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ADVANCES IN THE FIELD OF PHOSPHONITRILE POLYMERS

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I. INTRODUCTION

Hetero-chain organic-inorganic polymers have been widely studied lately. Of particular importance amongst them are organophosphorus compounds which possess a number of valuable properties, such as incombustibility, and fire- and heat-resistance.

Organophosphorus polymers containing the $-P=N-$ bond are especially interesting, owing to their heat-resistance. The compounds of this type which have been studied the most thoroughly are phosphonitrilic chloride and the polymers based on it; these have high elasticity and are known in the literature as "inorganic rubber"[1-6].

At present a homologous series of phosphonitrilic polymers has been prepared, proceeding from tri- and tetra-mer to macromolecular compounds. They have a number of important properties and are used industrially, *e.g.* in the electrical industry, as additives to lubricating oils, in fire-proofing textiles, and so on. The applications of phosphonitrilic chloride and its polymers have been reviewed by Rémond[4].

Polymeric phosphonitrilic chlorides are a class of inorganic hetero-chain linear macromolecular compounds which can exist as polymers both in the liquid and solid state[7].

Polymers which contain the $-P=N-$ bond and various organic branching groups are classified as organic-inorganic polymers. This review deals with phosphonitrilic derivatives and the polymers based on them.

II. METHODS OF PREPARATION

1. Phosphonitrilic Halides

The basic method for the preparation of phosphonitrilic chloride is the reaction of phosphorus pentachloride with ammonium chloride:

$$PCl_5 + NH_4Cl \rightarrow PNCl_2 + 4HCl.$$

This reaction can be carried out either in the presence or absence of organic solvents[8-11]. Audrieth, Steiman, and Toy[1] and Rémond[4] have reviewed the methods of preparation of phosphonitrilic chloride.

Liebig[12], in 1834, was the first to react phosphorus pentachloride with gaseous ammonia in an effort to prepare the amides of phosphoric acid. However, instead of the expected amides he obtained small quantities of a compound which was stable towards hydrolysis.

A number of workers showed later[13-16] that the compound obtained by Liebig was phosphonitrilic chloride and

that its molecular formula was that of a trimer $-(PNCl_2)_3$. In order to prepare phosphonitrilic chloride, Stokes[8-10] reacted phosphorus pentachloride with ammonium chloride at 150°–200°, in a sealed tube. Liberation of hydrogen chloride during this reaction rendered the method dangerous and inconvenient. Stokes[8-10] isolated and characterised the cyclic trimer and tetramer of phosphonitrilic chloride.

Schenk and Römer[11] improved this method by using an autoclave instead of a sealed tube. A thorough study of this reaction showed that the yield of cyclic trimer and tetramer depended upon the weight ratio of the starting components, reaction temperature, and duration of heating[17]. The most favourable conditions, yielding about 95% of cyclic trimer, were: 52.1 g of phosphorus pentachloride and 50–100 g of ammonium chloride, heated 4–6 h at 145°–160°.

The use of organic solvents in this reaction is very advantageous, providing mild homogeneous conditions and minimising explosion risks. Schenk and Römer[11] used 1,1,2,2-tetrachloroethane as solvent. If the reaction is carried out with an excess of ammonium chloride at 135° for 20 h, a mixture of polymeric phosphonitrilic chloride homologues is obtained, consisting of 75% of trimer and 25% of tetramer.

Teja and Peters[18] recommend the use of $AlCl_3$, PCl_5, or quinoline as catalysts to obtain polymeric phosphonitrilic chloride homologues with polymerisation coefficient $n = 7$ or more. Under such conditions the yield of phosphonitrilic chloride heptamer reaches 55–60%.

The molar ratio of the starting components, the reaction temperature, and the duration of heating have the same significant effect upon the yield when organic solvents are used.

Yokoyama and Yamada[19] showed that when the temperature, duration of heating, and the excess of ammonium chloride are increased, the yield of cyclic trimer decreases owing to side reactions. The maximum yield of phosphonitrilic chloride trimer (40%) is obtained at 132°–134°, with a molar ratio of PCl_5 to NH_4Cl of 1 : 1.15.

If phosphorus pentachloride ammonolysis is not complete, large yields of linear polymers of the composition $(PNCl_2)_n.PCl_5$, which are insoluble in petroleum ether, are obtained. The same linear polymers are formed by the action of phosphorus pentachloride on cyclic polymers[20]. Individual members of this series have not been prepared in the pure state as they are unstable to heat and easily split off phosphorus pentachloride even in slightly polar solvents.

The linear polymers differ from the cyclic ones in being highly polar and more reactive. Polymers with small n are converted to a mixture of cyclic polymers when treated with ammonium chloride. When $n > 2$, chain formation predominates over cyclisation.

Yokoyama and Yamada[19] studied the effect of different solvents, such as chlorobenzene, chloroform, and carbon tetrachloride, on the synthesis of phosphonitrilic chlorides, and showed that no reaction took place in chloroform and carbon tetrachloride. Chlorobenzene can be used instead of tetrachloroethane. It is probable that the most important factor in the synthesis of phosphonitrilic chloride is not the nature of the solvent, but the reaction temperature.

The mechanism of the reaction of phosphorus pentachloride with ammonium chloride is still incompletely understood. Paddock and Searle[20] suggest that the reaction proceeds in stages, the first stage consisting of the formation of ammonium hexachlorophosphate,

$$NH_4Cl + PCl_5 \rightarrow NH_4PCl_6,$$

which subsequently decomposes into NH_2PCl_4 or, more probably, into $NH=PCl_3$.[1]

The latter compound can react either with itself, or with PCl_5, to yield $PCl_4-N=PCl_3$:

$$\underset{(I)}{PCl_5 + NH=PCl_3} \rightarrow \underset{(II)}{PCl_4N=PCl_3} + HCl.$$

Compounds (I) and (II) are the first members of the two series of polymers: $H(NPCl_2)_nCl$ and $PCl_4(NPCl_2)_nCl$. The higher polymers are formed by the successive reaction of such products with the starting components or with the intermediate compounds.

Among other methods of preparation of phosphonitrilic chlorides, the reaction of phosphorus pentachloride with NH_2HgCl may be noted[1]:

$$PCl_5 + NH_2HgCl \rightarrow PNCl_2 + HgCl_2 + 2HCl.$$

Moureu and Wetroff[21,22] showed that at temperatures above 700°, phosphorus nitrides react slowly with chlorine to form phosphonitrilic chlorides.

$$PN + Cl_2 \rightarrow PNCl_2.$$

Phosphonitrilic bromides and some phosphonitrilic halides containing both bromine and chlorine, can be prepared, in like manner to phosphonitrilic chloride, by the reaction of phosphorus pentabromide or pentachloride with ammonium bromide in organic solvents[23,24].

To prepare phosphonitrilic halides containing both bromine and chlorine, Rice, Daasch, Holden, and Kohn[23] reacted a mixture of phosphorus trichloride and bromine, or a mixture of phosphorus tribromide and pentachloride, with ammonium chloride. As a result they obtained the following phosphonitrilic halides: $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$, and $P_3N_3Cl_2Br_4$. Phosphonitrilic fluorides and fluorochlorides have also been reported in the literature[5,26-32].

Audrieth and his collaborators[1] did not succeed in obtaining a phosphonitrilic derivative by the reaction of phosphorus pentachloride with ammonium fluoride; in this reaction ammonium hexafluorophosphate was formed instead.

The reaction of trimeric phosphonitrilic chloride with silver fluoride resulted in products of indeterminate composition. By heating lead fluoride with phosphonitrilic chloride at 130°–180°, a mixture of liquid products was obtained, from which the following compounds were isolated: $P_4N_4Cl_2F_6$, $P_4N_4Cl_4F_4$, and $P_3N_3Cl_4F_2$,[1] and $P_3N_3F_6.2HF.2H_2O$.

Phosphonitrilic fluorides are also formed by the reaction of phosphonitrilic chloride (trimer and tetramer) with potassium fluorosulphinate at 120°–125°:

$$PNCl_2 + 2KSO_2F \rightarrow PNF_2 + 2KCl + SO_2.$$

The degree of polymerisation of the phosphonitrilic halide remains unaltered[25].

Of particular note among the new methods for the synthesis of phosphonitrilic fluorides is that of Mao, Dresdner, and Young[28], whereby $(PNF_2)_3$ and $(PNF_2)_4$ are prepared by heating P_3N_5 with nitrogen trifluoride or CF_3SF_5 to 700°.

Phosphonitrilic isothiocyanates are also known. Otto and Audrieth[33] prepared them by reacting phosphonitrilic chloride trimer with potassium isothiocyanate in acetone solution.

TABLE 1. Phosphonitrilic halides.

