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PART II

NITROGEN-PHOSPHORUS POLYMERS

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UNIVERSITY OF HEIDELBERG

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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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 1 October 1964 through 30 June 1966. The manuscript was released by the author in June 1966 for publication as a technical report.

This technical report has been reviewed and is approved.

William E. Gibbs

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Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

A variety of chemical systems containing phosphorus nitrogen bands have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include the preparation and reactions of a variety of compounds with four-membered ring systems containing alternate P and N atoms, compounds with four-membered ring systems containing P, N and C atoms, and compounds containing P-N-P chains; and the preparation of phosphonitrilic chlorides and their derivatives.

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SECTION I

INTRODUCTION

The purpose of the work covered by this report was the preparation of phosphorus nitride derivatives. The work was divided into four sections.

Section II Compounds with 4-Membered Ring Systems Containing P and N

Section III Compounds with 4-Membered Ring Systems Containing P, N and C

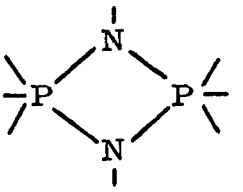
Section IV Compounds with P-N-P Chains

Section V Phosphonitrilic Chlorides $(NPCl_2)_n$ and Derivatives

SECTION II

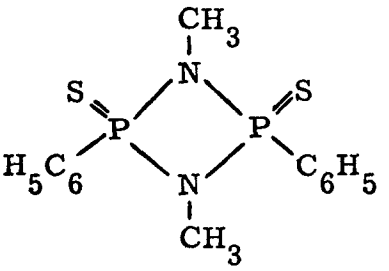
COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P AND N

First, we studied phosphorus-nitrogen compounds containing ring systems. Various phosphorus-nitrogen compounds are known (Reference 1) which comprise a four-membered ring system of the type indicated by formula I.

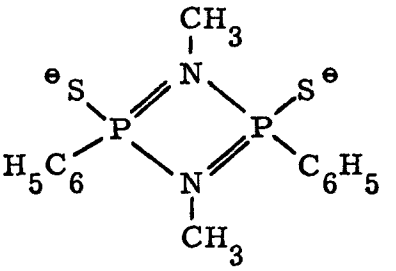


I

A series of such compounds has been prepared by Michaelis (Reference 2). It was found, for example, that the compound $[C_6H_5NP(O)C_6H_5]$ is dimeric and this fact would suggest that a tetracyclic system corresponding to formula I might apply for this substance. This formulation was justified by Trippett (Reference 3) for the compound $[CH_3NP(S)C_6H_5]_2$ on the basis of nuclear magnetic proton-resonance spectra. Accordingly, formula II can be ascribed to this compound. From the infrared spectrum, Trippett assumed that resonance exists between the forms IIa and IIb.

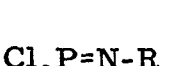


IIa

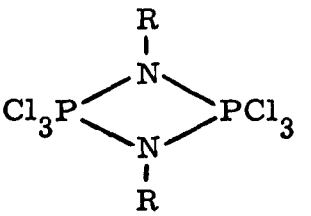


IIb

Substances with the basic structure I are also obtained in the reaction of phosphorus pentachloride with primary amines (Reference 1), whereby compounds of type III or IV can be prepared. Products of type IV are preferred when strongly basic amines (amines in which the basic constant of the aqueous solution lies between 10^{-4} and 10^{-9}) are employed (Reference 4) and the hydrochloride of such an amine is treated with PCl_5 in an inert solvent.

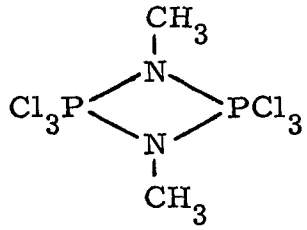


III



IV

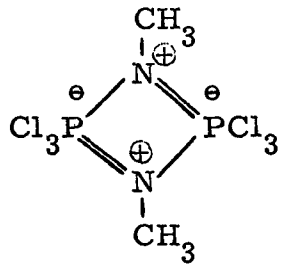
One of the most thoroughly investigated substances of type IV is compound V, which was first prepared by Chapman, Holmes, Paddock, and Searle (Reference 5).



V

All the phosphorus atoms in this compound are chemically equivalent, since the P^{31} NMR spectrum of a solution of the substance in $CHBr_3$ reveals only one signal (Reference 6) with a chemical shift 78.2 ppm (referred to 85% phosphoric acid as standard). The strongly positive chemical shift shows that 5-coordinate phosphorus is contained in this compound. This is further supported by a comparison with PCl_5, whose solution in carbon disulfide gives rise to a peak at +80 ppm. Moreover, the proton-resonance spectrum found by Trippett (Reference 3) is in agreement with formula V.

The P-N bond strengths in V have been estimated by Fowell and Mortimer (Reference 7); these authors found the value 74.3 kcal/mole for these linkages. The P-N bond in the tetracyclic system V would thus appear to be stronger than in the case of the normal P-N single bond, for which 66.8 kcal/mole was determined from studies of $P[N(C_2H_5)_2]_3$. It is very probable that these differences do not arise from a difference in hybridization of the phosphorus atoms, and it would seem reasonable to assume that in 2, 2, 2, 4, 4, 4-hexachloro-1, 3, -dimethyl-cyclodiphosphazane further stabilization by means of $d_{\pi}p_{\pi}$ bonds occurs in the manner indicated by formula VI.



VI

The structure of this compound was elucidated by Hess and Forst (Reference 8). Figure 1 shows the result of this investigation.

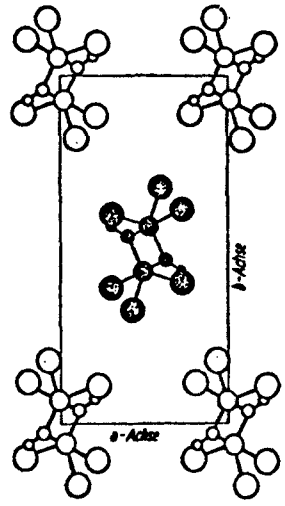


Figure 1. Crystal Structure of VI, Projection on [001]

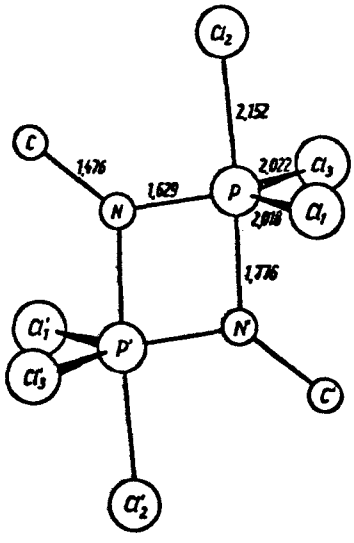


Figure 2. Compound VI, Atom Distances Å

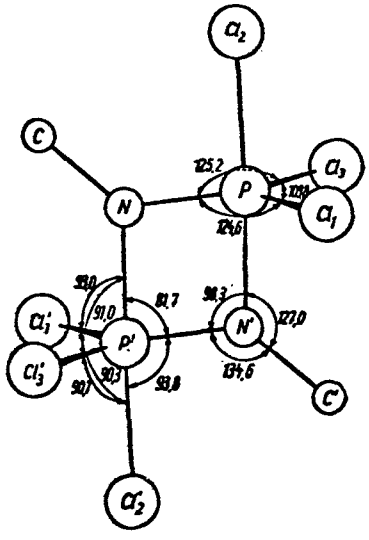
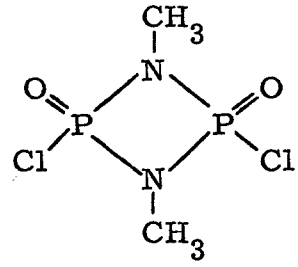


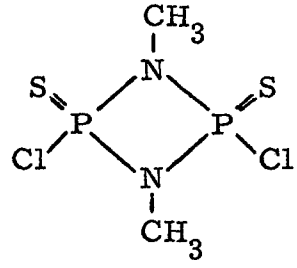
Figure 3. Compound VI, Bond Angles

It appeared likely that compounds V and VI would provide a basis for the conversion of 5-coordinate phosphorus into the 4-coordinate state. Toward this end, we treated the substance with sulfur dioxide and were able to obtain compound VII in excellent yield. VII is colorless and crystalline; it is extremely sensitive to moisture and hydrolyzes rapidly. The compound dissolves readily in benzene, and the P^{31} NMR spectrum of the solution reveals a single peak at +5.3 ppm. This result shows that in this case also, all the phosphorus atoms in the molecule are chemically equivalent. Comparison with other phosphorus compounds (Reference 6) indicates clearly that the phosphorus atoms in VII are 4-coordinate.



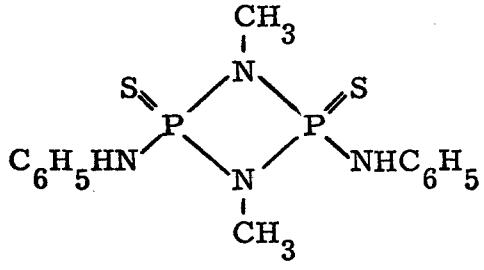
VII

We then attempted to prepare the sulfur compound analogous to VII by reacting 2, 2, 2, 4, 4, 4-hexachloro-1, 3-dimethylcyclodiphosphazane (V) with H_2S at room temperature. When dry pyridine was added to the reaction mixture, 2, 4-dithio-2, 4-dichloro-1, 3-dimethylcyclodiphosphazane (VIII) was formed in excellent yield together with pyridinium chloride; VIII also proved to be crystalline and sensitive to hydrolysis. Its P^{31} NMR spectrum in benzene showed one resonance signal at -51.5 ppm. These observations are in accord with the structural formula VIII. It has been generally observed that 4-coordinate phosphorus which bears a sulfur atom as one of its ligands gives rise to an NMR signal in this range, indicating that the phosphorus atoms in such compounds are only weakly shielded (Reference 9).

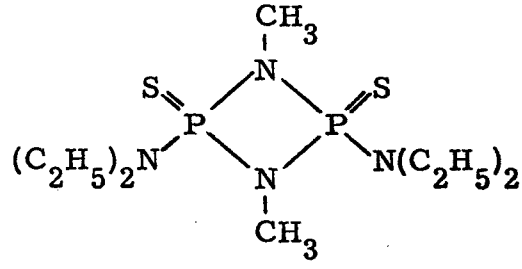


VIII

It was found that VIII reacted smoothly with amines. Compound IX was obtained by the action of a solution of aniline in benzene at room temperature. The corresponding diethylamine compound X was prepared in a similar way.

