

# THE PHOSPHONITRILIC CHLORIDES AND THEIR DERIVATIVES

L. F. AUDRIETH, R. STEINMAN, AND A. D. F. TOY

*William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois*

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## INTRODUCTION

The systematic classification and investigation of the compounds of nitrogen has been aided greatly by recognition of the fact that these substances are in many instances the nitrogen analogs of the better-known oxygen compounds. By formally setting up the so-called "nitrogen system of compounds" and proving experimentally that these compounds are related to ammonia as parent solvent in much the same way that oxygen compounds are related to water, Franklin (20) opened up a field of research which has occupied the attention of many investigators. By the use of this point of view, notable success has already been achieved in the study of sulfur-nitrogen (2a) and carbon-nitrogen compounds. Similar consideration of the many phosphorus-nitrogen compounds as ammonio derivatives indicates that order can be evolved from among the bewildering maze of experimental material which has been accumulated.

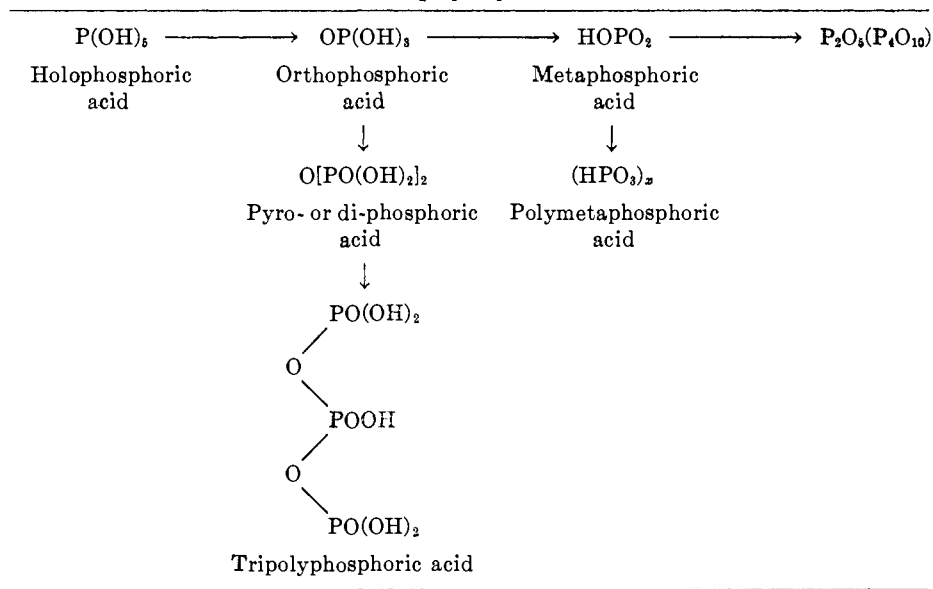
It is our purpose in this paper to discuss critically the chemistry of the phosphonitrilic chlorides. Some of these interesting substances were first obtained by Liebig (39), in an effort to prepare the amides of phosphoric acid by the action of ammonia on phosphorus pentachloride. The type formula,  $\text{PNX}_2$ , where X = halogen, reveals the fact that the phosphonitrilic halides are the nitrogen analogs of the phosphoryl halides ( $\text{POX}_3$ ) and, like the latter, are acid halides capable of undergoing a wide variety of solvolytic reactions. They differ from their oxygen analogs in their ability to undergo polymerization to form products of high molecular weight resembling rubber in appearance and properties. There is no evidence that the phosphonitrilic chlorides exist as stable monomers or dimers. The lowest polyhomolog to have been isolated is the trimer,  $(\text{PNCl}_2)_3$ , which possesses a ring structure like that of benzene. These are but a few of the very unusual properties which have aroused current interest in the phosphonitrilic halides.

Many of the reactions and properties of the compounds under discussion will become evident from a general consideration of the nitrogen analogs of phosphoric acid in which the radicals  $-\text{NH}_2$ ,  $=\text{NH}$ , and  $\equiv\text{N}$  replace the isosteric radicals  $-\text{OH}$  and  $=\text{O}$  in the known derivatives of pentavalent phosphorus. Thus, phosphorus pentamide may be regarded as the nitrogen analog of the monohydrate of phosphoric acid, if we assume that the latter may be represented by the empirical formula  $\text{P}(\text{OH})_5$ . Deammonation processes (removal of ammonia), as outlined in table 1, lead to the various ammonophosphoric acids and eventually to the phosphoric anammonide,  $\text{P}_2\text{N}_5$ , just as phosphoric acid is related by processes of dehydration, either directly or indirectly, to the polymetaphosphoric and polyphosphoric acids and to the acid anhydride  $\text{P}_2\text{O}_5$ .

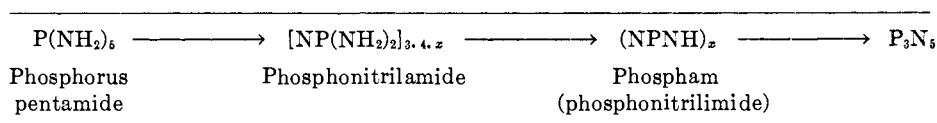
It is possible also to effect partial replacement of the aquo radicals by the corresponding nitrogen analogs to give a whole series of mixed ammonoaquo-phosphoric acids. Only a few of these are represented in table 2 and not all of these possible compounds are too well characterized. Indeed, a careful reinvestigation of these substances would seem highly desirable, since the literature contains so many conflicting statements and claims.

The problem of evaluation of the older literature is complicated by the fact that no consistent system of nomenclature has ever been employed to cover all actual

TABLE 1  
A. The aquophosphoric acids



B. The ammonophosphoric acids

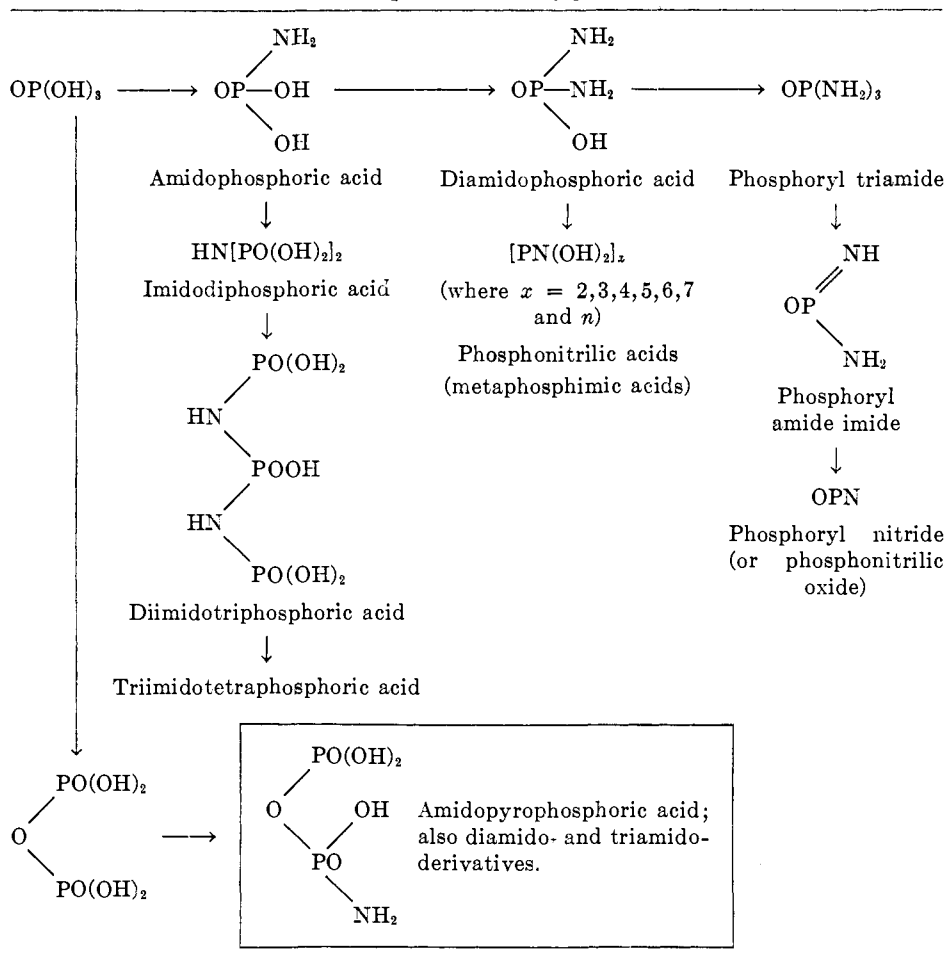


and hypothetical compounds. Proposals for the naming of nitrogen-phosphorus compounds have recently been made by the authors (2), in an effort to lay the groundwork for the systematization of the chemistry of these substances. The PN group is called the phosphonitrile radical, and compounds containing this combination of atoms are given this stem name where it can be shown definitely by chemical reactions that they are related. The phosphonitrilic halides are, therefore, related to the phosphonitrilamides,  $[PN(NH_2)_2]_x$ , and to the phosphonitrilic acids,  $[PN(OH)_2]_x$ , formerly called the metaphosphimic acids.

