

POLYMERIC PHOSPHORUS-NITROGEN COMPOUNDS

Dr. Margot Becke-Goehring
University of Heidelberg

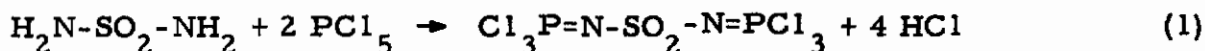
SYNTHESIS OF CHLORIDES, ESPECIALLY OF
POLYMERIC PHOSPHORUS NITRILIC CHLORIDES

We were able to elucidate completely the mechanism of formation of polymeric phosphorus nitrilic chlorides.

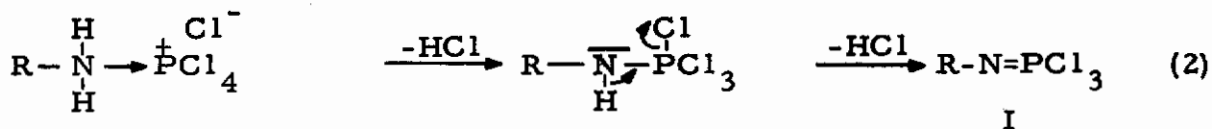
Phosphorus pentachloride has a well known structure.¹ In the vapor state the molecule is in the form of a trigonal bipyramid. Pure liquid PCl_5 exhibits a Raman spectrum which has been interpreted on the basis of a trigonal bipyramid structure. In the crystal, however, phosphorus pentachloride has an ionic structure corresponding to $[\text{PCl}_4]^+ [\text{PCl}_6]^-$. When phosphorus pentachloride is dissolved in polar solvents, it acts as an electrolyte and is present in ionic form. Transference number experiments indicate that $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$ are formed when phosphorus pentachloride is dissolved in nitrobenzene.

We suggested that with ammonia and derivatives of ammonia respectively phosphorus pentachloride may react as a salt $[\text{PCl}_4]^+ [\text{PCl}_6]^-$. An ionic mechanism should be especially observed when a polar solvent is employed.

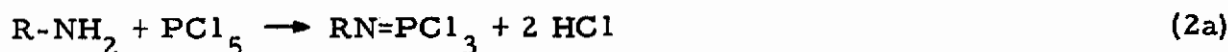
Sulfuryl amide reacts with phosphorus pentachloride:



Urea reacts in an analogous manner. From the monoamide of sulfuric acid $\text{Cl}_3\text{P=N-SO}_2\text{Cl}$ is formed. The H-atoms located on the nitrogen atom are substituted by PCl_3 . The reaction of phosphorus pentachloride which was first studied by Kirsanov presumably proceeds such that the $[\text{PCl}_4]^+$ reacts as a Lewis acid with the amide:²



With amines in an analogous manner reaction is observed:³



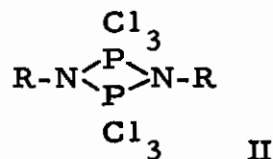
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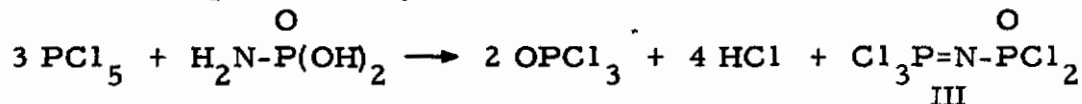
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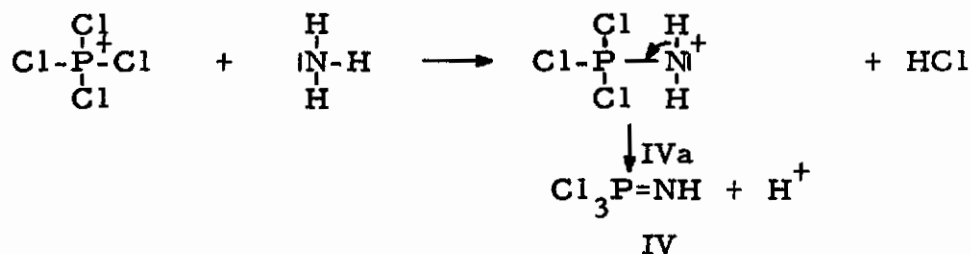
Strong bases (amines) and phosphorus pentachloride, however, are producing dimeric substances:⁴