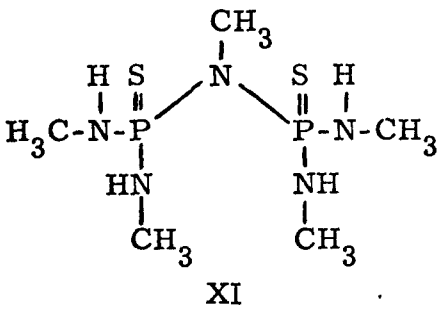


IX

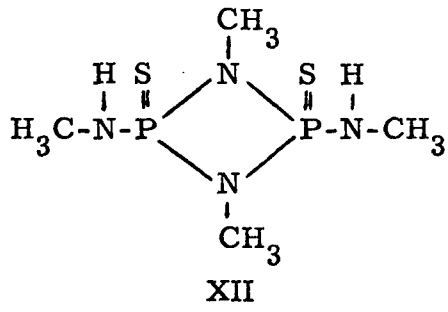


X

On the other hand, the reaction with excess monomethylamine in the absence of a solvent at -50°C resulted in cleavage of the four-membered ring and formation of N-methylimidodithiophosphoric tetra-N-methylamide (XI). When heated in vacuum (15 mm Hg) at 180° to 200°C, this product split off methylamine to regenerate the tetracyclic compound XII.



XI



XII

In all of these sulfur-containing compounds the phosphorus nuclei are only weakly shielded. This is clearly shown by the P^{31} NMR spectra; for example, IX (in dichloroethane) has a chemical shift of -54 ppm, XII (in benzene) indicates -60 ppm, and X (in methylene chloride) -63 ppm. These data would suggest that it is not strictly correct to incorporate a P=S double bond in the formulation of these compounds; rather, the bond would appear to be strongly polar and can be better represented by the form $\overset{+}{P}\text{-}\overset{\theta}{S}$.

The structure of compound VIII was elucidated by X-ray investigation. Figure 4 shows the result.

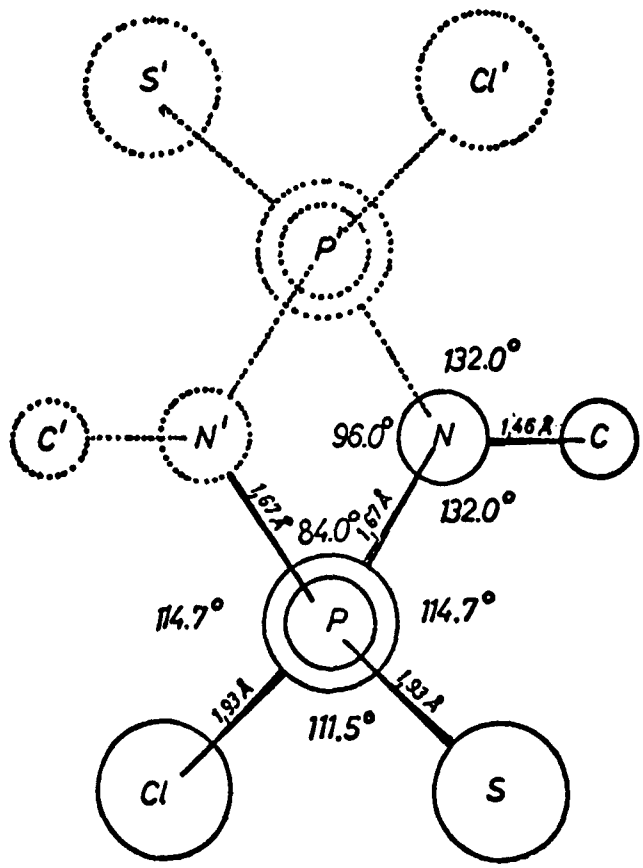
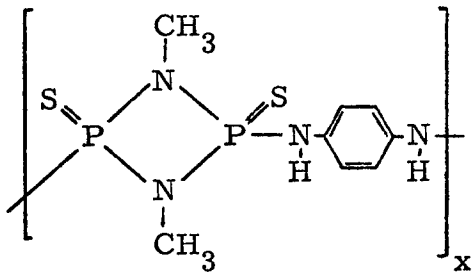


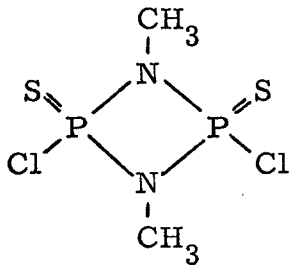
Figure 4. Structure of Compound VIII With Bond Angles and Bond Length (The ring is planar.)

Following the successful preparation of compound IX, it appeared expedient to react VIII with diamines under the same conditions which led to substitution in the case of the conversion of VIII into IX. Accordingly, a reaction with paraphenylene diamine was carried out, which furnished XIII, a nonhygroscopic solid.



XIII

Accordingly, some time was devoted to the preparation of polymers utilizing compound VIII and diamines as the starting materials.



VIII

These reactions were carried out with hexamethylene diamine, ethylene diamine, hydroquinone, p-phenylene diamine, and silver cyanamide.

Ethylene chloride was employed as solvent for the reaction of VIII with hexamethylene diamine. The reaction was exothermic and led to the product $\left[P_2N_4S_2C_8H_{20}\right]_x$. This polymer was found to be insoluble in most solvents (including water) but it dissolved slightly in warm dimethylsulfoxide. The substance became thermoplastic and malleable at 180°, but at 220° it began to decompose.

By treating VIII with ethylene diamine in a solution of carbon tetrachloride, we were able to obtain the compound $\left[P_2N_4S_2C_4H_{12}\right]_x$ in good yield. This material was stable up to 260° but the malleable state was not attained before decomposition set in. As in the previous instance, the substance proved to be insoluble in water, methanol, acetone, and other common solvents, indicating slight solubility only in dimethylsulfoxide.

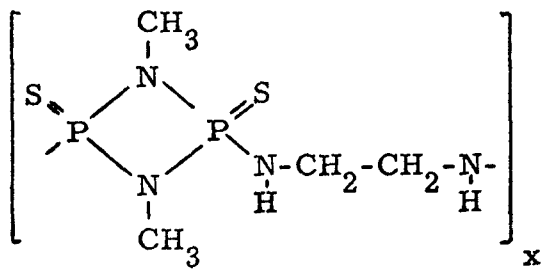
Reaction of VIII with hydroquinone in a mole ratio of 1:1 furnished $\left[P_2N_2S_2O_2C_8H_{10}\right]_x$. In this case, the reactants were mixed directly and heated to 190° in the absence of a solvent. The mixture fused and the melt evolved HCl, whereupon it rapidly became viscous. The material finally solidified to a yellowish-white substance, from which unreacted hydroquinone was subsequently removed by washing with ether. The polymer was stable up to 330° and did not exhibit thermoplastic properties at any temperature. This substance did not dissolve in water, methanol, acetone or other solvents excepting dimethylsulfoxide and dioxane, in which it was slightly soluble.

When VIII was reacted with hydroquinone in a mole ratio of 1:2, a frothy solid mass was produced which revealed a somewhat higher degree of thermal stability than that of the product obtained in the case of the reaction in a 1:1 mole ratio. Further studies with the "frothy" material are in progress.

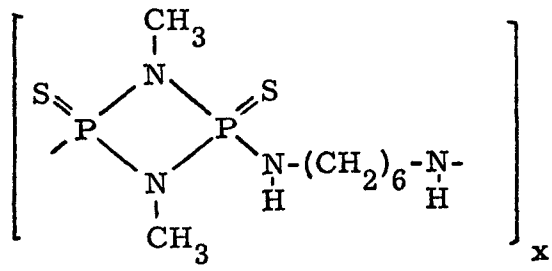
The reaction of VIII was p-phenylene diamine in ethylene chloride was exothermic and led to a white solid product having the composition $\left[P_2N_4S_2C_8H_{12}\right]_x$. However, this substance was not obtained pure, and could not be freed from accompanying p-phenylene diamine hydrochloride.

Ag_2NCN did not react with compound VIII in the presence of a solvent; however, reaction occurred when the components were mixed directly and fused. Solid polymeric products were formed which are presently being investigated.

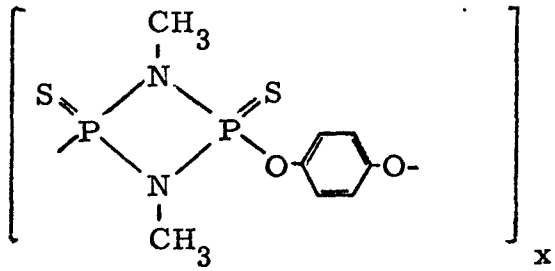
The infrared spectra of all these products indicate that the ring system present in VIII is retained in all instances; the absorption bands which are characteristic for the four-membered ring system were observed in the spectrum of each of the polymers. It was also evident that the diamines reacted in the expected manner, that is, one molecule of diamine per molecule of the cyclic compound VIII. Apparently, polymer chains containing the four-membered ring are produced which are then linked via amino groups XIV, XV. The establishment of an $-O-C_6H_4-O-$bridge between two four-membered ring systems as in XV, is also possible.



XIV

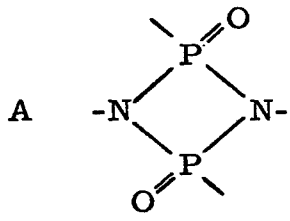


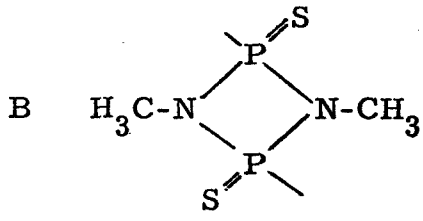
XV



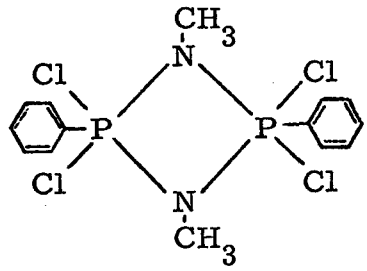
XVI

All these compounds with the units B may be compared with the DAPO-derivatives with the unit A which were prepared by Parts, Nielsen and Miller (Reference 10).





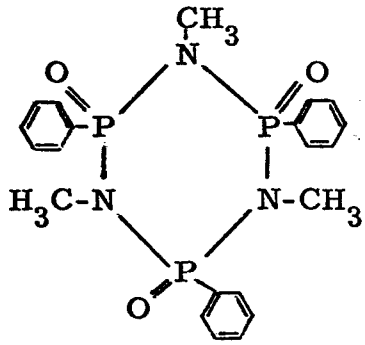
Another type of derivatives of the ring system I was obtained when $C_6H_5PCl_4$ was used instead of PCl_5 as reactant. When  -PCl_4 and $[CH_3NH_3]Cl$ were reacted, substance XVII was formed.



(mp 222°)

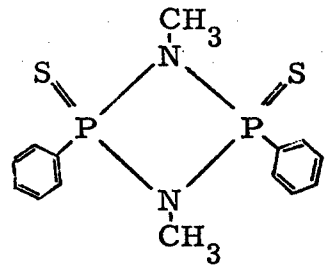
XVII

We have studied the reaction of XVII with SO_2. A compound $C_6H_5P(O)NCH_3$ was formed which is trimeric in the cold XVIII. With H_2S, however, compound XIX was obtained.



