THE PHOSPHAZENES (PHOSPHONITRILIC COMPOUNDS)

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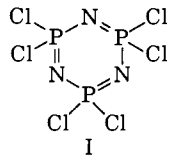
I. INTRODUCTION

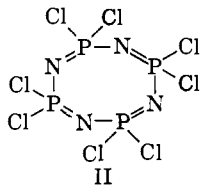
A. HISTORICAL

The phosphazenes have distinguished ancestry. The reaction between phosphorus pentachloride and ammonia was described by Rose in 1834 (303), and in an editorial comment, Liebig reported work carried out in conjunction with Wöhler (206). The major reaction product was phospham (Section VII-E), and a small quantity of a stable crystalline compound containing nitrogen, phosphorus, and chlorine was obtained (206). The formula was given incorrectly, but Gerhardt and Laurent (121, 122, 205) established that the empirical composition was $NPCl_2$, and Gladstone and Holmes (136, 137) and Wichelhaus (380) measured the vapor density and deduced the molecular formula, $N_3P_3Cl_6$. Several workers became active in the field (37, 131, 132, 133, 134, 135, 138, 309), aromatic amino derivatives were characterized (80, 168, 169), and a bromophosphazene was prepared (36, 38).

The cyclic structure of hexachlorotriphosphazene (I) was proposed by H. N. Stokes, whose classical work in the last years of the nineteenth century provided the foundations of phosphazene chemistry (351, 352, 353, 354, 355, 356, 357). Stokes established that hexachlorocyclotriphosphazene was the first member of a series, $(NPCl_2)_n$, and homologs (n = 3-7) were identified. Ammonolysis and hydrolysis were studied, and salts of tautomerized acids were prepared. Polymerization to an inorganic rubber occurred on heating chlorophosphazenes, and depolymerization occurred on stronger heating under reduced pressure. It was shown subsequently that equilibria are attained when different chlorides are heated at 600° (311, 312), and the structures and physical properties of the inorganic rubber were studied (217, 218, 219, 220). Monomeric phosphazenes (phosphine imines), $RN{=}PR_3'$, were prepared by Staudinger and his co-workers from reaction of azides with tertiary phosphines (340, 341, 342, 343). Compounds of formulas NPX_2 and $N_2P_2X_4$ have not yet been isolated.



I



II

Schenk and Römer modified the chlorophosphazene synthesis (308) and methods involving the use of an inert solvent are used widely today. Moureu and his co-workers carried out a series of investigations of ammonolysis, hydrolysis, and polymerization of chlorophosphazenes, and the thermal decomposition of aminophosphazenes (101, 102, 103, 104, 105, 106, 107, 108, 109, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 239, 378). Schmitz-DuMont and his co-workers studied the conversion of chlorides to fluorides (310, 313, 314, 315), and Bode and his co-workers prepared aryl derivatives of chlorophosphazenes, and investigated aminolysis to obtain chemical evidence of cyclic structures (46, 47, 50, 51, 52, 54).

X-Ray diffraction patterns of hexachlorocyclotriphosphazene (I) and octachlorocyclotetraphosphazene (II) were investigated (180), and a complete structure determination of the latter by Ketelaar and de Vries established that the puckered eight-membered ring contained alternate nitrogen and phosphorus atoms, with two chlorine atoms attached to each phosphorus (190, 191). Electron diffraction measurements of hexachlorocyclotriphosphazene by Brockway and Bright (57) and Schomaker (316) gave satisfactory agreement with the planar model (I) proposed by Stokes (353).

Interest in the phosphazenes has renewed during the past five years, and modern theories and techniques have enabled significant advances to be made in a relatively short time. Approximately one hundred and fifty publications have appeared since the beginning of 1959. Phosphazenes were discussed in recent Presidential Addresses to the Chemical Society (98) and the Society of Chemical Industry (302), at a Gordon Conference in August, 1960, and at the Chemical Society Symposium on Inorganic Polymers, held in the University of Nottingham in July, 1961 (151, 326).

B. SCOPE OF REVIEW

Cyclophosphazenes and open-chain derivatives of quinquevalent phosphorus based on one or more $-N{=}\overset{|}{\underset{|}{P}}-$ units are within the scope of this review. Monophosphazenes (phosphine imines) are included, but not, in general, phosphazines (375d) and compounds containing $-SO_2-N{=}\overset{|}{\underset{|}{P}}-$ groups prepared by the Kirsanov reaction (375c).

An important review by Audrieth, Steinman, and

Toy appeared in these pages in 1943 (19). Paddock and Searle have given an excellent account of more recent work (259) and shorter articles are concerned with aspects of phosphazene chemistry (14, 15, 55, 130, 146, 254, 256, 295, 322, 323, 324, 325). It is hoped that this review contains references to most important publications from the time of Liebig, up to and including papers listed in the November, 1961, issue of *Current Chemical Papers*. The reviewers have endeavored to consult each paper in the original.

II. NOMENCLATURE

Many structural varieties of phosphorus–nitrogen compounds are known and the difficulties of nomenclature have been discussed by Audrieth, Steinman, and Toy (18). The name phosphonitrilic chloride was suggested by Stokes (351) and the compound $N_3P_3Cl_6$ has been called the trimer of phosphonitrilic chloride, trimeric phosphonitrilic chloride, and tri(phosphonitrile)hexachloride. The name phosphonitrile suggests a phosphorus–nitrogen triple bond, for which there is at present no evidence except in short-lived gaseous monomeric phosphorus nitride, N≡P. Names such as phosphorus chloronitride, phosphorus chloride nitride, phosphoronitridic dichloride, chlorophosphinic nitride, and nitrilophosphoric chloride have been used. There is no satisfactory method of naming the many derivatives which have now been prepared.

Using nomenclature familiar from silicon–nitrogen compounds (silazanes) and boron–nitrogen compounds (borazanes), the name phosphazane is proposed for phosphorus–nitrogen compounds. To this could be added thiazanes (S–N compounds), alazanes (Al–N compounds), arsazanes (As–N compounds), arsoxanes (As–O compounds), *etc.*

The name phosphazane can be used for compounds derived from quinquevalent and tervalent phosphorus, with qualification by Roman numerals where necessary.

NH_2–PH_4	phospha(V)azane
NH_2–PH_2	phospha(III)azane

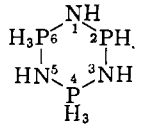
Unless specified otherwise, the names di- and triphosphazane, *etc.*, imply head-to-tail linkages of phosphazane units, N–P–N–P. . . . It is suggested that numbering should begin at nitrogen. The naming of a structure does not necessarily indicate the existence of a chemical compound; *cf.* phosphorane, PH_5.

A. QUINQUEVALENT PHOSPHORUS DERIVATIVES

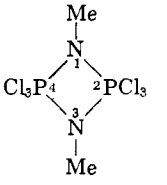
Roman numerals are omitted from names in this section.

NH_2—PH_4	phosphazane
NH=PH_3	phosphazene
N≡PH_2	phosphazyne

$\overset{1}{N}H_2$–$\overset{2}{P}H_3$–$\overset{3}{N}H$–$\overset{4}{P}H_3$–$\overset{5}{N}H$–$\overset{6}{P}H_4$ triphosphazane



cyclotriphosphazane

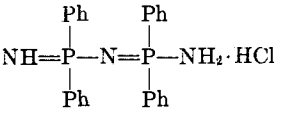


2,2,2,4,4,4-hexachloro-1,3-dimethylcyclodiphosphazane (117, 158)

$\overset{1}{N}H=\overset{2}{P}H_2-\overset{3}{N}=\overset{4}{P}H_3$ diphosphaza-1,3-diene or diphosphazadiene

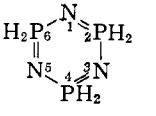
—N=PCl_2—N=PCl_2— poly-(dichlorophosphazene)

NEt=PPh_3 1-ethyl-2,2,2-triphenylphosphazene (10, 340)

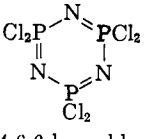


4-amino-2,2,4,4-tetraphenyldiphosphaza-1,3-diene hydrochloride (197)

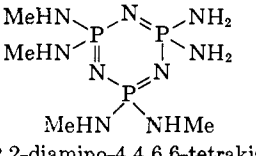
Kekulé-type resonance is assumed for phosphazene ring systems, and numbers indicating the positions of double bonds usually are omitted.



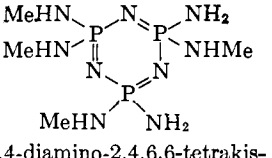
cyclotriphosphaza-1,3,5-triene or cyclotriphosphazatriene



2,2,4,4,6,6-hexachlorocyclotriphosphazatriene, or hexachlorocyclotriphosphazatriene



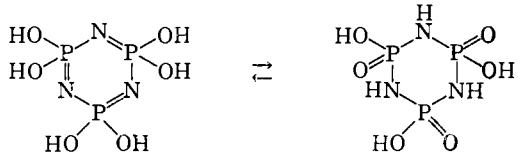
2,2-diamino-4,4,6,6-tetrakismethylaminocyclotriphosphazatriene (28, 30)



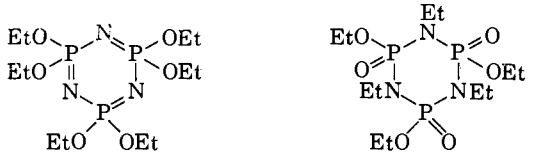
2,4-diamino-2,4,6,6-tetrakismethylaminocyclotriphosphazatriene (28, 30)

Acids derived from the halides have been described as phosphonitrilic acids (IIIA) and their tautomers as

metaphosphimic acids (IIIB), but this does not indicate that they are derived originally from the same structure (269). The salts probably contain mesomeric anions, but it is suggested that for nomenclature purposes they should be regarded as salts of hydroxyoxophosphazanes (IIIB).



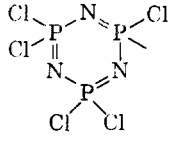
IIIA, 2,2,4,4,6,6-hexahydroxycyclotriphosphazatriene ⇄ IIIB, 2,4,6-trihydroxy-2,4,6-trioxocyclotriphosphazane



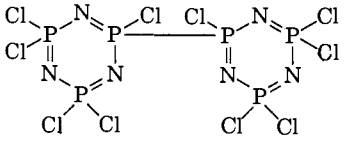
2,2,4,4,6,6-hexaethoxycyclotriphosphazatriene; 2,4,6-triethoxy-1,3,5-triethyl-2,4,6-trioxocyclotriphosphazane (112, 279)

Radicals:

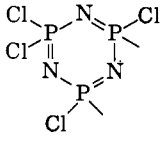
—NH—PH_4	phosphaz-1-yl
NH_2—PH_3—	phosphaz-2-yl
—N=PH_3	phosphazen-1-yl
NH=PH_2—	phosphazen-2-yl



pentachlorocyclotriphosphazatrienyl

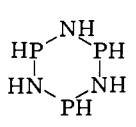


bi-(pentachlorocyclotriphosphazatrienyl)

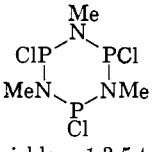


2,4,6,6-tetrachlorocyclotriphosphazatrienylene

B. TERVALENT PHOSPHORUS DERIVATIVES



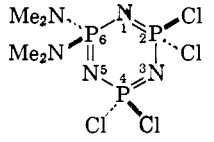
cyclotriphospha(III)azane



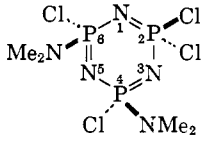
2,4,6-trichloro-1,3,5-trimethylcyclotriphospha(III)azane

C. STEREOCHEMISTRY

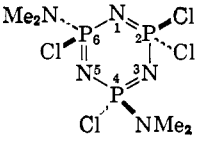
The six-membered phosphazene ring is approximately planar, with two exocyclic bonds on each phosphorus atom projecting above and below the ring. It is possible that the ring might pucker under the influence of suitable substituents, but if conformational isomerism and optical isomerism are neglected, three disubstituted derivatives are possible. The substituents are enumerated in the usual order of organic chemistry and the first substituent which can act unambiguously as a point of reference projects, by definition, below the plane of the ring. The *cis–trans* notation is employed where necessary to define the positions of remaining groups.