Formula	M.p., °C	B.p., °C at 13 mm Hg	B.p., °C at 760 mm Hg	Reference
$(PNCl_2)_3$	114.0	127	265	1, 6, 12, 17, 34–38
$(PNCl_2)_4$	123.0	188	328.5	1, 6, 37, 38
$(PNCl_2)_5$	40.5	223	polymerises	6, 37
$(PNCl_2)_6$	91.0	261	»	6, 37
$(PNCl_2)_7$	−18.0	289	»	6, 37
$(PNF_2)_3$	26.8	—	50.9	25, 27–29, 34–36
$(PNF_2)_4$	30.4	—	89.7	25–29, 34–36
$(PNF_2)_5$	—	—	120.1	37
$(PNF_2)_6$	—	—	147.2	37
$(PNF_2)_7$	—	—	170.7	37
$(PNF_2)_8$	—	—	192.8	37
$(PNF_2)_9$	—	—	214.4	37
$(PNF_2)_{10}$	—	—	230.8	37
$(PNF_2)_{11}$	—	—	246.7	37
$(PNF_2)_{18}$	—	—	—	6, 35
$(PNBr_2)_3$	191.0	—	—	24
$(PNBr_2)_4$	202.0	—	—	24
$P_3N_3Cl_5Br$	122.5	—	—	23
$P_3N_3Cl_4Br_2$	134.5	—	—	23
$P_3N_3Cl_4F_2$	165.5	—	—	23
$P_4N_4Cl_2F_6$	−12.1	—	106	1
$P_4N_4Cl_4F_4$	−24.9	—	130.5	1
$P_6N_7Cl_9$	237.0	—	—	34
$[PN(CNS)_2]_3$	42.0	—	—	33

All phosphonitrilic halides known at present are listed in Table 1.

As already mentioned, the reaction of phosphorus pentachloride with ammonium chloride yields a mixture of polymeric phosphonitrilic halide homologues, with the degree of polymerisation n = 3 or more. Crystallisation, sublimation, and distillation are usually employed for the separation of the mixtures.

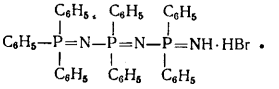
Trimer and tetramer are usually separated from the higher polymers by extraction with cold benzene[8–10], in which the latter are soluble (n = 5, 6, 7 or more). This method, however, is not suitable when large quantities of the higher polymers are present, as the viscosity of the solution increases considerably and makes filtration difficult. Glacial acetic acid was also used for the separation of trimer and tetramer from the higher polymers[1]. Steam distillation is recommended for the separation of the trimer only[1].

Good results were obtained in the separation of phosphonitrilic chlorides by gas chromatography. Gimblett[38] used a column packed with 30% E.301 Silicone on Celite 545, using nitrogen as carrier gas, at a flow rate of 1.5 litre h^{-1}.

2. Alkyl- and Aryl-Phosphonitriles

The synthesis of alkyl- and aryl-phosphonitriles can be carried out either by replacing the chlorine in phosphonitrilic chloride with alkyl or aryl radicals using the Grignard and Friedel-Crafts reactions (for phenyl radicals[2,39–42]), or by the reaction of trichlorodialkyl- and trichlorodiaryl-phosphoranes with ammonia[43–45]. Until recently the former method was the more widely used.

In 1929 Rosset[39] was the first to prepare hexaphenyltriphosphonitrile, from trimeric phosphonitrilic chloride and phenylmagnesium bromide, in molar ratio 1 : 4. The reaction was carried out in toluene at 110°–115°, and yielded 20–25% of hexaphenylphosphonitrile. Bode and Bach[40] repeated Rosset's experiments and made a thorough study of this reaction, including the effects of the component ratio, the temperature, and the nature of the solvent. In all cases they obtained the compound which corresponded to the formula $(C_6H_5)_7N_3P_3H.HBr$, m.p. 185°–187°, and to which they ascribed the following structural formula:



The yield of the cyclic trimer, hexaphenyltriphosphonitrile, was very low, regardless of the reaction conditions.

By allowing tetrameric phosphonitrilic chloride to react with phenylmagnesium bromide, Bode and Thamer[41] obtained two tetraphenyl derivatives, m.p. 176° and 205°, and two octaphenyl derivatives, m.p. 230° and 310°, which differed in their fluorescence.

In their attempt to prepare arylphosphonitriles, Bode and Bach[40] also allowed phosphonitrilic chloride to react with benzene in the presence of $AlCl_3$, and obtained products incompletely substituted by phenyl radicals. The quantity of the catalyst had no effect on the reaction rate. With ratios of aluminium chloride to trimeric phosphonitrilic chloride of 2 : 1 and 6 : 1, tetrachlorodiphenyltriphosphonitrile was obtained, m.p. 92.5°.

It is clear from these examples that Grignard and Friedel-Crafts' reactions are unsatisfactory for the preparation of aryl phosphonitrilic derivatives. Recent efforts of research workers have therefore been directed towards the alternative synthetic route, namely the reaction of tetrachloroarylphosphoranes, trichlorodiaryl-, and trichlorodialkyl phosphoranes with ammonia.

Bode and Bach[40] prepared the non-pairwise-substituted phenyl derivatives of trimeric phosphonitrilic chloride by reacting tetrachlorophenylphosphorane with ammonium chloride at 140° in tetrachloroethane. Haber, Herring, and Lawton[43] reacted trichlorodiphenylphosphorane with ammonium chloride in tetrachloroethane solution at 130°–135° and obtained very low yields of cyclic phosphonitrile derivatives (trimer and tetramer).

In the reaction in liquid ammonia, a white crystalline product was obtained, which upon heating under reduced pressure at 275° was converted in 65% yield to a polymer mixture. On fractional crystallisation, this product yielded 48% of cyclic tetramer and 7% of cyclic trimer. Searle[44] used this reaction for the synthesis of the alkyl derivatives of phosphonitrile. He reacted the components in tetrachloroethane at 120°–200°, and obtained very low yields of cyclic trimer and tetramer, and a mixture of linear polymers as the main reaction product. The linear polymers were converted to cyclic products in 70–75% yield on boiling with triethylamine or ammonium chloride in chloroform solution.

Korshak, Gribova, and their collaborators[45] reacted trichlorodibutyl- and trichlorodiethyl-phosphorane with ammonium chloride in dichlorobenzene solution and isolated linear products in which the molar ratio of phosphorus to nitrogen was 3 : 2 and 3 : 3 respectively.

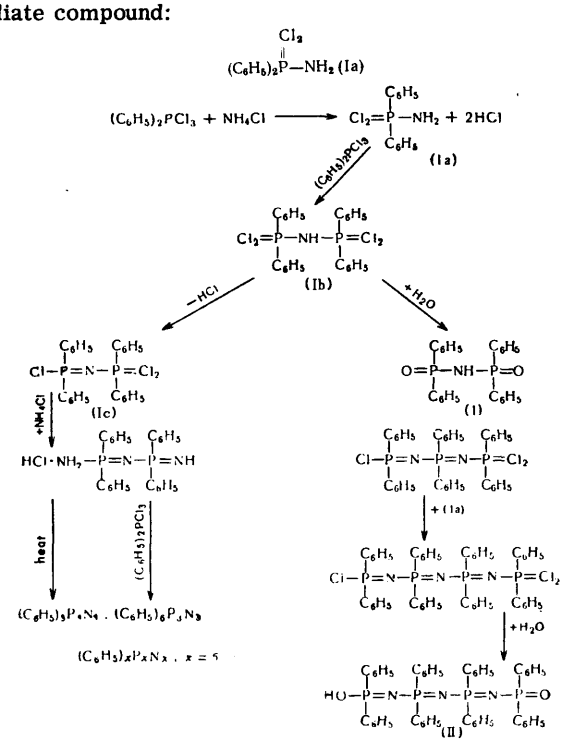
In order to study the mechanism of the reaction of trichlorodiaryl- and trichlorodialkyl-phosphorane with ammonium chloride in organic solvents, Korshak, Gribova, Artamonova, and Bushmarina [45] reacted trichlorodiphenylphosphorane with ammonium chloride in chlorobenzene or dichlorobenzene at 120°–180° for 8–20 h, with various molar ratios of the reactants. They carried out the reaction with gaseous ammonia in chlorobenzene at 0°.

The reaction of equimolar quantities of trichlorodiphenylphosphorane and ammonium chloride in chlorobenzene solution at 120°–125° for 12 h, results in 60% of a compound, m.p. 270°–272°, which corresponds to the formula $(C_6H_5)_4 \cdot P_2O_2NH$ (I). On hydrolysis it yields diphenylphosphinic acid. This reaction, carried out for 12–15 h at 160°–170° in dichlorobenzene, yields 70% of a compound which, on being recrystallised from benzene and alcohol, melts at 171°–171.5°. On the basis of analysis for the elements and ebullioscopic molecular weight determination in benzene, the formula ascribed to this compound is $(C_6H_5)_8 \cdot P_4N_3O_2H$ (II).

The reaction at 175°, for 20 h, of trichlorodiphenylphosphorane and ammonium chloride in molar ratio 1 : 5 results in the formation of 70% of octaphenyltetraphosphonitrile (III) and another compound which, after recrystallisation from dioxane, melts at 233°–235°, and whose formula is $(C_6H_5)_4P_2N_3H_4Cl$ (IV): the compound (IV) is formed in 60% yield in the reaction of trichlorodiphenylphosphorane with gaseous ammonia at 0° in organic solvents. It is unstable to heat, and when heated at 3–5 mm Hg and 270°–400° for 14 h, it is converted to octaphenyltetraphosphonitrile.

The authors assume the reaction to proceed in three main steps:

1. Chain initiation occurs as a result of the reaction of the NH_2 group with a chlorine atom in the trichlorophenylphosphorane molecule, giving rise to an intermediate compound:



2. The chain growth is thus a stepwise reaction, each stage giving rise to an independent compound. At the beginning the reaction consists basically of the interaction of the starting molecules with each other or with the molecules of the compounds formed, as is usual in polycondensations. Accordingly, the reaction product is a mixture of molecules with differing chain lengths. In principle, the chain growth can continue until all the reactive groups are used up. In fact, however, only small chains are formed at this stage (pentamers and hexamers) and the eight-membered cyclic product.