(mp 227°)

XVIII



(mp 203°)

XIX

Many of these phosphorus-nitrogen compounds incorporating a four-membered ring system according to I were obtained starting with the reaction of PCl_5 with primary amine. Closer study of this reaction system revealed that V is the main product although a further crystalline substance can be isolated from the mother liquors. Thus the principal reaction, leading to the tetracyclic compound V, can be expressed by the equation

$$2\ PCl_5 + 2[H_3NCH_3]Cl \longrightarrow P_2(NCH_3)_2Cl_6 + 6\ HCl$$

whereby the following reaction can also participate:

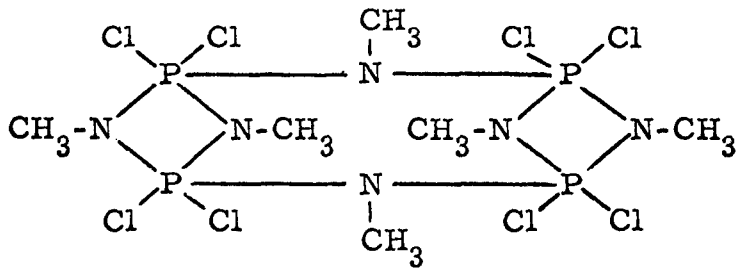
$$4\ PCl_5 + 6\left[H_3NCH_3\right]Cl \rightarrow P_4(NCH_3)_6Cl_8 + 18\ HCl \text{ (Reference 11).}$$

The new compound is produced from PCl_5 and methylammonium chloride in a yield of 2 to 4 percent based on PCl_5; it can be recrystallized from larger amounts of benzene and melts with decomposition at 395° in a sealed tube.

Ebullioscopic molecular weight determinations in benzene and in dichloroethane were carried out in an attempt to elucidate the structure of this substance. The value found was 584, which would indicate that the formula employed in the above equation is correct.

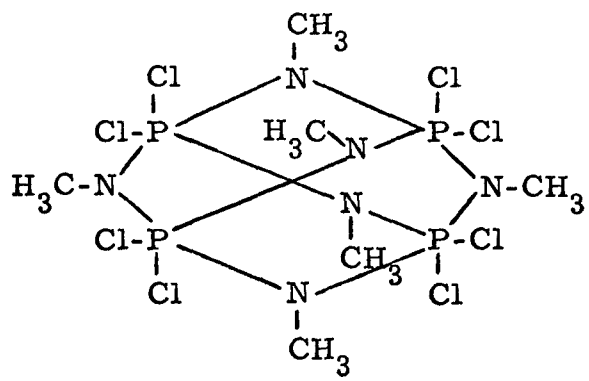
The P^{31} NMR spectra of solutions of the compound in benzene and in pyridine revealed only one resonance signal at +74.5 ppm. It can be inferred from this result that 5-coordinate phosphorus is present in the compound and that the phosphorus atoms are either chemically equivalent or that they are at least situated in chemically similar environments.

Accordingly, formulae XX, XXI or XXII may be considered for $P_4(NCH_3)_6Cl_8$

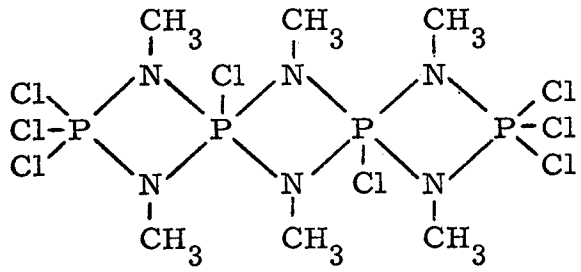


XX

The NMR spectrum and the high melting point appeared to support formula XXI (Reference 11), although the infrared spectra were more in accord with XX and XXII. By comparison, Chapman et al., found the following infrared bands for V: 434m, 575s, 658s, 700m, 747vw, 847vs, 1162s, 1184s, 1210s, 1439m, 1461m, 2812w, 2941m, 2996m (cm^{-1}).



XXI

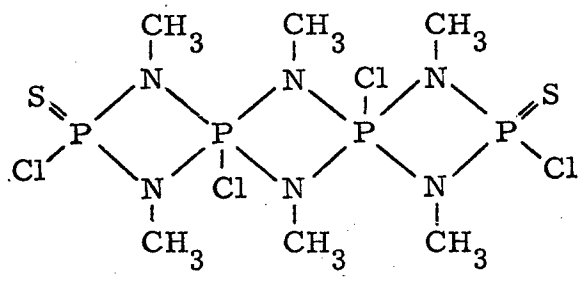


XXII

In addition to these bands, we observed absorption at 920 cm^{-1} (m) and at 1290 cm^{-1} (m). In contrast to Chapman et al., we employed KBr for the sample pellet.

Corresponding infrared studies of $P_4(NCH_3)_6Cl_8$ revealed bands at 2960 and 2820 cm^{-1}, which can be ascribed to C-H and N-CH vibrations, respectively. We also found further bands at 1460m, 1425m, 1235s, 1215vs, 1187vs, 1170vs, 877s, 843s, 715s, and 654s (cm^{-1}). The spectra of V and $P_4(NCH_3)_6Cl_8$ display a number of similar features, particularly with respect to a common, very strong absorption at 850 cm^{-1} which can be ascribed to the P-N vibration and which is attributed by Trippett to the tetracyclic phosphorus-nitrogen system. It therefore seemed feasible that the new compound might also consist of a phosphorus-nitrogen four-membered ring system, suggesting formulae XVI and XVIII.

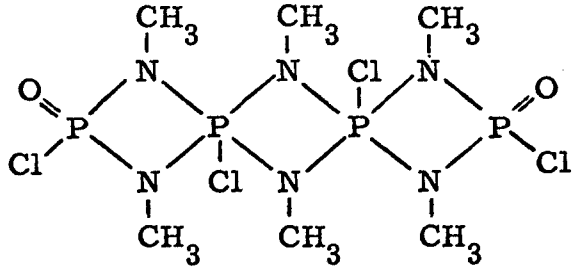
Additional structural studies were carried out with the help of chemical reactions. First, the interaction of $P_4(NCH_3)_6Cl_8$ and H_2S in pyridine was investigated. The product was a pale yellow, crystalline solid with the composition $P_4(NCH_3)_6S_2Cl_4$. The P^{31} NMR spectrum of a solution of this substance in dichloroethane was characterized by one resonance maximum at -55.3 ppm and another of equal intensity at +68 ppm. This result shows that the compound contains two types of phosphorus atoms which are chemically nonequivalent. Half of the P atoms are linked to sulfur and are 4-coordinate (corresponding to the signal at -55.3 ppm); the remaining P atoms are 5-coordinate, giving rise to the resonance peak at +68 ppm. On this basis, formula XXIII was ascribed to the compound.



XXIII

The fact that $P_4(NCH_3)_6Cl_8$ could not be made to react with more than two moles of H_2S provided strong support for formula XXII as a correct representation of $P_4(NCH_3)_6Cl_8$. Treatment of $P_4(NCH_3)_6Cl_8$ with SO_2 led to the crystalline substance $P_4(NCH_3)_6O_2Cl_4$ in high

yield. The P^{31} NMR spectrum of a solution of this product in pyridine contained peaks of equal intensity with the chemical shifts +73 ppm and -4 ppm. This result speaks unequivocally for formula XXIV.



XXIV

These results could be proved by X-ray analysis. These results, obtained with compound XXII are shown in Figures 5 and 6. In Figure 7 the environment of phosphorus P_2 is shown in detail. Figure 8 allows a comparison with the phosphorus atom in PCl_5.