IVA, 2,2,4,4-tetrachloro-6,6-bis-(dimethylamino)cyclotriphosphazatriene

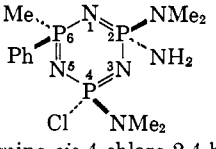


IVB, 2,2,4-*cis*-6-tetrachloro-4,6-bis-(dimethylamino)cyclotriphosphazatriene



IVC, 2,2,4-*trans*-6-tetrachloro-4,6-bis(dimethylamino)cyclotriphosphazatriene

The *cis–trans* notation is not required for compound IVA. In compound IVB, the 4-chloro substituent acts as point of reference, the remaining chlorine atom at 6 is *cis*, and the positions of the two dimethylamino groups are thus defined. A similar argument applies to IVC. In the next example, V, the 2-amino group is the reference point and this, by definition, projects below the plane of the ring. The 4-chloro atom is *cis* with respect to the amino group. The two dimethylamino groups in positions 2 and 4 are located unambiguously. The 6-methyl group is *cis* with respect to the amino group, and the 6-phenyl group needs no further description.



V, 2-amino-*cis*-4-chloro-2,4-bis-(dimethylamino)*cis*-6-methyl-6-phenylcyclotriphosphazatriene

D. GENERAL REMARKS

It is not expected that the proposed nomenclature will be applied rigorously in every case, but it would

be available for use in abstracts and for the naming of complex structures. The positions of double bonds could be specified where necessary. Suitably shortened names can be used, and in this review the $(NPCl_2)_n$ family will be called chlorophosphazenes. The compounds $N_3P_3Cl_6$ and $N_4P_4Cl_6$ will be called hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene.

III. STEREOCHEMISTRY AND REACTION PATTERNS

The cyclotriphosphazene ring is approximately planar, and although it may be sufficiently flexible to permit deformation by suitable substituents, the possibility of conformational isomerism has been neglected for both cyclotriphosphazenes and cyclotetraphosphazenes. Figure 1 illustrates possible isomers

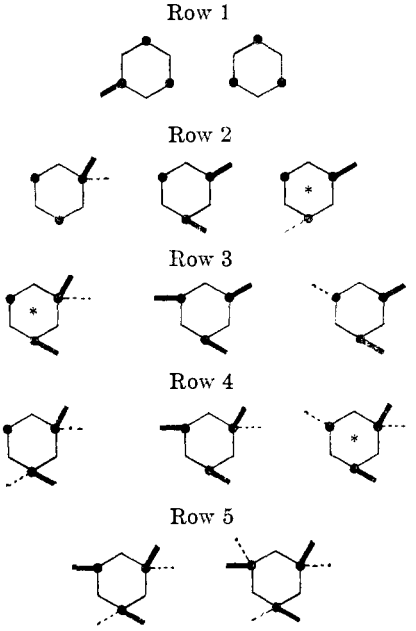


FIGURE 1

when the chlorine atoms in hexachlorocyclotriphosphazene are replaced by a second substituent. For the sake of clarity, hexachlorocyclotriphosphazene is drawn as a hexagon with positions of phosphorus atoms indicated by dots. Chlorine atoms are omitted and positions of the second substituent are represented by solid or dotted lines. Asterisks indicate the absence of elements of symmetry and the possibility of optical isomerism, although no examples of optical isomers have been reported. Possible substitution products when up to four chlorine atoms in octachlorocyclotetraphosphazene are replaced by a second substituent are shown similarly in Fig. 2.

A distinction can be made between *cis–trans* isomerism, and position isomerism. Two different 2,4,6-trichloro - 2,4,6 - triphenylcyclotriphosphazenes (VI) (175, 328) and three different 2,4,6,8-tetrachloro-

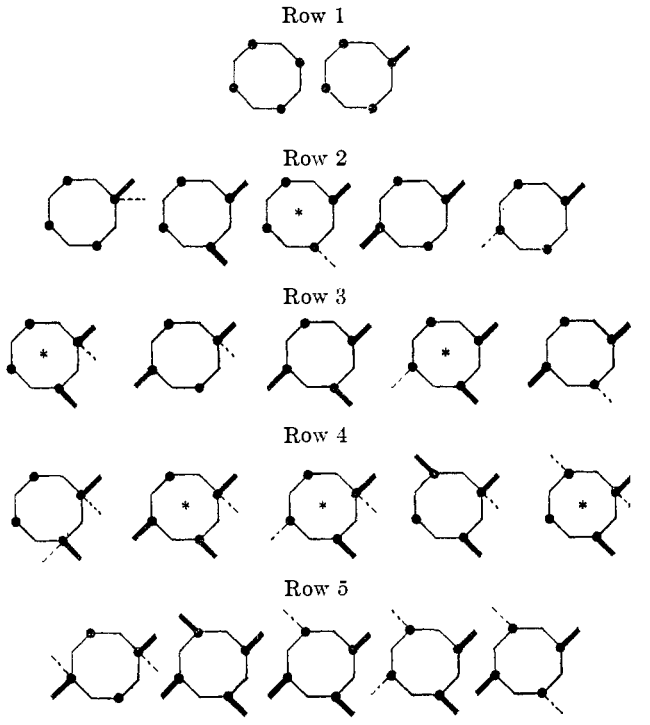
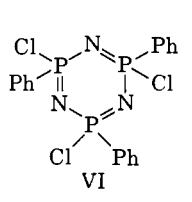
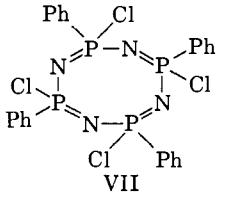


FIGURE 2

2,4,6,8 - tetraphenylcyclotetraphosphazenes (VII) have been prepared (327, 328). One chlorine atom and one phenyl group are attached to each phosphorus atom, but the absolute configurations are not known. These compounds and some of their derivatives are discussed in Sections VI-A and VII-B. It may be seen from Fig. 1 that two *cis–trans* isomers would be expected for compounds of formula $N_3P_3Ph_3Cl_3$, and from Fig. 2 that four *cis–trans* isomers would be expected for non-geminal compounds of formula $N_4P_4Ph_4Cl_4$



VI



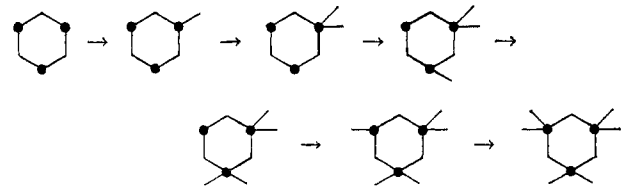
VII

A. REACTION PATTERNS OF CYCLOTRIPHOSPHAZENES

Two different reaction schemes have been considered for the progressive replacement of chlorine atoms in hexachlorocyclotriphosphazene. The differences depend on whether replacement occurs preferentially at phosphorus containing one chlorine atom (geminal replacement) or at phosphorus containing two chlorine atoms (non-geminal replacement). The two reaction schemes, with *cis–trans* isomers omitted, are illustrated in Fig. 3.

The preparation of phenyl derivatives $N_3P_3Ph_2Cl_4$ (VIII), $N_3P_3Ph_4Cl_2$ (IX), and $N_3P_3Ph_6$ (X) is discussed in Section VI B and it has been established that geminal

Scheme 1, geminal replacement



Scheme 2, non-geminal replacement

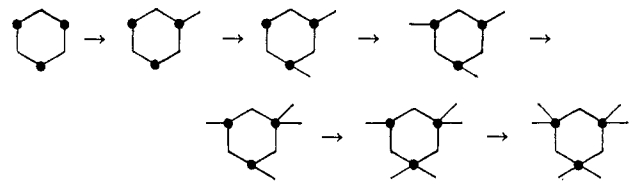
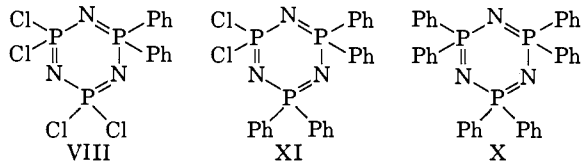


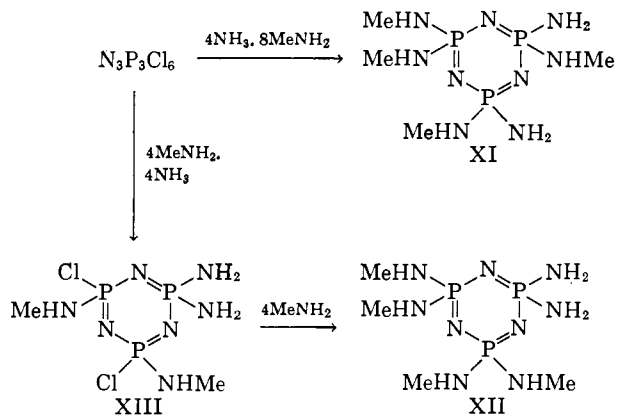
FIG. 3.—Reproduced, with permission, from the *J. Chem. Soc.* (281).

replacement (scheme 1) is predominant in phenylation by the Friedel-Crafts reaction (50, 330).



VIII XI X

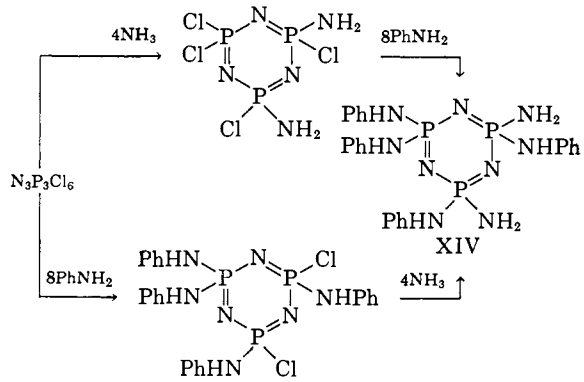
Non-geminal replacement (scheme 2) occurs preferentially in reactions with ammonia and some amines. Two isomeric bisaminotetrakismethylaminocyclotriphosphazenes (XI, XII) were prepared from reaction with ammonia and methylamine, and it is clear that position isomers would not be formed as a result of geminal replacement. The configuration of the 2,2-bisamino-4,6-dichloro-4,6-bismethylamino intermediate (XIII) was confirmed by the phosphorus nuclear magnetic resonance spectrum (28, 30).



XI XIII XII

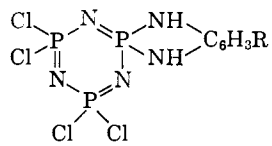
The proton magnetic resonance spectra of a series of dimethylaminophosphazene derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1, 2, 3, 4, and 6), provided conclusive evidence of non-geminal replacement (scheme 2) in reactions of hexachlorocyclotriphosphazene with dimethylamine (379).

Non-geminal replacement by amino and anilino groups would lead to the formation of 2,4-bis(amino)-2,4,6,6-tetrakis(anilino)cyclotriphosphazene (XIV), whether prepared from bis(diamino) or tetrakis(anilino) intermediates, although formation of a single bis(amino)tetrakis(anilino)cyclotriphosphazene was considered to result from geminal replacement (47, 51).



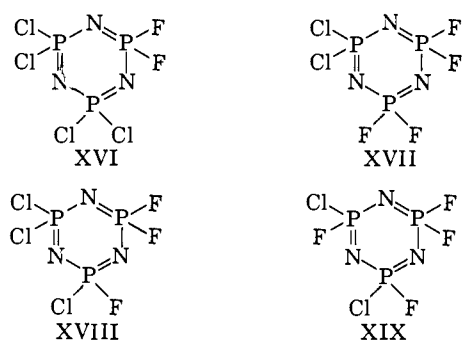
XIV

Examples of preferential geminal replacement by amines occur in the reaction of hexachlorocyclotriphosphazene with aromatic *o*-diamines (51) to give spiro derivatives (XV).



XV, R = H, Me

Mixed chlorofluorides prepared from hexachlorocyclotriphosphazene were assigned structures on the basis of nuclear magnetic resonance spectra (70, 160). The high yields of 2,2-difluoro-4,4,6,6-tetrachlorocyclotriphosphazene (XVI) and 2,2,4,4-tetrafluoro-6,6-dichlorocyclotriphosphazene (XVII) provide evidence of preferential geminal replacement (scheme 1). 2,2,4 - Trifluoro - 4,6,6 - trichlorocyclotriphosphazene (XVIII) was obtained also, but the isolation of a small quantity of 2,2,4,6-tetrafluoro-4,6-dichlorocyclotriphosphazene (XIX) suggested concurrent non-geminal replacement (70).