3. Chain rupture in this reaction is obviously connected with the tendency to form very stable eight-membered cyclic products. The predominant formation of the cyclic tetramer rather than the trimer is evidently to be accounted for by steric factors.

All the alkyl and aryl derivatives of phosphonitrile known at present are listed in Table 2.

3. Phosphonitrilamides and Their *N*-Substituted Derivatives

The synthesis of phosphonitrilamides from phosphorus pentachloride and gaseous or liquid ammonia in organic solvents is very widely known [1,6,46–50]:

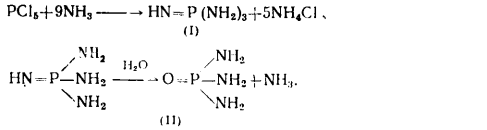
$$3PCl_5 + 24NH_3 \rightarrow [PN(NH_2)_2]_3 + 15NH_4Cl.$$

So is also the preparation from a solution of phosphonitrilic chloride (trimer or tetramer) and liquid ammonia [46]:

$$(PNCl_2)_3 + 12NH_3 \rightarrow [PN(NH_2)_2]_3 + 6NH_4Cl.$$

In the reaction of phosphorus pentachloride with liquid ammonia in different organic solvents a mixture of the polymeric homologues of phosphonitrilamides is usually formed [51].

Becke-Goehring and Niedenzu [50] studied the mechanism of the reaction of phosphorus pentachloride with ammonia in the presence of small quantities of water and suggested the following reaction scheme:

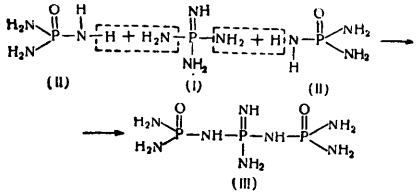


The triamide of imidophosphoric acid (I) formed in the early stages of the reaction is easily hydrolysed to phosphoramide (II). In the presence of very small quantities

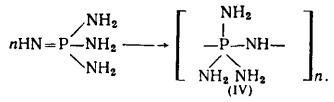
TABLE 2. Alkyl and aryl derivatives of phosphonitrile.

Formula	M.p., °C	Reference	Formula	M.p., °C	Reference
$(C_6H_5)_2P_3N_3Cl_4$	92.5	40	$(C_6H_5)_4P_2NO_2H$	270–272	45
$(C_6H_5)_3P_3N_3H \cdot HBr$	185.0	40	$(C_6H_5)_4P_2N_3H_3Cl$	233–235	45
$(C_6H_5)_3P_3N_3Cl(OH)_2$	294.0	40	$(C_6H_5)_6P_3N_3$	228–232	40, 43, 44
$(C_6H_5)_8P_4N_4$	310.0	41, 43, 45	$(CH_3)_6P_3N_3$	195–196	44
$(C_6H_5)_8P_4N_4$	230.0	41	$(CH_3)_8P_4N_4$	163–164	41
$(C_6H_5)_4P_4N_4Cl_4$	176.0	41	$(C_4H_9)_6P_3N_2ClO$	171–172	45
$(C_6H_5)_4P_4N_4Cl_4$	205.0	41	$(C_4H_9)_6P_3N_2O_2H$	86–87	45
$(C_6H_5)_8P_4N_3O_2H$	171–171.5	45	$(C_2H_5)_6P_3N_3HCl$	132–134	45

of water, the unhydrolysed compound (I) condenses with compound (II), forming the amide of triimidotriphosphoric acid (III):



Compound (I) can also polymerise:



The hydrolysis of the polymer (IV) results in the formation of ammonium polydiimidophosphate:

$$[-P(NH_2)_3-NH-]_n \rightarrow [-P(NH_2)_2(OH)-NH-]_n \rightarrow$$
$$\rightarrow [-P(NH)(ONH_4)-NH-]_n.$$

By carrying out the reaction of PCl_5 with an excess of liquid ammonia at -50° in chloroform solution, Audrieth and Sowerby obtained 36% of phosphonitrilamide trimer[46].

Another method for the synthesis of phosphonitrilamides is the ammonolysis of phosphonitrilic chlorides (trimer and tetramer). This reaction is slow, and, as shown by Audrieth and Sowerby[46], the complete substitution of chlorine atoms takes 48 h if an excess of liquid ammonia is used and the reaction is carried out under pressure at room temperature. The same result is obtained by slowly adding an ether solution of phosphonitrilic chloride to an excess of liquid ammonia at room temperature with vigorous agitation[46].

The products of partial ammonolysis are obtained by the reaction of aqueous or gaseous ammonia with the ether solution, or gaseous ammonia with the benzene solution of phosphonitrilic chloride trimer[1,6]. From the mixture of products obtained in this way, a diaminotetrachloro derivative, $P_3N_3(NH_2)_2Cl_4$, was isolated[6].

The ammonolysis of the ether solution of phosphonitrilic chloride tetramer with ammonia yields a mixture of products: diaminohexachlorophosphonitrile[52], tetraaminotetrachlorophosphonitrile[52], and phosphonitrilamide tetramer[46]. As in the case of phosphonitrilic chloride trimer, the reaction with liquid ammonia is very slow[1,46].

It can be seen from these examples that the ammonolysis of phosphonitrilic chlorides proceeds in stages: very harsh reaction conditions are required for the complete ammonolysis to take place.

N-Substituted phosphonitrilamides are prepared by ammonolysis of phosphonitrilic chlorides (trimer and tetramer) with aliphatic and aromatic amides[1,6,47,48,53,54,55].

$$(PNCl_2)_3 + 12RNH_2 \rightarrow [PN(NHR)_2]_3 + 6RNH_2HCl.$$

The reaction can be carried out either in the presence or absence of organic solvents[48]. Complete substitution of chlorine atoms in phosphonitrilic chloride is only achieved

TABLE 3. Phosphonitrilamides and their *N*-substituted derivatives.

Formula	M.p., °C	Reference	Formula	M.p., °C	Reference
$P_3N_3(NH_2)_6$	161.5	1,46,47	$P_3N_3(NH-C_6H_4-CH_3)_6$	249	48
$P_3N_3Cl_4(NH_3)_3$	—	10	$P_3N_3(NH-C_6H_4)_6$	241	1
$P_3N_3Cl_4[N(CH_3)_2]_2$	98—103	46,47,53	CH_3		
$P_3N_3Cl_3[N(CH_3)_2]_3$	107	47			
$P_3N_3Cl_2[N(CH_3)_2]_4$	104	53	$P_3N_3Cl_4[(NH_2)C_6H_4CH_3]_2$	211	48
$P_3N_3[N(CH_3)_2]_6$	104	53	$P_3N_3(N<CH_2-CH_2>CH_2)_6$	231—266	1,48
$P_4N_4[N(CH_3)_2]_8$	237	53			
$P_3N_3Cl_3[N(CH_3)_2](NH_2)_2$	87	47	$P_3N_3Cl_4[(NH)_2C_6H_4]$	350	52
$P_3N_3Cl_2(NHCH_3)_2(NH_2)_2$	140	47	$P_3N_3(NHNH-C_6H_4)_6$	200	1
$P_3N_3[N(CH_3)_2]_2[NHCH_3]Cl_3$	82	47			
$P_3N_3(NH_2)_2(NHCH_3)_4$	204	47	$P_3N_3Cl_2(C_6H_6)_2(NH_2)_2$	162	48
$P_3N_3(NH_2)_2(NHCH_3)_4$	161.5	47	$P_3N_3Cl_2(C_6H_5)_2(NHC_6H_5)_2$	193	48
$P_3N_3(C_6H_5)_2(NH_2)_4$	275	47	$P_3N_3(NH_2)_2(C_6H_5)_2(NHC_6H_5)_2$	218	48
$P_3N_3(C_6H_5)_2[N(CH_3)_2]_4$	120	47	$P_3N_3(NH_2)_2(NHC_6H_5)_4$	256	48
$P_3N_3(C_6H_5)_2(NHCH_3)_4$	174	47	$P_3N_3(NH_2)_2(NHC_6H_5)_2\cdot(-NH-C_6H_4-NH-)_2$	160	48
$P_3N_3(C_6H_5)_2(NHCH_3)_2(NH_2)_2$	140	47			
$P_3N_3(C_6H_5)_2(NH_2)_2[N(CH_3)_2]_2$	137	47			
$P_3N_3Cl_4[N(C_2H_5)_2]_2$	134	53	$P_3N_3(N_3)_6$	oil	56
$P_3N_3Cl_3[N(C_2H_5)_2]_3$	162	6	$P_3N_3(NHNH_2)_6$	360	57
$P_3N_3(NHC_2H_5)_6$	119	6	$P_3N_3(NSC)_6$	42	33
$P_3N_3Cl_4(NHCH_2CH_2NH_2)_2$	188	48	$P_3N_3(NC_6H_5)_3$	—	54,57
$P_3N_3Cl[NHCH_2CH(CH_3)_2]_2$	—	1	$P_3N_3Cl_4(NHR)_2$	—	1
$P_3N_3Cl_4(NHC_4H_9)_2$	—	6	where RNH_2 = ester of amino-acid		
$P_3N_3Cl_4[N(C_6H_{11})_2]_2$	200	1,53	$P_4N_4(NH_2)_2Cl_6$	—	52
$P_3N_3(NHC_6H_{11})_6$	166	50	$P_4N_4(NH_2)_4Cl_4$	—	52
$P_3N_3Cl_2(NH-C_6H_5)_4$	191	48	$P_4N_4(NH_2)_2(NH_2)_2Cl_2$	—	52
$P_3N_3(NH-C_6H_5)_6$	268	1	$P_4N_4(NHC_6H_5)_8$	250	1
$P_3N_3Cl_2(NH-C_6H_4-CH_3)_4$	174	48	$P_3N_3(NHN=CHC_6H_5)_6$	250 (decomp)	57
			$P_3N_3(NHN=CHC_6H_4OH)_6$	255	57

under harsh reaction conditions[6]. The easiest to prepare are the disubstituted amino derivatives.