In a consideration of the chemistry of the phosphonitrilic chlorides we shall

discuss (1) the preparation, (2) the physical properties, (3) the polymerization, and (4) the chemical reactions, particularly the solvolytic reactions, which these compounds undergo.

TABLE 2  
Mixed ammonoquo derivatives of phosphoric acid



### I. PREPARATION, PURIFICATION, AND SEPARATION OF PHOSPHONITRILIC CHLORIDES

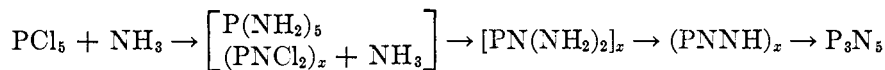
#### A. PREPARATION

All methods for the preparation of the phosphonitrilic chlorides involve the partial ammonolysis of phosphorus pentachloride. All procedures yield mixtures of the various polyhomologs which must be subjected to subsequent separation and purification to obtain the individual members.

1. *Preparation by the reaction of phosphorus pentachloride with ammonia*

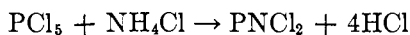
Justus von Liebig (39) attempted to prepare the amides of phosphoric acid by passing gaseous ammonia over phosphorus pentachloride. Instead of obtaining the expected amides, he isolated a relatively small quantity of a remarkably stable product which could be steam-distilled or boiled with acids and alkalis without undergoing appreciable decomposition. Wöhler (39) analyzed Liebig's new compound and assigned to it the formula  $P_3N_2Cl_5$ . Gerhardt (21, 22) and later Laurent (38) showed by analysis that the true composition may be represented by the empirical formula  $PNCl_2$ . On the basis of vapor-density measurements, Gladstone and Holmes (29, 30, 31) and Wichelhaus (74) proved the compound to be trimeric and assigned to it the formula  $(PNCl_2)_3$ .

In all of these experiments only small yields of phosphonitrilic chloride were obtained. More highly ammonated products, such as phospham, are always formed even in those instances in which the pentachloride is dissolved in some non-aqueous solvent, such as carbon tetrachloride, and then treated with ammonia (47) or with ammonium carbamate (19) to moderate the reaction. It is significant, however, that small quantities of phosphonitrilic chloride are always obtained, indicating that this substance is either an intermediate or a secondary reaction product in the ammonolysis of the phosphoric halide.



2. *Preparation from phosphorus pentachloride and ammonium chloride*

To prevent the formation of completely ammonated products, Stokes (64, 65, 68) used ammonium chloride as a source of ammonia.



He carried out the reaction in closed tubes between 150° and 200°C. High pressures were built up, owing to formation of hydrogen chloride, and the tubes had to be opened at frequent intervals during the process in order to let the gas escape. The procedure was both costly and dangerous, in that the tubes frequently exploded. The resulting product, the weight of which was about 30 per cent of that of the original charge, consisted of a buttery mass containing crystalline material. Stokes extracted the trimer and tetramer with gasoline and fractionally recrystallized from anhydrous benzene the residue left after removal of the solvent. He verified the existence of the trimer and also isolated the tetramer,  $(PNCl_2)_4$ , from the benzene fraction. The pentamer, hexamer, and heptamer, together with an oily material the composition and molecular weight of which were represented by  $(PNCl_2)_{11}$ , were obtained from the gasoline mother liquor.

Schenck and Römer (57) were not satisfied with Stokes' method because it was dangerous, it was costly, and it produced low yields. In one of their early attempts, they heated 600 g. of phosphorus pentachloride with 150 g. of ammonium chloride in an acid-tight autoclave. They obtained their best yields at 120°C., the temperature which Stokes found to be the optimum one. The

hydrogen chloride produced as a result of the reaction was vented when it had attained a pressure of 25 atm. The heating was continued until no appreciable pressure changes were observed. About 200 g. of a crude product, contaminated with phosphorus pentachloride and ammonium chloride, was obtained. This material was subjected to fractional distillation at 2 mm. pressure. Distillation commenced at 130°C., resulting in the deposition of a white solid in the receiver, and was continued until a bath temperature of 200°C. had been attained, above which the residue in the flask foamed, then thickened, and finally assumed a dark color.

The distillate was washed with water to remove unreacted phosphorus pentachloride and then dried. This purified product, consisting of a mixture of trimer and tetramer, was then redistilled at 10 mm.; a fraction boiling at 124°C. was found to be the pure trimer, melting at 114°C. A second fraction, boiling at 185°C. and melting at 123.5°C., was found to be the pure tetramer. Both isomers were recrystallized from benzene.

The direct reaction between ammonium chloride and phosphorus pentachloride was also investigated by Besson and Rosset (4), who merely heated together a mixture of equal weights of the reactants in a retort provided with a cooling apparatus. The product which sublimed from the reaction mixture was distilled to effect separation of the trimer and tetramer. No details of the temperature or the yield were given.

This procedure has recently (63a) been studied and found to give excellent results if the proper ratio of reactants is employed and the temperature and time of heating are controlled carefully. Specific directions follow: An intimate mixture of phosphorus pentachloride (52.1 g. or 0.25 mole) and ammonium chloride (50-100 g.) is placed in the bottom of a 50-cm. Pyrex tube (50 mm. in diameter) and then covered with a capping of ammonium chloride 1 to 3 in. in thickness. The tube is immersed in an oil bath to such a depth that the ammonium chloride cap is kept largely above the liquid level. The outlet from the reaction tube is connected to a wash bottle containing sulfuric acid which serves as an indicator for the rate of evolution of hydrogen chloride. The mixture is then heated for 4 to 6 hr. at a bath temperature of 145-160°C., resulting in a conversion of 90 to 95 per cent of the phosphorus pentachloride into a mixture of the various polyhomologs of  $\text{PNC}_2$ . As the reaction nears practical completion, the bubbling of hydrogen chloride through the sulfuric acid trap slows down markedly. Considerable amounts of the trimeric form sublime into the cooler portions of the reaction vessel. The residue is then extracted with low-boiling petroleum ether (50-70°C.), which removes quantitatively the trimeric and tetrameric homologs. Evaporation of the solvent yields mixtures of these corresponding quite consistently to 38 to 43 per cent of theory, based upon the amount of phosphorus pentachloride used (11-12.5 g. of the trimer-tetramer mixture, when the quantities specified above are employed). The higher polyhomologs can be obtained from the residue by extraction with benzene, carbon tetrachloride, or chloroform. Evaporation of these solutions invariably results in the formation of thick viscous oils or rubbery solids.

If the mixture of phosphorus pentachloride and ammonium chloride is heated

rapidly to red heat, small yields of the various polyhomologs can also be obtained. However, the major product appears to be phospham.

3. *Preparation by the reaction of phosphorus pentachloride with ammonium chloride in the presence of an inert solvent*

The yields obtained by Schenck and Römer far exceeded those reported by Stokes, but the method was not altogether satisfactory since it involved too many operations. Schenck and Römer (57) decided to carry out the reaction in an indifferent solvent in which the phosphorus pentachloride would be soluble and which would boil in the neighborhood of the most satisfactory reaction temperature. They chose *s*-tetrachloroethane as the solvent. Four hundred grams of phosphorus pentachloride and 120–130 g. of ammonium chloride were introduced into a liter of the solvent, and the mixture was placed in a round-bottom flask which was immersed in an oil bath. The flask was attached to a reflux condenser to the outlet of which was fitted a calcium chloride tube, in turn connected with suitable absorbents for hydrogen chloride.