XVI XVII XVIII XIX

The reaction pattern of hexachlorocyclotriphosphazene is considered to depend on both polar and

steric effects (281). Both replacement schemes may be followed, but frequently one scheme is predominant. When the polar effects of chlorine and the replacing group are similar, the position of replacement depends on the relative sizes: if the replacing group is smaller than chlorine, geminal replacement occurs, but if the replacing group is larger, replacement will occur at a different phosphorus atom. When the replacing group is of similar size but provides a higher electron density at the attached phosphorus atom, subsequent nucleophilic attack at the same phosphorus is discouraged, and non-geminal replacement would be preferred. When the electron density on phosphorus is lowered by a replacing group, geminal replacement at the same phosphorus is encouraged.

B. REACTION PATTERNS OF CYCLOTETRAPHOSPHAZENES

Phosphorus nuclear magnetic resonance spectra established the 2,6:2,4,4,6,8,8 configurations of three bisarylaminohexachlorocyclotetraphosphazenes, and non-geminal replacement has been suggested for other disubstituted and tetrasubstituted aminophosphazenes (187, 188).

IV. SYNTHESIS OF PHOSPHAZENE RINGS

Cyclophosphazenes are synthesized conveniently by methods involving ammonolysis and cyclization of quinquevalent phosphorus halides. Difficulties of interpreting the reaction mechanism are common to all reactions of this type, and it is not known which of many possible species in solution lead directly to the formation of phosphazenes. Phosphorus pentachloride vapor has a covalent trigonal bipyramid structure, and the compound is monomeric in certain non-polar solvents, but crystalline phosphorus pentachloride contains PCl_4^+ PCl_6^- ions, crystalline phosphorus pentabromide contains PBr_4^+ Br^- ions, and both compounds ionize in polar solvents (265). Thermal dissociation occurs also.

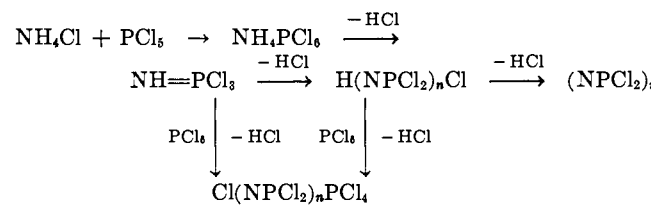
$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

Two different series of compounds, cyclic phosphazenes, $(NPCl_2)_n$, and open-chain phosphazenes of reported composition $Cl_4P(NPCl_2)_nCl$, are formed from reaction between phosphorus pentachloride and ammonium chloride (212). The open-chain compounds can be distinguished by solubility behavior, greater reactivity with water, and by their ultraviolet spectra (212, 259). No individual members of the open-chain series have been separated from the reaction, and it has been suggested (33) that they might be a mixture of end-stoppered polymers, $H(NPCl_2)_nCl$ (31) and compounds such as $N_3P_4Cl_{11}$ (XX) (33).

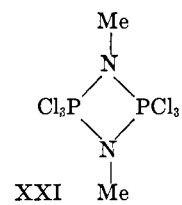
$$Cl_2P(N{=}PCl_3)_3 \text{ or } ClP(N{=}PCl_3)_3{}^+Cl^-$$
XX

The effects of different reaction conditions have been investigated (388, 395). Near room temperatures in solvents of high dielectric constant, *e.g.*, nitrobenzene, one of the major products is NP_3Cl_{12} (32) for which the structure $Cl_3PN{=}PCl_3{}^+PCl_6^-$ has been suggested on the basis of the nuclear magnetic resonance spectrum and the conductivity in nitrobenzene. Reaction of this compound with sulfur dioxide gave $Cl_3PN{=}POCl_2$ (32), which has been prepared also by reaction of phosphorus pentachloride with amino derivatives of phosphoric acid, $H_2NPO(OH)_2$, $(H_2N)_2PO(OH)$, and $(H_2N)_3PO$ (33, 114), and by reaction of phosphorus chlorides with hydroxylamine salts (189) or dinitrogen tetroxide (27). Two aminolysis products have been prepared (27, 33). Reaction of phosphorus pentachloride with $(H_2N)_3PO$ gave also a small quantity of hexachlorocyclotriphosphazene, and reaction with $(H_2N)_3PS$ gave $N_3P_4Cl_{11}$ (XX) (33).

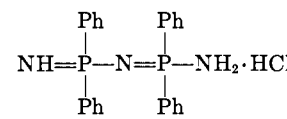
The proposed mechanism involves initial formation of ammonium hexachlorophosphate, and decomposition to $NH{=}PCl_3$ which then polymerizes with elimination of hydrogen chloride, or reacts with phosphorus pentachloride (259).



Ammonium hexachlorophosphate is unstable, but tetramethylammonium hexachlorophosphate has been reported (100). Reaction of phosphorus pentachloride with methylammonium chloride gave a hygroscopic product, $(NMePCl_3)_2$, which has been formulated as a saturated cyclic phosphazane (XXI) (68). A similar reaction with phenylammonium chloride gave a product of analogous composition, $NPhPCl_3$, but the molecular weight was not determined (126).



XXI



XXII

Reaction of diphenyltrichlorophosphorane with liquid ammonia gave an open-chain diphosphazadiene addition compound (42, 197) for which structure XXII has been proposed (197). Octaphenylcyclotetraphosphazene and a smaller quantity of hexaphenylcyclotriphosphazene were obtained on pyrolysis (42, 197). Other possible intermediates are discussed in Section VI-A.

An important variation of this method involves chlorination of aminobisperfluoromethylphosphine and dehydrohalogenation of the intermediate *in situ* to give perfluoromethylphosphazenes (151, 365)

$$(CF_3)_2PNH_2 + Cl_2 \rightarrow (CF_3)_2P(NH_2)Cl_2 \xrightarrow[-2HCl]{2Et_3N} [NP(CF_3)_2]_n \quad (n = 3, 4, x)$$

The intermediate has not been prepared by direct ammonolysis and it is not known whether compounds of this type occur as intermediates in the ammonolysis of quinquevalent phosphorus halides.

It is clear that the degree of polymerization of cyclophosphazenes depends on a number of factors. Under conditions investigated, ammonolysis and cyclization of phosphorus pentachloride gives preferentially a six-membered ring (212, 355), but with $PhPCl_4$ and Ph_2PCl_3 the cyclotetraphosphazene ring is preferred (152, 327, 328). With phosphorus pentabromide the relative proportions of different ring systems depend on the reaction conditions (23, 186). Reaction of methylammonium chloride gives a cyclic diphosphazane (XXI) (68). Monophosphazenes are formed from reaction of triphenyldihalogenophosphoranes with arylamines in the presence of triethylamine (171, 172).

$$Ph_3PX_2 + ArNH_2 \xrightarrow[-2HCl]{2NEt_3} ArN{=}PPh_3$$

The same products are obtained from reactions of tertiary phosphines with azides (170, 340, 342).

Disproportionation of phenyl derivatives of cyclotetraphosphazene, and the interconversion of halogenophosphazenes are discussed in Sections V-D, VI-C, and IX.

Reactions of ammonium chloride with niobium (358), tantalum (141), and molybdenum (140) pentachlorides have been investigated in attempted preparations of phosphazene analogs.

V. HALOGENOCYCLOPHOSPHAZENES

A. PREPARATION OF CHLORIDES

The synthesis by Liebig of hexachlorocyclotriphosphazene from phosphorus pentachloride and ammonia or ammonium chloride is of historical interest (206), and modifications included the use of sealed tubes (351, 352, 355) or use of an inert solvent such as *sym*-tetrachloroethane (246, 308). Other preparative methods include the reaction of ammono-basic mercuric chloride with phosphorus pentachloride (136, 317, 138), the high temperature chlorination of phosphorus nitrides (232, 234, 239, 378), and reaction between tetrasulfur tetranitride, thionyl chloride, and phosphorus trichloride (143).

Stokes discovered that hexachlorocyclotriphosphazene was the first of a homologous series, $(NPCl_2)_n$, of which lower members (n is 3–6) were isolated in a pure state, and an impure heptamer was obtained. Recent improvements in technique have led to the isolation and purification of compounds $N_7P_7Cl_{14}$ and $N_8P_8Cl_{16}$ (212), and there is indirect evidence of higher members (n is 9–17). The relative proportions depend on reaction conditions; cyclic phosphazenes are extracted with light petroleum, and separated by solvent extraction, fractional crystallization, fractional distillation, chromatography, *etc.* (45, 127, 212).

The compound $N_7P_6Cl_9$ also reported by Stokes (355) has been assigned a tricyclic structure like that of cyameluric chloride (199, 200).

The compound NP_2Cl_7 has been prepared from reaction between phosphorus trichloride and tetrasulfur tetranitride, and from the high temperature reaction between hexachlorocyclotriphosphazene and phosphorus pentachloride in phosphorus oxychloride (148).

A new reaction leading to the formation of chloro- and bromophosphazenes from tervalent phosphorus azides is discussed in Section VI-D.

B. PREPARATION OF BROMIDES

The preparation of hexabromocyclotriphosphazene from reaction of phosphorus pentabromide with ammonia (38) and ammonium bromide (147) has been reported. Octabromocyclotetraphosphazene has been characterized (46, 49), and lowering of the degree of dissociation of phosphorus pentabromide by addition of excess of bromine gave increased yields of both compounds (23, 186).

Preparation of the compound NP_2Br_7 has been reported (186).

Mixed chlorobromides, $N_3P_3Cl_{6-n}Br_n$ (n = 1, 2, 4), have been prepared from reactions of ammonium chloride and ammonium bromide with suitable quinquevalent phosphorus halides (301).

C. IODIDES

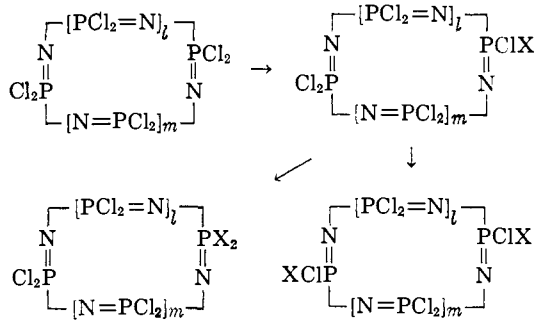
Quinquevalent phosphorus compounds containing phosphorus–iodine bonds have not been prepared, and there is no evidence for the existence of iodophosphazenes despite their mention in the patent literature (21, 74, 209). Reaction of chlorophosphazenes with sodium iodide in acetone or sulfur dioxide solution is slow and accompanied by the liberation of iodine (45, 259), and precipitation of sodium chloride. It is possible that these observations can be explained by initial reaction of chlorophosphazene with the solvent.

D. FLUORIDES

Reactions of phosphorus pentafluoride with ammonium fluoride (204) and of anhydrous hydrogen fluoride with hexachlorocyclotriphosphazene (53) give ammonium hexafluorophosphate. Fluorophosphazenes and chlorofluorophosphazenes were prepared from the reaction of lead difluoride with hexachlorocyclotriphosphazene (310, 313, 314, 315). A feature of this work was the change in ring size and the formation of fluorochlorocyclotetraphosphazenes. These polymerized at 300° to form a rubber, which depolymerized to chlorofluorocyclotriphosphazenes.

The reaction of potassium fluorosulfite, KSO_2F, with chlorophosphazenes to give corresponding fluorides without change of ring size (319, 320) has been simplified by use of a mixture of potassium fluoride and sulfur dioxide (69, 153). By this method, mixtures of higher chlorides were converted to fluorides $(NPF_2)_n$ (n = 3–17), which could be separated by means of fractional distillation and gas–liquid chromatography. Cyclic structures were deduced from the infrared spectra; and, because the lower chlorides could be converted to fluorides without change in ring size, the existence of higher cyclic chlorides was inferred (69). Mixed chlorofluorides have been prepared similarly (70). Geminal replacement (scheme 1, Section III-A) is preferred, although small quantities of products are formed by non-geminal replacement (scheme 2).

Good yields of cyclic fluorides were prepared from chlorides without change in ring size by reaction with sodium fluoride in nitrobenzene using aqueous hydrogen fluoride as catalyst (223) and by reaction with argentous fluoride. Direct reaction of chlorophosphazenes with argentic fluoride was vigorous, and decomposition occurred, but chlorofluorides were converted to fully fluorinated phosphazenes by the use of argentic fluoride (275). Hexafluorocyclotriphosphazene and octafluorocyclotetraphosphazene have been prepared by reaction of nitrogen trifluoride or CF_3SF_5 with N_5P_3 at 700° (214).