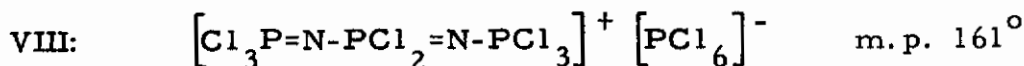
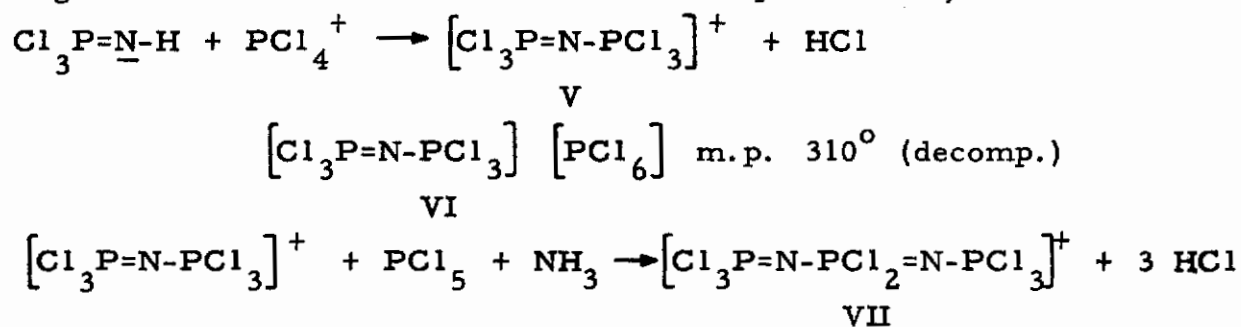
Accordingly, monoamido phosphoric acid reacts in tetrachloroethane solution rapidly and almost quantitatively in accordance with the equation:⁵



We were able to show that ammonia or ammonium chloride and phosphorus pentachloride may react in an analogous manner:

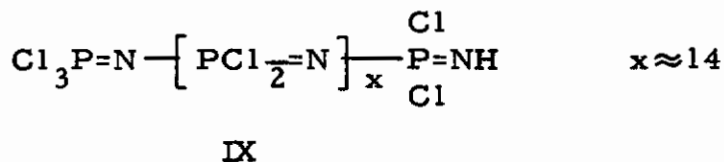


The intermediate Product IV reacts with further PCl_4^+ to form the cation V, which combines with the anion $[\text{PCl}_6]^-$ to give the stable salt VI. This reaction occurs already at 40-60° C in polar solvents in almost quantitative yield. The salt VI easily reacts with further NH_4Cl , giving a cation VII under P-N-chain lengthening. VII was isolated in the form of a salt represented by VIII.⁶

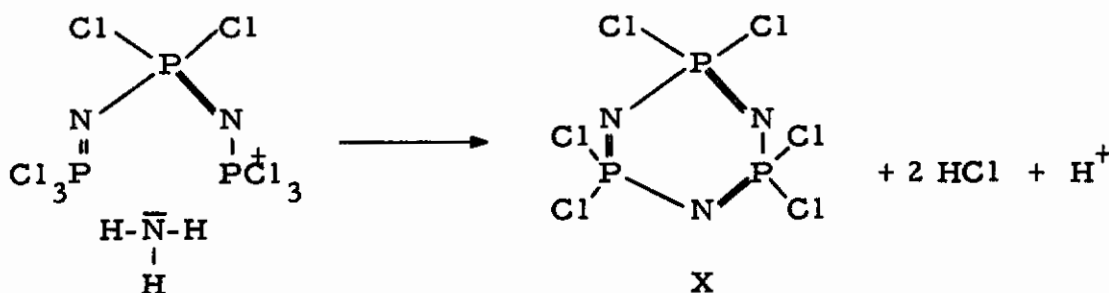


This reaction could be carried out with about 80% yield. The reaction of further ammonium chloride with VIII can now take two courses. In the one