The external bath was maintained at 135°C. and the mixture was refluxed for 20 hr. The major reaction was complete after 7 hr., but continued heating was necessary to drive off the dissolved hydrogen chloride. The mixture was then cooled and filtered to remove the excess ammonium chloride. After removal of the solvent by distillation at 11 mm. and 50°C., a buttery mass was again obtained, which consisted mainly of an oil suspension of crystalline material. The residue was washed with cold benzene, in which the trimer and tetramer are relatively insoluble and the higher polymers very soluble. The partially purified mixture, weighing about 100 g. and consisting of about 75 per cent trimer and 25 per cent tetramer, was then recrystallized from benzene and the purified product distilled at 10 mm. At this pressure the trimer distils at 124°C. and the tetramer at 185°C.

This procedure has since been used by all investigators with but few minor changes. Experiences by the authors (19, 62) indicate that it is advisable to remove the solvent either at as low a temperature as possible or very rapidly at temperatures of about 80°C., in order to prevent polymerization of the product, with consequent decrease in yields of the lower polyhomologs.

4. *Preparation by miscellaneous reactions*

The phosphonitrilic chlorides have also been obtained by the interaction of ammonobasic mercuric chloride with phosphorus pentachloride (29, 30, 31) in accordance with the equation:



At high temperatures (above 700°C.) nitrides of phosphorus are slowly attacked by chlorine (48, 72, 73) to give a sublimate consisting largely of the trimeric halide. Small traces of the phosphonitrilic halides are also obtained when phosphoryl nitride is treated with chlorine above 800°C. (72).

## B. SEPARATION AND PURIFICATION OF THE PHOSPHONITRILIC CHLORIDES

All methods of preparation thus far devised give mixtures of various polymers of  $(\text{PNCl}_2)_x$ , where  $x = 3, 4, 5, 6, 7$ , and higher. Considerable difficulty is encountered in separating these polymers, not only because of their similarity, but because separation, if effected at higher temperature, always results in appreciable polymerization. Under any circumstances a preliminary separation of the trimer and tetramer from the remainder of the reaction product is advisable before fractional distillation, sublimation, or crystallization is attempted.

Most investigators have made use of the fact that cold benzene will extract the higher polymers ( $x = 5, 6, 7$ , and higher), whereas the trimer and tetramer are considerably less soluble. Such a separation is only partially successful, since considerable quantities of the lower forms go into solution, yet it was this procedure which enabled Stokes (64, 65, 68) to isolate the various polymers in the pure state. In those cases where large quantities of the higher polymers are present, the latter tend to cause formation of an extremely viscid solution in benzene which makes filtration difficult if not impossible.

The authors (62) have attempted to use a number of other solvents to effect similar separations, but only in the case of anhydrous acetic acid has any real success been achieved. The trimer and tetramer are appreciably soluble in acetic acid, whereas the higher members appear to undergo reaction and are much less soluble. Fractional crystallization from acetic acid will effect a crude separation into trimer- and tetramer-rich fractions, which can then be further purified by fractional distillation. It should be pointed out that removal of residual acetic acid is apparently necessary, since products containing traces of the acid appear to polymerize more rapidly.

If only the trimer is desired, resort can be had to a process of steam distillation (39) of the mixed product. The trimer is quite volatile in steam and is not attacked rapidly, whereas the tetramer is hydrolyzed to the corresponding phosphonitrilic acid.

After the trimer and tetramer have been separated from the higher polymers, the process of fractional distillation can be employed to obtain the pure compounds. A survey of the data in table 3, giving the melting and boiling points of the various polymers, indicates that separation of trimer from tetramer is readily effected by distillation at reduced pressure.

## II. PHYSICAL PROPERTIES OF PHOSPHONITRILIC CHLORIDES

## A. MELTING AND BOILING POINTS

The melting and boiling points of the phosphonitrilic chlorides are given in table 3. Those of the trimer and tetramer are known with considerable accuracy, whereas those of the higher polymers are known only approximately and have never been verified since first reported by Stokes (68).

The vapor pressure of trimeric phosphonitrilic chloride has recently (63a) been redetermined with great care over the range 75.2 to 189.3°C. For the solid-vapor curve the vapor pressure is given by the expression  $\log p = -3978 (1/T) +$

11.187 (where  $t = 75.2$  to  $114.9$ ); for the liquid-vapor equilibrium,  $\log p = -2880 (1/T) + 8.357$  (where  $t = 114.9$  to  $189.3$ ). On the basis of these data the triple point, representing the melting point of the trimer, corresponds to a temperature of  $114.9^\circ\text{C}$ . The normal boiling point obtained by extrapolation of the liquid-vapor curve to 760 mm. pressure is  $252.7^\circ\text{C}$ ., which is somewhat lower than the previously accepted value,  $256^\circ\text{C}$ ., reported by Stokes (68) in 1897.

The molal heat of vaporization calculated from the slope of the liquid-vapor curve is 13.2 kilocalories; the molal heat of sublimation is 18.2 kilocalories; the molal heat of fusion obtained by difference is 5.0 kilocalories.

TABLE 3  
*Properties of the phosphonitrilic chlorides (68)*

FORMULA	SPECIFIC GRAVITY	MELTING POINT °C.	BOILING POINTS	
			At 13 mm. °C.	At 760 mm. °C.
(PNCl <sub>2</sub> ) <sub>3</sub> .....	1.98 (29)	114	127	256
(PNCl <sub>2</sub> ) <sub>4</sub> .....	2.18 (64)	123.5	188	328.5
(PNCl <sub>2</sub> ) <sub>5</sub> .....		40.5-41	223-224.3	Polymerizes
(PNCl <sub>2</sub> ) <sub>6</sub> .....		90-91	261-263	Polymerizes
(PNCl <sub>2</sub> ) <sub>7</sub> .....		-18	289-294	Polymerizes

TABLE 4  
*Solubilities of phosphonitrilic chlorides, expressed in grams per 100 grams of solvent (16)*

SOLVENT	TRIMER	TETRAMER
	grams	grams
Ether.....	46.37	12.4
Dioxane.....	29.55	8.23
Benzene.....	55.0	21.42
Toluene.....	47.3	17.8
Xylene.....	38.85	13.85
Saturated petroleum hydrocarbons.....	27.9	8.39
Carbon tetrachloride.....	38.88	16.55
Carbon disulfide.....	52.05	22.00

It is interesting to note that the trimer and tetramer form a eutectic mixture melting at  $88.5$ – $89^\circ\text{C}$ ., corresponding to a trimer mole fraction between 0.6 and 0.7 (16, 19, 62).

#### B. SOLUBILITIES

Solubilities of the various polymers have been discussed qualitatively under their separation. Few quantitative measurements have been made and these have been collected in table 4.

The halogenated aliphatic hydrocarbons, such as chloroform, carbon tetrachloride, and *s*-tetrachloroethane, the aliphatic and aromatic hydrocarbons, such as petroleum ether, benzene, toluene, and xylene, and ethers, such as diethyl



ether and dioxane, may be designated as solvents in which the phosphonitrilic chlorides are soluble. It is also reported that the trimer is soluble in phosphoryl chloride (4, 25, 49, 52), turpentine (27, 49), liquid sulfur dioxide (6, 52), and concentrated sulfuric acid (64). Attention has already been directed to the preferential solubility of the trimer and tetramer in anhydrous acetic acid. The phosphonitrilic halides are also soluble in various alcohols, phenols, and amines, but these classes of compounds are hardly suitable solvents as some reaction always takes place, especially at higher temperatures (see section IV).

The addition of the trimer to lubricating oils, in which the compound is quite soluble, is said to reduce wear at rubbing surfaces (2b).

### C. CRYSTALLOGRAPHIC FORM AND STRUCTURE

The trimer,  $(\text{PNCl}_2)_3$ , crystallizes in six-sided plates belonging to the rhombic system with axial ratios  $a:b:c = 0.4417:1:1.8165$  (32, 75), whereas the tetramer crystallizes in the tetragonal system (35, 37). The hexamer forms rhombic crystals with the axial ratios  $a:b:c = 0.5482:1:1.1757$  (32, 71).