Geminal replacement (X = F)

Non-geminal replacement (X = NMe_2)

FIG. 4.—Reproduced, with permission, from the *J. Chem. Soc.* (281).

E. PSEUDOHALIDES

No products have been obtained from attempted reactions of chlorophosphazenes with silver cyanide (80) or hydrogen cyanide (384), but reaction of sodium azide with hexachlorocyclotriphosphazene gave an oily explosive hexa-azide (150).

$$N_3P_3Cl_6 \xrightarrow{NaN_3} N_3P_3(N_3)_6$$

2,4 - Diamino - 2,4,6,6 - tetrachlorocyclotriphosphazene was converted similarly to a less explosive diaminotetra-azidophosphazene (67).

Chlorophosphazenes dissolved in suitable non-aqueous solvents, *e.g.*, acetone, react with alkali metal or ammonium thiocyanates to give fully substituted isothiocyanates. The isothiocyanate structure has been established by the infrared spectra, and these compounds react with ammonia, *n*-butylamine, aniline, phenylhydrazine, and ethanol. It is reported that polymerization of isothiocyanatophosphazenes to form an elastomer occurs at 150° (16, 253, 367).

$$N_4P_4Cl_8 \xrightarrow{KSCN} N_4P_4(NCS)_8 \xrightarrow{8NH_3} N_4P_4(NHCSNH_2)_8$$

F. CHEMICAL PROPERTIES

Halogenophosphazenes are comparatively stable to electrophilic and nucleophilic attack. Replacement of halogen and the formation of phosphorus–carbon, phosphorus–nitrogen, and phosphorus–oxygen bonds are discussed in Sections VI, VII, and VIII. Properties of chlorides have been most investigated. Octachlorocyclotetraphosphazene appears more susceptible than hexachlorocyclotriphosphazene to nucleophilic attack. Complete replacement of chlorine is easier in the former, perhaps for steric reasons. Hydrolysis is slow, partly because of the hydrophobic nature of the compounds; hexachlorocyclotriphosphazene can be steam distilled. Octachlorocyclotetraphosphazene is less stable to hydrolysis, and fluorides appeared less stable than chlorides (259, 320).

Unsuccessful attempts to prepare derivatives of hexachlorocyclotriphosphazene by reaction with sodium, sodium amalgam, potassium, silver, and zinc, have been reported (80, 133, 300). Reaction with sodium in liquid ammonia has been used in the determination of chlorine (364) and reaction with zinc and acetic acid gives phosphine (351).

Addition compounds of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene with perchloric acid have been reported (51). Early work indicated addition compound formation between hexachlorocyclotriphosphazene and nitrogen dioxide and sulfur trioxide (39). The compound $N_3P_3Cl_6 \cdot 3SO_3$ has been isolated (25, 144). Melting point diagrams of a number of binary mixtures of chlorophosphazenes and aminochlorophosphazenes gave no indication of compound formation (107). Studies of chlorophosphazenes with hydrogen chloride or sulfuric acid are reported to indicate association (259). No solid complexes of hexachlorocyclotriphosphazene with stannic chloride or antimony pentachloride were observed. A ternary complex of hexachlorocyclotriphosphazene with aluminum chloride and benzene (147) and a binary complex with aluminum chloride (50) have been reported.

G. PHYSICAL PROPERTIES

Melting points and boiling points of halogenophosphazenes and configurations of mixed halides are given in Tables 1 and 2. Tables 2 and 3 contain values of the density of liquid phosphazenes and viscosity data appear in Table 3. Density measurements of solid

phosphazenes are included with crystallographic data in Table 25 (Section XI-C). Vapor pressure data for halogenocyclophosphazenes and polydichlorophosphazene are given in Table 4. Tables 5 and 6 contain physical constants of other phosphorus–nitrogen halogen derivatives, and of pseudohalides and their derivatives. Solubilities of chlorophosphazenes in organic solvents have been reported (107, 259, 351, 396).

Hexafluorocyclotriphosphazene, hexachlorocyclotriphosphazene, and octafluorocyclotetraphosphazene have similar heats of fusion. The unusual properties of both fluorochlorocyclotetraphosphazenes merit further investigation. These compounds provide the only recorded examples of reported dissociation in the vapor state (310, 313, 314), and their boiling points are relatively low. The boiling points of fluorochlorocyclotriphosphazenes suggest that the lower-boiling difluoride, $N_3P_3F_2Cl_4$, may have a non-geminal configuration. This compound and the higher-boiling geminal tetrafluoride were both obtained from $N_4P_4F_4Cl_4$ by polymerization and subsequent depolymerization. It is possible that two fluorine atoms are geminal and two are non-geminal in $N_4P_4F_4Cl_4$, or that fluorine migration occurs at high temperatures.

TABLE 1

HALOGENOCYCLOTRIPHOSPHAZENES AND HALOGENOCYCLOTETRAPHOSPHAZENES

Compound	M.p., °C.	B.p., °C.	Configuration	References
$N_3P_3F_6$	27.8	50.9		(69, 153, 223, 319, 320)
$N_3P_3F_4Cl_2$		114.7	2,2,4,4:6,6	(70, 313)
$N_3P_3F_4Cl_2$		84.4	2,2,4,6:4,6	(70)
$N_3P_3F_2Cl_3$		150.1	2,2,4:4,6,6	(70)
$N_3P_3F_2Cl_4$		181.6	2,2:4,4,6,6	(70)
$N_3P_3F_2Cl_4$		140–142		(313)
$N_3P_3Cl_6$	114	256.5		(41, 57, 64, 191, 200, 212, 351, 354)
$N_3P_3Cl_5Br$	122.5–123.5			(301)
$N_3P_3Cl_4Br_2$	134.5–136.5			(301)
$N_3P_3Cl_2Br_4$	167.5–169			(301)
$N_3P_3Br_6$	192			(23, 38, 46, 186)
$N_4P_4F_8$	30.5	89.7		(69, 153, 216, 223, 319, 320)
$N_4P_4F_6Cl_2$	−12.4 to −12.1	105.8[a]		(314)
$N_4P_4F_4Cl_4$	−25.2 to −24.9	130.5[a]		(313)
$N_4P_4Cl_8$	124	328.5		(188, 191, 200, 212, 351, 354)
$N_4P_4Br_8$	202			(23, 46, 49, 186)

[a] Estimated from vapor pressure data.

VI. PHOSPHAZENE DERIVATIVES CONTAINING PHOSPHORUS–CARBON BONDS

Apart from the isolation of hexaphenylcyclotriphosphazene (304, 305), nothing was known about cyclic phosphazenes containing phosphorus–carbon bonds until Bode and his co-workers investigated the ammonolysis and cyclization of phenyl derivatives of phosphorus pentachloride, Friedel–Crafts type phenylation of chlorophosphazenes, and reactions of phenyl Grignard reagents and phenyllithium compounds with chlorophosphazenes (50, 54, 369). This work has been re-investigated and expanded recently (2, 268, 327, 328, 330). Two novel methods of synthesis have been developed by the Corona group: one based on the decomposition of tervalent phosphorus azides (151, 162, 163, 366) and the other on the dehydrohalogenation of aminodichlorobisperfluoroalkylphosphoranes (151, 365). Monophosphazenes (phosphine imines), which bear a structural relationship to other linear and cyclic phosphazenes, are also considered in this section.

TABLE 2

HIGHER HALOGENOPHOSPHAZENES

Compound	M.p., °C.	B.p., °C. (mm.)	n^{20}_{4358}	$n^{20}D$	d^{20}_4	References
$N_5P_5F_{10}$	−50	120.1	1.3550	1.3482	1.8259	(69)
$N_5P_5Cl_{10}$	41.3	223–224.3 (13)				(200, 212, 354)
$N_6P_6F_{12}$	−45.5	147.2	1.3604	1.3533	1.8410	(69)
$N_6P_6Cl_{12}$	92.3	281–282 (26)				(200, 212, 354)
$N_7P_7F_{14}$	−61	170.7	1.3644	1.3570	1.8496	(69)
$N_7P_7Cl_{14}$	8–12	289–294 (13)			1.890	(200, 212, 354)
$N_8P_8F_{16}$	−16.9	192.8	1.3677	1.3602	1.8567	(69)
$N_8P_8Cl_{16}$	57–58					(212)
$N_9P_9F_{18}$	<−78	214.4	1.3699	1.3622	1.8589	(69)
$N_{10}P_{10}F_{20}$	−51	230.8	1.3710	1.3633	1.8638	(69)
$N_{11}P_{11}F_{22}$	<−78	246.7	1.3723	1.3645	1.8644	(69)
$N_{12}P_{12}F_{24}$		143–148 (12.65)				(69)
$N_{13}P_{13}F_{26}$		154–159 (12.65)				(69)
$N_{14}P_{14}F_{28}$		166–170 (12.65)				(69)
$N_{15}P_{15}F_{30}$		136–142 (1.7)				(69)
$N_{16}P_{16}F_{32}$		143–148 (1.85)				(69)
$N_{17}P_{17}F_{34}$		152–157 (1.85)				(69)

TABLE 3

DENSITY AND VISCOSITY

Compound	Temperature range, °C.	$d^t = d^0 - \alpha t$ d^0	$10^3\alpha$	$-\log \eta$ (c.p.) $= -(A/T) + B$ A	B	ΔH, visc. kcal./mole	Ref.
$N_4P_4F_4Cl_4$	0–30	1.9568	1.36				(313)
$N_5P_5F_{10}$	20–80	1.8811	2.76	556	1.728	2.54	(69)
$N_6P_6F_{12}$	10–60	1.9009	2.10	602	1.512	2.75	(69)
$N_4P_4F_6Cl_2$	$d^{18.6} = 1.8742$						(314)

A. AMMONOLYSIS AND CYCLIZATION OF SUBSTITUTED QUINQUEVALENT PHOSPHORUS HALIDES

Ammonolysis and cyclization of phosphorus halides

TABLE 4

VAPOR PRESSURE DATA

Compound	Temperature range, °C.	$\log_{10} p(\text{mm.}) = (A/T) + B$ A	B	ΔH, sub., kcal./mole	ΔH, vap., kcal./mole	ΔS, vap., cal./deg.	ΔH, fus., kcal./mole	Reference
$N_3P_3F_6$	0–m.p.	2810	11.82	12.9				(320)
		2806	11.81	12.8				(153)
	M.p.-50	1670	8.04		7.6	23.5	5.3	(320)
		1679	8.065		7.68	23.7	5.1	(153)
$N_3P_3Cl_6$	75-m.p.	3978	11.187	18.2				(350)
	M.p.-190	2880	8.357		13.2	24.9	5.0	(350)
	M.p.-b.p.	2830	8.215		12.9	23.9		(225)
$N_4P_4F_8$	0-m.p.	3013	11.76	13.8				(320)
		3046	11.85	13.9				(153)
	M.p.-90	1952	8.26		8.9	24.6	4.9	(320)
		1947	8.247		8.91	24.5	5.0	(153)
$N_4P_4F_6Cl_2$	60–77	1911	7.923		8.74	23.07		(314)
$N_4P_4F_4Cl_4$	88–123	1911	7.615		8.74	21.66		(313)
$N_4P_4Cl_8$	M.p.-275	3400	8.560		15.6	25.9		(225)
$N_5P_5F_{10}$	25–120	2141.7	8.3373		9.8	24.9		(69)
$N_7P_7F_{14}$					11.6	26.2		(69)
$N_8P_8F_{16}$					12.0	25.8		(69)
$N_9P_9F_{18}$					12.7	26.1		(69)
$N_{10}P_{10}F_{20}$					13.5	26.9		(69)
$N_{11}P_{11}F_{22}$					14.6	28.0		(69)
$(NPCl_2)_x$	330–470	3380	7.24	15.5				(225)

TABLE 5

OTHER HALOGEN DERIVATIVES

Compound	M.p., °C.	B.p., °C. (mm.)	References
$NP_2(O)Cl_4$	35.7	102(1) $n^{38}D$ 1.5256 d^{38} 1.796	(27, 33, 189)
NP_3Cl_{12}	310–315		(32)
NP_4Cl_{11}	200–202		(33)
$N_2Me_4P_2Cl_6$	160 dec.		(68, 117)
$N_7P_6Cl_9$	237.5	251–261(13)	(199, 200, 355)

TABLE 6

PSEUDOHALIDES AND DERIVATIVES

Compound	M.p., °C.	References
$N_3P_3(N_3)_6$	< −20	(150)
$N_3P_3(NH_2)_2(N_3)_4$ (2,4:2,4,6,6)	81–82	(67)
$N_3P_3(NCS)_6$	42	(253, 367)
$N_3P_3(NHCSNH_2)_6$	190 dec.	(367)
$N_3P_3(NHCSNHBu^n)_6$	155	(367)
$N_3P_3(NHCSNHPh)_6$	151	(367)
$N_3P_3(NHCSOEt)_6$	174	(367)
$N_3P_3(NHCSN_2H_2Ph)_6$	165 dec.	(367)
$N_4P_4(NCS)_8$	90	(367)
$N_4P_4(NHCSNH_2)_8$	120 dec.	(367)
$N_4P_4(NHCSNHBu\text{-}n)_8$	105	(367)
$N_4P_4(NCS)_2(NHCSNHBu\text{-}n)_4$	155	(367)
$N_4P_4(NHCSNHPh)_8$	139	(367)
$N_4P_4(NHCSOEt)_8$	189	(367)
$N_4P_4(NHCSN_2H_2Ph)$	153 dec.	(367)

is the main synthetic route to chloro- and bromophosphazenes, and the method has been extended to the preparation of phosphazenes containing phosphorus–carbon bonds. The first attempt to prepare phenylphosphazenes gave a mixture of products, and on treatment with acetic acid a small quantity of a partially hydrolyzed derivative, $N_3P_3Ph_3ClO_2H_2$, was obtained (50).