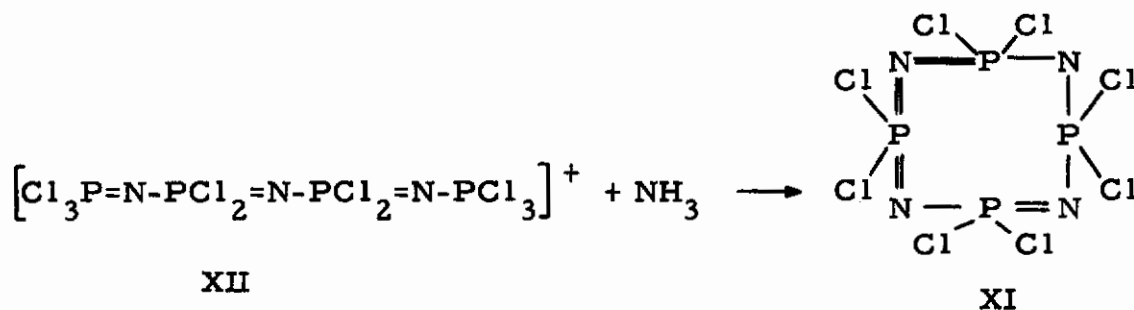
instance the chain-lengthening reaction can occur in accordance with the scheme described above, leading to the formation of oily phosphorus nitrilic chlorides. This is particularly the case, when temperatures from 160-200° C are employed and when HCl is not removed. The chains are terminally saturated with the ions of hydrogen chloride and have the following structure IX:⁷



In the other instance, reaction between the cation VII and NH₄Cl can lead to trimeric phosphorus nitrilic chloride X.

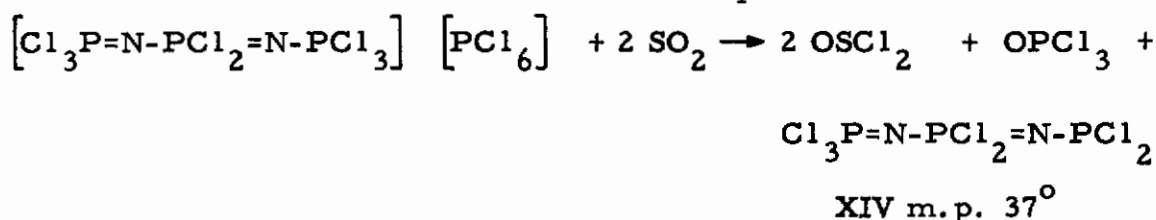
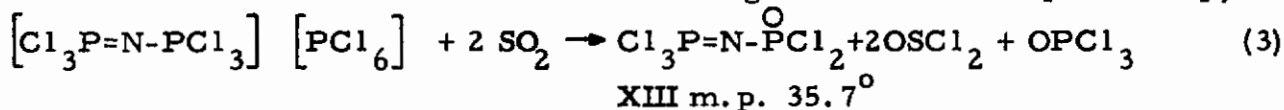


A further chain-lengthening reaction produces finally tetrameric phosphorus nitrilic chloride XI, in that a cation XII if formed which reacts further with NH₄Cl under ring closure. The yield of the tetramer is of course not high, since XII is only a by-product.