The trimer (35, 52) and the tetramer (35, 37) have also been subjected to x-ray studies. These data may be summarized as follows:

	TRIMER	TETRAMER
Space group.....	$V_H^{16}$	$C_{4h}^4$
Dimensions of unit cell in Å:		
$a_0$ .....	14.00 (14.30)	10.82 (10.79)
$b_0$ .....	6.16 (6.25)	
$c_0$ .....	12.94 (13.03)	5.59 (5.93)
Molecules in unit cell.....	4	2
Density:		
Calculated.....		2.20
Found.....	1.98	2.18

Interatomic distances have been calculated for the tetramer (37) and are found to be (in Å. units):

(a) For bonded atoms:

$\text{P-Cl}_1$ , 1.97<sub>5</sub>       $\text{P-N}$ , 1.66

$\text{P-Cl}_2$ , 2.01<sub>5</sub>       $\text{P-N}'_1$ , 1.69

(b) For non-bonded atoms:

$\text{Cl}_1\text{—Cl}_2$ , 3.17       $\text{N—Cl}_2$ , 2.71

$\text{P—P}'$ , 2.93       $\text{N}'\text{—Cl}_1$ , 2.88

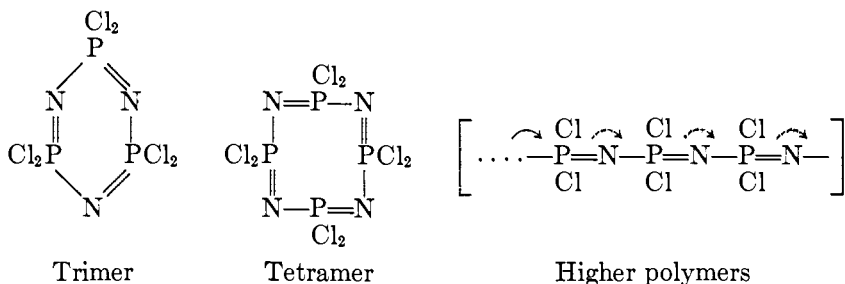
$\text{N—N}'$ , 2.85       $\text{N}'\text{—Cl}_2$ , 3.14

$\text{N—Cl}_1$ , 3.18

The valence angles for the various combinations of atoms are:

$\text{P—N—P}'$ .....	123°
$\text{N—P—N}'$ .....	117°
$\text{Cl}_1\text{—P—Cl}_2$ .....	105°30'

These data lead to the conclusion that the tetramer is in the form of a puckered ring.<sup>1</sup> In all polymers, two chlorine atoms are attached to each phosphorus atom. Resonance occurs between the two possible arrangements of the double bonds in the rings, analogous to that in aromatic compounds.



All experimental evidence points to the fact that both the trimer and the tetramer possess cyclic structures with alternate phosphorus and nitrogen atoms, whereas the higher members, including the "inorganic rubber", possess chain structures. It should be recalled that a distinct change in physical properties (see table 3) occurs in going from the tetramer to the pentamer, and also that these same lower forms exhibit marked qualitative differences in solubility from the higher polyhomologs. The trimer and the tetramer are also less easily polymerized than are the higher members, presumably because ring rupture is necessary before polymerization can occur.

#### D. PHYSIOLOGICAL CHARACTERISTICS

Reference has been made by many investigators (3, 39, 49) to the characteristic aromatic odor of the phosphonitrilic chlorides. If the vapor is inhaled in appreciable quantities, definite injury to the respiratory organs occurs and nausea is induced (49). Renaud (52) goes even further in emphasizing that great care should be taken in any operations involving vaporization of the phosphonitrilic chlorides. In his work on the cracking of the highly polymerized forms, Renaud mentions severe eye pains, a very general pronounced apathy, and finally difficulty in breathing, as resulting from excessive exposure to the gaseous decomposition products. These effects are not immediate and do not become apparent until several hours after exposure. Respiratory discomforts are alleviated by breathing air containing small amounts of ammonia gas.

It is interesting in this connection to report the results obtained by Dr. C. W. Kearns<sup>2</sup> of the Department of Entomology of the University of Illinois in a study of the pesticidal properties of the trimer. Trimeric phosphonitrilic chloride was found to be considerably more toxic to the Greenhouse Leaf Tyer than acid lead arsenate, which was used in control tests. The trimer was found

<sup>1</sup> The singular stability of the tetramer seems to militate against the concept of an eight-membered ring. Copley (8) prefers to consider the polyhomologs above the trimer as having bridged or polycyclic structures with no ring containing more than six atoms.

<sup>2</sup> Private communication.

to have a medium lethal dosage of 0.08 mg. per gram of body weight, as compared with a dosage of 0.205 g. per gram in the case of the control agent. However, injury to foliage occurs to a marked extent, making it improbable that the phosphonitrilic chlorides will ever be of any practical value as pesticides.

### III. POLYMERIZATION OF PHOSPHONITRILIC CHLORIDES

The phosphonitrilic chlorides form as complete a polyhomologous series as is known in the realm of chemistry. In addition to definite compounds the composition of which may be represented by the formulas  $(\text{PNCl}_2)_x$ , where  $x = 3$  to 7, there have been obtained: (a) a high-molecular-weight oil, the average composition of which is represented by the formula  $(\text{PNCl}_2)_{11}$ ; (b) gums; (c) waxes; (d) the inorganic rubber  $(\text{PNCl}_2)_n$ , the molecular weight of which is estimated to be at least 20,000; and (e) an infusible non-elastic material the nature of which has not yet been definitely determined.

Stokes (68) was the first investigator to show that the mixture of phosphonitrilic chlorides is converted to a rubber-like material slowly at 250°C., and very rapidly at 350°C. Short treatment of this product with benzene enabled him to extract lower polymers, while long treatment caused the rubber-like mass to swell and gelatinize. Evaporation of the benzene, however, gave back the rubber-like substance. The elastomer appears to absorb both ether and lower forms of  $\text{PNCl}_2$ . It is decomposed by hot water, and swells, gelatinizes, and then dissolves in warm dilute aqueous ammonia. Depolymerization begins at 350°C. and proceeds rapidly below red heat, leaving no residue if a pure substance has been used.

Renaud (50, 52) studied the polymerization of the trimer in a closed tube at 270°C. and found that liquids, gums, or insoluble or infusible products could be obtained, depending on the length of heating. He mentions the use of a trimer which had been carefully dried in order to eliminate the influence of water which, according to him, effects the polymerization process. When cooled in liquid air these products take on the aspects of a glass. A transition from the gummy form to a glass seems to occur at -47°C. Renaud assumed that the trimer on heating gives rise to chains of varying length, which are capable of enmeshing the lower polymers.

Schenck and Römer (57) studied the polymerization of the trimer and tetramer at various temperatures by placing samples in small sealed tubes and suspending these in the vapors of constant-boiling liquids. Their results are given in table 5.

Below 250°C. short heating of the trimer and the tetramer gives no polymeric material, whereas the oily polyhomologs go rapidly over to rubbery masses below 200°C. Schenck and Römer describe the inorganic polymer as an elastic and pliable material like rubber. It is colorless in the pure state and is insoluble in the usual solvents. The elastomer does swell in benzene and eventually dissolves to give a dispersion which resembles that of gelatin in water. The product is stable towards acids and alkalies, but is decomposed by long boiling with water. According to these investigators the inorganic rubber is stable in

air for a limited time only, since it loses its elasticity and decomposes to a brittle mass. Slow heating of the polymer to red heat does not bring about decomposition to lower polymers, but converts the rubbery material into a porous horny mass.

Meyer and coworkers (42, 43) produced polymers by heating either the trimer or the tetramer at 300°C. for 8 hr. In appearance these were not distinguishable from slightly vulcanized rubber. Under tension the products give fiber-like diffraction patterns in which the most probable arrangement is a succession of  $\text{PNCl}_2$  units held together by primary valence forces. The elementary cell is rhombic, belonging to the  $C_{2v}^9$  space group with the following cell dimensions:  $a_0 = 11.07 \text{ \AA}$ .,  $b_0 = 4.92 \text{ \AA}$ . (fiber axis), and  $c_0 = 12.72 \text{ \AA}$ .