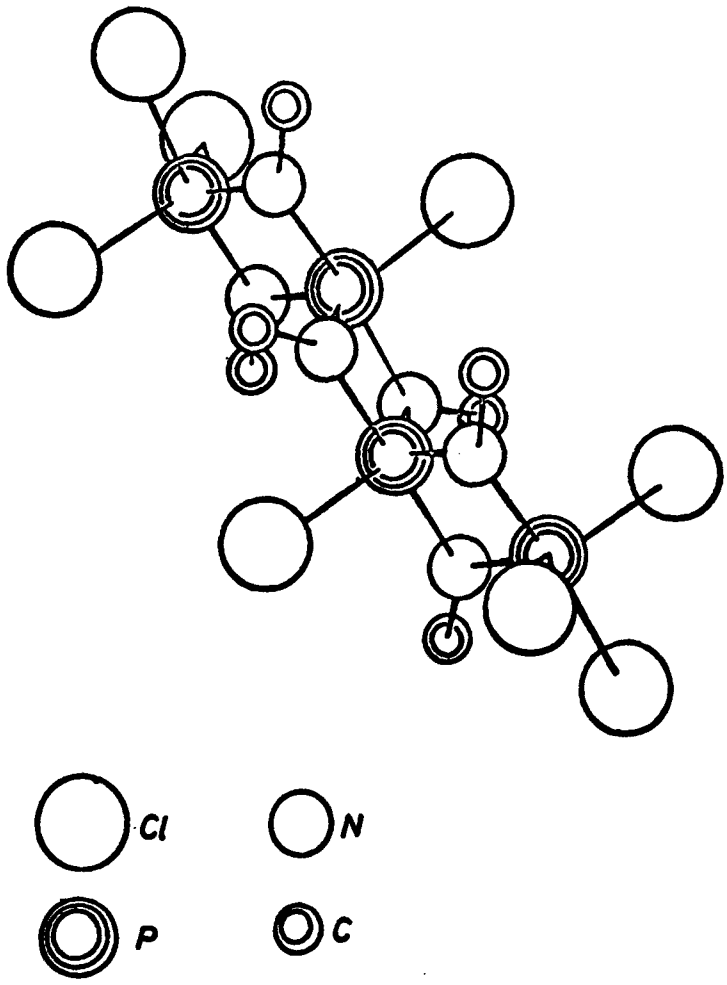


Figure 5. Structure of Compound XXII

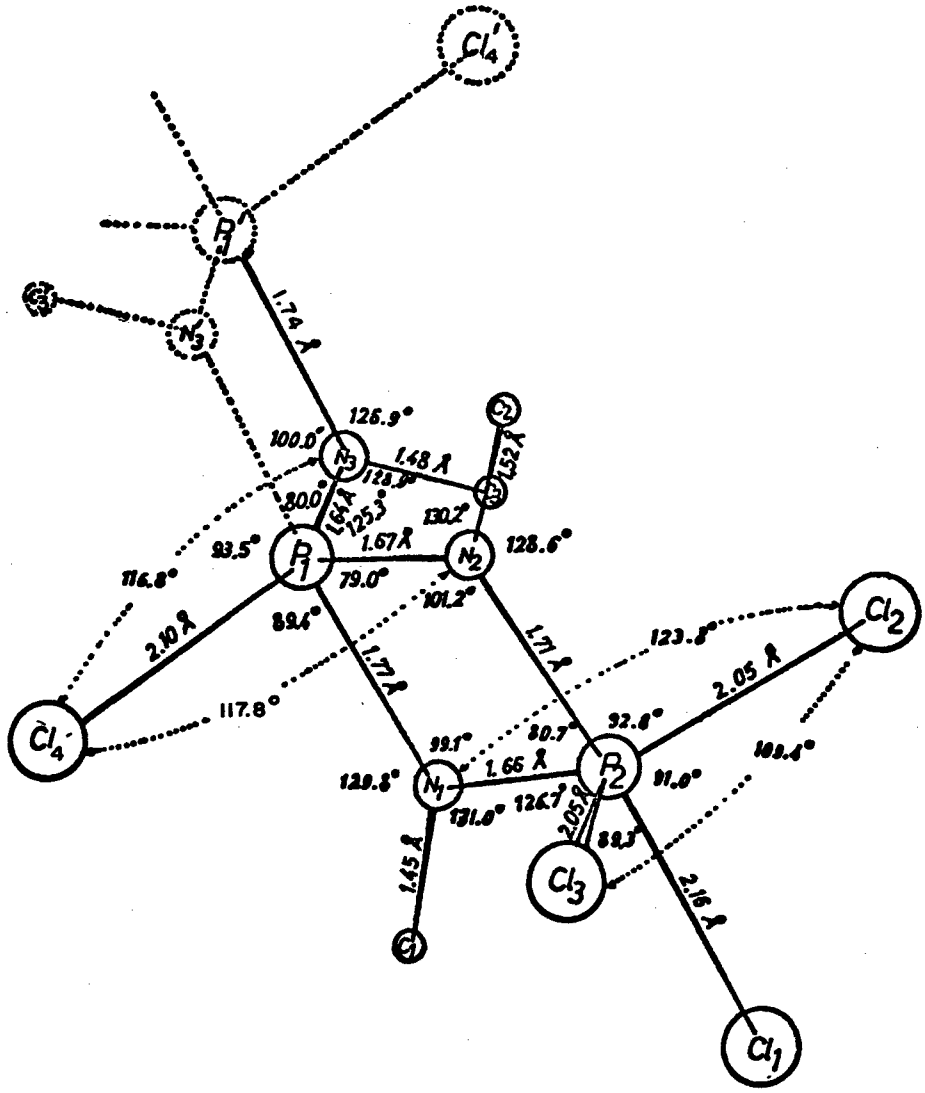


Figure 6. Part of the Molecule of XXII With Bond Lengths and Bond Angles

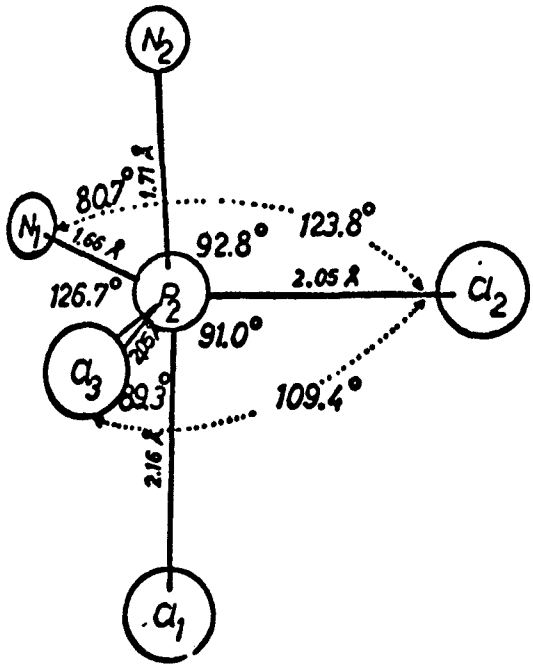


Figure 7. Part of the Molecule of XXII

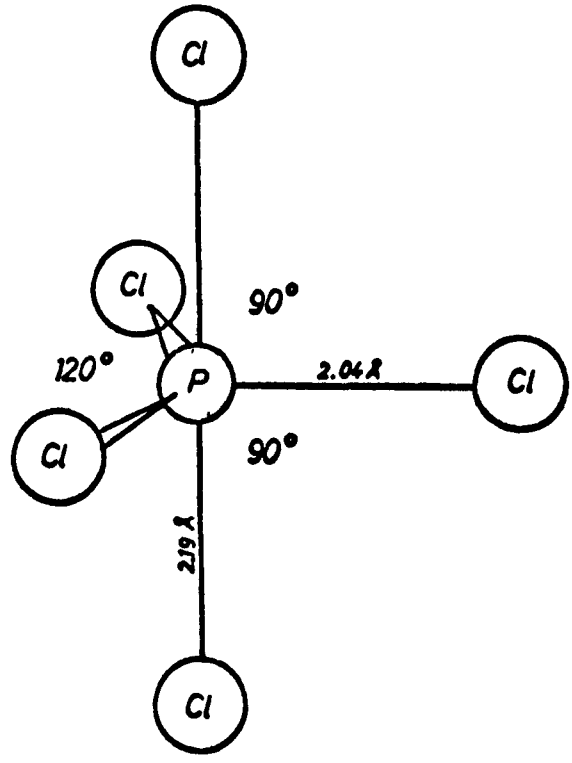


Figure 8. PCl_5

A. 2, 2, 2, 4, 4, 4-HEXACHLORO-1 3-DIMETHYLCYCLODIPHOSPHAZANE (V)

A mixture of 74.3 g of methylammonium chloride (1.1 mole) and 208.5 g of PCl_5 (1 mole) was placed in 750 ml of dry tetrachloroethane and heated to boiling. Evolution of HCl set in at 60° and continued for about 6 hours. After this time the solution was allowed to cool to about 40° and then concentrated in a thin-layer evaporator under partial pressure (20 mm Hg) until crystals appeared. The mixture was then cooled to 0° and the crystals filtered off. The yield of V is about 150 g, corresponding to 90 percent of theory. The product can be recrystallized from benzene, CCl_4, di- and tetrachloroethane, and acetonitrile. With the latter solvent and repeated recrystallization, it is possible to obtain a sample which melts at 178° (uncorr) as opposed to the melting point of 160° reported by Chapman et al. (Reference 5). It is essential that the melting point determination be carried out in a sealed tube. In all other aspects, this substance is identical with that obtained by the authors mentioned above (Reference 5).

B. 2, 4-DIOXO-2, 4-DICHLORO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (VII)

A total of 100 g of $P_2(NCH_3)_2Cl_6$ (V) was dissolved in 500 ml of dry methylene chloride; dry SO_2 was then passed into the cooled solution (ice bath) with stirring. At first, a portion of the starting material remained undissolved, but this was consumed in the course of the reaction. SO_2 is sparged into the clear, colorless solution until approximately twice the theoretical amount has been absorbed. The reaction mixture is then allowed to stand at 0°

overnight, after which the solvent is removed in a thin-layer evaporator under aspirator vacuum. The residue consists of a pale yellow oil which soon crystallizes; this product can be recrystallized from cyclohexane or, preferably, sublimed at 60°/0.01 mm Hg. The melting point is unsharp (101°-103°). Yield: 92.5 percent, based on $P_2(NCH_3)_2Cl_6$.

Analysis of $P_2(NCH_3)_2O_2Cl_2$ (222.9)

calc:	12.57 N	27.79 P	31.81 Cl	10.77 C	2.71 H
found:	12.49 N	27.40 P	31.83 Cl	10.72 C	2.70 H

Molecular weight (ebullioscopically in benzene and dichloroethane): 222±1.5 (mean from 6 determinations).

C. 2, 4-DITHIO-2, 4-DICHLORO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (VIII)

A total of 103 g of dry pyridine was added to a solution of 100 g of V (0.3 mole) in 1 liter of dry benzene. Dry H_2S was passed into the stirred solution at room temperature. After a short time, a precipitate of pyridinium chloride appeared, which was formed in an approximately theoretical amount in the course of 15 hours. The precipitate was then filtered off and washed repeatedly with benzene. The filtrate was subsequently evaporated in aspirator vacuum, care being taken to exclude moisture throughout each phase of the operations. A yellowish crystalline residue was obtained following removal of the solvent; this product can be recrystallized from cyclohexane or (preferably) from petroleum ether. Purification can also be achieved by sublimation at 70°/0.1 mm Hg. Melting point: 120° to 122° (unsharp). Yield: 60 g (78.3% of theory).

Analysis of $P_2S_2(NCH_3)_2Cl_2$ (255.1)

calc:	24.29 P	10.98 N	25.14 S	27.80 Cl
found:	24.14 P	10.77 N	24.75 S	27.50 Cl

Molecular weight (ebullioscopically in benzene and dichloroethane): 256±0.5 (mean for 7 determinations).

D. 2, 4-DITHIO-2, 4-DIANILINO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (IX)

A total of 37 g of aniline was added dropwise with stirring in the course of 20 min to a solution of 25.5 g $P_2(NCH_3)_2S_2Cl_2$ (VIII) in 800 ml of dry benzene. The reaction mixture was allowed to stand under continuous stirring for 24 hours, after which it was heated to boiling for a short time and filtered while still hot through a frit to separate the anilinium chloride formed in the reaction. The solvent was removed in aspirator vacuum, leaving a colorless crystalline residue. When this was dissolved in 600 ml of hot carbon tetrachloride and the solution allowed to cool, star-shaped crystals separated. These were recrystallized in the same way. Yield: 8 g (25% of theory). The substance melted at 146° and was readily soluble in dichloroethane, benzene, and CCl_4. It is not hygroscopic, although it is slowly darkened by the action of light.

Analysis of $P_2(NCH_3)_2S_2(NHC_6H_5)_2$ (368.4)

calc:	15.21 N	16.81 P	17.40 S	45.64 C	4.92 H
found:	14.96 N	17.00 P	17.37 S	45.66 C	4.88 H

Molecular weight (ebullioscopically in benzene): 368 (mean from 3 determinations).

E. 2, 4-DITHIO-2, 4-BIS-DIETHYLAMINO-1, 3-DIMETHYLCYCLOPHOSPHAZANE (X)

A solution of 6 g diethylamine in 100 ml of benzene was dropped in the course of 20 min with stirring into a solution of 13 g of $P_2(NCH_3)_2S_2Cl_2$ in 350 ml of dry benzene at room temperature. The reaction was mildly exothermic and a white precipitate was formed, which was filtered off on a frit after two hours. The filtrate was concentrated to 50 ml in aspirator vacuum and allowed to cool, whereupon crystals separated. These were recrystallized from 700 ml of cyclohexane. The substance melts at 169° and is not hygroscopic. Yield: 12 g (75% of theory).

Analysis of $P_2(NCH_3)_2S_2[N(C_2H_5)_2]_2$ (328.4)

calc:	17.06 N	18.86 P	19.53 S	36.57 C	7.98 H
found:	16.77 N	19.20 P	19.78 S	37.01 C	8.04 H

Molecular weight (ebullioscopically in benzene): 328 (graphic mean from 3 determinations).

F. N-METHYLIMIDODITHIOPHOSPHORIC TETRA-N-METHYLAMIDE (XI)

A total of 13.4 g of VIII was added in one portion to 100 ml of methylamine which had been condensed at -50° under exclusion of moisture. The clear solution which resulted was allowed to stand at room temperature until most of the excess methylamine had evaporated and then residual amine was pumped off in vacuum. The white solid which remained was boiled with several separate portions of benzene, care being taken to apply heat for only a short time in order to avoid loss of amine by chemical fission. The benzene solutions were subsequently concentrated in vacuum, whereupon the product crystallized out on cooling. Purification was accomplished by recrystallization from carbon tetrachloride or methylene chloride. Yield: 12.5 g (86.4% of theory). Melting point: 92°.

Analysis of $P_2S_2(NCH_3)(NHCH_3)_4$ (275.3)

calc:	22.50 P	25.44 N	23.29 S
found:	22.70 P	25.22 N	23.64 S

Molecular weight (ebullioscopically in benzene): 278±6 (mean from 4 determinations).