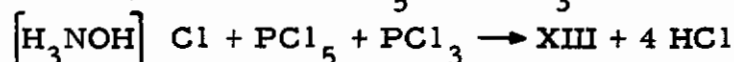
The constitution of all mentioned products was established by nuclear magnetic resonance spectra. Furthermore, VI was reacted with SO₂ whereby XIII was formed as expected product. XIV was obtained when the salt VIII was treated with SO₂. The constitution of products arising from the reaction with SO₂ were

likewise determined with the aid of nuclear magnetic resonance spectroscopy.



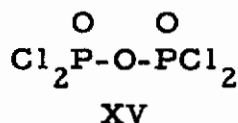
XIII is found to be formed in numerous reactions in phosphorus chemistry.

First, we were able to obtain this compound in the reaction between PCl_5 and the amides of orthophosphoric acid.⁵ The second method of preparing this acid chloride XIII proceeds from hydroxyl ammonium chloride, which is reacted with equimolar quantities of PCl_5 and PCl_3 at elevated temperatures:

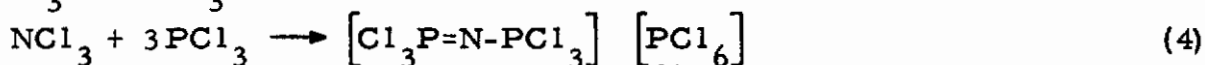


A third method is given in equation (3).

A further method consists of the reaction of PCl_3 with N_2O_4 . PCl_3 reacts with N_2O_4 such that the tetrachloride of diphosphoric acid (XV) is formed. Furthermore, according to Klement a compound $\text{P}_4\text{O}_4\text{Cl}_{10}$ was thought to be produced.⁸ This compound has been widely investigated, since it is interesting in that it cannot be explicitly formulated. Hence, several theories concerning its constitution were proposed; these dealt especially with the examination of the molecular spectra. We found, however, that the compound " $\text{P}_4\text{O}_4\text{Cl}_{10}$ " contains nitrogen and that the product has the formula P_2NOC_5 and the constitution XIII. $\text{P}_4\text{O}_4\text{Cl}_{10}$ does not exist.⁹ XIV has not been found to have been formed in any other reactions.

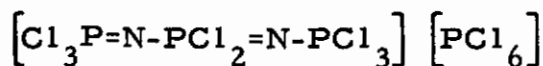


The intermediate products of the synthesis of phosphorus nitrilic chlorides, e. g. VI and VIII, may be obtained by other reactions too. VI may be obtained when NCl_3 and PCl_3 is allowed to react in an inert solvent:

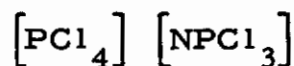


VIII is formed when S_4N_4 and PCl_3 is reacted.¹⁰ NMR measurements established

formula VIII. The older formulations are not in agreement with these measurements:¹¹



VIII right



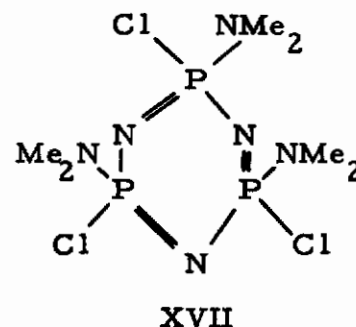
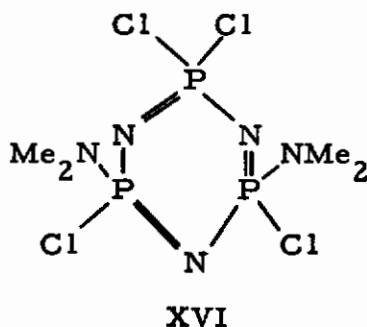
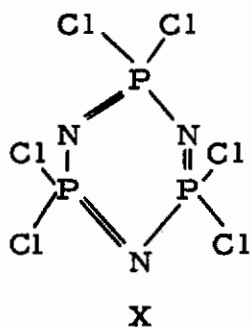
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SYNTHESIS OF SOME POLYMERIC DERIVATIVES OF THESE CHLORIDES

All phosphorus nitrogen chlorides are useful as starting materials for the research on phosphorus nitrogen polymers.