The preparation of aromatic phosphonitrilamides requires higher temperatures[48]. The reaction with aliphatic amines can occur under milder conditions if organic solvents are used. The *N*-substituted phosphonitrilamides reported in the literature are listed in Table 3. A large number of these compounds have been prepared lately.

It was believed until recently that the substitution at each phosphorus atom in phosphonitrilic chloride occurs in pairs. Becke-Goehring[47], however, showed that in the reaction of phosphonitrilic chloride with amines, substitution can occur simultaneously at different phosphorus atoms.

Ray and Shaw[53] obtained di- and tri-substituted phosphonitrilamides using secondary amines, diethylamine and dicyclohexylamine. With primary amines, ethylamine and cyclohexylamine, they succeeded in preparing the completely substituted products. In the reaction of phosphonitrilic chloride with diethylamine and dicyclohexylamine, the substitution obviously takes place at different phosphorus atoms. The rate of substitution in phosphonitrilic chloride and its derivatives depends on several factors, such as nucleophilic activity of the amine, steric effects, and the polarity of the substituent[48,53]. It should be noted that under identical conditions, the substitution in phosphonitrilic chloride tetramer proceeds faster than in the trimer[53]. Diamines, as well as monoamines, react with phosphonitrilic chloride, forming *N*-substituted phosphonitrilamides[6].

In the reaction with ethylenediamine, two chlorine atoms are substituted by *N*-aminoethylamino groups[6]. The reaction with aromatic diamines is similar[48]. If the substitution of halogen atoms attached to phosphorus does not proceed pairwise, di- and tri-substituted phosphonitriles are obtained in different stereoisomeric forms.

Audrieth[6] suggested the possible stereoisomers of the phosphonitrile trimer (see Fig. 1).

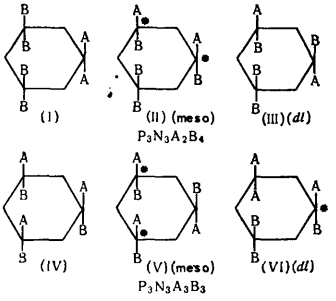
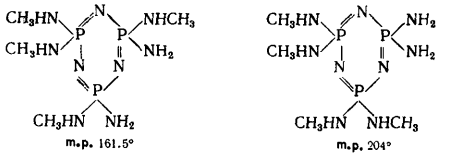


Fig. 1. Structural and stereoisomers of di- and tri-substituted phosphonitriles (asymmetric phosphorus atoms are indicated by an asterisk).

Becke-Goering[47] obtained two isomers, m.p. 161.5° and 204°, by the reaction of tetrachlorodiaminophosphonitrile and dichlorodiaminodimethylaminophosphonitrile, respectively, with methyl amine.



The products from the reaction of phosphonitrilic chloride and hydrazine[57] or sodium azide[56] also belong to *N*-substituted phosphonitrilamides.

The phosphonitrile trimer and tetramer react with esters of amino-acids yielding products in which some of the halogens are replaced with amino-ester radicals[1]. The trimer usually yields disubstituted derivatives, and the tetramer, tetrasubstituted ones.

4. Esters of Triphosphonitrilic Acids

The reaction of phosphonitrilic chloride — trimer and tetramer — with alcohols and phenols has been thoroughly studied[1,58-62]. Wissemann[1] studied the reaction with alcohols both in the presence and absence of proton acceptors such as pyridine, and showed the reaction to proceed in the following manner:

$$PNCl_2+2ROH \longrightarrow [PN(OR)_2]+2HCl\,, \quad PN(OR)_2+HCl \longrightarrow PN\begin{matrix}OR\\OH\end{matrix}+RCl$$

$$PNCl_2+2ROH \longrightarrow PN\begin{matrix}OR\\OH\end{matrix}+RCl+HCl\,, \quad 2PN\begin{matrix}OR\\OH\end{matrix} \longrightarrow O\begin{matrix}PN(OR)\\PN(OR)\end{matrix}+H_2O$$

$$2PN(OR)_2 \longrightarrow O\begin{matrix}PN(OR)\\PN(OR)\end{matrix}+R_2O.$$

The trimer and tetramer react with absolute methanol to form partially substituted products, the incomplete esters of tri- and tetra-phosphonitrilic acids.

Dishon[59] developed a method for the synthesis of phosphonitrilic esters in the presence of a proton acceptor at 0°. Hexamethyl and hexabutyl esters of triphosphonitrilic acid were prepared by this method. Phosphonitrilic esters can also be prepared by reacting phosphonitrilic chloride with alcoholates. In this way, Rätz and Hess[61] prepared the hexaethyl ester of triphosphonitrilic acid.

Aromatic esters of phosphonitrilic acids can be prepared by reacting phosphonitrilic chlorides with phenols, in the presence of pyridine[1], or with sodium phenoxide[62].

Table 4 lists all the phosphonitrilic esters known at present.

TABLE 4. Esters of tri- and tetra-phosphonitrilic acids.

Formula	M.p., °C	Ref.
$P_3N_3(OCH_3)_6$	127—128/0.1 mm	59
$P_3N_3(OC_2H_5)_6$		61
$P_3N_3Cl_2(OC_2H_5)_4$		61
$P_3N_3(OC_4H_9)_6$	170—171/0.3 mm	59
$P_3N_3(OCH_2—CH=CH_2)_6$	—	63
$P_3N_3[(OH)(OCH_3)]_6$	—	1
$P_4N_4[(OH)(OCH_3)]_8$	—	1
$P_3N_3(OC_6H_5)_6$	—	62
$P_3N_3(OC_6H_4CH_3)_6$	—	62
$P_3N_3(OC_6H_4NO_2)_6$		
$P_3N_3(OC_6H_4CH_2C_6H_5)_6$	—	62
$P_3N_3Cl_2(CH_2OCHOHCH_2OH)_2(OCH_3)_2 4C_5H_5N$	—	62
$P_4N_4Cl_2(CH_2OCHOHCH_2OH)_4(OCH_3)\cdot 4C_5H_5N$	—	1
$[PN(CCH_3)(OC_{10}H_{17})]$	—	1
$P_4N_4(OCH_3)_8$	41	36
$P_3N_3(OCH_2CHBrCH_2Br)_3$	—	63

5. Macromolecular Phosphonitrile Derivatives

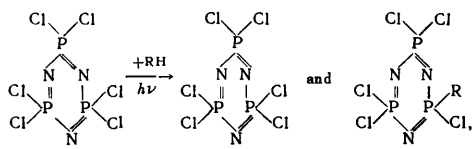
The usual method of preparing macromolecular derivatives of phosphonitrile is by polymerisation. Polymerisation of phosphonitrilic halides has been very widely studied[1,5,6,18,25-32,35,37,62,64-71]. The best known amongst the halogen derivatives of phosphonitrile is polyphosphonitrilic chloride, often called "inorganic rubber". In 1897 Stokes[9] showed for the first time that a mixture of phosphonitrilic chlorides was transformed on heating to 250°–350° into a rubber-like material. The polymerisation of phosphonitrilic halides can be carried out in the presence[66,67] or absence[66,68] of organic solvents.

Patat and Kollinsky[66] studied the polymerisation of phosphonitrilic chloride in the presence of solvents and showed the polymerisation rate to be determined by the reaction temperature, the monomer concentration, and the nature of solvent. During the polymerisation of phosphonitrilic chloride in solvents such as benzene, toluene, xylene, and hexane, at 280°–340°, an excess hydrogen chloride pressure was observed on opening the tube, whilst the viscosity of the solution was only slightly changed, thus indicating a possible reaction between the phosphonitrilic chloride and the solvent, according to the equation[67]

$$n\,RH + (PNCl_2)_m \xrightarrow[O_2]{\sim 300^\circ} P_mN_mCl_{2m-n}R_n + n\,HCl.$$

A more thorough study of the reaction of phosphonitrilic chloride trimer with toluene at 300° during 36 h showed that a mixture of products was formed, from which $P_3N_3Cl_5C_7H_7$, $P_3N_3Cl_4(C_7H_7)_2$, and others were isolated[66].

Dishon and Hirshberg[72] found that in the photochemical reaction of the phosphonitrilic chloride trimer and tetramer with benzene and decahydronaphthalene both soluble and insoluble products were formed. From the soluble part phenyl- and decahydronaphthyl-phosphonitrilic chlorides were isolated:



where R = phenyl and decahydronaphthyl. The percentage of carbon and hydrogen is higher in the insoluble part than in the soluble one, indicating stepwise substitution of chlorine atoms by R radicals.

Polymerisation in hydrocarbons and their derivatives is catalysed by oxygen. Patat and Kollinsky[66] showed that the polymerisation in these solvents did not take place in the absence of oxygen.

Polymerisation of phosphonitrilic chloride was studied in such solvents as tetrachloroethylene, hexachloroethane, tetrabromoethylene, hexachlorobenzene, hexabromoethane, phosphorus trichloride, phosphorus oxychloride, and concentrated H_2SO_4. The best results were obtained in a solution of carbon tetrachloride. In this solvent, colourless, high-molecular-weight polymers were obtained.