G. 2, 4-DITHIO-2, 4-BIS-N-METHYLAMINO-1, 3-DIMETHYLCYCLODIPHOSPHAZANE (XII)

Sublimation of XI at 180° to 200°/15 mm Hg led to XII in ca 80 percent yield. The product was recrystallized from dichloroethane or acetonitrile. Melting point: 224°.

Analysis of $P_2S_2(NCH_3)_2(NHCH_3)_2$ (244.3)

calc:	25.37 P	22.94 N	26.25 S
found:	25.36 P	23.04 N	26.50 S

Molecular weight (ebullioscopically in acetone): 243±2 (mean from 4 determinations).

H. $P_4(NCH_3)_6Cl_8$ (XXII)

A mixture of 208.5 g PCl_5 and 75 g of methylammonium chloride (not previously dried) was placed in 750 ml of tetrachloroethane and heated to boiling. The evolution of HCl ceased after about 6 hours. The reaction mixture was cooled to 0° and the crystallized product (V) filtered.

The filtrate was evaporated in aspirator vacuum in a thin-layer evaporator to about half the original amount and then cooled to 0°C. This procedure led to a further quantity of V. Next, tetrachloroethane was evaporated off in the same way and the residue warmed with 200 ml of carbon tetrachloride. In the absence of residual tetrachloroethane, this treatment permits removal of remaining traces of V and oily by-products from the finely crystalline crude product. The latter consists of a white material corresponding to XXII. The yield is variable, amounting to about 3 g (ca 2% of theory). XXII can be recrystallized from benzene. In a sealed tube, the substance melts with decomposition at 395°.

Analysis of $P_4(NCH_3)_6Cl_8$ (581.8)

calc:	21.30 P	14.45 N	48.75 Cl	12.38 C	3.12 H
found:	21.24 P	14.36 N	47.63 Cl	12.9 C	3.29 H

Molecular weight (ebullioscopically in benzene and in dichloroethane): 584±16 (mean from 6 determinations).

I. $P_4(NCH_3)_6O_2Cl_4$ (XXIV)

A total of 5.8 g of XXII was dissolved to the limit of solubility in 400 ml of dry benzene. Dry SO_2 was sparged into the stirred mixture at room temperature for 2 to 3 hours. The resulting clear solution was then evaporated to dryness in an aspirator vacuum. The white solid residue was recrystallized twice from 50 ml of benzene and dried in vacuo. Yield: 3 g (65% of theory). The substance is hygroscopic; melting point: 185° to 220° with decomposition. XXIV is readily soluble in pyridine, methylene chloride, dichloroethane, and benzene.

Analysis of $P_4(NCH_3)_6O_2Cl_4$ (471.98)

calc:	17.80 N	26.25 P	30.05 Cl	15.27 C	3.34 H
found:	17.23 N	26.77 P	29.63 Cl	15.66 C	3.81 H

J. $P_4(NCH_3)_6S_2Cl_4$ (XXIII)

A total of 11.6 g of XXII was suspended in 800 ml of dry benzene. After the addition of 13 g of dry pyridine, dried H_2S was passed into the stirred mixture for 12 hours. The solution turned yellow and pyridinium chloride was precipitated; this was subsequently filtered off on a frit, care being taken to exclude moisture. The filtrate was evaporated to dryness in vacuum, leaving a yellowish solid residue. This crude product was recrystallized first from 200 ml of benzene and then from cyclohexane. Yield: 6 g (60% of theory). The compound melts at 230° with decomposition; it dissolves readily in benzene, tetrachloroethane, and dichloroethane and less easily in cyclohexane. $P_4(NCH_3)_6S_2Cl_4$ is somewhat hygroscopic.

Analysis of $P_4(NCH_3)_6S_2Cl_4$ (504.12)

calc:	24.58 P	16.67 N	12.72 S	28.13 Cl	14.29 C	3.5 H
found:	24.79 P	16.62 N	12.79 S	28.26 Cl	14.64 C	3.5 H

Molecular weight (ebullioscopically from dichloroethane): 497 (mean from 3 determinations).

Infrared Spectra (in KBr)

$P_4(NCH_3)_6Cl_8$: 2960s, 2820vw, 1460m, 1425m, 1285sh, 1202s, 1173m, 1077w, 1018w, 922w, 877s, 843vs, 793w, 715vs, and 654m (cm^{-1})

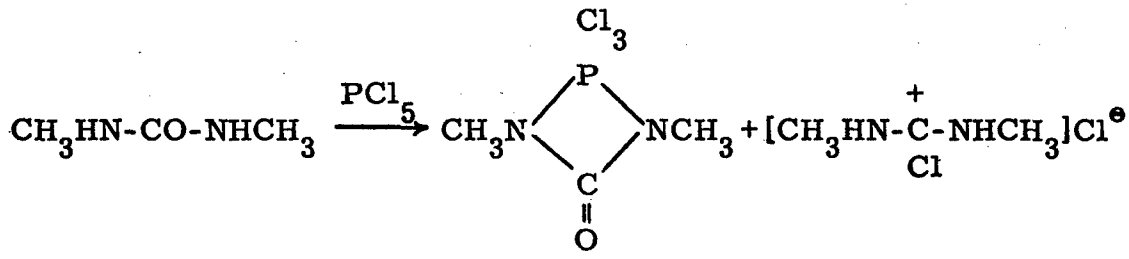
$P_4(NCH_3)_6S_2Cl_4$: 2900s, 1460s, 1425w, 1378m, 1278vw, 1200s, 1156s, 890m, 845vs, br, 787m, 758m, 730s, and 684s (cm^{-1})

$P_4(NCH_3)_6O_2Cl_4$: 2950s, 1465s, 1315m, 1251m, 1210m, 872s, 832s, 793m, 696m, and 680m (cm^{-1})

SECTION III

COMPOUNDS WITH FOUR-MEMBERED RING SYSTEMS CONTAINING P, N AND C

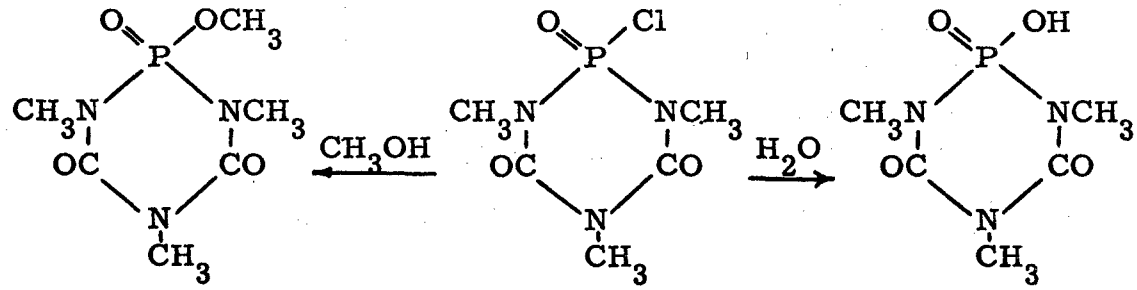
We investigated the reaction between N, N'-dimethyl urea and phosphorus pentachloride. When these reagents were reacted in dry carbon tetrachloride, HCl was evolved and a compound was formed to which formula XXV can be ascribed (Reference 12).



XXV

This compound is obtained when the oily crude product which initially separates (yield: 90%) is distilled in vacuo. The distillation residue is a solid from which a second phosphorus compound with the composition $C_5H_9ClN_3O_3P$ can be isolated by sublimation in vacuo at 80° to 100°. This same product was also obtained when compound XXV was heated in a sublimation apparatus for several days at 160° to 180° at a pressure of 0.01 mm Hg.

Under these conditions, XXV decomposes; the cold trap in the vacuum line afterwards contained a material which was identified as phosphorus oxytrichloride. $C_5H_9ClN_3O_3P$ was collected on the cold finger. The sublimation residue consisted of a yellow-brown frothy solid. It proved possible to determine the constitution of $C_5H_9ClN_3O_3P$, for which formula XXVI was established. The substance is colorless and crystalline; it dissolves in benzene and in other organic solvents but is insoluble in petroleum ether. The action of water causes evolution of hydrogen chloride. When the latter is removed in vacuum, a colorless oil is produced which solidifies to fully transparent crystals. Formula XXVIII was ascribed to this material. Corresponding treatment with methyl alcohol leads to the colorless crystalline compound XXVII.



XXVII XXVI XXVIII

The polymer which is formed together with XXVI in the thermal decomposition of XXV is insoluble in all common organic solvents. However, this polymer reacts with water and alcohols to furnish new polymeric products which are soluble.

The polymer P_1 produced in the thermal decomposition of XXV has the following composition: 20.28% C; 2.87% H; 15.68% N; 16.7% P; 26.5% Cl; 17.5% O.

Decomposition occurs when P_1 is heated first to 150° and then gradually to 400°. A solid product is thereby formed which is stable between 400° and 520°, first decomposing above 600°.

When heated in an open flame, the substance becomes black but does not burn. At red heat, OPN is produced which does not undergo further combustion.

When subjected to the action of boiling methanol for several hours, polymer P_1 gives rise to a viscous, sticky paste which is soluble in alcohols and whose solution can be readily applied to a large variety of surfaces, e.g., wood or cloth. The paste itself can also be directly applied. The paste (designated as P_2) has the following composition: 19.7% C; 5.9% H; 17.2% N; 12.3% P; 13.3% Cl; leaving 32.5% which presumably consists of oxygen.

P_2 decomposes at temperatures between 230° and 400°. The first product of decomposition is stable up to 540°, above which it too decomposes.

P_1 is completely dissolved by the action of boiling water. When the excess of water is removed in vacuum, a transparent film is obtained which is stable up to 250°. This film (designated as P_3) has the composition 17.2% C; 5.05% H; 21.9% N; 13.4% P; 11.7% Cl; remainder (presumably O): 30.8%.

It is not yet possible to establish structural formulae for these polymeric products of pyrolysis of substance XXV. Nonetheless, experimental results indicate that pyrolysis of the four-membered ring system XXV provides a pathway to an interesting group of polymers which have the advantage of being convertible into alcohol-soluble and even water-soluble materials.

A. PREPARATION OF COMPOUND XXV

A solution of 88 g (1 mole) NN'-Dimethylurea in 1750 ml CCl_4 was placed in a 2-l round-bottomed, three-necked flask, fitted with a reflux-condenser, a $CaCl_2$-drying-tube and a mechanical stirrer. To this well-stirred and cooled mixture was added 220 g (about 1.1 mole) phosphorus pentachloride. The rate of addition was so adjusted that the temperature of the solution did not rise over 70°. After thirty minutes of gently refluxing, the mixture was cooled in order to crystallize the greenish oil on the surface $\left[(CH_3\text{-}NH)_2CCl_2\right]$, the liquid was separated and the solvent removed.