At first, the reactions of phosphorus nitrilic chlorides X and XI were studied. We studied the effect of nucleophilic reagents on these quasiaromatic ring systems.

It was found: 2, 3, 4, or 6 Cl-atoms of $[\text{NPCl}_2]_3$ (X) are easily substituted by nucleophilic ligands. Strongly nucleophilic reagents attack in 1 and 3 position. Further substitution follows in 5 position of the six membered ring system.¹²

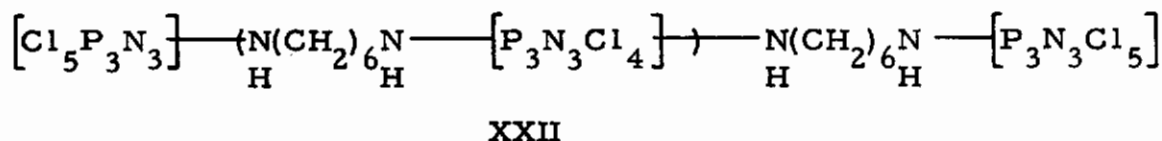
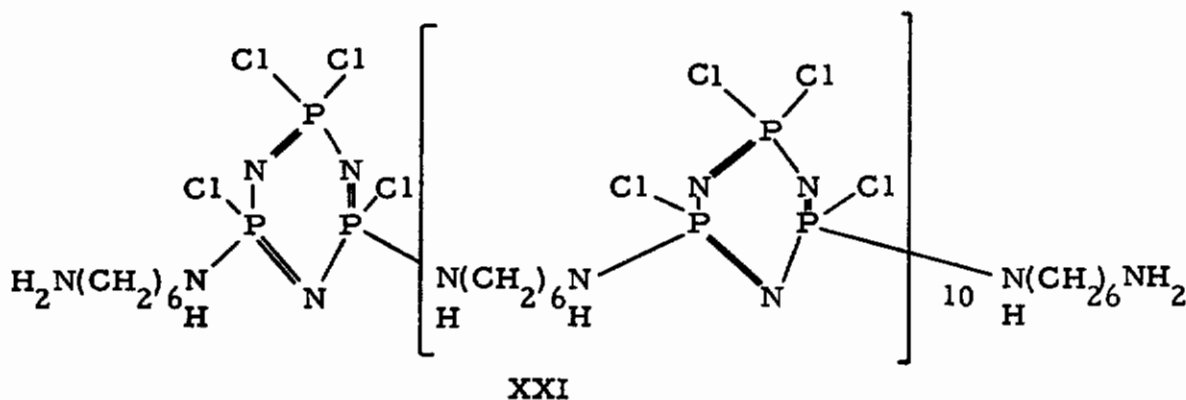
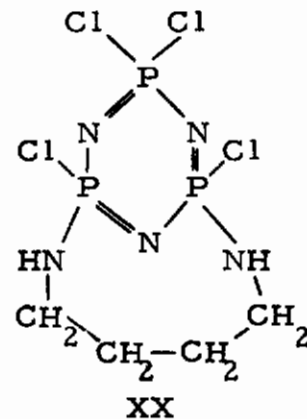
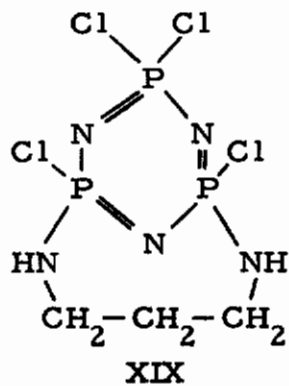
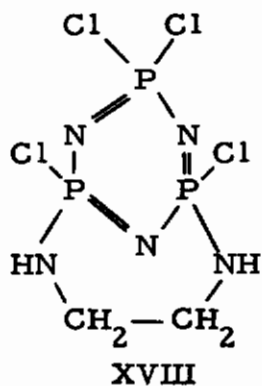


Substitution rules were derived from the behavior of trimeric and tetrameric phosphorus nitrilic chlorides.¹² The rules were checked by the synthesis of isomers and by nuclear magnetic resonance spectra of the products. After we knew these rules of substitution of chloride atoms by strong nucleophilic reagents, it was possible to think out a reasonable way of preparing polymers.