TABLE 5  
*Polymerization of the trimeric and tetrameric phosphonitrilic chlorides*

NO.	LIQUID USED	BOILING POINT OF LIQUID °C.	TIME OF HEATING	NATURE OF PRODUCT
1	Aniline	182	1 hr.	No change in melting point
2	Nitrobenzene	209	1 hr.	No change in melting point
3	Diphenyl	254.9	4 hr.	Turbidity in the liquid mass; when cooled gave a wax-like product with no sharp melting point; softened at 150–200°C. and was a clear liquid above 200°C.
4	Diphenyl		5 hr.	Kneadable mass which could still be melted
5	Diphenyl		6 hr.	One-piece elastic mass; did not melt; when heated to red heat gave a hard and brittle mass; longer heating did not change nature of this material
6	Phthalic anhydride	284.5	2 hr.	
7	Diphenylamine	302	1 hr.	
8		350	Few minutes	

Study of the temperature-tension curve showed the phosphonitrilic chloride polymer to be wholly analogous to rubber. When the polymer is heated at a constant degree of deformation, the tension increases to a degree which is more than proportional to the absolute temperature. It is assumed that the crystalline portions "melt" and also undergo tension. On cooling, the tension remains at first higher than in the process of heating, and decreases in an amount proportional to the temperature. The polymer then exists in an amorphous metastable state; crystallization, and restoration of the original degree of tension, occur only gradually. Contraction is produced not through intermolecular forces, but through thermal agitation of links of the flexible chain. There is a tendency to produce the preferred condition in which the chains are completely disoriented rather than the less probable oriented arrangement.

Meyer states that depolymerization of the inorganic rubber is effected at room temperature by solvents like dioxane. In many respects the behavior of the polyphosphonitrilic chloride resembles that of plastic sulfur.

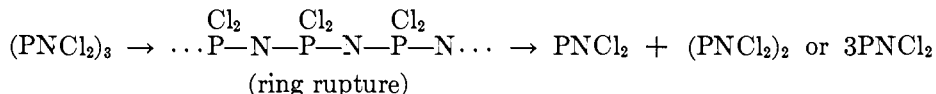
Ficquelmont (14, 15) studied the behavior at room temperature of products obtained by the polymerization of  $(\text{PNCI}_2)_x$  (where  $x = 3$  to 7) at  $350^\circ\text{C}$ . If the elastomer is allowed to stand at room temperature it gradually loses its elastic properties and shows crystalline structure. This crystalline material dissolves slowly in organic solvents, such as ether and dioxane, from which some trimer and tetramer can be isolated. That this is not a depolymerization, however, is, according to Ficquelmont, indicated by the following facts: (1) The rubber-like material is not completely crystalline and the amorphous and insoluble portion can be preserved without change. (2) The crystalline material recovers its "amorphous" character by heating to  $50\text{--}90^\circ\text{C}$ ., a temperature which corresponds to the melting range of mixtures of the lower polymers. The heat-treated material will then again slowly become partly crystalline. The rubber is, therefore, a mixture of soluble, slowly crystallizing material and an insoluble non-crystalline substance. (3) If the product is heated slowly to around  $500^\circ\text{C}$ ., a black, insoluble, infusible, and non-elastic material is obtained. If heated rapidly, most of the elastomer distills to give a mixture of lower polymers.

Ficquelmont believes that the black infusible non-elastic product is the ultimate end product of polymerization and that the lower polyhomologs, including the elastomer, are intermediate forms. In fact, the inorganic rubber is assumed to consist of a network of highly polymerized, fibrous material, enclosing within its meshes the less highly polymerized members. This hypothesis is believed to account for its behavior on standing at ordinary temperatures and also on rapid heating.

Schmitz-Dumont (59) heated the trimer under such conditions as to cause reaction to occur in a homogeneous gas phase (1 g. of trimer sealed in a 100-cc. quartz tube and heated at  $600^\circ\text{C}$ .). Polymerization then takes place without the formation of the elastomer. The resulting mixture contains some unchanged trimer, some tetramer, and higher polymeric forms, both crystalline and liquid. Systems of similar components were obtained when the tetramer or the rubber-like polymer were subjected to the same conditions. It is, therefore, to be assumed that a true equilibrium exists. An increase in concentration of one of the lower polymers, or an increase in pressure, should cause a change in the quantity of higher polymers formed, an assumption which was borne out experimentally. A rise in temperature causes a decrease in the quantity of the higher polymers, indicating that the process of polymerization is an exothermic process. The higher polymers are depolymerized by heating in a vacuum at  $380^\circ\text{C}$ .

It is obvious from a review of the literature that various investigators are in agreement only on the conditions under which the "elastomer" is obtained (by heating to  $350^\circ\text{C}$ . under pressure), and that it presumably possesses a fiber-like structure. The problem is complicated by the fact that the mechanism of polymerization of the trimer and of the tetramer, both of which possess ring structures, must be different in some respects from that of the higher chain-like structures. There seems to be little question but that ring rupture is involved,

with probable formation of monomeric, dimeric, trimeric, and/or tetrameric chains of high activity.



Evidence for this sort of a mechanism is only circumstantial and rests on the fact that higher polymers are obtained when the trimer is heated to temperatures above 250°C. On the other hand, the so-called inorganic rubber undergoes depolymerization in part when heated rapidly above 380°C. to give always appreciable quantities of the trimer and tetramer, as well as oily and wax-like polyhomologs. Whether the inorganic rubber contains chains of high molecular weight enmeshing lower polymers, or whether these are formed by a process of depolymerization on standing at room temperature, does not yet seem to have been established clearly.

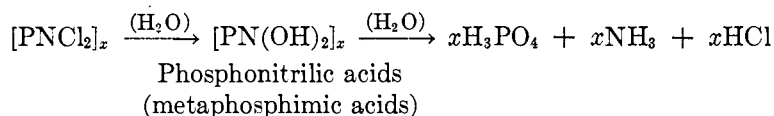
It seems, however, that a chain mechanism is involved, but to date no investigations have been reported which give a clue as to the manner in which such a polymerization is initiated (except by heating) and continued and why it stops. One is reminded of a vinyl-type polymerization, but the formation of stable cyclic structures as intermediates has never been observed in the case of vinyl polymers. No experimental attempts have ever been made to determine if a free-radical, biradical, or chain mechanism can be applied to the polymerization of  $\text{PNCl}_2$ . In fact, it is questionable if the polymerization of  $\text{PNCl}_2$  is quite like anything yet encountered in the realm of organic chemistry.

It is probable, however, that any polymerization involves thermal activation of terminal atoms in longer chains and ring rupture of cyclic structures. It is easier to polymerize the pentamer and higher forms than the trimer and tetramer. The fact that mixtures of various polyhomologs are always obtained indicates that such a process should be capable of a kinetic study, provided means are found for determining accurately and quantitatively one or more of the members of the series.

#### IV. CHEMICAL PROPERTIES OF PHOSPHONITRILIC CHLORIDES

##### A. HYDROLYSIS

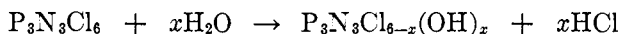
In line with their behavior as acid chlorides the phosphonitrilic halides undergo reactions of hydrolysis to yield partially and completely hydroxylated products—the latter being known as the phosphonitrilic acids (2). More vigorous reaction gives intermediate polyammonophosphoric acids (4, 49, 64, 65, 66) with phosphoric acid, hydrochloric acid, and ammonia as the end products.



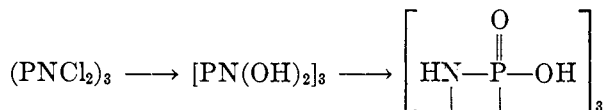
## 1. Hydrolysis of trimeric phosphonitrilic chloride

(a) *Tri(phosphonitrile) dihydroxytetrachloride*,  $P_3N_3Cl_4(OH)_2$ , is obtained when an ether solution of the chloride is agitated vigorously with water (49, 64, 65). The water solution contains both hydrochloric and trimeric phosphonitrilic acids, while the ether layer holds in solution the unchanged chloride and the dihydroxytetrachloride. The latter compounds are separated by extraction with benzene, in which the dihydroxy derivative is only slightly soluble. No statement can be made with respect to the location of the OH groups on the tri(phosphonitrile) ring.