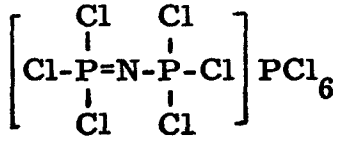
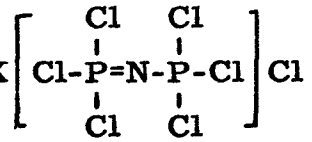
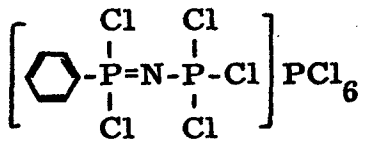
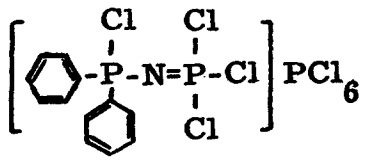
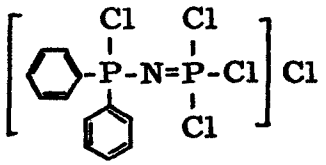
The high vacuum distillation was done in two or three portions for better yield (polymers). The product was a colorless liquid and very hygroscopic.

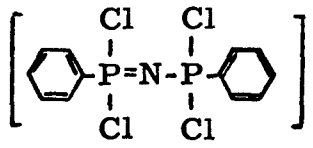
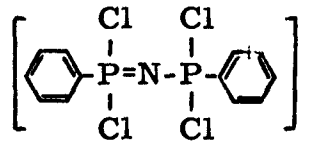
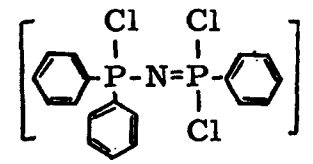
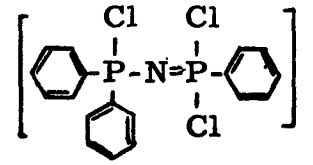
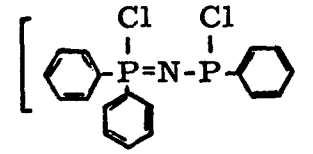
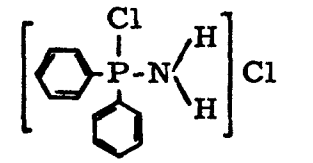
bp 55°/1 mm Hg; yield: 76 g = 34%; chem shift P^{31} NMR +60 ppm (related to 85% H_3PO_4).

SECTION IV

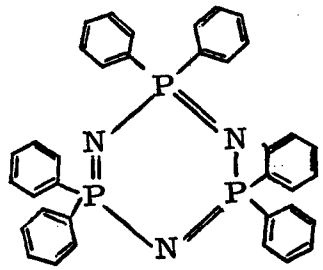
COMPOUNDS WITH P-N-P-CHAINS

According to the research proposal the preparation of the following phosphorus nitride salts was realized. The structures were established.

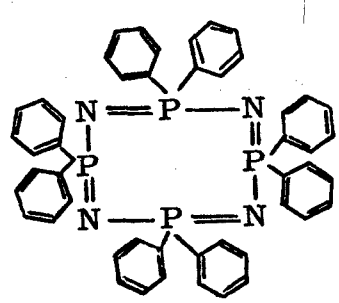
	Substance	mp/bp	nmr P^{31} δ
XXIX		solid with water fast hydrolysis	δ = -21.4, +300
XXX		solid with water fast hydrolysis	δ = -21,4
XXXI		solid mp 124°	δ = -41, 8, -24, 7, +300
XXXII		solid mp 163°-166°	δ = -42, 3, -14, 3, +300
XXXIII		solid	δ = -42, 3, -14, 3

	Substance	mp/bp	nmr P^{31} δ
XXXIV	 PCl_6	solid mp 132°	δ = -41, 7, +300
XXXV	 Cl	solid mp 210°	δ = -41, 7
XXXVI	 Cl	solid but not crystalline	δ = -46, 4, -38, 1
XXXVII	 PCl_6	solid	δ = -46, 4, -38, 1, +300
XXXVIII	 Cl	solid pyrolysis yields 3,A and 3, B hydrolysis yields IL	δ = -43, 3
XXXIX	 Cl	solid when heated to 270°, 3, A and 3, B are formed	δ = -51, 0

Substance	mp/bp	nmr P^{31} δ

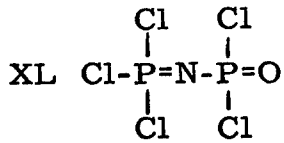


3, A



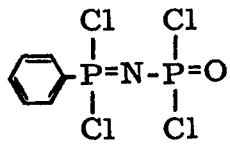
3, B

The following oxygen containing compounds were obtained.

XL 

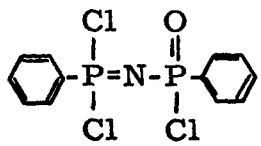
mp +35, 7
bp_1 102°
n_D^{25} 1.5305

δ = +0, 1, +14, 2

XLI 

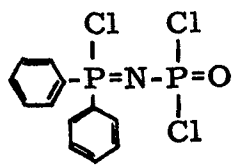
bp 0.001 148°-150°
n_D^{22} 1.5838
pyrolysis yields longer chains

δ = -20, 0, +8, 4

XLII 

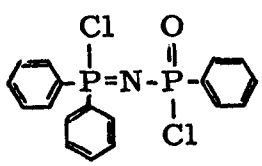
liquid
$bp_{0.01}$ 210°

δ = -14, 9, -11, 9

XLIII 

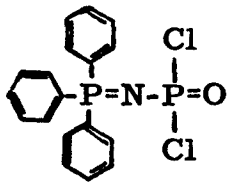
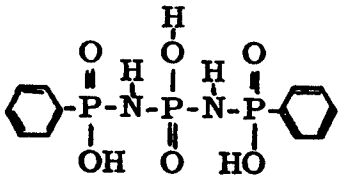
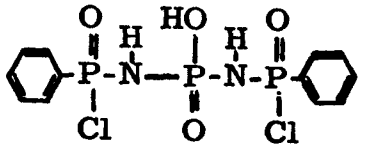
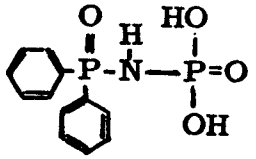
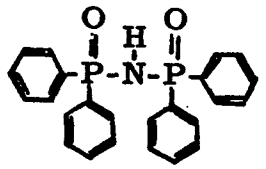
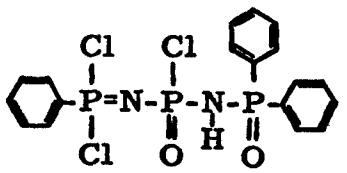
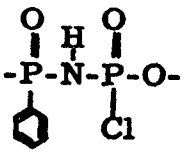
liquid
$bp_{0.01}$ 205°-215°
pyrolysis yields B
hydrolysis yields XX

δ = -29, 0, +8, 7

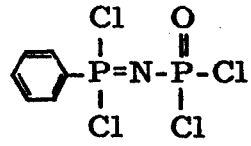
XLIV 

solid but not crystalline

δ = -31, 4, -18, 4

Substance		mp/bp	nmr P^{31} δ
XLV			δ = -12, 9, +9, 6
XLVI		solid	
XLVII		solid	
XLVIII		solid mp 201°	
XLIX		solid mp 171°	
L		solid	
LI		solid	

The polymeric compound LI was built from compound XLII.



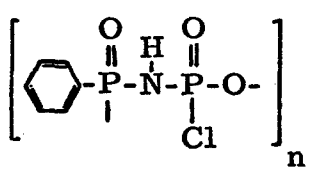
XLII

This substance was heated at 90° to 100° in a distillation apparatus which was directly connected with a high vacuum pump, whereby distilled water was simultaneously introduced very slowly directly into the hot oily liquid. Under these conditions reaction occurred with the evolution of hydrogen chloride. The HCl and water vapor were condensed in a trap cooled with liquid nitrogen. When this procedure was maintained for 20 to 30 minutes while the bath temperature was raised slowly from 150° to 200°, the walls of the flask gradually became covered with small bubbles and the originally dark brown oil swelled to a greyish froth.

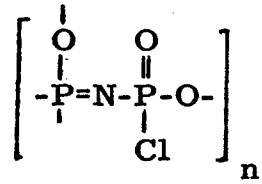
The polymeric product thus formed was isolated by allowing the flask to cool, bringing the system to atmospheric pressure, and pulverizing the brittle, spongy mass under petroleum ether. The polymer is hygroscopic; it swells in contact with most organic solvents such as acetone, benzene, methylene chloride, chloroform, carbon tetrachloride, etc. The polymer does not dissolve in boiling water although it does interact under these conditions, as is evidenced by a decrease in the chlorine content. A consistent analysis of the polymer was very difficult to obtain, because the composition varied considerably according to the conditions of the synthesis. If the temperature is too low, viscous, greyish-brown products result in place of the hard, froth-like substance capable of swelling. However, if the procedure described above is followed exactly, the results of analysis agree with the formula $C_6H_6ClNP_2O_3$ and it can be concluded that the polymer must be of type LI.

Thermogravimetric studies of substance LI revealed that initial decomposition occurs at 340° to 400° followed by a second stage of decomposition at 540° to 690°. In the temperature range corresponding to the first decomposition, the loss in weight amounted to 33.6 percent. This can be interpreted by loss of the phenyl group. The resulting polymer, which is stable up to 540°, is then apparently of type LII.

Thus, polymer LII originates from a substance capable of swelling and which in this form can be applied to the surfaces of wood and cloth, etc. This procedure is therefore a means of preparing a useful fireproofing material.



LI



LII

In this way we were able to obtain a new type of polymer which appears particularly promising because the compound still contains a chlorine atom; this halogen can very probably be substituted with the result that the solubility and other desirable qualities of the products should be enhanced.

The formation of compound XL is interesting and shows characteristic aspects to the whole class of compounds.

The reaction of amides of orthophosphoric acid and of thiophosphoric acid with PCl_5 has been investigated by Becke-Goehring et al. (Reference 13). It was shown that orthophosphoric acid monoamide LIII reacts readily with PCl_5 according to Equation (1).

$$3\ PCl_5 + H_2N\text{-}\overset{\overset{O}{\|}}{P}(OH)_2 \rightarrow 2\ OPCl_3 + 4\ HCl + Cl_3P{=}N\text{-}\overset{\overset{O}{\|}}{P}Cl_2 \qquad (1)$$

LIII XL

This reaction led to the formation of compound XL which is also obtained by the action of PCl_3 upon N_2O_4 (Reference 14) as well as in the reaction of hydroxylammonium salts with phosphorus pentachloride (Reference 15).

The formation of XL according to Equation (1) represents a type of reaction which was first observed by Kirsanov in studies dealing with sulfuric acid amides (Reference 16). According to this scheme, the reaction of an acid amide with PCl_5 involves primary dissociation of PCl_5 into $\left[PCl_4\right]^+$ and $\left[PCl_6\right]^-$ (Reference 17). Nucleophilic attack by the nitrogen of the acid amide upon the PCl_4 cation then leads to the intermediate product LIV, which splits off HCl to form a trichlorophosphazo compound LV, (Reference 18).

$$R\text{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}} \rightarrow \overset{+}{PCl_4} \xrightarrow[-H^+]{-HCl} R\text{-}N{=}PCl_3 \qquad (2)$$

LIV LV

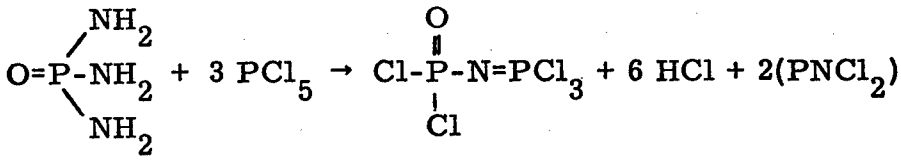
PCl_5 reacts with LIII not only in the sense of a Kirsanov reaction; it reacts simultaneously in the usual manner with the hydroxyl groups present, causing them to be replaced by Cl.