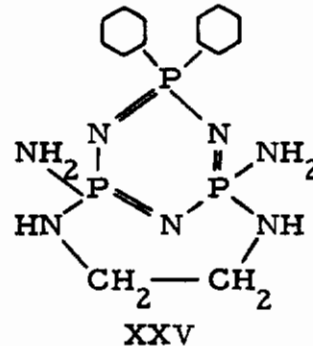
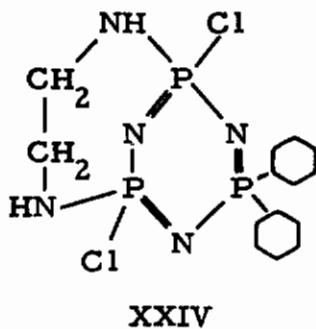
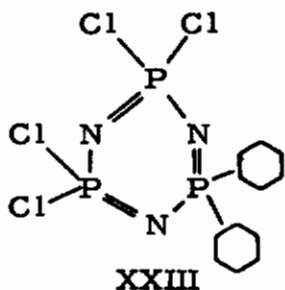
We investigated the reaction of X with polymethylenediamines. According to the rules of substitution, we found the reaction products XVIII, XIX and XX. With hexamethylenediamine, however, (or octamethylenediamine or $\text{H}_2\text{N}-\text{C}_6\text{H}_{10}-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{NH}_2$) a polymeric substance was obtained. Two

Contrails

substances XXI and XXII were obtained, and their structures were elucidated.



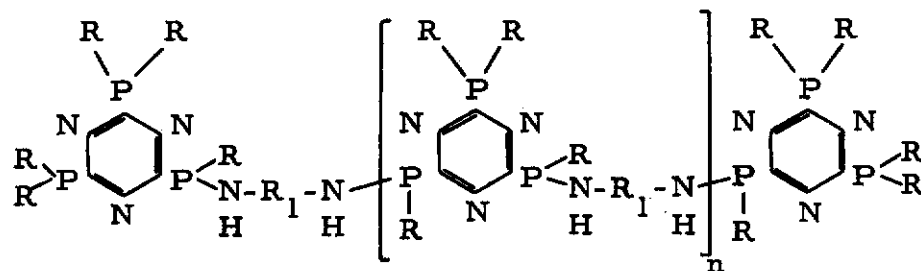
A variety of derivatives of such compounds was obtained. With diphenyl phosphorus nitrilic tetrachloride (XXIII) analogous reactions were observed. Monomers (XXIV), (XXV) are obtained with ethylenediamine; polymers are obtained with diamines which contain a longer chain $(\text{CH}_2)_n$.



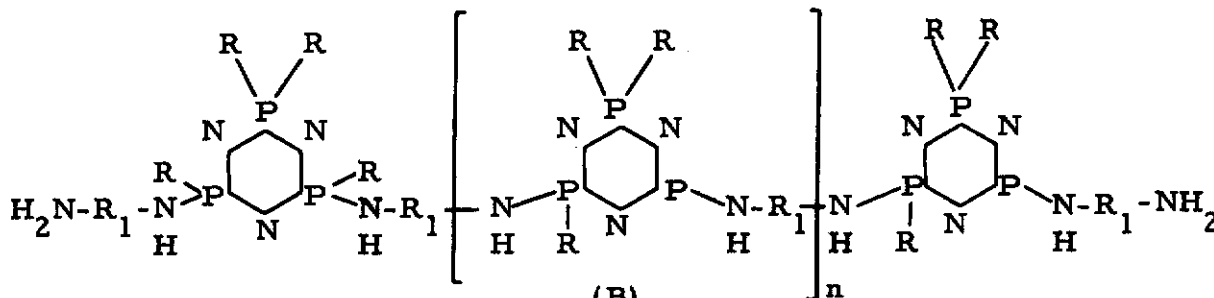
Some of the polymers are resins. When heated to about 150° the polymers become

thermoplastic. Of course, the behaviour depends largely upon the substituents.