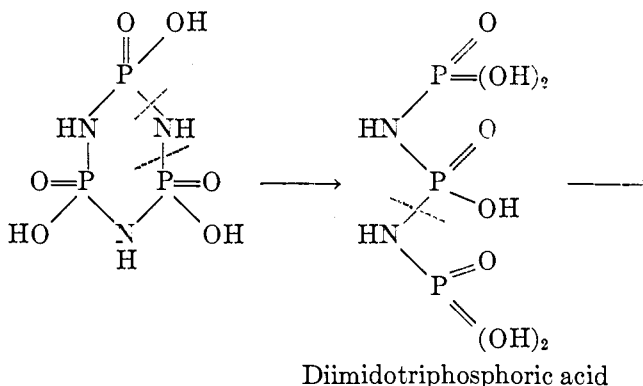
The compound is rather unstable and must be considered as only one of a large number of possible intermediate products (64, 65):

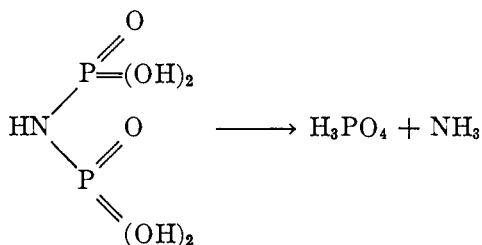


(b) *Trimeric phosphonitrilic acid*,  $P_3N_3(OH)_6$  (29, 49, 58, 64, 65, 66) is an unstable compound better known in the form of its salts. The sodium salt (49, 66) can be obtained quite readily by shaking an ether solution of the chloride with an aqueous solution of sodium acetate. The reaction is slow, but complete conversion to the trisodium salt can be effected. With the exception of a tetrasodium salt (66) and a hexasilver salt (66, 69), all other derivatives are those of a tribasic acid. For this reason, Stokes (66) felt that the structure of the acid could best be represented as a cyclic imidophosphoric acid rather than as a phosphonitrilic acid.



When aqueous solutions of the trimer of phosphonitrilic acid are strongly acidified, decomposition takes place to yield phosphoric acid and ammonia as end products (66). Less vigorous action leads to the formation of appreciable quantities of diimidotriphosphoric acid and imidodiphosphoric acid, both of which may be isolated in the form of their salts and both of which must be considered intermediate products of hydrolysis (66).





Imidodiphosphoric acid

These compounds are mixed ammonoquosphoric acids corresponding to tri- and di-polyphosphoric acids, respectively, and like the latter undergo hydrolytic reversion to phosphoric acid.

### 2. Hydrolysis of tetrameric phosphonitrilic chloride

(a) *Tetrameric phosphonitrilic acid*,  $[\text{PN}(\text{OH})_2]_4 \cdot 2\text{H}_2\text{O}$  (64, 65, 67), is an extraordinarily stable compound and is obtained by the action of water upon solutions of the tetrameric chloride in ether. It is obtained in the form of colorless needles which are but slightly soluble in cold water (0.64 g. per 100 g. of water at 20°C.). The tetrameric chloride is much more readily hydrolyzed than the trimeric compound; consequently, steam distillation has been used to effect their separation. Furthermore, the presence of the tetramer can always be detected in mixtures, owing to the fact that it hydrolyzes rapidly to give the slightly soluble acid.

Tetrameric phosphonitrilic acid is markedly resistant to the action of acids, although it will on long and vigorous action finally undergo hydrolysis to ammonia and phosphoric acid (67). Because of its unusual stability and the probable instability of the intermediate hydrolytic products, isolation of the latter has not been possible. The acid forms three series of salts in which two, four, and eight hydrogen atoms have been replaced (18, 67).

### 3. Phosphonitrilic acids from hydrolysis of solutions of $(\text{PNCl}_2)_3$ and $(\text{PNCl}_2)_4$ in pyridine

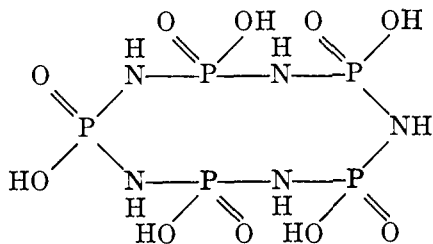
Schenck and Römer (57) treated solutions of the trimer and of the tetramer in pyridine with water and obtained products containing no halogen and analyzing for the pyridine salts of phosphonitrilic acids. Molecular-weight determinations were not possible, because of the insolubility of these salts in various solvents. These products lose pyridine readily in a vacuum over sulfuric acid or when heated under reduced pressure, yielding hygroscopic powders which are easily soluble in water to give acid solutions. These acids coagulate albumin, indicating that they are substances of higher molecular weight. In properties these "acids" are quite different from those prepared by other investigators.

### 4. Phosphonitrilic acids from hydrolysis of the higher phosphonitrilic chlorides

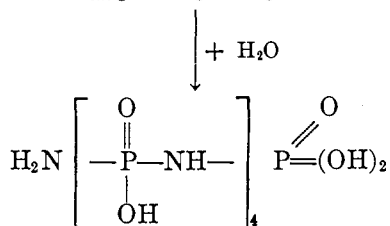
The higher phosphonitrilic chlorides undergo fairly rapid hydrolysis when their ethereal solutions are treated with caustic soda. Only Stokes (69, 70)



seems to have studied these higher phosphonitrilic acids, and his experimental results and analyses leave much to be desired. Stokes considered it highly probable that the pentameric and hexameric phosphonitrilic acids exist as open-chain radicals in alkaline solution and in the lactam form in neutral and acid media. Thus, the phosphonitrilic acid pentamer was represented as



in acid solution, and as

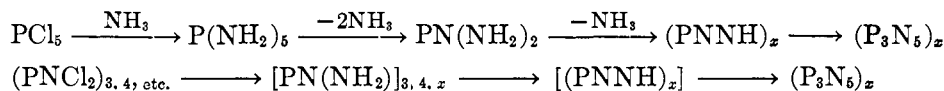


i.e., an amidotetrimidopentaphosphoric acid in the form of its salts.

While salts of the various acids have been isolated (69, 70), it should be pointed out that their composition is rather indefinite. It is interesting to note that solutions of the very unstable free acids in water can be obtained by decomposing the silver salts with hydrogen sulfide. The hydrolytic decomposition of the pentameric phosphonitrilic acid yields the tetrameric phosphonitrilic acid as one of the products (69, 70).

#### B. AMMONOLYSIS OF PHOSPHONITRILIC HALIDES

The action of ammonia on the phosphonitrilic halides leads to partially and completely ammonated products, the latter being known as the phosphonitrilamides. The phosphonitrilamides and their deammonation products, phospham and triphosphorus pentanitride, have been subjected to considerable study in connection with the complete ammonolysis of phosphorus pentachloride.



If the product of ammonolysis of phosphorus pentachloride is hydrolyzed (47), two substances are obtained, one of which is the hydrate of trimeric phosphonitrilamide,  $[\text{PN(NH}_2)_2]_3 \cdot \text{H}_2\text{O}$ , while the other is the tetraammonium salt of the tetrameric phosphonitrilic acid,  $\text{P}_4\text{N}_4\text{O}_8\text{H}_4(\text{NH}_4)_4 \cdot 4\text{H}_2\text{O}$ . It is quite probable therefore that a whole series of phosphonitrilamides, analogous to the phosphonitrilic acids, is capable of existence.

*1. Ammonolysis of trimeric phosphonitrilic chloride*

(a) *Tri(phosphonitrile) diamidotetrachloride*,  $P_3N_3(NH_2)_2Cl_4$  (16, 44, 47, 55, 64, 65): The action of aqueous or gaseous ammonia upon an ethereal solution, or of gaseous ammonia upon a benzene solution, of the trimeric phosphonitrilic chloride yields the partially ammonated product. The compound is soluble in ether, hot benzene, and hot carbon tetrachloride, but only slightly soluble in cold benzene, cold carbon tetrachloride, and cold water. It can be recrystallized, with some decomposition, from hot water. Ficquelmont (16) gives the following quantitative solubilities of the diamidotetrachloride at 18°C. in grams per 100 g. of solvent: ether, 64.7; dioxane, 48.0; benzene, 1.55; toluene, 1.09; xylene, 0.73; petroleum ether (b.p., 80–90°C.), 0.09; carbon tetrachloride, 0.05; carbon disulfide, 0.13. The compound gives a negative chloride test in aqueous solution with silver nitrate, except on boiling. It fuses with decomposition at 162°C. and begins to lose hydrogen chloride when heated in a vacuum at 170°C. Even at 600°C. all of the chlorine is not removed; when the diamidotetrachloride is heated in a current of ammonia at 800–825°C., conversion to  $P_3N_5$  is finally effected.

It is interesting in this connection to point out that a small quantity of this same substance [ $P_3N_3(NH_2)_2Cl_4$ ] was obtained as a by-product in the treatment of a cold solution of phosphorus pentachloride in carbon tetrachloride with gaseous ammonia (47). While most of the pentachloride reacted with precipitation of a mixture of the phosphonitrilamides, the carbon tetrachloride retained in solution a small quantity of  $P_3N_3(NH_2)_2Cl_4$ . This substance is possibly an intermediate in the ammonolysis of phosphorus pentachloride.