Compound XL is also obtained when PCl_5 is reacted with orthophosphoric acid diamide LVI in place of LIII, but the yield is only about 50 percent according to Equation (3).

$$HO\text{-}\overset{\overset{O}{\|}}{P}(NH_2)_2 + 3\ PCl_5 \rightarrow Cl\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{P}}\text{-}N{=}PCl_3 + 5\ HCl + POCl_3 + (PNCl_2) \qquad (3)$$

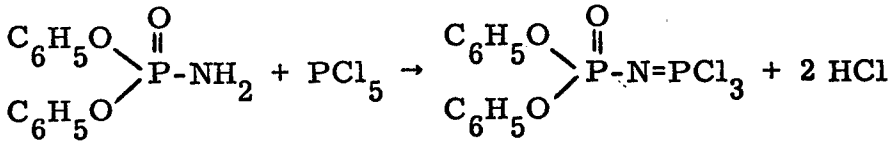
LVI XL

This reaction with PCl_5 proceeds in the sense of a Kirsanov reaction and in addition replacement of a hydroxyl and an amido group by Cl occurs. Orthophosphoric acid triamide behaves analogously.



(4)

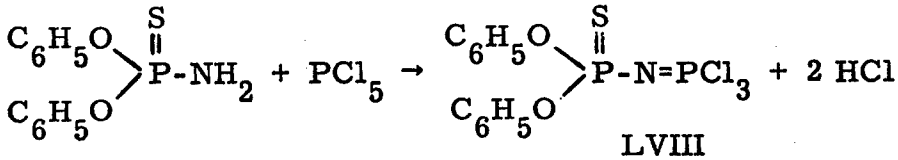
A. V. Kirsanov was able to show that substituted phosphoric acid amides can also react with PCl_5 according to Equation (2) (Reference 19); he obtained compound LVII when orthophosphoric acid amide diphenyl ester was reacted with PCl_5.



(5)

LVII

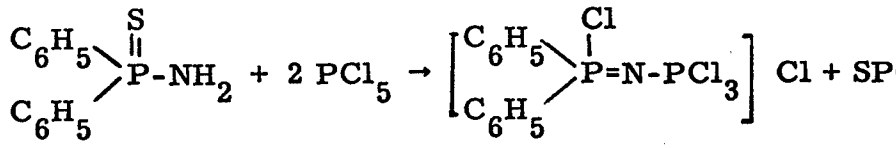
Kirsanov also prepared the corresponding thiophosphoryl compound(LVIII) in a similar manner (Reference 19).



(6)

LVIII

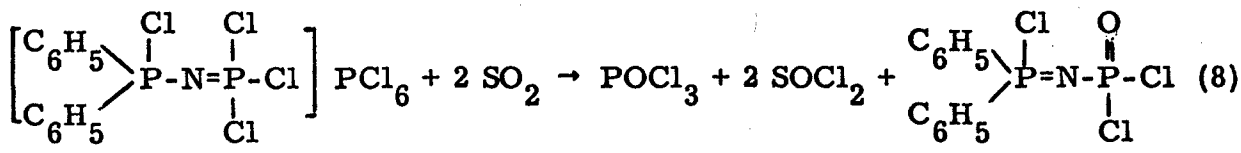
An analogous reaction occurs when diphenylthiophosphinic amide is introduced in place of thiophosphoric ester amide, but in addition, further PCl_5 causes substitution of the sulfur and formation of the phosphorus nitride salt XXXIII.



(7)

XXXIII

With more PCl_5 compound XXXII is formed. The reaction of XXXII with SO_2 proceeds according to Equation (8).

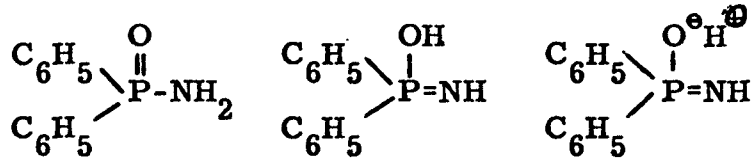


(8)

XXXIV XLIII

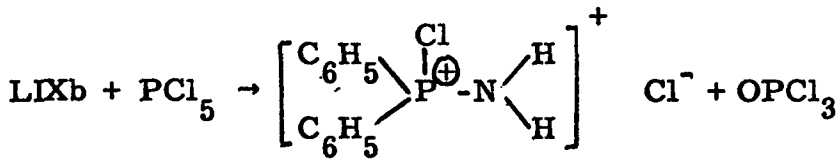
Compound XLIII was formed which is a liquid (bp 210°/0, 01 mm Hg). Careful hydrolysis of XIV leads to compound LXIII, a colorless crystalline substance (mp 201°-203°). It is possible that the high melting point of compound LXLIII is due to hydrogen bonding.

It was found that diphenylphosphinic amide LIX reacts with PCl_5 in a manner entirely different from that of the phosphoric and thiophosphoric derivatives already studied. Diphenylphosphinic amide apparently exists in the tautomeric forms LIXa and LIXb.



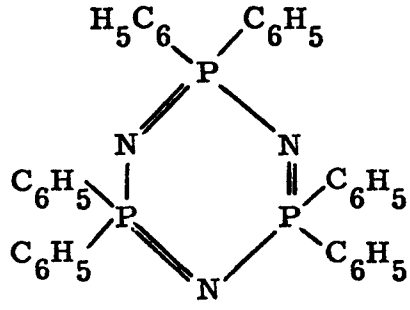
LIXa LIXb LIXc

LIXb and LIXc are chlorinated very readily by PCl_5, furnishing chlorodiphenylphosphine imine hydrochloride (III) (Equation 6).

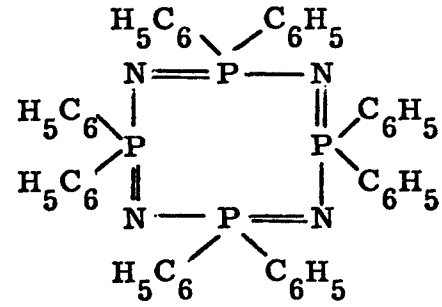


LX

LX is a colorless, crystalline solid which evolves HCl even at temperatures below 100°; when heated slowly to 270° to 280° under slightly reduced pressure, the substance decomposes to give hexaphenyl tris(phosphorus nitride) (LXI) in 51 percent yield and octaphenyl tetrakis (phosphorus nitride) (LXII) in ca 30 percent yield.



LXI



LXII

LX hydrolyzes with evolution of NH_3 when treated with warm 2 M KOH solution; acidification with HCl causes precipitation of diphenylphosphinic acid (mp 190°).

The P^{31} NMR spectrum of a solution of LX in methanol showed a chemical shift of $\delta = -51,0$ ppm, referred to 85 percent H_3PO_4. This indicates that the extent of electronic shielding of the phosphorus atom in this compound is small and that the positive ionic charge is to be ascribed to the phosphorus and not to the nitrogen atom. The infrared spectrum of III closely resembles that of triphenylphosphine imine hydrochloride with the exception that an additional band is present at 1400 cm^{-1} in the former case.

A. $\left[(C_6H_5)_2P(Cl)\text{-}NH_2\right]Cl$ (LX)

Thirty-three g (0.153 mole) of $(C_6H_5)_2P(O)NH_2$ were dissolved in 400 ml of chloroform in a two-necked flask fitted with a stirrer and a drying tube; 32 g (0.153 mole) of PCl_5 were added with stirring, whereupon remaining traces of amide dissolved immediately. Within half a minute following the addition of the PCl_5, the solution became noticeably warm; cooling was then applied with an ice water bath and stirring continued for two minutes. At the end of this time stirring was stopped and the cooling bath removed, after which 400 ml of CCl_4 were dropped into the reaction mixture in the course of two hours. It is expedient to let the CCl_4 run in along the side of the flask, as this enhances crystallization of the product. LX then separates in the form of colorless needles; these were subsequently filtered off on a frit and washed with CCl_4 and petroleum ether. Attempts to dry the compound in vacuo lead to a loss of from 2 to 4 percent HCl. Yield: 80 percent of theory.

B. PREPARATION OF $\left[(C_6H_5)_2P(Cl)=N\text{-}PCl_3\right]PCl_6$ (XXXII)

A solution of 14, 4 g (0, 062 mole) of $(C_6H_5)_2P(S)NH_2$ in 200 ml of dry chloroform was placed in a flask provided with a stirrer and a reflux condenser fitted with a drying tube; 40 g (0, 19 mole) of PCl_5 were added with stirring and the mixture was heated slowly to 50° to 60°. After the vigorous evolution of HCl had subsided (1/2-1 hour), the mixture was boiled under reflux for a further two hours. Most of the solvent was then distilled off, and the cooled oily residue treated with dry benzene. This first benzene extract was poured off and the residue shaken again twice with fresh portions of benzene. After the third wash, the reaction product separated into pale greenish-yellow crystals. The yield of the already very pure crude product is 90 to 100 percent; the substance can be recrystallized from small amounts of chloroform (100 ml).

Analysis of X: $C_{12}H_{10}Cl_{10}NP_3$ (615.72)

calc:	23.41 C	1.64 H	57.58 Cl	2.28 N	15.09 P
found:	24.65 C	2.18 H	57.5 Cl	2.28 N	14.6 P

This substance is very hygroscopic and can be handled only in an absolutely dry atmosphere. It is difficultly soluble in nonpolar solvents such as benzene, carbon tetrachloride, and petroleum ether and soluble in tetrachloroethane, chloroform, and phosphorus oxychloride. X melts at 163° to 166°. The molecular weight measured in nitrobenzene is 285 (calc 615.72), since the salt dissociates in this solvent. The assumption that dissociation into two univalent ions occurs was confirmed by measurement of the equivalent conductivity in nitrobenzene ($\varkappa = 0.5 \cdot 10^{-7} \Omega^{-1} cm^{-1}$). $\Lambda_c(20°) = 21\,\Omega^{-1}$, cm^{-1}, $mole^{-1}$ ($c = 0.8 \cdot 10^{-2}$ mole/e).

C. PREPARATION OF $\left[(C_6H_5)_2P(Cl)=N\text{-}PCl_3\right]Cl$ (XXXIII)

The chloride XXXIII is obtained in the same way as XXXII when a mole ratio of $(C_6H_5)_2P(S)NH_2$:PCl_5 of 1:2 is employed. After washing with benzene, XXXIII remains as an oil. The product crystallizes when the remaining traces of solvent are pumped off in vacuo.