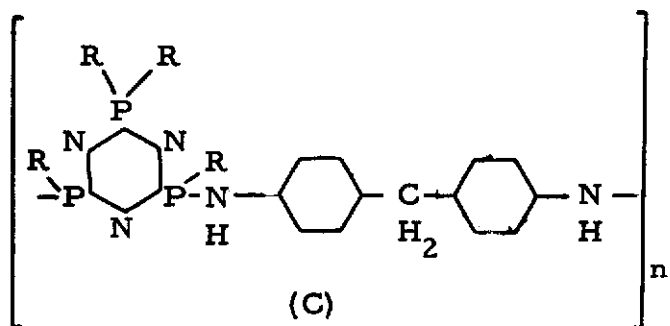
Types of polymers which could be obtained with phosphorus nitrilic chlorides as starting material:



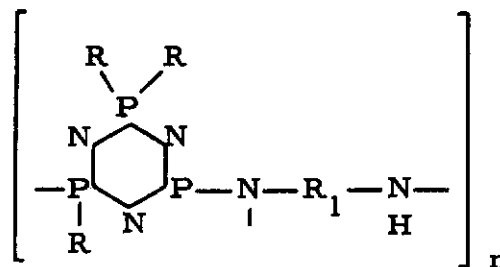
(A)



(B)



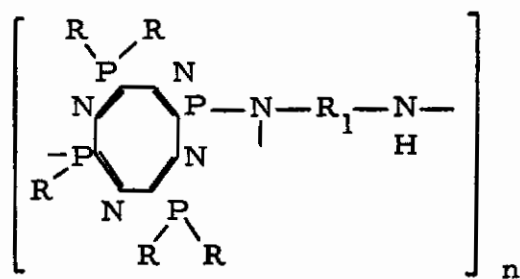
(C)



(D)

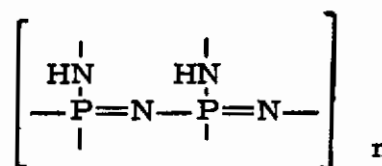
A, B, C, D are derivatives of trimeric phosphorus nitrilic chloride.

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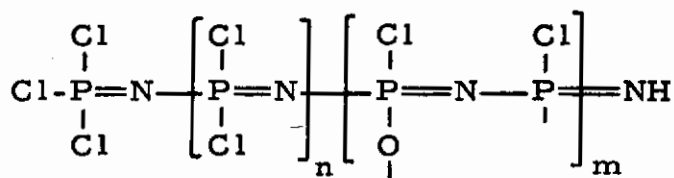
(E)

E is a derivative of tetrameric phosphorus nitrilic chloride.



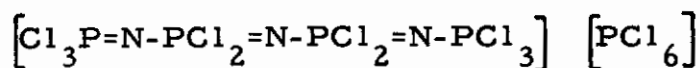
(F)

F may be obtained starting with the trimer or the tetramer respectively.

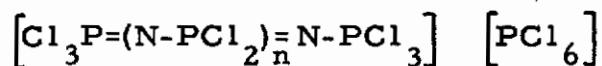


(G)

G is a derivative of the linear phosphorus nitrilic chloride. With traces of water, IX is polymerized producing G.



