}{-}N{-}}\right]^+ \quad \text{as well as} \quad \left[\mathrm{{-}N{-}\overset{N-}{\underset{N-}{P}}{-}Cl}\right]^+$$

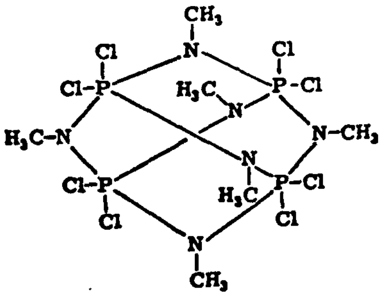
6. The Reaction with Monomethyl Ammonium Chloride

It was already pointed out in chapter IIb, 1, that monomethyl amine, that is to say its hydrochloride, reacts with PCl_5 to yield the four membered ring system VIII. A closer investigation of the same reaction in a tetrachloroethane solvent, however, revealed that other products could also be formed. When PCl_5 and $[H_3NCH_3]Cl$ were heated in tetrachloroethane in a mole ratio 1:1.3 for several hours at 60°C, compound VIII was the first product to be isolated upon cooling and reduction of solvent volume. After a period of days a second product crystallized out of the remaining mother liquor, and its composition was $P_4(NCH_3)_6Cl_8$ (References 10, 11). When the reaction mixture was carefully heated for longer periods of time (15 hours), this material could be obtained in yields as high as 10%; finally if the reaction medium was rapidly heated, a mixture of polymeric materials - yet of unknown composition and of a variable nature - was produced in addition to VIII (Reference 48).

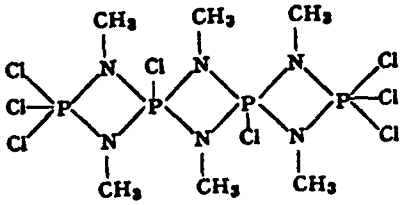
The molecular weight of $P_4(NCH_3)_6Cl_8$ was determined ebullioscopically both in benzene and dichloroethane, and the ^{31}P-nuclear magnetic resonance spectrum was examined as well. The latter analysis revealed a signal at $+74.5 \cdot 10^{-6}$, indicating the presence of phosphorus with a coordination number of five (the chemical shift for PCl_5 is $+80 \cdot 10^{-6}$). On the basis of the above physical parameters we considered formulas XLIII, XLIV, and XLV as likely candidates for the structure of this substance.



XLIII



XLIV

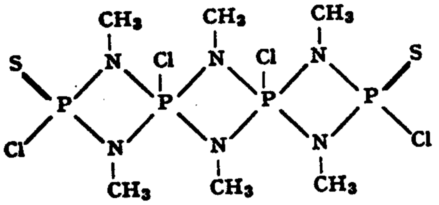


XLV

The nuclear magnetic resonance spectrum as well as the high melting point of this substance (395°C) seemed to indicate that structure XLIV was the proper one; the infra-red spectrum, on the other hand, suggested either XLIII or XLV (Reference 11), because of its remarkable similarity to compound VIII - especially in the strong absorption at 850 cm^{-1} attributed to the P-N vibrations of the four membered ring system.

When $P_4(NCH_3)_6Cl_8$ was exposed to H_2S, four, and only four, chlorine atoms could be replaced by sulfur. The product of the reaction was $P_4(NCH_3)_6S_2Cl_4$, the ^{31}P NMR spectrum of which revealed tetra-coordinated phosphorus bonded to a sulfur atom (a chemical shift of $-55.3 \cdot 10^{-6}$) and penta-coordinated phosphorus with a chemical shift of $+68 \cdot 10^{-6}$. XLVI seemed to be the only structure consistent with this data, suggesting that structure XLV was the correct one for $P_4(NCH_3)_6Cl_8$.

By x-ray analysis of $P_4(NCH_3)_6Cl_8$ structure XLV was indeed established (Reference 57).



XLVI
(m.p. 230°C - decomposition)

The structural backbone of XLV consists of three planar phosphorus-nitrogen rings, linked to one another by common phosphorus atoms. The system has a center of symmetry, and the configuration around the phosphorus atoms is trigonal bipyramidal. Figure 7 shows half of the molecule, while Figure 8 shows the bond lengths and bond angles aroung the P_1 atom;

Figure 9 gives the same information for the P_2 atom.

The environment of the P_1 atom is very similar to that of the phosphorus in compound VIII. The trigonal pyramid is distorted; and although the equatorial ligands are all in a plane, the axial ligands are not on a line. Comparison with Figure 3 shows that this is also the case for compound VIII.