Hydrolysis of an ether solution of  $P_3N_3(NH_2)_2Cl_4$  with an aqueous solution of sodium acetate (12) gives the trisodium salt of diimidotriphosphoric acid, rather than the trimeric phosphonitrilate.

(b) *Trimeric phosphonitrilamide*,  $[PN(NH_2)_2]_3$ : Liquid ammonia at first reacts quite readily (5) with the chloride, but the reaction soon slows down owing to agglomeration of the product. Only by long action (1 month to 6 weeks) in a sealed tube, carried out in such a way that the product is continually refluxed with liquid ammonia, is action completed. The amide is completely insoluble in liquid ammonia, whereas ammonium chloride is soluble. Removal of excess ammonia gives a product the composition of which corresponds to the empirical formula  $PN_3H_4$ ,  $[PN(NH_2)_2]$ . This product is very soluble in water but can be precipitated as the monohydrate  $[PN(NH_2)_2]_3 \cdot H_2O$  (47) by the addition of alcohol to the aqueous solution. When heated in a vacuum for several days at 220°C. the compound loses ammonia and the residue approaches gradually the composition of phospham,  $(PNNH)_x$ . Studies in this laboratory (63) indicate that this deammonation process is irreversible. Loss of ammonia is accompanied by a process involving simultaneous aggregation to give products of increasingly higher molecular weight.

A solution of  $(PNCl_2)_3$  in hot benzene reacts slowly with ammonia gas to give eventually an insoluble mixture of  $[PN(NH_2)_2]_3$  and ammonium chloride. An attempt to extract the ammonium chloride with methyl alcohol apparently

results in some reaction with the phosphonitrilamide. It is claimed that the two components formed are  $\text{PNNH}_4\text{OH}$  and  $\text{PN}(\text{NH}_2)(\text{NHCH}_3)$  in the ratio 3 moles to 10 moles (55).

When ammonia gas is passed over melted  $(\text{PNCl}_2)_3$  the latter is converted into a greyish-white infusible powder approaching the composition of phospham (9, 10). It is significant that the product, even when treated in an ammonia atmosphere at  $450^\circ\text{C}$ ., still contains from 2 to 3 per cent of chlorine (44).

### 2. Ammonolysis of tetrameric phosphonitrilic chloride

The action of ammonia upon an ethereal solution of  $(\text{PNCl}_2)_4$  leads to progressive ammonolysis with formation of the diamidohexachloride (11), the tetraamidotetrachloride (11, 55), and probably the tetrameric phosphonitrilamide (11, 12). A monoamido and triamido derivative are also assumed to form as intermediate products. The tetraamido compound,  $\text{P}_4\text{N}_4(\text{NH}_2)_4\text{Cl}_4$  (11, 55), is assumed to decompose on heating, first with loss of hydrogen chloride to give an intermediate compound with the formula  $\text{P}_4\text{N}_4(\text{NH}_2)_2(\text{NH})_2\text{Cl}_2$  and eventually with formation of phospham.

As in the case of the trimeric halide, reaction of the tetramer with liquid ammonia is slow (47). If the reaction is allowed to take place at the boiling point of liquid ammonia, ammonolysis will occur (47). Deammonation of what is presumably the tetrameric phosphonitrilamide gives no indication of the formation of intermediate compounds (63). Deammonation at  $200^\circ\text{C}$ . is accompanied by aggregation to give a product which approaches the composition of phospham.

The various amides hydrolyze to give the ammonium salts of the tetrameric phosphonitrilic acid (12).

## C. AMINOLYSIS OF PHOSPHONITRILIC CHLORIDES

The type reaction



has been shown to hold when the trimer and tetramer are allowed to react with such amines as *p*-toluidine, *o*-toluidine, aniline, and piperidine as well as with phenylhydrazine. It has been shown by molecular-weight determinations that the products obtained from the trimer are different from those derived from the tetramer; consequently, no depolymerization is involved in these aminolytic reactions. Table 6 gives formulas and melting points of a number of such products which may be called *N*-substituted phosphonitrilamides.

It should be pointed out that reactions of aminolysis should resemble those of ammonolysis and should give products in which only partial replacement of the chlorine has occurred. Work by Steinman (63), using such amines as cyclohexylamine, dicyclohexylamine, isobutylamine, and diethylamine, definitely indicates that complete aminolysis is difficult to attain. Lipkin (41) has recently patented a process for producing a light-colored solid, synthetic resinous material substantially insoluble in organic solvents by condensing phospho-

nitrilic chloride with butylamine and heating the condensation product to 200–400°C. under reduced pressure to effect its polymerization.

#### D. REACTION WITH AMINO ACID ESTERS (55)

Both the trimer and tetramer react with amino acid esters in either chloroform or benzene, giving products in which only part of the chlorine is replaced. In the case of the trimer (reaction a) only two of the six chlorine atoms are replaced, whereas four of those in the tetramer (reaction b) are presumably affected.

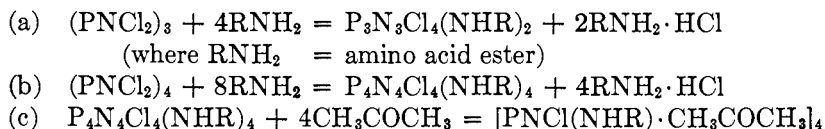


TABLE 6  
*N*-Substituted phosphonitrilamides

FORMULA	AMINE	MELTING POINT	REFERENCES
		°C.	
$[\text{PN}(\text{NHC}_6\text{H}_4 \cdot \text{CH}_3)_2]_3$ .....	<i>p</i> -Toluidine	243	(33, 34)
$[\text{PN}(\text{NHC}_6\text{H}_4 \cdot \text{CH}_3)_2]_3$ .....	<i>o</i> -Toluidine	241–2	(9, 10)
$[\text{PN}(\text{NHC}_6\text{H}_5)_2]_3$ .....	Aniline	268 (267)	(9, 10, 33, 34, 56, 57, 63)
$[\text{PN}(\text{NHC}_5\text{H}_{10})_2]_3$ .....	Piperidine	231	(9, 10, 33, 56, 57)
$[\text{PN}(\text{NH} \cdot \text{NHC}_6\text{H}_5)_2]_3$ .....	Phenylhydrazine	200	(9, 10, 56, 57)
$[\text{PN}(\text{NHC}_6\text{H}_5)_2]_4$ .....	Aniline	244	(56, 57, 63)

The respective products are recovered from the reaction medium as oils. Treatment of these oils with acetone gives the crystalline acetone addition products (reaction c) in the case of the tetramer, but not for the trimer. Esters of glycolic and aspartic acids, of alanine, and of tyrosine have been found to undergo the reactions given in (a) and (b).

#### E. ADDITION COMPOUNDS WITH TERTIARY AMINES

The phosphonitrilic halides, like other acid halides, form addition complexes with such tertiary amines as pyridine, quinoline, and tribenzylamine (55). In view of the fact that compounds obtained from the trimer and tetramer possessed the same melting points, the assumption was made by Schäperkötter (55) that formation of these complexes results in degradation to the simple monomeric adducts:  $\text{PNCl}_2 \cdot 2\text{NR}_3$ . Molecular-weight determinations in camphor appear to verify this assumption. Unpublished work by Burg (6) lends credence to such an assumption, since polymerization of such addition compounds appears to proceed more rapidly.

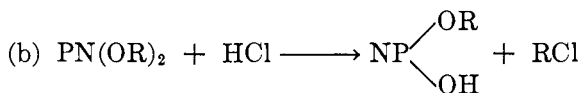
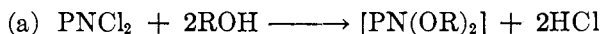
However, the trimer and tetramer are quite soluble in pyridine and such solu-

tions have been used for the preparation of the corresponding phosphonitrilic acids in the form of their pyridine salts (57),—and these are different! Also, the action of alcohols (75) upon pyridine solutions of the halides appears to give the respective esters of the phosphonitrilic acids.

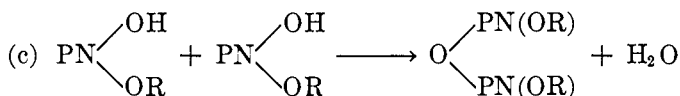
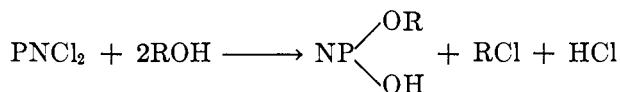
These pyridine solutions are extraordinarily reactive. Clear solutions are obtained only in the absence of moisture, as a trace of water immediately gives a cloudy precipitate. The use of  $\text{PNCl}_2$  for the purpose of drying pyridine has been suggested (57).