D. PREPARATION OF $(C_6H_5)_2P(Cl)=N-P(O)Cl_2$ (XLIII)

Dry SO_2 was passed into $\left[(C_6H_5)_2P(Cl)=N-PCl_3\right]PCl_6$ in a flask fitted with a gas inlet and a gas outlet tube. The crystalline mass liquefied; after the mixture had become homogeneous, SO_2 was passed in for a further hour. SO_2, $SOCl_2$ and $OPCl_3$ were then removed in an aspirator vacuum. The residue was distilled rapidly in vacuo at 205° to 215°/0.01 mm Hg, care being taken to select a short distillation path. Yield: 90 percent of theory.

Analysis of XLIII: $C_{12}H_{10}Cl_3NOP_2$ (352.54)

calc:	40.88 C	2.86 H	30.17 Cl	3.97 N	4.54 O	17.57 P
found:	40.81 C	2.91 H	30.22 Cl	3.98 N	-- O	17.92 P

The cryoscopically determined molecular weight in benzene was 368 (calc 352.5). The compound is a pale yellow, oily liquid. It is considerably less sensitive towards hydrolysis than the salt and is soluble in benzene, dioxan, and carbon tetrachloride.

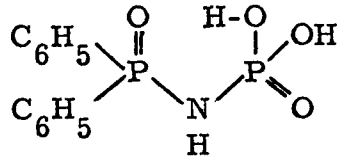
E. PREPARATION OF $(C_6H_5)_2P(O)-NH-P(O)(OH)_2$

$(C_6H_5)_2P(Cl)=N-P(O)Cl_2$ was diluted with twice its quantity of dioxan and this mixture treated in turn with twice its amount of water. The mixture was shaken and kept at room temperature. The acid separated slowly as a white solid. This material was then washed thoroughly with water and recrystallized from ethanol. When well dried, the white needles melted at 201° to 203°.

Analysis of XV: $C_{12}H_{13}NO_4P_2$ (297.19)

calc:	48.49 C	4.41 H	4.71 N	21.53 O	20.86 P
found:	48.44 C	4.58 H	4.80 N		20.77 P

Titration gave an equivalent weight of 296 with methyl orange as indicator and 147 with phenolphthalein. This is in agreement with the calculated molecular weight of 297.2 and the formula LXIII.



LXIII

F. $\left[(C_6H_5)_2PN\right]_3$ (LXI) AND $\left[(C_6H_5)_2PN\right]_4$ (LXII)

A sample, 8.5 g, of phosphine imine hydrochloride (LX) was heated slowly to 275°. This temperature was maintained for two hours and the HCl formed pumped off under partial vacuum. The melt solidified to a brittle, greyish mass which was subsequently extracted with 200 ml of benzene in a Soxhlet apparatus. Progressive removal of the benzene in vacuum lead to crystallization first of LXI (3.1 g, 51% of theory) and then of LXII (1.8 g, 30% of theory).

Analysis of LXI: $C_{36}H_{30}N_3P_3$ (597.59)

calc:	72.36 C	5.06 H	7.03 N	15.55 P
found:	72.38 C	5.14 H	7.05 N	15.76 P

Molecular weight (ebullioscopically in benzene): 571; mp 223° to 227°, P^{31} NMR spectrum (benzene): maximum at -14.2 ppm (referred to 85% H_3PO_4), (Reference 5).

Analysis of LXII: $C_{48}H_{40}N_4P_4$ (796.78)

calc:	72.36 C	5.06 H	7.03 N	15.55 P
found:	72.66 C	4.73 H	6.91 N	15.37 P

Molecular weight (ebullioscopically in benzene): 843; mp 315° to 318°

G. INFRARED SPECTRA

For $\left[(C_6H_5)_2P(Cl)NH_2\right]Cl$ (LX): 3170s, 3060s, 1590w, 1560w, 1480w, 1440s, 1400s, 1130s, 1028s, 947s, 750s, 730s, 690s (cm^{-1})

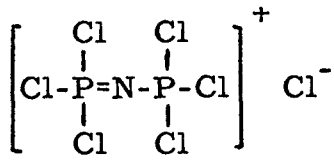
For $\left[(C_6H_5)_3PNH_2\right]Cl$: 3090s, 3000s, 1595w, 1560w, 1495w, 1450s, 1130s, 1000s, 970s, 760s, 725s, 695s (cm^{-1})

SECTION V

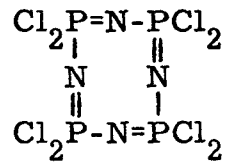
PHOSPHONITRILIC CHLORIDES $(NPCl_2)_n$ AND DERIVATIVES

According to the research proposal we had to study new and efficient methods for preparing phosphorus nitride chlorides containing P-N ring systems. We used the compound NP_2Cl_7 as starting material.

NP_2Cl_7 is prepared by the reactions of $[NH_3OH]Cl$ with PCl_5 or via $PCl_5 + NH_4Cl$ (Reference 20). The structure is shown by formula XXX.



XXX

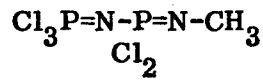


LXVI

It was suspended in s-tetrachloroethane and mixed with an excess of $[CH_3NH_3]Cl$. At a reaction temperature of 110° to 120° the following reaction was observed.

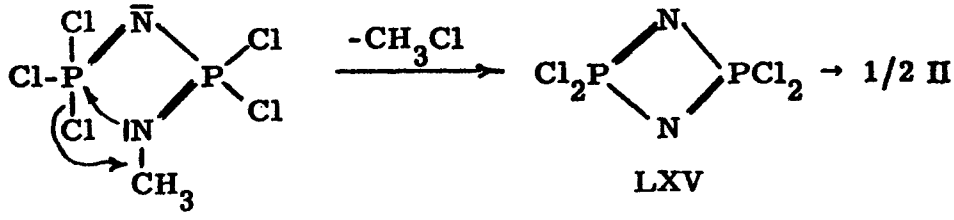
$$2[Cl_3P{=}N{-}PCl_3]Cl + 2[CH_3NH_3]Cl \longrightarrow II + 2\ CH_3Cl + 6\ HCl$$

The first reaction product was compound LXIV.



LXIV

But LXIV is not stable. When heated, CH_3Cl is released and LXV is formed. However, LXV dimerizes immediately.

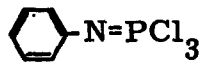


LXV

Thus a good method was obtained for the preparation of tetrameric phosphorus nitride chloride LXVI. The yield of $[NPCl_2]_n$ was nearly quantitative. A large amount of $[NPCl_2]_4$ was obtained; $[NPCl_2]_n$ formed, however, contained approximately 15 percent of $[NPCl_2]_3$. The amount of $[NPCl_2]_5$, $[NPCl_2]_6$, $[NPCl_2]_7$ and $[NPCl_2]_8$ was very small.

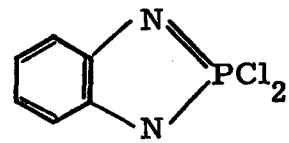
With $[C_2H_5NH_3]Cl$ a similar reaction was observed.

Aniline reacted smoothly with NP_2Cl_7. However, the yield of LXVI was small. Compound LXVII was formed besides LXVI.[2]



(m. p. 179°)

LXVII



H (mp 216° decomp)

LXVIII

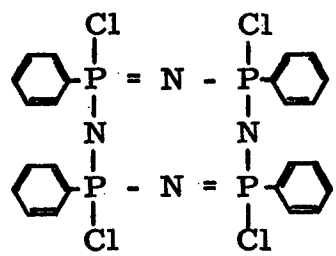
o-Phenylenediamine and NP_2Cl_7 formed compound LXVIII and no polymeric phosphonitrilic chlorides. By the reaction of cyclohexylamine and NP_2Cl_7 a crystalline compound $[C_6H_{12}N_2P_2Cl_6]_2$ was prepared. We tried to elucidate the structure of this compound, but we did not succeed.

Further, we prepared compound XXXV. This substance was obtained by the reaction

XXXV

The reaction of this compound XXV with NP_2Cl_7 was studied. The reaction was observed:

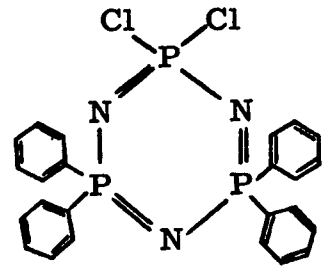
$$2\ VII + 2[CH_3NH_3]Cl \rightarrow LXIX + 2\ CH_3Cl + 6\ HCl$$



LXIX

Only one of the possible 4 isomers of LXIX was formed, e.g., a compound with mp 248°.

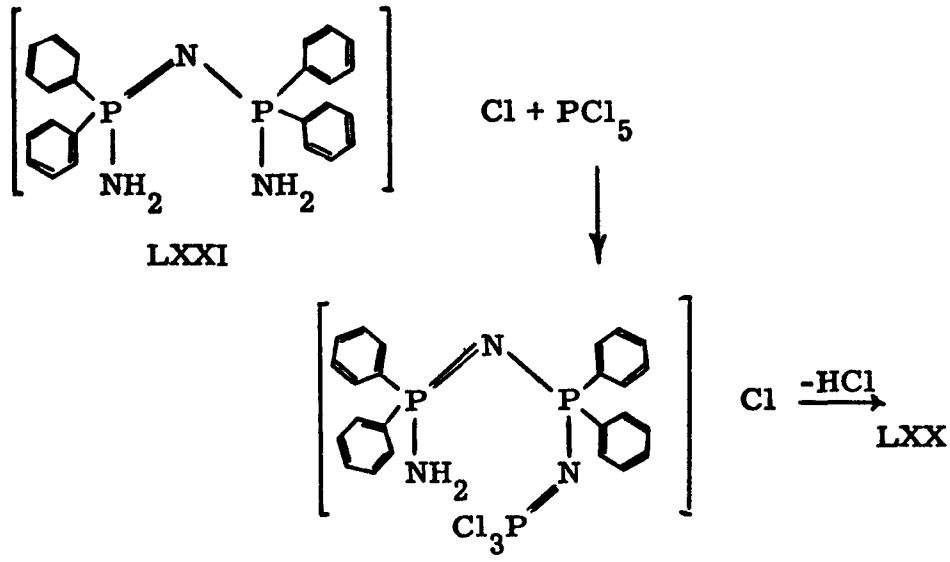
To summarize, a good method for the preparation of tetrameric phosphonitrilic compounds was found. Other polymers were not obtained in good yield. Further, a method for the preparation of compound LXX was developed.



(mp 144°)

LXX

This compound LXX was obtained by reaction of LXXI (Reference 21) with PCl_5. We were able to obtain LXX in better yield when tetrachloroethane was used as a solvent. We were able to show that the first reaction product was LXXII. At 120° to 130° (5 hours) ring closure was obtained and LXX was formed.



LXXI

LXXII

The preparation of other derivatives of phosphorus nitrilic chlorides, e.g., LXI and LXII was already mentioned.

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13. ABSTRACT

A variety of chemical systems containing phosphorus nitrogen bands have been investigated as potential intermediates for the synthesis of polymeric materials having extreme thermal and chemical stability. These investigations include the preparation and reactions of a variety of compounds with four-membered ring systems containing alternate P and N atoms, compounds with four-membered ring systems containing P, N and C atoms, and compounds containing P-N-P chains; and the preparation of phosphonitrilic chlorides and their derivatives.

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