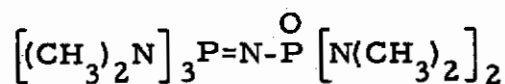
(H)



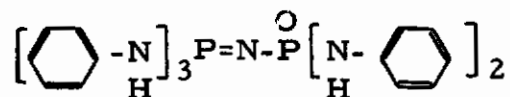
(I)

H and I are products of the reaction of NH_4Cl and PCl_5 . Further, it can be shown by NMR spectroscopy that when trimeric phosphorus nitrilic chloride is reacted with PCl_5 by heating the two substances in a closed tube at about 220° , the salts I are formed.

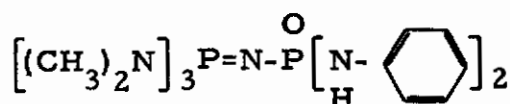
Other polymers could be obtained with $\text{Cl}_3\text{P}=\text{N}-\overset{\text{O}}{\text{P}}\text{Cl}_2$ (XIII) as starting material. Each chlorine atom in this compound can be substituted by an amino group (XXVI). It became apparent in the preparation of the anilide (XXVIb) that polymers are easily formed if the procedure of preparation is carried out at temperatures in excess of 0°C . The amides XXVII are condensed to polymeric substances when heated to $150-200^\circ\text{C}$ (XXVIII).



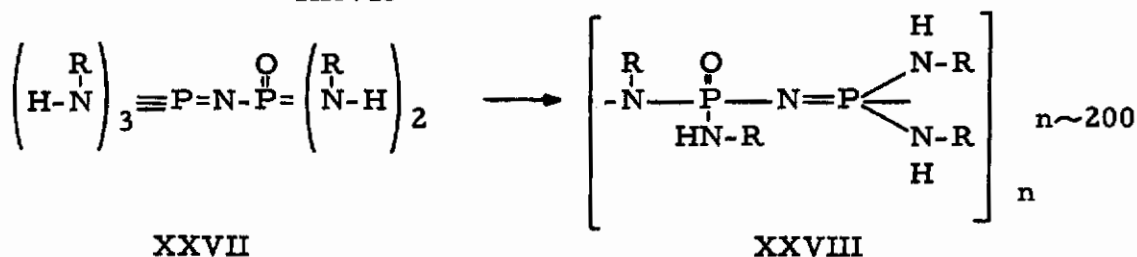
XXVIa



XXVIb



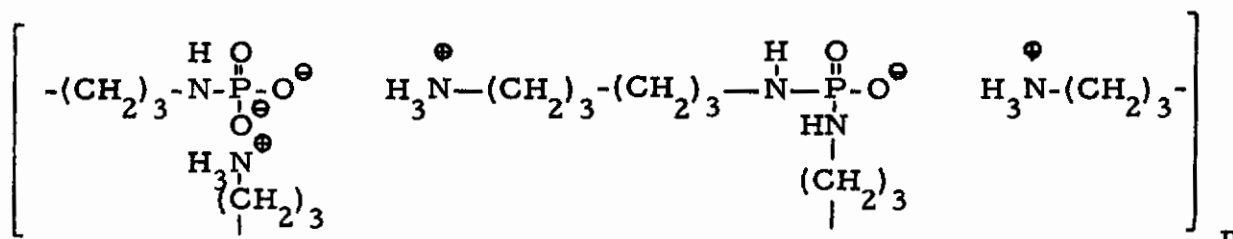
XXVIc



XXVII

XXVIII

With hexamethylenediamine a pentamide was formed. This amide was sensitive towards water, and with water a stable polymeric substance XXIX was formed.



Another polymeric material is formed when $\text{Cl}_3\text{P}=\text{N}-\overset{\text{O}}{\text{P}}\text{Cl}_2$ is brought to reaction with urea or with $\text{K}[\text{OCN}]$. However, $(\text{Cl})_2(\text{C}_6\text{H}_5)\text{P}=\text{N}-\overset{\text{O}}{\text{P}}(\text{Cl})(\text{C}_6\text{H}_5)$ which was prepared just recently may be a better starting material for such polymers.

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