#### F. REACTION WITH ALCOHOLS, PHENOLS, AND THE RESPECTIVE THIO COMPOUNDS

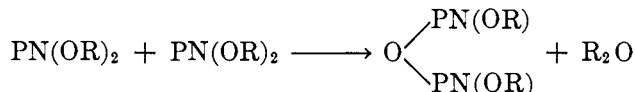
It can be said with certainty that no ester of the phosphonitrilic acids has been positively identified and characterized, despite the fact that reactions of the phosphonitrilic chlorides with the alcohols have been the subject of considerable study. Wissemann (75) allowed alcohols to react either directly or in the presence of pyridine with the phosphonitrilic halides. On the basis of his observations a number of possible reactions are believed to take place:



or



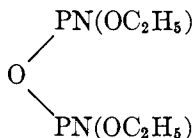
or



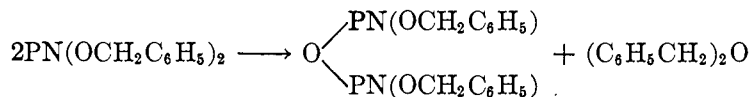
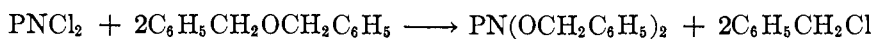
Thus, direct reaction of  $(\text{PNCl}_2)_3$  with absolute methanol gives at first appreciable quantities of methyl chloride. The mixture then becomes turbid as considerable quantities of hydrogen chloride are evolved. Long heating leads to the separation of a crystalline material which, after washing with methyl alcohol and ether and drying, is shown by analysis to have the empirical composition  $[\text{PN}(\text{OH})(\text{OCH}_3)]$ . Under similar conditions the tetramer yields a product the composition of which is intermediate between  $[\text{PN}(\text{OH})(\text{OCH}_3)]$  and  $[\text{PN}(\text{OCH}_3)_2]$ . The latter mixture is insoluble in water, whereas the substance obtained from the trimer is readily soluble.

When ethyl alcohol reacts with either the trimer or tetramer a solid product is

finally obtained which sinters between 222–225°C. and can be represented by the empirical formula:



Direct reaction of benzyl alcohol gives largely benzyl chloride. Dibenzyl ether, on the other hand, reacts with either the trimer or the tetramer in accordance with the following series of equations:



Interaction of glycerol and  $(\text{PNCl}_2)_3$  in dry pyridine takes place when the solution is warmed. The precipitate so obtained is dissolved in methyl alcohol for purification, giving a product the composition of which by analysis corresponds to the formula:



The tetramer is much less reactive, but under the same conditions gives a compound the composition of which may be represented by the formula:



Interaction of  $(\text{PNCl}_2)_3$  with acetoacetic ester in the presence of pyridine yields a brownish powder which is soluble in organic solvents. The compound is represented by the formula:



No definite compound is obtained with the tetramer,  $(\text{PNCl}_2)_4$ .

From phenol (6 moles) and  $(\text{PNCl}_2)_3$  (1 mole) in the presence of pyridine, Wissemann (75) claims to have obtained a greenish oil, boiling at 130–140°C. at 15 mm., the composition of which corresponds to that of an addition compound,  $[\text{PNCl}_2 \cdot 2\text{C}_6\text{H}_5\text{OH}]_3$ . The tetramer was found to react much less readily, giving no definite product.

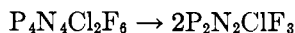
With  $\alpha$ -naphthol in the presence of pyridine a substance is obtained which, upon treatment with methanol, gives a product the composition of which may be represented by the empirical formula  $[\text{PN}(\text{OCH}_3)(\text{OC}_{10}\text{H}_7)]$ . Reaction with pyrogallol was also observed, but the composition of the product was not determined.

Viscous liquids of relatively high boiling points, stable towards moisture and heat, insoluble in water, but soluble in fatty oils, mineral oils, gasoline, benzene, and ether, are obtained by refluxing and treating at higher temperatures the mixed phosphonitrilic halides with metal compounds of alcohols, phenols, thiophenols, or mercaptans (40). It is claimed that such products may be

used as addition agents for lubricating oils or greases, and as plasticizers for resins, lacquers, varnishes, and rubber, and as fluid media for hydraulic brakes.

#### G. THE PHOSPHONITRILIC FLUORIDES (60, 61)

Experimental efforts to replace chlorine in the phosphonitrilic chlorides by fluorine have led to some rather unusual results. Interaction of ammonium fluoride with phosphorus pentachloride results in the formation of ammonium hexafluorophosphate (1). Reaction of the trimer with silver fluoride under varying conditions yields products of indefinite composition. However, if lead fluoride and the trimeric chloride are heated together at temperatures between 130° and 180°C., a liquid mixture is obtained which on distillation yields a colorless distillate having a peculiar odor resembling that of hydrogen cyanide, boiling at 106°C., and melting at -12.4° to -12.1°C. This compound was shown by analysis and molecular-weight determinations to be the tetra(phosphonitrile) dichlorohexafluoride,  $P_4N_4Cl_2F_6$ . In the vapor state the molecular weight decreases with rising temperature, indicating that depolymerization takes place, possibly in accordance with the equation:



If the original material is heated in a copper bomb (for 17 hr.) at 300°C., a colorless rubber-like mass forms. This elastomer is very much less stable than the corresponding one obtained from the chlorides, since it can be completely depolymerized to give volatile products merely by heating over a low flame.

In addition to the above compound another product is obtained, boiling at 130.5°C., melting at -25.2° to -24.9°C., and having a composition corresponding to the formula  $P_4N_4Cl_4F_4$ . This substance also appears to dissociate into simpler units, possibly  $P_2N_2Cl_2F_2$ , when heated in the vapor state to temperatures between 207° and 302°C. When the substance is heated under pressure at 300°C. an elastomer is obtained which, when decomposed at 400°C., breaks down into two liquid fractions, one boiling at 115-117°C., the other at 140-142°C. Molecular-weight determinations and analyses indicate that the first is the compound  $P_3N_3Cl_2F_4$ , while the second is  $P_3N_3Cl_4F_2$ .

If the reaction between  $(PNCl_2)_3$  and  $PbF_2$  is carried out in a glass apparatus, a crystalline product, melting at 32.5°C., is obtained, the composition of which corresponds to the formula  $P_3N_3F_6 \cdot 2HF \cdot 2H_2O$ . The formation of this compound is ascribed to the presence of moisture in the reaction mixture.

#### H. MISCELLANEOUS REACTIONS

At a temperature of 110-115°C. trimeric phosphonitrilic chloride reacts slowly with phenylmagnesium bromide in anhydrous toluene in an atmosphere of hydrogen. After purification of the hydrolyzate, a product is obtained which fuses at 230°C. and corresponds in composition and molecular weight to the hexaphenyl triphosphonitrile,  $[PN(C_6H_5)_2]_3$  (53, 54). Attempts to prepare alkyl derivatives by reaction of the trimer with zinc ethyl were not successful (9, 10, 64, 65). Reaction with bromobenzene and sodium also gave no definite compound (64, 65).

Couldridge (9, 10) attempted unsuccessfully to replace chlorine in the phosphonitrilic halides by reaction with silver cyanide. Wissemann (75) claims to have prepared the pyridine and quinoline addition compounds of the phosphonitrilic cyanide by reaction of the trimer in either solvent with hydrogen cyanide.

Action of sodium, of sodium amalgam (9, 10), and of potassium (25, 27) causes decomposition. Renaud (52) found the reaction between the trimer and sodium at 120°C. to be quite vigorous. Some sodium chloride is formed, but the residual product still contains considerable chlorine.

Zinc dust reacts with the phosphonitrilic chlorides dissolved in glacial acetic acid to give some phosphine (64, 65).

The trimer of phosphonitrilic chloride also forms unstable addition compounds with sulfur trioxide and nitrogen dioxide (4). At 150°C. the sulfur trioxide compound decomposes to give chlorine, nitrogen, sulfur dioxide, thionyl chloride, and sulfuryl chloride, together with a soluble vitreous material.

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