Diphenyltrichlorophosphorane and ammonium chloride give low yields of phenylphosphazenes. Reaction with liquid ammonia gives colorless crystalline moisture-sensitive intermediates which yield a mixture of products including octaphenylcyclotetraphosphazene and some hexaphenylcyclotriphosphazene on heating. Both compounds are soluble in benzene and glacial acetic acid and neither is attacked by boiling water (152). The liquid ammonia method gave a crystalline intermediate, $N_3H_4P_2Ph_4Cl$, for which open-chain structures were proposed, and which gave similar yields of cyclic products on heating (42). A similar crystalline intermediate (XXIII), having the same composition and molecular weight, was obtained during a detailed investigation of the ammonolysis of diphenyltrichlorophosphorane (197). Proposed reaction paths are shown in Fig. 5, and postulated structures of compounds which were not isolated are shown in brackets.

Penta-coördinated phosphorus compounds are rare (375b) and the salt-like structure XXIII seems likely in view of the high basicity of cyclic phosphazenes (99, 282) and the formation of addition compounds by monophosphazenes (Section VI-G). Structure XXIVA was proposed for the compound $N_3HP_4O_2Ph_8$ but the tautomer XXIVB is a possible alternative.

Reactions of corresponding alkyl compounds (197) are shown in Fig. 6. The basic nature of some cyclophosphazenes (99, 282) suggests that compound XXV might have a cyclic structure, $N_3P_3Et_6 \cdot HCl$, and a tautomeric form (XXVIB) of compound XXXVIA is considered.

Shaw and Stratton re-investigated the reaction of phenyltetrachlorophosphorane with ammonium chloride: three isomers of formula $N_4P_4Ph_4Cl_4$, and a derivative, $N_3P_3Ph_3Cl_3$, were isolated (327, 328). A different derivative, $N_3P_3Ph_3Cl_3$, has been obtained from a similar reaction (175), and these compounds provide the first examples of *cis–trans* isomerism in the phosphazene field. The non-geminal configurations were

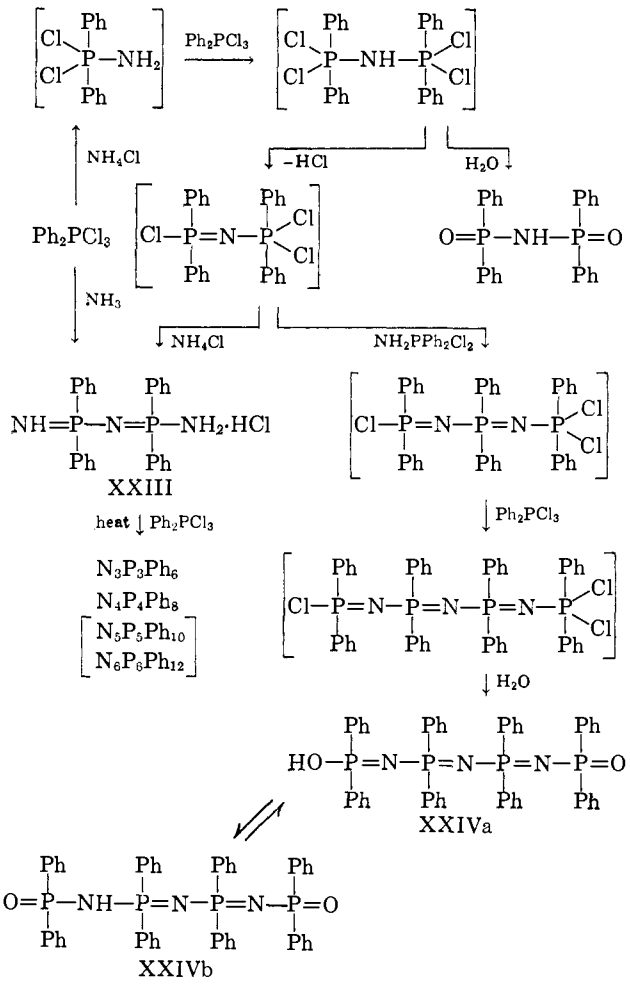


FIGURE 5

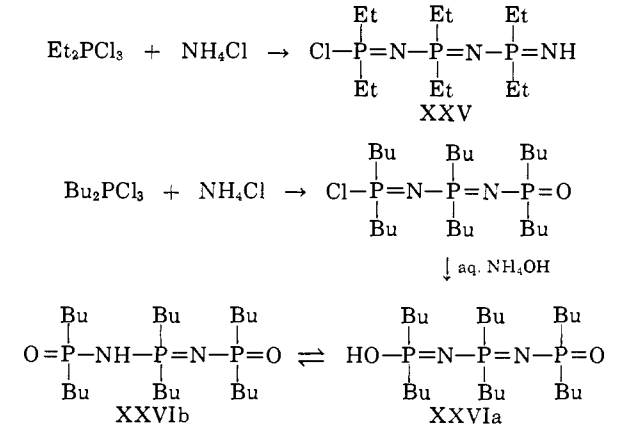


FIGURE 6

demonstrated by the method of synthesis and by the formation of phenylphosphonic acid on hydrolytic degradation.

Reaction of liquid ammonia with diethyltrichlorophosphorane gave unidentified chlorine-containing, moisture-sensitive products; on heating, a 37% yield of hexaethylcyclotriphosphazene and a 20% yield of octaethylcyclotetraphosphazene were obtained. Both compounds were soluble in water, ligroin, benzene, chloroform, carbon disulfide, carbon tetrachloride, and ethyl alcohol; on pyrolysis, both compounds gave black resinous products and one mole of ethane per mole of cyclic phosphazene (43). A similar reaction of dimethyltrichlorophosphorane gave 3–5% yields of cyclic phosphazenes, but treatment with triethylamine and ammonium chloride increased the yields to 70–75% (318).

A variation of the synthetic method involving the chlorination and subsequent dehydrogalogenation of aminobisperfluoromethylphosphine (151, 365) is discussed in Section IV.

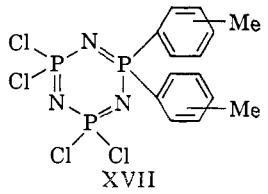
B. FRIEDEL–CRAFTS REACTION

Friedel–Crafts-type reactions of aromatic hydrocarbons include a number of reactions with organometallic and inorganic halides such as boron trichloride (240) and phosphorus trichloride (198a) but few similar reactions of quinquevalent phosphorus halides have been reported (198b).

Hexachlorocyclotriphosphazene and refluxing benzene give 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazene in the presence of aluminum chloride (50). The preparation has been repeated (29, 330) and moderate yields of 2,2,4,4-tetraphenyl-6,6-dichlorocyclotriphosphazene are obtained after longer reaction time (330). The geminal configuration of phenyl groups in both compounds was established by hydrolytic degradation to diphenylphosphinic acid (29, 330). The best method of preparation of hexaphenylcyclotriphosphazene is by reaction of hexachlorocyclotriphosphazene with benzene and aluminum chloride in an autoclave (330).

Three chlorophenyl derivatives, $N_3P_3(p\text{-}C_6H_4Cl)Cl_5$, $N_3P_3(p\text{-}C_6H_4Cl)_2Cl_4$, and $N_3P_3(p\text{-}C_6H_4Cl)_4Cl_2$, have been prepared by the Friedel-Crafts reaction, and hydrolytic degradation to appropriate phosphorus acids established *para* substitution and a preferred geminal reaction pattern (scheme 1). Reaction with toluene or *m*-xylene gave mixtures whose analyses corresponded to di- and tetrasubstituted tolyl- and xylyl-phosphazenes. The four chlorine atoms of the diphenyl derivative, $N_3P_3Ph_2Cl_4$, were replaced by toluene to give a mixture of isomeric 2,2-diphenyl-4,4,6,6-tetratolylcyclotriphosphazenes. None of the tolyl and xylyl derivatives was shown to be a single pure compound and individual isomers could not be separated, although it was established that geminal substitution occurred. Hydrolysis of 2,2-ditolyl-4,4,6,6-tetrachlorocyclotriphosphazene (XXVII) gave a quantitative yield of phosphoric acid, but the phosphonic acid fractions contained a mixture of isomeric acids.

Arylphosphazenes were not obtained from reactions of hexachlorocyclotriphosphazene with mesitylene,



XVII

durene, biphenyl, naphthalene, furan, or thiophene (2), and decomposition of the aromatic compound was probably catalyzed by the presence of aluminum chloride (370). Similar behavior has been observed in Friedel–Crafts reactions of boron trichloride (240).

Attempts to prepare chloroalkylphosphazenes by the Friedel–Crafts method were unsuccessful (64).

No pure compounds have been obtained from Friedel–Crafts reactions of octachlorocyclotetraphosphazene, and isolation of products is complicated by hydrolysis (2).

Discussion of the mechanism of these Friedel–Crafts reactions is restricted by lack of evidence. It has been suggested that hexachlorocyclotriphosphazene forms a ternary complex with aluminum chloride and benzene (147), and a binary complex with aluminum chloride has been observed in carbon disulfide solution (50). It is possible that the active intermediate is similar to those involved in acylation (20). Hydrogen in an aromatic hydrocarbon might be replaced by means of a complex involving a quasi-phosphonium ion whose reactivity might be reduced inter- or intramolecularly by the lone pair of electrons on nitrogen.

C. ORGANOMETALLIC REAGENTS

No products were obtained from the earliest reactions of hexachlorocyclotriphosphazene with organometallic reagents (80, 351), but in 1925, Rosset obtained a small quantity of hexaphenylcyclotriphosphazene from reaction of phenylmagnesium bromide with hexachlorocyclotriphosphazene (304, 305). The preparation has been repeated successfully (197, 274). It has been suggested that reaction of hexachlorocyclotriphosphazene with phenylmagnesium bromide does not occur under normal conditions of a Grignard reaction in ether. Toluene caused decomposition, but mixtures of anisole and toluene gave small yields of hexaphenylcyclotriphosphazene. The main reaction product, containing bromine and chlorine, could not be purified by recrystallization. Treatment with silver perchlorate gave a perchlorate derivative containing seven phenyl groups and three phosphorus–nitrogen units. Destructive distillation yielded triphenylphosphine oxide, but not aniline. It was assumed that the seventh phenyl group was attached to phosphorus and an open chain structure, $Ph_3P{=}N{-}PPh_2{=}N{-}PPh_2{=}NH\cdot HClO_4$, was suggested. The heptaphenyl derivative was not obtained by addition of phenylmagnesium bromide to hexaphenylcyclotriphosphazene, which suggests that ring cleavage occurred before the chlorine atoms were replaced completely (50). It seems likely that the presence of one geminal PCl_2 group may lead to cleavage of the ring by organometallic compounds. Reaction occurs between hexachlorocyclotriphosphazene and phenyllithium, but the expected substitution products are not obtained. Formation of a small quantity of diphenylphosphinic acid on hydrolysis indicates that some phenylation occurs (50), and phenylphosphazenes have been obtained by reaction of phenyllithium with fluorophosphazenes (45).