When the polymerisation is carried out in solution, its rate is substantially affected by the temperature and the monomer concentration. Fig. 2 shows the dependence of the reaction rate on temperature and concentration. The yield of polymer rises with increase of temperature and concentration. It is clear from Fig. 2 that the rate equation is of the second order. The activation energy is $E = 40 \pm 3$ kcal. The rate constant in carbon tetrachloride is $k = 4 \times 10^{14} \times 10^{-40\,000/2.3RT}$. The rate increases when oxygen is added (see Fig. 3), but when the reaction is carried out in an atmosphere of pure oxygen, a general fall in the reaction rate is observed. The molecular weight of the soluble part of the polymer reached 130 000. Table 5 shows that the molecular weight of the polymer depends on the concentration of the monomer in solution.

Polymerisation of phosphonitrilic chloride can also be carried out in bulk (block polymerisation), without organic solvents[68-71].

Patat and Frömbling[68] studied the kinetics of the polymerisation of phosphonitrilic chloride at 250°–300° in the absence of air. The reaction rate increases with increasing temperature (Fig. 4).

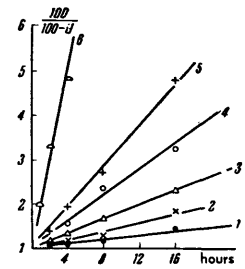


Fig. 2. Polymerisation of triphosphonitrilic chloride in solution at different temperatures: 1) 15% trimer at 270°; 2) 5% trimer at 300°; 3) 10% trimer at 300°; 4) 15% trimer at 300°; 5) 30% trimer at 330°; 6) 15% trimer at 330°. U = percentage conversion.

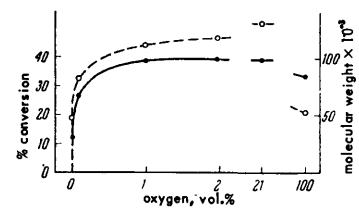


Fig. 3. Effect of oxygen on the polymerisation of triphosphonitrilic chloride in solution.

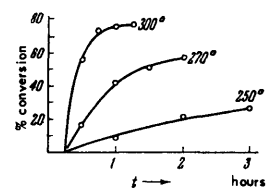


Fig. 4. Block polymerisation of triphosphonitrilic chloride at different temperatures.

This reaction can also proceed in the absence of oxygen, and is of the second order (see Fig. 5). Its activation energy is 42 ± 2.5 kcal. The addition of small quantities of carbon tetrachloride to the system causes a sharp drop in the polymerisation rate. Polymerisation of phosphonitrilic chloride in the absence of air is catalysed by alcohols, organic acids, and other compounds[69].

Konecny and Douglas[69] found that the following compounds initiated the polymerisation of phosphonitrilic chloride at 210° for a reaction time of 48 h (the weight of the catalyst used per gram of the sample is given in brackets): ether (2.1 mg), benzoic acid (10 mg), acetic acid (0.96 mg), chloroacetic acid (20 mg), nitromethane (1.6 mg), ethyl acetate (2.4 mg), n-butyl ether (40 mg), acetone (3.0 mg), methyl ethyl ketone (1.9 mg), ethanol (2.6 mg), di-t-butyl peroxide (2.3 mg), zinc (130 mg), tin (40 mg), and sodium (200 mg).

Fig. 6 shows the effect of different catalysts, ether, ethanol, and tin, on the polymerisation rate of phosphonitrilic chloride trimer. The results of the polymerisation of trimer, tetramer, and their mixture in the presence of 8.4 mg ether are given in Fig. 7, which shows that the trimer polymerises faster than the tetramer.

Manley[73] has shown that the polymerisation of phosphonitrilic chloride is not initiated by high-energy electrons.

The molecular weights of the samples of phosphonitrilic chloride polymers obtained by block polymerisation in the absence of air are of the order 1×10^6; if the polymerisation is carried out in solution in the presence of oxygen, the molecular weight reaches the values $1 \times 10^4 - 1 \times 10^5$.[68] Block polymerisation in the absence of oxygen, as well as polymerisation in solution, gives an insoluble polymer in yields which depend on the reaction temperature and not on monomer concentration or reaction time[68]. With a rise in the polymerisation temperature the yield in macromolecular products is decreased.

Patat and Frömbling[68] showed that thermal polymerisation of phosphonitrilic chloride followed a radical mechanism. The chain initiation is the result of the rupture of the P–N–bond of the trimer ring, which gives rise to a radical-like chain (I) or a chain in which the nitrogen atom is

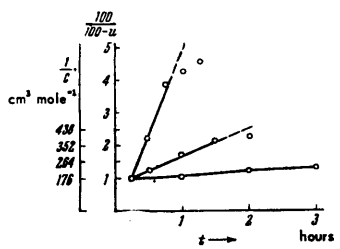


Fig. 5. Kinetics of the block polymerisation of triphosphonitrilic chloride. U = percentage conversion.

TABLE 5. Dependence of the degree of polymerisation on concentration[68].

Concentration %	Mol.wt.
5	45600
10	108000
15	123000
30	131000

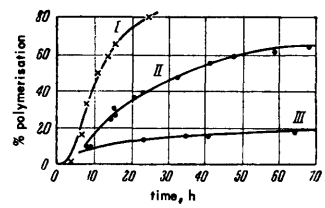


Fig. 6. Polymerisation of phosphonitrilic chloride (trimer, tetramer, and their mixture) catalysed by 8.4 mg of ether: I) trimer; II) trimer-tetramer mixture (initially containing 53% of trimer); III) tetramer.

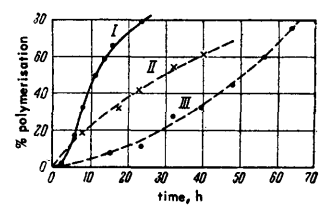
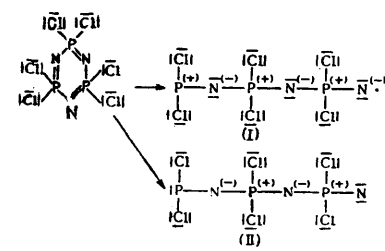


Fig. 7. Catalytic polymerisation of phosphonitrilic chloride trimer in the presence of: I) 8.4 mg of ether; II) 2.6 mg of ethanol; III) 20 mg of tin.

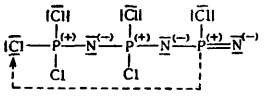
electron-deficient, but in which the phosphorus atom has an octet (II)*.



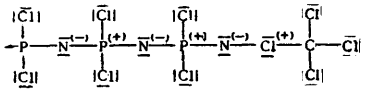
The chain growth is bimolecular, and chain termination is

* The symbolism used in the next four formulae (a line to represent an electron pair is that of Patat and Frömbling[68] (Ed. of Translation).

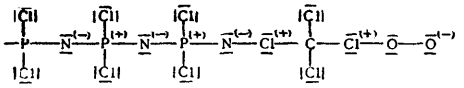
a result of monomolecular rearrangement, leading to the formation of the P=N–bond at the end of the chain:



Patat and Frömbling[68] explain the inhibiting effect of carbon tetrachloride by the deactivation of polymer radicals through the electron deficiency in nitrogen being made up:



The product formed by the addition of carbon tetrachloride to the growing chain becomes unstable in the presence of oxygen, and the polymerisation can consequently start again:



Phosphonitrilic halides containing bromine and fluorine can also polymerise[25,27,32,35]. Seel and Langer[25] found the phosphonitrilic fluoride trimer to polymerise on heating at 350° for 15 h into a rubber-like product. Meyer[27] heated phosphonitrilic fluoride in an autoclave at 260° and obtained a rubber-like polymer. The ability to polymerise remains even if the halogen in phosphonitrilic chloride is replaced by alkyl or aryl groups. Octaphenyltetraphosphonitrile and tetraphenyltetrachlorotetraphosphonitrile polymerise on heating to 300°[41]. Bode and Bach[40] showed that a solid white mass formed on heating diphenyltetrachlorotriphosphonitrile for 3 h at 250° in a sealed tube. Korshak, Gribova, Artamonova, and Bushmarina[45] studied the polymerisation of octaphenyltetraphosphonitrile by heating it in a sealed tube at 320°–500°. The time required for polymerisation varied from 6 to 127 h. The results of these experiments are given in Table 6. It is evident that at 320° the polymerisation of octaphenyltetraphosphonitrile is already taking place, yielding penta- and hexa-mers, which melt at 100°–140°. If the temperature is increased from 320° to 400°, the yield of these products rises from 6.0 to 50.5%. Hexaphenyltriphosphonitrile is formed as well as the mixture of penta- and hexa-mers.

If the heating is continued for 41 h at 400°, a product which does not melt up to 300°–400°, and which is insoluble in ordinary organic solvents, is also formed. Its yield rises with the rise in polymerisation temperature from 400° to 500°. The polymerisation of octaphenyltetraphosphonitrile is a result of the rupture of the eight-membered ring, which is subsequently transformed into a six-membered one.

Searle[44] showed that the methyl derivatives of phosphonitrile trimer do not polymerise to a rubber-like product when heated up to 350°–400°, but are decomposed instead.

Polymeric esters of triphosphonitrilic acid are obtained

TABLE 6. The polymerisation of octaphenyltetraphosphonitrile.