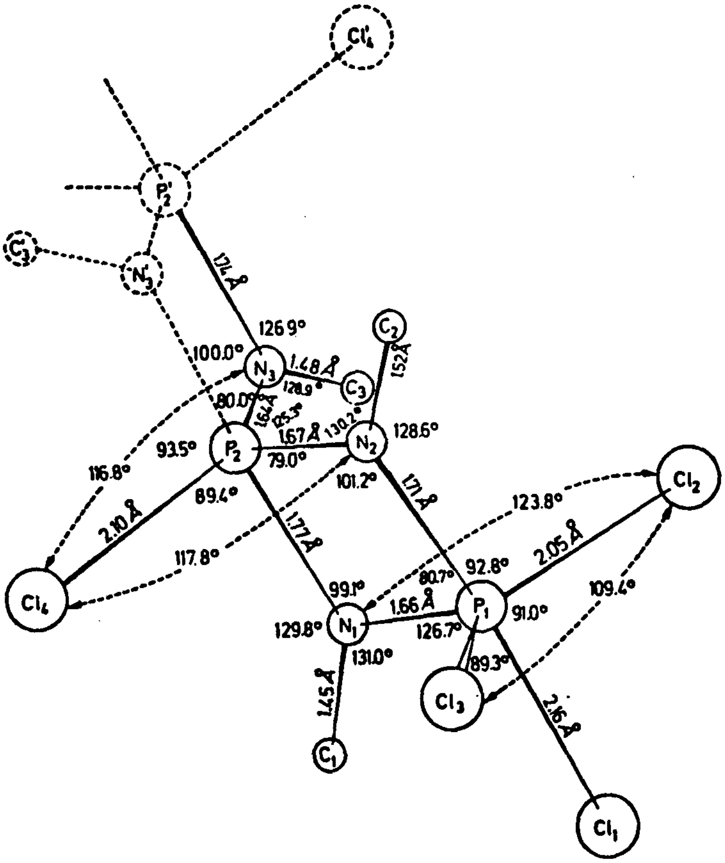


Fig. 7: Half of molecule XLV, which has a center of symmetry.

Weiß and Hartmann (Reference 57) suggest that the four membered phosphorus-nitrogen ring systems possess delocalized π bonds, and that the degree of this bonding is the same in various P-N bonds. The different bond lengths originate in the sp^3d hybridization and depend on the equatorial or axial position of the nitrogen atoms*. The P-Cl bond lengths compare favorably with those of PCl_5 (Figure 1).

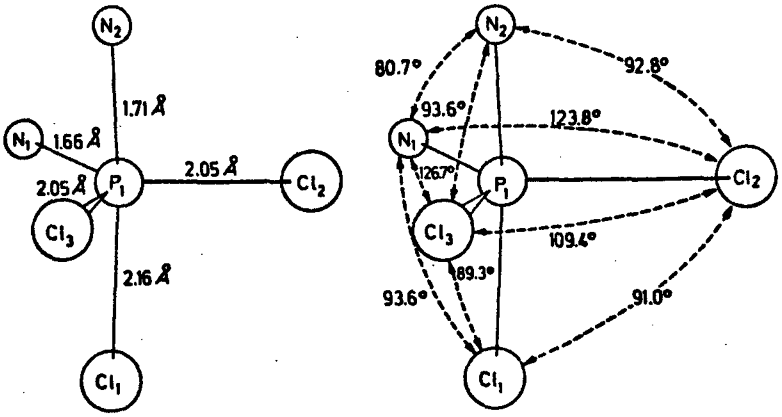


Fig. 8: Bond lengths and angles around P_1.

Since the P_2 atom is common to both four membered rings, the trigonal bipyramidal is even more distorted around P_2 than it is around P_1.

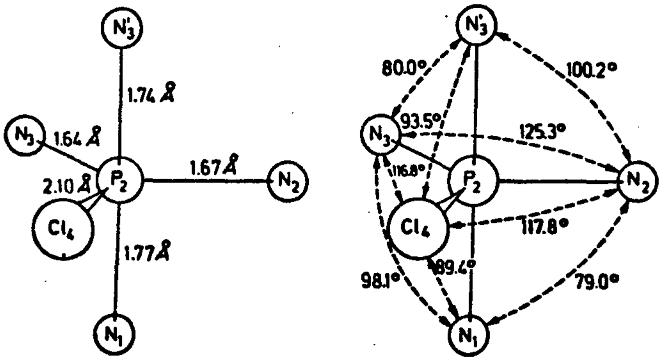


Fig. 9: Bond lengths and angles around P_2.