Reaction of phenylmagnesium bromide with octachlorocyclotetraphosphazene gave two tetraphenyl derivatives, two octaphenyl derivatives, and two phenylated cleavage products (54, 369). The two tetraphenyl compounds, which differed in melting point and solubility, could be obtained by recrystallization from the same solvent and it is likely that they are position isomers rather than different crystalline modifications of the same substance. The higher melting compound gave diphenylphosphinic acid on complete hydrolysis.

Conformational isomerism has been suggested (257) to account for the existence of two octaphenyl derivatives. The higher melting octaphenyl compound has been obtained from ammonolysis and cyclization of diphenyltrichlorophosphorane (152). The lower-melting compound has not yet been reported by other authors. The melting point is similar to that of hexaphenylcyclotriphosphazene, but it was stated that the mixed melting point with a sample of hexaphenylcyclotriphosphazene showed that the two compounds are different. Hydrolysis of tetrachlorotetraphenylcyclotetraphosphazenes gave some hexaphenylcyclotriphosphazene and phosphoric acid, and hydrolysis of a higher concentration of the phosphazenes gave octaphenylcyclotetraphosphazene, suggesting depolymerization and repolymerization of suitable fragments (54, 369).

Work up to this stage can be summarized by saying that with aryl organometallic compounds, small yields of definite compounds could be obtained. Some of these compounds appeared to be formed by ring opening, but most of the phosphazene was unaccounted for. No reaction was reported between hexachlorocyclotriphosphazene and methyllithium; and with sodium acetylide an uncharacterized, insoluble, polymeric product was obtained (64). Reaction with alkyl and aryl Grignard reagents gave low yields of high-melting solids, or viscous, undistillable oils, containing chlorine (394).

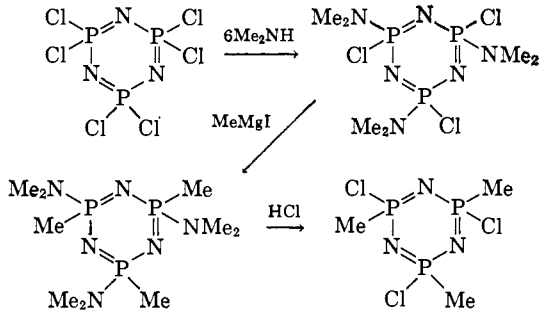
A variety of organolithium compounds react with hexachlorocyclotriphosphazene. Reaction with *n*-butyllithium takes place at −30° and viscous oils and solids of indefinite melting points are obtained. The molecular weights vary from 1000 to 3500, and the degree of butylation, *n*-Bu:P from approximately 1:1 to 2:1. All the products were soluble in benzene and some in

petroleum ether. Analyses of compounds containing a low *n*-Bu:P ratio suggested that some hydrolysis had occurred. Most of the products contained small quantities of chlorine which could be removed as triethylamine hydrochloride, suggesting a salt-like structure. The chemical properties of these polymers show some resemblance to the properties of monomeric phosphazenes (Section VI-G). The polymeric mixtures were partially separated by chromatography and crystallization, but none yielded any individual molecular weight species and all decomposed on attempted distillation (268).

It is well-known that removal by organometallic reagents of one or all three of the chlorine atoms in phosphorus trichloride is relatively easy, but that difficulties are experienced in replacing two chlorine atoms. Protection of one of the three positions by a dimethylamino group and reaction with an organometallic reagent, followed by removal of the dimethylamino group with hydrogen chloride under carefully controlled conditions, gave dialkylchlorophosphine (65).

$$PCl_3 \rightarrow Cl_2PNR_2 \rightarrow R_2PNR_2 \rightarrow R_2PCl$$

This reaction was applied by Tesi and Slota to 2,4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazene, whose configuration has been established (30, 281). The corresponding methyl derivative, $N_3P_3Me_3(NMe_2)_3$, was obtained from a Grignard reaction, and anhydrous hydrogen chloride in refluxing xylene removed the three dimethylamino groups. 2,4,6-Trichloro-2,4,6-trimethylcyclotriphosphazene was recovered as a crystalline solid. The authors state that similar reactions take place with phenyl- and vinylmagnesium bromide (368).



D. SYNTHESIS FROM TERVALENT PHOSPHORUS AZIDES

Preparation by this method of linear and cyclic phosphazenes (162, 163, 366) represented the most significant advance in synthetic procedure since discovery of the ammonolytic method. Phosphorus substituents which are unstable to high reaction temperatures or the action of hydrogen chloride or liquid ammonia, can be prepared by treating a tervalent phosphorus compound with a metal azide to give the azidophosphine which is not usually isolated, and polymerization occurs on heating. It is probable that this reaction involves a mechanism whereby the azido group is attacked by the lone pair of electrons of nucleophilic phosphorus which becomes quinquevalent.

$$Y_2PX + MN_3 \rightarrow Y_2PN_3 + MX \quad nY_2PN_3 \xrightarrow{\text{heat}} (NPY_2)_n + nN_2$$

Herring (162) obtained polymeric products by this method from reactions of PBr_3, $PhPCl_2$, and Ph_2PCl. Polydibromophosphazene gave the known elastomer $(NPBr_2)_x$ (23, 186) on heating under vacuum; polymeric $(NPPhCl)_x$ had an average molecular weight of 5,000; on heating polymeric $(NPPh_2)_x$ under vacuum a 33% yield of octaphenylcyclotetraphosphazene was obtained. Tesi, Haber, and Douglas isolated bisperfluoromethylphosphine azide which decomposed to polymeric bisperfluoromethylphosphazene, $[NP(CF_3)_2]_x$, the first perfluoroalkylphosphazene. The white amorphous solid was insoluble in common organic solvents, and appeared to be unaffected on boiling with sulfuric, nitric, and perchloric acids. The action of 10% caustic soda caused some decomposition and one mole of fluoroform was obtained per $NP(CF_3)_2$ unit (366).

E. MISCELLANEOUS REACTIONS

Homogeneous films of chlorocyclophosphazenes do not undergo reaction during 40 hr. irradiation with a mercury arc, but some reaction occurs with solutions in hydrocarbon solvents (96). No pure compounds were obtained, but analysis of the products indicated that some chlorine atoms had been replaced by hydrocarbon residues. It is probable that reaction proceeds by a free radical mechanism, and the authors suggested that the phosphazene rings were unchanged. This work may be compared with that of Kharasch on reactions of hydrocarbons with phosgene and oxalyl chloride (192).

Reaction with the solvent was observed during a study of polymerization of chlorophosphazenes in benzene, toluene, xylene, and hexane (264). The products appear similar to those mentioned above, but it was suggested that substitution was accompanied by cleavage of the phosphazene ring. In the absence of oxygen no reaction was observed, and the authors postulated a free radical mechanism.

F. PHYSICAL PROPERTIES

Melting points of alkyl- and aryl-phosphazenes, and of alkyl- and aryl-chlorophazenes, with configurations when known, are reported in Tables 7 and 8.

G. MONOPHOSPHAZENES (PHOSPHINE IMINES)

Monophosphazenes, discovered by Staudinger and Meyer, and investigated in detail by Staudinger and Hauser, are isosteric with phosphine methylenes, $R_3P{=}CH_2$, and phosphine oxides, $R_3P{=}O$ (340, 342). 2,2,2-Triphenylphosphazene, $HN{=}PPh_3$, acts as a ligand like triphenylphosphine oxide in the forma-

TABLE 7

ALKYL AND ARYL PHOSPHAZENES

Compound	M.p., °C.	Configuration	References
$N_3P_3Me_6$	195–196		(318)
$N_3P_3Me_5Cl$	156–157	2,4,6:2,4,6	(368)
$N_3P_3Et_6$	117.5–119		(43)
$N_3P_3(CF_3)_6$	64		(365)
$N_3P_3(C_3F_7)_6$	Oil		(365)
$N_3P_3Ph_6$	232–233		(42, 50, 54, 152, 197, 268, 274, 304, 305, 330, 369)
$N_3P_3Ph_4Cl_2$	142–143	2,2,4,4:6,6	(330)
$N_3P_3Ph_5Cl$	188	2,4,6:2,4,6	(328)
	161–163	2,4,6:2,4,6	(175)
$N_3P_3Ph_2Cl_4$	95	2,2:4,4,6,6	(29, 50, 330)
$N_3P_3(C_6H_4Cl)_4Cl_2$	188	2,2,4,4:6,6	(2)
$N_3P_3(p\text{-}C_6H_4Cl)_2Cl_4$	137	2,2:4,4,6,6	(2)
$N_3P_3(p\text{-}C_6H_4Cl)Cl_5$	91	2:2,4,4,6,6	(2)
$N_4P_4Me_8$	163–164		(318)
$N_4P_4Et_8$	Oil		(43)
$N_4P_4(CF_3)_8$	109		(365)
$N_4P_4Ph_8$	319.5–321		(42, 54, 152, 197, 328, 369)
	230		(54, 369)
$N_4P_4Ph_4Cl_4$	176	Geminal	(54, 369)
	205	Geminal	(54, 369)
	148	2,4,6,8:2,4,6,8	(327)
	248	2,4,6,8:2,4,6,8	(327)
	202	2,4,6,8:2,4,6,8	(328)
$[NP(CF_3)_2]_x$	95–100		(365, 366)
$(NPPh_2)_x$	85–110		(162)
$(NPPhCl)_x$	60–110 (softening)		(162)

TABLE 8

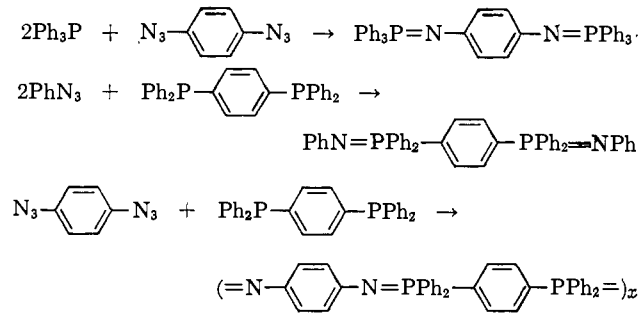
OPEN-CHAIN ALKYL AND ARYL PHOSPHAZENES

Compound	M.p., °C.	References
$NP_2Ph_4O_2H$	270–272	(197)
$N_2P_3Bu_6OCl$	171–172	(197)
$N_2P_3Bu_6O_2H$	86–87	(197)
$N_3P_2Ph_4H_4Cl$	233–235	(197)
	245–246.5	(42)
$N_3P_3Et_6HCl$	132–134	(197)
$N_3P_4Ph_8O_2H$	171–171.5	(197)

tion of coördination compounds of cobalt(II), nickel(II), and copper(II) (12).

Reaction of tertiary phosphines with alkyl, aryl, and acyl azides gives unstable phosphazides, RN=N—N=PR_3, some of which have been isolated, and which decompose to phosphazenes, RN=PR_3, with evolution of nitrogen. Reaction is more vigorous in the formation of alkyl- than of aryl-phosphazenes (340, 342). Kinetic studies indicated a second-order reaction for a series of *para*-substituted phenyl azides. Electron-withdrawing groups like $-NO_2$ increased the reaction rate, and electron-supplying groups like $-NMe_2$ decreased the reaction rate (170). Reactions of diazides and diphosphines have been investigated, and polymeric phosphazenes have been prepared (151, 163).

Tertiary phosphines and hydrazoic acid (340), chloramine (5, 9, 331, 332), or hydroxylamine-O-sulfonic acid (5,6) give phosphazene addition compounds, regarded as aminophosphonum salts $[R'R''NPR_3]^+X^-$. Free phosphazenes have been liberated from the salts by treatment with ammonia (7), sodamide in liquid



ammonia (8, 9), or magnesium hydride (331). Reaction of triphenyldihalogenophosphoranes with primary aromatic amines in the presence of pyridine gives aminophosphonium salts, but in the presence of triethylamine, phosphazenes are obtained (171, 172).

$$Ph_3PX_2 + ArNH_2 + 2NEt_3 \rightarrow ArN{=}PPh_3 + 2Et_3NHX$$

Similar reactions with aromatic diamines give bisphosphazenes. Reactions of triphenyldihalogenophosphoranes with ammonia, primary aliphatic amines, hydrazine, and phenylhydrazine give aminophosphonium salts, even in the presence of triethylamine (172).