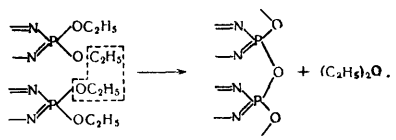
Reaction temperature, °C	Time, h	Composition of polymers, %			
		trimer	tetramer	penta- and hexa-mer mixture	high-melting product
320	62.5	10.4	72.5	6.0	—
320	127.0	20.8	56.5	17.5	—
380	92.5	6.2	51.8	35.7	—
380	117.5	4.6	54.4	40.2	—
400	15.0	9.3	29.5	50.5	—
400	41.0	4.4	9.2	9.4	71.0
420	22.5	1.1	12.7	10.9	67.5
460	10.0	—	—	3.8	93.5
500	6.0	—	—	2.3	97.5

TABLE 7. Alcoholysis of polyphosphonitrilic chloride[75].

Alcohol	% substituted chlorine	% chlorine substituted by alkoxy groups	PO:P	C:H
Ethanol	99.5	79.5	1.59:1	2:5.1
Isopentanol	98.0	63.0	1.26:1	5:11.2
2-Ethylhexanol	88.0	68.5	1.37:1	8:17.1

either by the polymerisation of the cyclic esters (trimer and tetramer) of phosphonitrilic acid, or by the alcoholysis of the phosphonitrilic chloride polymers[1,59–63]. Brown[62] polymerised the hexaphenyl triphosphonitrilic ester by heating it to 320°, and obtained a solid thermoplastic resin.

Polymers of *p*-cresyl- and *o*-, *m*-, and *p*-nitrophenyl esters of triphosphonitrilic acid have been described[62]. According to Brown[62], the nitrophenyl phosphonitrilic esters are easier to polymerise. When heating the hexaethyl triphosphonitrilic ester to 125°, Rätz and Hess[61] observed the separation of ethyl ether and the formation of a polymeric, amorphous, hygroscopic product, barely soluble in water, but forming a strongly acid solution. They suggested the following scheme for this reaction:



Dishon[59] prepared polymers from the hexamethyl, hexabutyl, and hexaallyl esters of triphosphonitrilic acid.

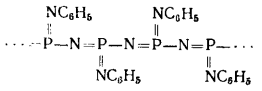
The polymerisation of triphosphonitrilic esters can be conducted in the presence of $AlCl_3$, $ZnCl_2$, and BF_3 as catalysts[61]. These polymers can also be obtained, as indicated above, by the alcoholysis of phosphonitrilic chloride polymers[63,74,76]. Goldschmidt and Dishon[75,76] made a thorough study of the alcoholysis of phosphonitrilic chloride polymers with several aliphatic alcohols in different solvents and in the presence of pyridine as a proton acceptor. Their results are given in Table 7, which shows that, under the stated conditions, the chlorine atoms in polyphosphonitrilic chloride can be almost completely replaced, partly by alkoxy

groups and partly by oxygen. Goldschmidt and Dishon[75] observed a deterioration in the mechanical properties of polymers obtained by treating polyphosphonitrilic chloride with aliphatic alcohols in the presence of pyridine. They explained this by a difference in the properties of the layers of the polyester formed and those of the unreacted polyphosphonitrilic chloride. There is no deterioration in the mechanical properties of the polymer, and the alcoholysis proceeds faster, if carried out in toluene solution with a previously swollen polyphosphonitrilic chloride.

For the preparation of macromolecular phosphonitrilic polyesters soluble in organic solvents, the authors[75] recommended cautious heating of insoluble macromolecular polyesters with tetrachloroethane and other chlorine-containing solvents. The polymer dissolves as the cross-links between the parallel chains of the polymer are destroyed. Soluble phosphonitrilic polyesters are also formed by the alcoholysis of polyphosphonitrilic chloride previously swollen in a solvent.

Hamalainen[74] obtained phosphonitrilic polyesters by treating polyphosphonitrilic chloride with 2,3-dihalogeno alcohols in the presence of pyridine. Esterification of the phosphonitrilic chloride polymer can be carried out with sodium alcoholate in the corresponding alcohol[75], but the polyesters obtained by this method have a higher intrinsic viscosity and a smaller number of alkoxy groups than those obtained in the reaction with alcohol and pyridine.

Phosphonitrilamides and *N*-substituted phosphonitrilamides can polymerise to form resinous products[50,54,55,58,77]. Lipkin[55] obtained solid transparent polymers, insoluble in organic solvents, by heating to 200°–400° under reduced pressure the products of the reaction between phosphonitrilic chloride and butylamine. If the product of the reaction between phosphonitrilic chloride and acetanilide is heated, hydrogen chloride and acetyl chloride are liberated, and a thermoplastic solid is formed, which softens at 90°–110° and whose structure is probably that of a polyphenylphospham[54,58]:



Products of the reaction between phosphonitrilic chloride (trimer and tetramer) and chloroaniline, urea, guanylurea, guanidine, etc. have been described[77].

Among other polymers containing a $-\overset{|}{\underset{|}{P}}=N-$ bond may be mentioned phospham $[-N=P(=NH)-]_x$ [78,79], and phosphoryl nitride $(O=P\equiv N)_x$, a solid product which decomposes at 750°.[80]

Phosphoryl nitride polymer is formed on heating the triamide of phosphoric acid at 600°. Similarly, on heating at 100°, the triamide of thiophosphoric acid polymerises with the liberation of ammonia; at 800° impure phosphorus nitride is formed.

Audrieth and Sowerby[46] observed that after prolonged heating of phosphonitrilamide strong deamination occurred, and a high-molecular-weight compound, polyphospham, was formed. Polymeric phosphonitrilic thiocyanate, $[-N=P(NCS)_2]_x$, is also known[33].

III. PROPERTIES

1. Physical Properties

The physical properties of phosphonitrile derivatives, trimer and tetramer, as well as the higher polymeric homologues, have been widely studied[1,6,20,81–93]. Brockway and Bright[82] investigated the structure of phosphonitrilic chloride trimer by electron diffraction. They found the trimer to consist of a planar six-membered ring, with phosphorus and nitrogen alternating, and all P–N bonds equivalent. Two chlorine atoms are attached to each atom of phosphorus, at right angles to the plane of the P_3N_3 ring. Ketelaar and de Vries[94] showed phosphonitrilic chloride tetramer to possess an eight-membered non-planar ring, in which the P–N bonds are equivalent, as in the trimer.

Daasch[89,95], Shaw[90], and others[20,23,57] studied the infra-red spectra of phosphonitrilic chloride trimer and tetramer and their derivatives, and showed the absorption maximum at 1200–1350 cm^{-1} to be caused mainly by stretching vibrations of the P–N group. Daasch and Smith[95] studied the infra-red absorption spectra of phosphonitrilic esters and showed the frequency of the stretching vibrations of the P–N group to change insignificantly with change in the size of the alcohol radical from CH_3O to $C_8H_{17}O$. This frequency characterises the vibrations of the ring and depends mainly on the electronegative properties of the atoms attached to the ring; it increases with rising electronegativity, as shown in Table 8.

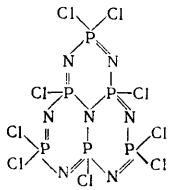
The structure of the higher polymeric homologues of phosphonitrilic chloride, pentamer, hexamer, and nitrilohexamer, is still little known. Audrieth and Toy[1] think that they have a linear structure. Kruse[34], on the basis of ultra-violet and infra-red spectra, and the dipole moments of the lower polymeric phosphonitrile homologues,

TABLE 8. Frequencies of the stretching vibrations of phosphonitrilic halides.

Compound	Frequency of stretching vibration, cm^{-1}	
$P_3N_3Cl_6$	1218[89]	1220[90]
$P_3N_3Br_6$	1170[20]	1184[90]
$P_3N_3(OMe)_6$	1242[95]	1275, 1235[90]
$P_3N_3(NMe)_6$	1195[90]	
$P_3N_3Cl_2(NMe)_4$	1220, 1198[90]	
$P_3N_3Cl_4(NMe_2)_2$	1210[90]	
$P_3N_3Cl_4(NHMe)_2$	1215 (shoulder), 1205[90]	
$P_3N_3Cl_4(NEt_2)_2$	1255; 1226 (shoulder)[90]	
$P_3N_3Cl_4Ph_2$	1220, 1189[90]	
$P_3N_3F_6$	1287[90]	
$P_3N_3Cl_5Br$	1205[23]	
$P_3N_3Cl_4Br_2$	1202[23]	
$P_3N_3Cl_2Br_4$	1180[23]	
$P_3N_3(N_2H_3)_6$	1218[57]	
$P_4N_4Cl_8$	1305[89], 1315[90]	
$P_4N_4Br_8$	1277[90]	
$P_4N_4(OMe)_8$	1377[90]	
$P_4N_4Cl_4Ph_4$ (m.p. 248°)	1313, 1294, 1282[90]	
$P_4N_4Cl_4Ph_4$ (m.p. 148°)	1292[90]	
$P_4N_4(NMe_2)_8$	1265[90]	
$P_5N_5C_{10}$	1325[20]	
$P_6N_6C_{12}$	1324[20]	
$(PNCl_2)_{8-9}$	1291[20]	
$(PNCl_2)_{8-9}PCl_5$	1240[20]	
$(PNCl_2)_n$ (rubber)	1365–1380[20]	

attribute to them a non-planar ring, rather than a chain structure. There is very little difference in the infra-red absorption spectra of different phosphonitrilic chloride polymers.