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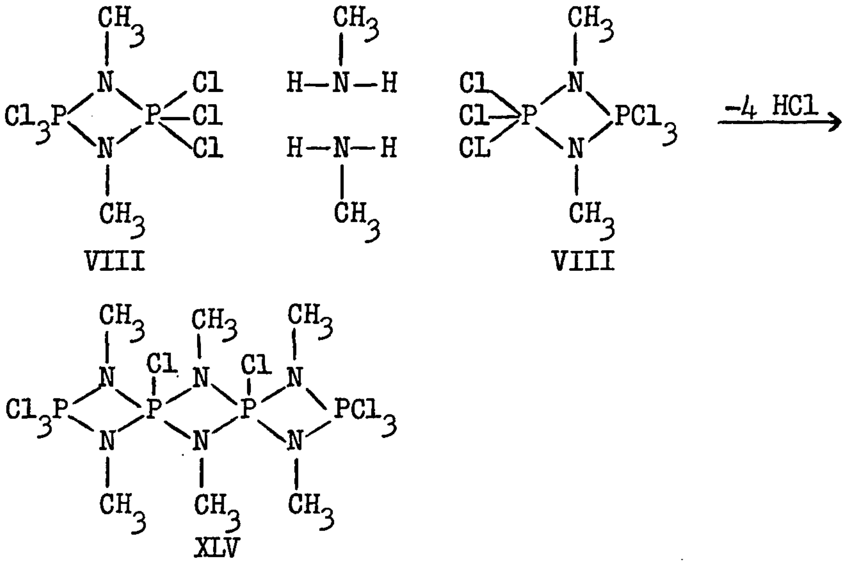
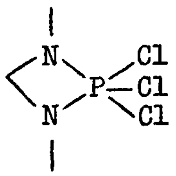
* A ratio of 1.1 for axial to equatorial bond length is average (Reference 34).

We envision the formation of XLV as follows: first the amine forms an adduct with PCl_5 by the mechanism discussed above, leading to the formation of VIII; next two molecules of VIII combine with monomethyl amine (released from the hydrochloride salt in the process of heating) to yield XLV; finally in the presence of PCl_5 XLV can be converted back into VIII (Reference 48).

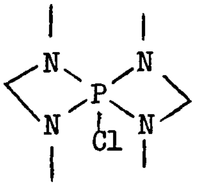


XLV

The existence of compound XLV, XLVI (as well as the readily synthesized oxygen analogue of XLVI (Reference 11, 48) demonstrates that phosphorus with a coordination number of five can exist with the following ligands around it.

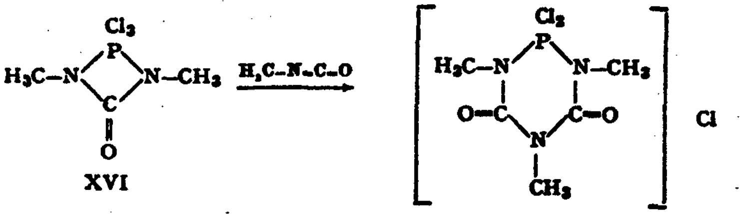


and



In previously observed systems phosphorus has an sp^{3}d and nitrogen an sp^2 hybridization; the compounds are not ionic, but covalent in nature.

When the structure portrayed above are present, the phosphorus atom is always involved in the four membered ring system*. Indeed one can attempt to enlarge the ring, for example, by treating with $H_3C{-}N{=}C{=}O$ (Reference 42); in the process, however, the penta-coordinated phosphorus is converted to tetra-coordinated phosphorus:



XVI

7. Summary

The nature of substitution reactions between nitrogen containing ligands and phosphorus pentachloride is essentially twofold. In many reactions, phosphorus, having a coordination number of five, is converted into phosphorus with the coordination number four; in the process ions or molecules are formed which have N-P bonds possessing a certain degree of double bond character. In other reactions the coordination number of five does not change, and four membered phosphorus-nitrogen containing ring systems are obtained. Such bonds between phosphorus and nitrogen have a $d_\pi p_\pi$ contribution.

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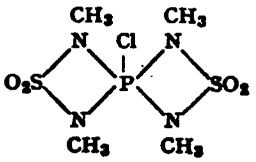
* This was confirmed recently when we reacted N,N'-dimethyl sulfamide with PCl_5. We obtained both compound VIII and XLVII in the process (Reference 54).



XLVII

(m.p. 170-171.5°-decomposition)

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13. ABSTRACT

The structure of phosphorus pentachloride has been investigated and reviewed. The two general types of reactions of phosphorus pentachloride, the formation of adducts and substitution reactions are discussed. The reactions of phosphorus pentachloride with ammonia derivatives of the structure $R-NH_2$, ammonia and its salts, hydroxylamine and its salts, hydrazine and its derivatives, phosphoryl amide and thiophosphoryl amide, and monomethyl ammonium chloride are described.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Phosphorus Nitride						
Phosphorus Compounds						
Inorganic Polymers						