Aminophosphonium salts are prepared from phosphazenes by the addition of hydrogen halides (9, 10, 11, 172, 340, 377), or alkyl halides, when alkylation of hydrogen also occurs. Decomposition to alkyl phosphazenes and alkyl halides occurs on heating (10, 172).

$$HN{=}PR_3 \xrightarrow{R'X} [R_2'NPR_3]X \rightarrow R'N{=}PR_3 + R'X$$

The basicity of phosphazenes decreases with nitrogen substituents alkyl > aryl > acyl. Soluble aminophosphonium salts, *e.g.*, chlorides, have been converted to less soluble salts, *e.g.*, picrates and perchlorates. The compound $[H_2NPPh_3]OSO_3H$ has been converted by boiling methanol to the methyl ester, $[H_2NPPh_3]$-OSO_3Me, and by benzoyl chloride to the 1-benzoyl phosphazene, PhCON=PPh_3 (6). Tertiary phosphines heated with NO-dibenzoylhydroxylamine, PhCONH-OCOPh, also give 1-benzoylphosphazenes, PhCON=PR_3 (377).

Phosphazenes in which hydrogen, alkyl, or aryl groups are attached to nitrogen are thermally stable, and distillation and sublimation have been achieved. Compounds in which acyl groups are attached to nitrogen decompose on heating to phosphine oxides and organic nitriles. Thioacyl derivatives have not been isolated, and decomposition to phosphine sulfide occurs (10, 331, 340).

$$PhCON_3 + PR_3 \rightarrow PhCON{=}PR_3 \rightarrow R_3PO + PhCN$$
$$PhCSN_3 + PR_3 \rightarrow [PhCSN{=}PR_3] \rightarrow R_3PS + PhCN$$

Monomeric phosphazenes are hydrolyzed to phosphine oxides and amine derivatives (8, 170, 172, 340, 342). The salts behave similarly, but are usually more stable (6, 10, 332), and increased hydrolytic stability is achieved if the phosphorus contains aryl rather than alkyl substituents. Hydrolytic stability decreases in the order of nitrogen substituents acyl > aryl > alkyl.

The compound $EtN{=}PEt_3$ decomposes on contact with moisture (340), but boiling acid is required for hydrolysis of $(ROCO)_2CR'N{=}PPh_3$ (170).

Monophosphazenes react readily with cumulative double bonds, *e.g.*, in carbon dioxide and isocyanates, but less readily with isolated or conjugated double bonds, when higher temperatures are required. Reaction occurs also with acid halides.

$RN{=}PR_3 + CO_2$	$\rightarrow RNCO + R_3PO$	(340, 342)
$RNCO$	$\rightarrow RNCNR + R_3PO$	(340, 342)
$R_2C{=}CO$	$\rightarrow R_2C{=}C{=}NR + R_3PO$	(340, 341, 343)
SO_2	$\rightarrow RNSO + R_3PO$	(340)
R_2CO	$\rightarrow R_2C{=}NR + R_3PO$	(340)
$PhCO_2H$	$\rightarrow PhCONHR + R_3PO$	(170)
CS_2	$\rightarrow RNCS + R_3PS$	(340, 342)
$RNCS$	$\rightarrow RNCNR + R_3PS$	(340, 342)
$HN{=}PR_3 + CO_2$	$\rightarrow [H_2NPR_3]NCO + R_3PO$	(9)
Ph_2CO	$\rightarrow Ph_2C{=}NH + R_3PO$	(9)
CS_2	$\rightarrow [H_2NPR_3]CNS + R_3PS$	(9)
$PhCOCl$	$\rightarrow PhCON{=}PR_3$	(6, 8)
H_2NSO_2Cl	$\rightarrow H_2NSO_2N{=}PR_3$	(10)

Reaction of triphenylphosphine with *p*-azidobenzoic acid gives the phosphazene, $p\text{-}HOCOC_6H_4N{=}PPh_3$, and a phosphazene-end-stoppered polyamide, which was also formed by pyrolysis of the phosphazene (172). The use of phosphazenes in the introduction of primary amine groups into organic compounds has been applied to the synthesis of amino acids (10, 170).

2,2,2-Triphenylphosphazene was converted by halogens to a mixture containing the 1-halogenophosphazene, $XN{=}PPh_3$, which reacted with triphenylphosphine to give a salt-like bromide, stable to boiling acid and decomposed only slowly by boiling alkali. Reaction with silver nitrate gave the corresponding nitrate. It was suggested that the compounds NP_2X_7 (X = Cl, Br) (Section V) might have analogous structures, and the great hydrolytic stability of the complex cation was ascribed to a resonance structure. The same compound has been obtained from reaction of triphenyldibromophosphorane and 2,2,2-triphenylphosphazene.

$$HN{=}PPh_3 + Br_2 \rightarrow BrN{=}PPh_3 + [H_2NPPh_3]Br$$

$$BrN{=}PPh_3 + PPh_3 \rightarrow [Ph_3P{-}N{=}PPh_3]Br \xrightarrow{AgNO_3} [Ph_3P{-}N{=}PPh_3]NO_3$$

$$Ph_3PBr_2 + 2HN{=}PPh_3 \rightarrow [Ph_3P{-}N{=}PPh_3]Br + [H_2NPPh_3]Br$$

Similar products have been obtained from reactions of 1-halogenophosphazenes with triphenylarsine and dialkyl sulfides (10, 11).

A number of phosphazenes where the phosphorus–nitrogen unit is part of a cyclic organic structure have been prepared, and their ultraviolet spectra discussed (91).

Physical constants of monophosphazenes and aminophosphonium compounds are reported in Tables 9 and 10.

TABLE 9

MONOPHOSPHAZENES

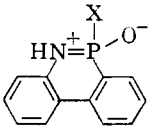
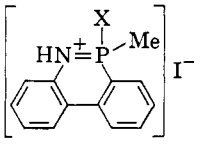
Compound	M.p., °C., or b.p., °C. (mm.)	References
$ClNPPh_3$	179–180 dec.	(11)
$BrNPPh_3$	170–172 dec.	(10, 11)
$INPPh_3$	174–175 dec.	(11)
$HNPPh_3$	122.5–123.5	(7, 8, 9, 331)
$MeNPEt_3$	94–96 (11)	(340)
$MeNPPh_3$	62–65	(340)
$EtNPMe_3$	56 (10)	(76)
$EtNPEt_3$	93.5 (11)	(340)
$EtNP(Pent\text{-}i)_3$	119 (0.23)	(340)
$EtNPPh_3$	96 198 (0.5)	(10, 76, 340)
$PhNPEt_3$	116 (0.08)	(340)
$PhNP(Pent\text{-}i)_3$	161 (0.04)	(340)
$PhNPEt_2Ph$	69–70	(340)
$PhNPPh_3$	131–132	(172, 342)
$o\text{-}MeC_6H_4NPPh_3$	129–130	(172)
$m\text{-}MeC_6H_4NPPh_3$	107–109	(172)
$p\text{-}MeC_6H_4NPPh_3$	134–135	(172, 342)
$3,5\text{-}Me_2C_6H_3NPPh_3$	130–131	(342)
$o\text{-}ClC_6H_4NPPh_3$	137–138	(172)
$m\text{-}ClC_6H_4NPPh_3$	118–119	(172)
$p\text{-}ClC_6H_4NPPh_3$	121	(170, 172)
$p\text{-}NCC_6H_4NPPh_3$	191–192	(172)
$o\text{-}NO_2C_6H_4NPPh_3$	151–152	(172)
$m\text{-}NO_2C_6H_4NPPh_3$	137–138	(172)
$p\text{-}NO_2C_6H_4NPPh_3$	159	(170, 172)
$2,4\text{-}(NO_2)_2C_6H_3NPPh_3$	200–201	(172)
$2,4,6\text{-}(NO_2)_3C_6H_2NPPh_3$	183–184	(172)
$p\text{-}Me_2NC_6H_4NPPh_3$	123–124 dec.	(172)
$p\text{-}PhN_2C_6H_4NPPh_3$	176–178	(172)
$p\text{-}MeOC_6H_4NPPh_3$	118	(170, 172)
$o\text{-}HOCOC_6H_4NPPh_3$	222	(170)
$o\text{-}MeOCOC_6H_4NPPh_3$	148	(170)
$p\text{-}EtOCOC_6H_4NPPh_3$	135–136	(172)
$2\text{-}(C_5H_4N)NPPh_3$	142–143	(172)
$1\text{-}C_{10}H_7NPPh_3$	141–143	(340)
$2\text{-}C_{10}H_7NPPh_3$	142–143	(172)
$PhCONPEt_3$	62.5–63	(340)
$PhCONPEt_2Ph$	73–74	(340)
$PhCONPPh_3$	194–195.5	(6, 340, 377)
$PhCONHNPPh_3$	177–180	(172)
$o\text{-}HOC_6H_4CONPPh_3$	207	(170)
$H_2NCONPPh_6$	180	(170)
$PhSO_2NPPh_3$	156–157	(170, 172)
$p\text{-}MeC_6H_4SO_2NPPh_3$	193	(9, 172)
$p\text{-}Ph_3PNC_6H_4SO_2NPPh_3$	254–256	(172)
$H_2NSO_2NPPh_3$	198	(10)
$o\text{-}Ph_3PNC_6H_4NPPh_3$	206	(172)
$p\text{-}Ph_3PNC_6H_4NPPh_3$	255–257	(163, 172)
$p,p'\text{-}Ph_3PNC_6H_4C_6H_4NPPh_3$	269–270	(172)
$2,3\text{-}Ph_3PNC_{10}H_6NPPh_3$	226–228	(172)
$p\text{-}PhNPPh_2C_6H_4PPh_2NPh$	208–210	(163)

TABLE 10

AMINOPHOSPHONIUM SALTS

Compound	M.p., °C.	Reference
$[H_3NPMe_3]Cl$	122	(9)
$[H_3NPEt_3]N_3$		(340)
$[H_3NP\text{-}n\text{-}Bu_3]Cl$	62–65	(332)
$[H_3NP\text{-}n\text{-}Bu_3][PF_6]$	72–73	(332)
$[H_3NP\text{-}n\text{-}Bu_3][anthraquinone\text{-}2\text{-}sulfonate]$	89–90	(332)
$[H_3NP(CH_2Ph)_3]Cl$	220–221	(331)
$[H_3NP(CH_2Ph)_3][picrate]$	179.5–180.5	(331)
$[H_3NP(CH_2Ph)_3][HPtCl_6]$	190–191	(331)
$[H_3NP(CH_2CH_2CN)_3][picrate]$	154	(331)
$[H_3NP[CH_2CH_2CN)_3][HPtCl_6]$	210 dec.	(331)
$[H_3NPMe_2Ph]Cl$	106	(9)
$[H_3NPMePh_2]Cl$	167	(9)
$[H_3NP(allyl)_2Ph][anthraquinone\text{-}2\text{-}sulfonate]$	181–183	(331)
$[H_3NP(allyl)_3Ph][HPtCl_6]$	192–193	(331)
$[H_3NPPh(CH_2)_4][PF_6]$	76	(332)

TABLE 10—*Concluded*

Compound	M.p., °C.	References
$[H_2NPPh(CH_2)_4]$[anthraquinone-2-sulfonate]	207–208	(332)
$[H_2NPPh(CH_2)_4]$[picrate]	171–172	(332)
$[H_2NPPh(CH_2)_6][PF_6]$	120–121	(332)
$[H_2NPPh(CH_2)_6]$[anthraquinone-2-sulfonate]	243 dec.	(332)
$[H_2NPPh(CH_2)_6]$[picrate]	150–151	(332)
$[H_2NPPh_3]Cl$	236	(9, 332)
$[H_2NPPh_3]Br$	248	(10, 172)
$[H_2NPPh_3]I$	254	(10)
$[H_2NPPh_3]N_3$	196 dec.	(340)
$[H_2NPPh_3][ClO_4]$	172–175	(332)
$[H_2NPPh_3][IO_4]$	163–165	(332)
$[H_2NPPh_3][NCO]$	120	(9, 332)
$[H_2NPPh_3][CNS]$	173	(9)
$[H_2NPPh_3][HSO_4]$	205	(6)
$[H_2NPPh_3][MeSO_4]$	146	(6)
$[H_2NPPh_3]$[picrate]	133	(6)
$[H_2NPPh_3][PF_6]$	185–187	(332)
$[H_2NPPh_3][HPtCl_6]$	190–193	(332)
$[H_2NPPh_3]$[anthraquinone-2-sulfonate]	214–216	(332)
$[H_2NPPh_3]$[nitroprusside]	193–195	(332)
$[MeHNPPh_3][PF_6]$	185–188	(332)
$[MeHNPPh_3][ClO_4]$	175–177	(332)
$[MeHNPPh_3][HPtCl_6]$	185–187	(332)
$[MeHNPPh_3]$[picrate]	118–120	(332)
$[n\text{-}BuHNPPh_3]Br$	141–143	(172)
$[C_6H_{11}HNPPh_3]Br$	176–177	(172)
$[PhHNPPh_3]Cl$	228–231	(340)
$[PhHNPPh_3]Br$	201–203	(172)
$[m\text{-}MeC_6H_4HNPPh_3]Br$	171–172	(172)
$[p\text{-}C_6H_5C_6H_4HNPPh_3]Cl$	180	(170)
$[H_2NHNPPh_3]Br$	210–212 dec.	(172)
$[PhHNHNPPh_3]Br$	218–219 dec.	(172)
$[(EtOCOCH_2)MeNPPh_3]I$	103–104	(340)
$[Et_2NPPh_3]I$	164–165	(10, 340)
$[Ph_3PNPPh_3]Br$	256	(10)
$[Ph_3PNPPh_3][NO_3]$	232	(10)
$[Me_2SNPPh_3]Br$	188 dec.	(10)
$[Et_2SNPPh_3]Br$	148	(10)
$[Et_2SNPPh_3]I$	158	(10)
$[Ph_3AsNPPh_3]Br$	226	(10)
$[HNPPh_3]_2[Co^{II}Cl_2]$	217	(12)
$[HNPPh_3]_2[Cu^{II}Cl_2]$	193	(12)
$[HNPPh_3]_4[Ni^{II}I_2]$	226	(12)
		