Molar polarisation, $P_{2\infty}$ (cm^3) has been determined for trimer (84 ± 0.5), tetramer (148.5 ± 4.5), pentamer (145.5 ± 4.5), and hexamer (131.5 ± 6.5). The low $P_{2\infty}$ value, 44 ± 3, for the nitrilohexamer is accounted for by its structure — condensed rings with low electron mobility.



Phosphonitrilic halide trimers containing chlorine and bromine also have the structure of a planar six-membered ring[20]. The heat of formation of phosphonitrilic chloride trimer is $\Delta H_f = -196.3 \pm 3$ kcal $mole^{-1}$.[20] The energy of the P–N bond is approximately 75–80 kcal $mole^{-1}$.

A study has been made of the distribution curves of phosphonitrilic chloride (trimer, tetramer, pentamer, and hexamer) between solutions of sulphuric acid and n-hexane[20] to determine the acid–base equilibrium. The results are given in Fig. 8, which shows that the trimer is a stronger base than the other oligomers. The difference in basicities, and the corresponding difference in the partition coefficients for the distribution between sulphuric acid of a chosen concentration and an inert solvent, can be used as a basis for the separation of the phosphonitrilic chlorides.

Yokoyama and Yamada[96] determined the solubility of phosphonitrilic chloride trimer in benzene, toluene, xylene, hexane, trichloroethylene, tetrachloroethane, chloroform, carbon tetrachloride, methanol, ethanol, acetone, ethyl ether, acetic acid, and dioxane. The best solvents are found to be benzene, toluene, tetrachloroethane, and chloroform. The solubility of phosphonitrilic chloride trimer in these solvents increases as the temperature is increased from 20° to 80°.

Exceptional heat resistance and chemical stability are the main characteristics of the cyclic phosphonitrile derivatives. Like benzene, phosphonitrilic chloride trimer consists of a six-membered ring, with the length of all P–N bonds equal. The energy of that bond, determined thermochemically and spectroscopically, is higher than that of the single P–N bond[5,20,97,98].

The rings of cyclic phosphonitriles are apparently very flexible, as is borne out by the existence of 17-membered rings. The cyclic phosphonitrile derivatives can be regarded as aromatic compounds. The aromatic rings of the phosphonitrile series seem to be able to assume any dimensions as the aromatic bonds in them are formed by the overlapping of the p-orbital of nitrogen and the d-orbital of phosphorus, whereas in benzene they are formed by the overlapping of the p-orbitals of carbon[35,97,98].

The oily phosphonitrilic chloride polymer obtained by the incomplete ammonolysis of phosphorus pentachloride, of empirical formula $PCl_4(PNCl_2)_nCl$, has a linear structure, as is illustrated by a comparison of the ultra-violet spectra of this polymer with those of phosphonitrilic chloride trimer (see Fig. 9)[20]. Fig. 9 shows that the ultra-violet

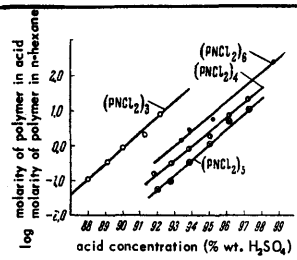


Fig. 8. Partition coefficients for the distribution of phosphonitrilic chlorides between sulphuric acid and n-hexane. The initial concentration of every polymer in n-hexane was 3.5×10^{-3} M.

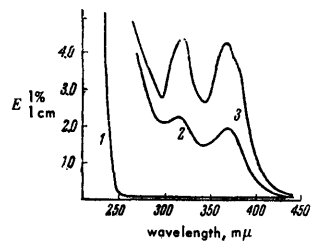


Fig. 9. Ultra-violet spectra of two samples of insoluble oil of the composition $PCl_4(NPCl_2)_nCl$ (of different molecular weight) and of phosphonitrilic chloride trimer: 1) cyclic trimer; 2) oil insoluble in petroleum ether (sample A); 3) insoluble oil (sample B).

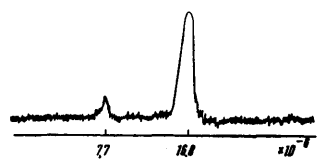
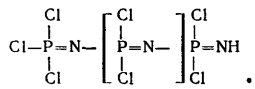


Fig. 10. Nuclear magnetic resonance spectra of oily phosphonitrilic chloride.

spectra of the linear polymer are characterised by two maxima, which are absent from the trimer spectra. The intensity of these maxima depends on the molecular weight of the polymer (see samples A and B) whereas their λ_{max} values remain unchanged. The linear structure of these polymers is confirmed by their preparation from cyclic derivatives by treatment with phosphorus pentachloride.

Becke-Goehring and Koch[88] studied the structure of phosphonitrilic chloride polymers $(PNCl_2)_n$ (when n averaged from 10 to 15) from their nuclear magnetic resonance. There are two resonance maxima (Fig. 10) which indicate the presence of two different phosphorus atoms in the molecule. On the basis of these results Becke-Goehring and Koch[88] consider the oily polymer to have the linear structure, corresponding to the formula



The weak resonance maximum is ascribed to the phosphorus atom on the far left in the formula, whereas the very intense maximum corresponds to all the other phosphorus atoms.

Meyer, Lothmar, and Pankow[91] used X-ray diffraction in a thorough study of the structure of macromolecular phosphonitrilic chloride. They showed the chain in "inorganic rubber" to be spiral, as in Fig. 11.

Using the relation between the modulus of elasticity and the molecular weight ($M \simeq 3RTd/\epsilon$) for ideal rubbers, Specker[92,93] found the molecular weight of the macromolecular polyphosphonitrilic chloride to be 37 000–78 000.

Patat and Kollinsky[66] established the following relationship between the intrinsic viscosity Z_η and the osmotic molecular weight for phosphonitrilic chloride polymers prepared by polymerisation in solvents:

$$Z_\eta = 0.165 \times 10^{-4} M^{-0.69}.$$

Fig. 12 shows that there is good agreement between the experimental and calculated results. On the basis of these results the authors consider that in benzene or toluene solution phosphonitrilic chloride polymers are present in the form of entangled balls[66].

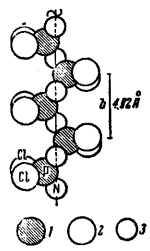


Fig. 11. The structure of the polyphosphonitrilic chloride chain: 1) phosphorus atoms; 2) chlorine atoms; 3) nitrogen atoms.

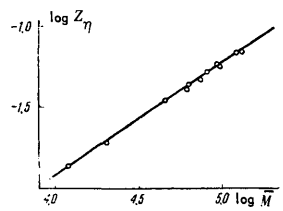


Fig. 12. The molecular weight and viscosity of phosphonitrilic chloride polymers.

From the polymerisation and depolymerisation data for polymeric phosphonitrilic chloride, Patat and Derst[99] consider its structure to resemble a series of interlocking rings. Such a structure would account for the limited solubility of polymeric phosphonitrilic chloride. The insoluble part swells to a certain extent only, as the interlocking rings cannot dissolve without breaking. Thus, the very high value obtained for the molecular weight of polymeric phosphonitrilic chloride is misleading. If the large rings were formed at low temperatures, and the small ones at higher temperatures, a relationship should exist between the overall rate [of dissolution? (Ed. of Translation)] and the temperature of polymerisation. In fact, the reaction rate constant depends solely on the concentration of the polymer. Patat and Derst[99] determined the solubility in benzene of polymeric phosphonitrilic chlorides obtained at different temperatures (see Table 9).

TABLE 9. Solubility of polymeric phosphonitrilic chlorides[99].

Temperature of polymerisation, °C	Fraction soluble in benzene, %	Reaction product
Below 250	100	no polymer formed
250–260	20–30	
300	20–30	
400	30–40	
500	40–50	
600	100	only low-molecular-weight homologues

2. Chemical Properties

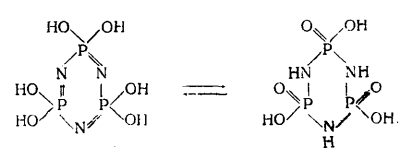
Owing to their structure, cyclic phosphonitrile derivatives are extremely stable chemically[1,6,20]. Their characteristic reactions are polymerisation, esterification, ammonolysis, substitution, hydrolysis, and others. The majority of these reactions proceed without ring rupture. We have already discussed polymerisation, ammonolysis, and esterification, and we shall now briefly mention another series of chemical transformations.

We must first note the hydrolysis of phosphonitrilic chlorides[1,8,10,20,100,101]:

$$(PNCl_2)_x \xrightarrow{H_2O} [PN(OH)_2]_x \xrightarrow{H_2O} H_3PO_4 + xNH_3 + xHCl.$$

phosphonitrilic acid (metaphosphimic acid)

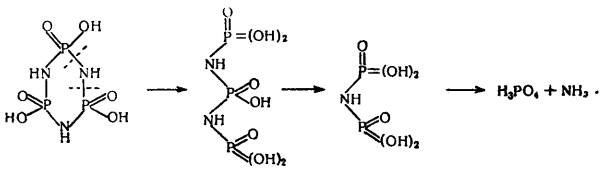
Stokes[8,10] obtained dihydroxytetrachlorotriphosphonitrile, $P_3N_3Cl_4(OH)_2$, as well as triphosphonitrilic acid, by the hydrolysis of phosphonitrilic chloride trimer in ether solution. Most of the authors call triphosphonitrilic acid metaphosphimic acid, and assume that it exists in two tautomeric forms[1,6]:



triphosphonitrilic acid trimetaphosphimic acid

Steger's work[102] on the infra-red spectra of this acid corroborates this hypothesis.

Triphosphonitrilic acid, $P_3N_3(OH)_6$, is a tribasic acid, very unstable, but forming stable salts (the hexasilver salt is also known). Its trisodium salt is easily formed by the extraction of the ether solution of phosphonitrilic chloride trimer with an aqueous solution of sodium acetate. The tetrasodium salt is also known, but it is evidently the derivative of the linear acid — $HO[PO(OH)NH]_3H$. Upon further hydrolysis of phosphonitrilic acid, imidophosphoric acids are formed, which are eventually transformed into phosphoric acid and ammonia[8,10]:



diimidotriphosphoric acid imidodiphosphoric acid

Using ion-exchange, paper chromatography, and other methods, Narath, Lohman, and Quimby[101] showed that the first step in the hydrolysis of sodium trimetaphosphimate is the gradual replacement of the P–N–P bond by P–O–P accompanied by the liberation of ammonia and the formation of the cyclic diimidotrimetaphosphate and imidotrimetaphosphate.

The cyclic phosphonitrilic chloride tetramer hydrolyses more easily than the trimer, and forms a very stable acid, $[NHP(O)OH]_4$.[8,10,100] The cyclic acid is tetrabasic.

Corbridge[100] obtained X-ray diffraction constants for dipotassium, dirubidium, and diammonium salts of tetrametaphosphimic acid. Octasilver tetrametaphosphimates are also known[8,10].

Infra-red spectra of tetraphosphonitrilates indicate the presence of hydrogen bonds (there is no maximum at 3620 cm^{-1}, corresponding to the free OH group, but there is intense absorption at 2600–3000 cm^{-1}, indicating the existence of hydrogen bonds between the P–OH groups). For this reason, Paddock[20] thinks that the difference between the tautomeric forms $NHPO(OH)-$ and $-N=P(OH)_2$ is less than might be expected from the formula. Yet the same salts of tri- and tetra-phosphonitrilic acids react with sodium hypochlorite to form *N*-chloro derivatives[61].

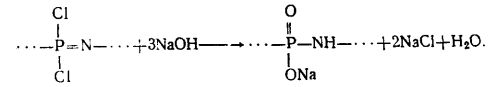
Seel and Langer[25] showed that the cyclic phosphonitrilic fluorides, trimer and tetramer, hydrolyse more easily to the corresponding acids than the chlorides; the trimer is more stable to hydrolysis than the tetramer. Tetraphosphonitrilic acid can be easily isolated from the products of hydrolysis.

Cyclic phosphonitrilic halides also react with nitrogen peroxide, forming an unstable complex[103]. Sulphur trioxide reacts with the chloride trimer at 40° forming a hygroscopic addition product of the composition $(PNCl_2.SO_3)_3$.[104] Bode, Bütow, and Lienau[48] reacted perchloric acid with a solution of phosphonitrilic chloride in acetic acid and isolated $(PNCl_2)_3.HClO_4$ and $(PNCl_2)_4.2HClO_4$.

The reaction of phosphonitrilic chlorides with a solution of sodium in liquid ammonia results in the rupture of the ring[6]. This reaction can be used for the quantitative determination of the halogen in phosphonitrilic halides.

Substitution, polymerisation, etc., proceed far more easily with linear derivatives of phosphonitrile, than with the cyclic ones, which is evidently connected with the loss of aromatic character by the former[88]. Thus, oily oligomers are so easily hydrolysed in water, that atmospheric moisture should be excluded during their preparation.

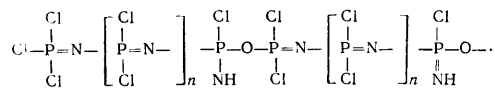
Polymetaphosphimic acid is formed by the hydrolysis of oily polymeric phosphonitrilic chloride (n = 10–15) with aqueous alkali:



During the hydrolysis of oily phosphonitrilic chloride with aqueous acid, in addition to the water-soluble products, a difficultly soluble material is also formed; this has acid properties and is a metaphosphimic acid hydrate.

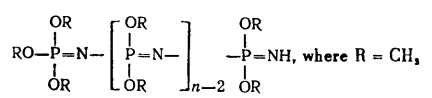
Salts of the soluble polymetaphosphimic acid with the following cations have been prepared: Ag, Cu^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}.[88]

Becke-Goehring and Koch[88] showed that in the hydrolysis of polymeric phosphonitrilic chloride with insufficient quantities of water, hydrogen chloride splits off, and an oxygen bridge is formed:



The product obtained is rubber-like, and soluble in organic solvents.

Goldschmidt and Dishon[75,76] studied the esterification of phosphonitrilic chloride polymer, and we have covered it in detail in the present review (see p. 6). Becke-Goehring and Koch[88] made a study of the esterification of the oily phosphonitrilic chloride polymer. Its alcoholysis with sodium methoxide in absolute methanol yields a viscous colourless liquid of the composition



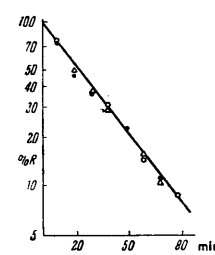
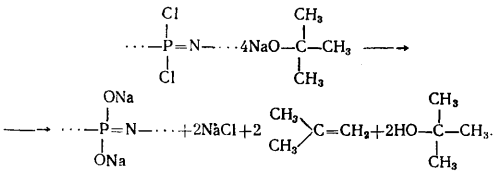


Fig. 13. Depolymerisation of phosphonitrilic chloride polymer samples obtained at 250°, 400°, and 500°. Depolymerisation temperature 350° [R = percentage of polymer? (Ed. of Translation)].

Mild alcoholysis with sodium t-butoxide yields sodium polymetaphosphimate and isobutylene[88].



On being heated above 350° phosphonitrilic chloride polymer depolymerises[67,68,99]. Patat and Derst[99] studied the effect of various factors (such as temperature and time of polymerisation, and the presence of oxygen) on the destruction of polymeric phosphonitrilic chloride. The temperature of polymerisation has no effect on the depolymerisation rate, as is shown in Fig. 13, neither has the time of polymerisation. It is true, however, that there was some difference in the quantities of the soluble polymer owing to the incomplete conversion during the polymerisation in too short a time. The results of Patat and Derst's study[99] on the depolymerisation kinetics, are given in Table 10.

Depolymerisation of phosphonitrilic chloride polymers is a first-order reaction. The beginning of the reaction consists of the rupture of the larger rings, giving rise to two active chain ends at the rate $v_i = k_i[P]$, where [P] is the concentration (weight) of the polymer. During depolymerisation, low-molecular-weight products, $(PNCl_2)_x$, with $x = 3-7$, are split off, according to a chain reaction with rate

$$v_{\text{depolym}} = k_{\text{depolym}}[P^*],$$

where [P*] is the concentration of "biactive" polymers; k_{depolym} is the depolymerisation rate constant. The reaction ends by the cyclisation of the low-molecular-weight residues from the initial ring.

The gross reaction rate,

$$v_R = v_{\text{depolym}} = k_{\text{depolym}}[P^*] = k_R[P],$$

depends only on the concentration of the high-molecular-weight phosphonitrilic chloride, and the gross reaction rate-constant is

$$k_R = 7.5 \times 10^5 e^{-26\,000/RT} \text{ sec}^{-1}.$$

The activation energy for depolymerisation is 26 ± 2 kcal × × mole^{-1}.

TABLE 10. Depolymerisation kinetics of phosphonitrilic chloride polymers[99].

Temp. of depolymerisation, °C	$t_{0.5}$, min *	Depolymerisation constant, sec^{-1}
250	1030	$1.1215 \cdot 10^{-5}$
300	99.5	$11.6105 \cdot 10^{-5}$
350	18.0	$64.1806 \cdot 10^{-5}$
275	350	$3.3007 \cdot 10^{-5}$
311	75	$15.4003 \cdot 10^{-5}$
330	32.5	$35.5462 \cdot 10^{-5}$

* $t_{0.5}$ = time of 50% depolymerisation.

3. Application

Rémond has made a thorough survey of the applications of phosphonitrilic chloride and its polymers[4]. Cyclic phosphonitrilic chlorides are of special interest because they form, on heating, macromolecular inorganic polymers with excellent elastic, heat- and fire-resistant qualities. These macromolecular compounds have functional groups which can be substituted by different organic radicals, thus making possible a combination of the properties of organic and inorganic polymers.

Phosphonitrilic chloride is used for the preparation of coatings and adhesive for glass, ceramics, asbestos, and metals[4]. Phosphonitrilic chloride polymers are used as additives to lubricating oils, and for the impregnation and fire-proofing of textiles. In combination with glass, asbestos, and other inorganic fibres, they are used for the preparation of insulating materials resistant to high temperatures[5].

Transparent solid materials have been obtained from the products of condensation of phosphonitrilic chloride with butylamine[55]. As a rule, the addition of phosphonitrilic chloride to polymers increases their heat-resistance[4]. The products of the reaction of phosphonitrilic chloride with alcohols, phenols, naphthols, mercaptans, and thiophenols are used as plasticisers for resins and varnishes[5].

Phosphonitrilic esters, prepared from the macromolecular phosphonitrilic chlorides and an alcohol in the presence of pyridine, can be used as plasticisers for nitrocellulose varnishes and films[75]. Allyl phosphonitrilates can be used to increase the adhesion of resins to glass fibres[4], and for fire-proofing textiles[63,74].

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THE CHEMISTRY OF β-KETOACETALS

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I. INTRODUCTION

The study of β-dicarbonyl compounds has furthered the