X = OPh	288–289	(91)
X = Ph	283	(91)
X = H	193–194	(91)
		
X = Me	230–233 dec.	(91)
X = Ph	214	(91)

VII. REACTIONS OF HALOGENOPHOSPHAZENES WITH NITROGENOUS BASES

A. AMMONOLYSIS

Ammonolysis of hexachlorocyclotriphosphazene was investigated by Stokes who isolated the diamino derivative, $N_3P_3Cl_4(NH_2)_2$ (351, 352); the bromine analog, $N_3P_3Br_4(NH_2)_2$, has been reported (147). Small quantities of the former have been isolated from reaction of gaseous ammonia with phosphorus pentachloride in carbon tetrachloride solution (40). Ammonolysis of chlorophosphazenes has been studied and a number of aminophosphazenes have been reported (17, 40, 101, 107, 221, 224, 229, 334). Hexa-aminocyclotriphosphazene and octa-aminocyclotetraphosphazene are very soluble in water (this may be contrasted with the slight solubility of melamine), but are virtually insoluble in common organic solvents, except glacial acetic acid with which there is some reaction (221, 334).

Ammonolysis of tetrachlorodiphenylcyclotriphosphazene gives a diamino derivative, $N_3P_3Ph_2Cl_2(NH_2)_2$, and a tetra-amino derivative, $N_3P_3Ph_2(NH_2)_4$, which exists in two crystalline modifications with different melting points. Complete ammonolysis is slow and a polymeric compound mixed with ammonium chloride was regarded as an intermediate (29). The basicity of aminophosphazenes is comparable with that of the parent amines, and addition compounds are formed with one molecule of hydrogen chloride even in the presence of ammonia (99, 221, 282). It is possible that the suggested polymeric intermediate is an addition compound, $N_3P_3Ph_2(NH_2)_4 \cdot HCl$, and a related product, also regarded as a polymeric compound mixed with ammonium chloride, might have a salt-like structure, $N_3P_3Ph_2(NH_2)_2(NMe_2)_2 \cdot 3HCl$. Addition of more than one molecule of hydrogen chloride occurs with excess of acid (45, 51, 99). Salts would be expected to regenerate the parent aminophosphazenes on treatment with ammonia, or primary, secondary, or tertiary amines, but the polymeric substances would behave differently with each base.

B. AMINOLYSIS

The earliest aminolysis experiments were described by Hoffman (168, 169) and Couldridge (80). The work was extended (210, 307, 308, 393), and it was observed that complete aminolysis is difficult for amines containing large substituents (349). Spiro derivatives of *o*-phenylenediamine and diaminotoluene were prepared, and in an investigation of the aminolysis of chlorocyclotriphosphazenes, the products contained even numbers of amino groups. It was assumed that geminal replacement had occurred (51), but more detailed studies with ammonia, methylamine, and dimethylamine indicated that a non-geminal reaction pattern is followed (scheme 2, Section III). Some mixed amino derivatives were prepared, and these included a pair of position isomers (XI, XII) (28, 29, 30).

Reactions of a large number of primary and secondary amines with hexachlorocyclotriphosphazene give aminophosphazenes, $N_3P_3Cl_{6-n}(NR_2)_n$ (n = 1–4, 6) (280, 281). Penta-amino derivatives were not obtained and elementary analyses of such compounds would be

close to those of hydrochlorides $N_3P_3(NR_2)_6 \cdot HCl$. Piperidinophosphazenes, $N_3P_3Cl_{6-n}(NC_5H_{10})_n$ (n = 1–6), have been reported recently (203).

Primary amines with unbranched alkyl groups give fully aminolyzed products at or near room temperature, and primary amines with branched alkyl groups give partially aminolyzed products under the same conditions. Higher temperatures were required for complete replacement. In refluxing ether, isopropylamine and *t*-butylamine gave excellent yields of tetraamino derivatives, and dichlorotetra-isopropylaminocyclotriphosphazene was converted to hexa-isopropylaminocyclotriphosphazene by reaction with excess of amine in a sealed tube at 120°. The tetra-*t*-butylamino derivative does not react with excess of *t*-butylamine under these conditions, but reaction with methylamine to give tetrakis-*t*-butylaminobismethylaminocyclotriphosphazene indicates the importance of steric effects in this type of reaction. Steric effects are even more pronounced with secondary amines. Temperatures of 60–80° are necessary for complete reaction with dimethylamine and piperidine, but sealed tube reactions did not always produce fully substituted phosphazene derivatives of higher amines (281). The reaction resembles that of amines with cyanuric chloride (333b) or 1-chloro-2,4-dinitrobenzene (56).

Chlorophosphazenes react with esters of amino acids to give substituted aminophosphazenes (203, 306), and with acetanilide to give acetyl chloride, hydrogen chloride, and uncharacterized, probably polymeric phosphazenes (60, 386). Diphenylurea gives phenyl isocyanate, and reactions of other amides have been reported (60).

Reactions of amines with octachlorocyclotetraphosphazene follow a similar pattern. Di-, tetra-, and octaaminophosphazenes (187, 188, 308), one monoamino derivative, $N_4P_4Cl_7NMe_2$ (283), and alkylamino and arylamino derivatives of the three non-geminal isomeric tetrachlorotetraphenylcyclotetraphosphazenes (327, 328) have been prepared.

No products were isolated from the reaction of hexafluorocyclotriphosphazene with ammonia or aniline (320), but partially substituted products have been obtained from reaction with dimethylamine and piperidine (45).

Alkyldimethylaminophosphazenes are converted by anhydrous hydrogen chloride to alkylchlorophosphazenes (368) and the reaction is discussed in Section VI-C. Similarly, the compound $N_3P_3Cl_4(NH_2)_2$ is reported to give hexachlorocyclotriphosphazene with hydrogen chloride or aniline hydrochloride (51).

Addition compounds with hydrochloric acid and perchloric acid are formed in the presence of excess of acid (51), and it has been observed that monohydrochlorides of hexa-aminocyclotriphosphazenes, $N_3P_3(NHR)_6 \cdot HCl$, are formed even in the presence of excess of amine. The hydrogen chloride can be removed by triethylamine (282). It is clear that aminophosphazenes are relatively strong bases, and an addition compound with boron trifluoride, $N_3P_3(NHEt)_6 \cdot BF_3$, has been prepared (2). In aqueous solution, aminophosphazenes are about two pK units weaker than the parent amines, but they are stronger bases than the parent amines in nitrobenzene solution and some other non-aqueous solvents (99). The relative basic strengths may depend on the structure of the aminophosphazene and on the nature of the solvent. It is possible that reported chlorine-containing intermediates, some of which have been regarded as open-chain end-stoppered phosphazene polymers (29, 42, 43, 152, 197, 318), are hydrochlorides.

Most of the compounds reported in Tables 11, 12, 13, 14, 15, and 16 are crystalline solids. Melting points re-

TABLE 11

AMINOPHOSPHAZENES

Compound	M.p., °C.	References
$N_3P_3(NH_2)_6$	ca. 220 dec.	(17, 221)
$N_3P_3(NHMe)_6$	258	(30, 281)
$N_3P_3(NMe_2)_6$	104	(30, 280, 281)
$N_3P_3(NHEt)_6$	118–119	(280, 281)
$N_3P_3(NEt_2)_6$	205	(281)
$N_3P_3(NHPr\text{-}n)_6$	59	(194, 281)
$N_3P_3(NHPr\text{-}i)_6$	81	(281)
$N_3P_3(NHBu\text{-}n)_6$	48	(194, 281)
$N_3P_3(NHBu\text{-}i)_6$	59	(281)
$N_3P_3(NHPent\text{-}n)_6$	38	(194)
$N_3P_3(NHHex\text{-}n)_6$	49	(194)
$N_3P_3(NHC_6H_{11})_6$	166	(280, 281)
$N_3P_3(NC_5H_4)_6$	147.5	(276)
$N_3P_3(NC_5H_{10})_6$	266	(51, 80, 168, 203, 281)
$N_3P_3(NHNHPh)_6$	200	(80)
$N_3P_3(NHCH_2CO_2Et)_6$	72–72.5	(203)
$N_3P_3[NH(CH_2)_2CO_2Me]_6$	Oil	(203)
$N_3P_3(NH\text{-}o\text{-}C_6H_4Me)_6$	241–242	(80)
$N_3P_3(NH\text{-}p\text{-}C_6H_4Me)_6$	249	(168, 281)
$N_3P_3(NMePh)_6$	141–142	(45)
$N_4P_4(NH_2)_8$	ca. 220 dec.	(17, 221)
$N_4P_4(NHMe)_8$	208	(188, 283)
$N_4P_4(NMe_2)_8$	238	(280, 283)
$N_4P_4(NHEt)_8$	122	(188)
$N_4P_4(NHPr\text{-}n)_8$	99.5	(188, 283)
$N_4P_4(NHBu\text{-}n)_8$	86	(188)
$N_4P_4(NHBu\text{-}i)_8$	94	(283)
$N_4P_4(NHBu\text{-}s)_8$	111	(283)
$N_4P_4(NHPent\text{-}n)_8$	79	(188)
$N_4P_4(NHHex\text{-}n)_8$	70	(188)
$N_4P_4(NHCH_2Ph)_8$	121.5	(188)
$N_4P_4(NC_5H_4)_8$	262	(276)
$N_4P_4(NC_4H_8O)_8$	>230 dec.	(188)
$N_4P_4(NC_5H_{10})_8$	295	(2, 188)
$N_4P_4(NH\text{-}o\text{-}C_6H_4Me)_8$	229 dec.	(188)
$N_4P_4(NH\text{-}m\text{-}C_6H_4Me)_8$	199	(188)
$N_4P_4(NH\text{-}p\text{-}C_6H_4Me)_8$	207	(188)

TABLE 12

MIXED AMINOPHOSPHAZENES

Compound	M.p., °C.	Configuration	References
$N_3P_3(NH_2)_2(NHMe)_4$	161.5	2,4:2,4,6,6	(28, 30)
	204	2,2:4,4,6,6	(28, 30)
$N_3P_3(NH_2)_2(NMe_2)_4$	144	2,4:2,4,6,6	(30)
$N_3P_3(NH_2)_2(NHMe)_2(NMe_2)_2$	76	2,2:4,6:4,6	(30)
$N_3P_3(NH_2)_2(NHPh)_4$	256–257	2,4:2,4,6,6	(51)
$N_3P_3(NHMe)_2(NMe_2)_4$	125	2,4:2,4,6,6	(30)
$N_3P_3(NHMe)_2(NMe_2)_2$	119	2,4,6:2,4,6	(30)
$N_3P_3(NHMe)_4(NMe_2)_2$	124	2,2,4,6:4,6	(30)
$N_3P_3(NHMe)_2(NHBu\text{-}t)_4$	199		(281)

TABLE 13

AMINOHALOGENOPHOSPHAZENES

Compound	M.p., °C., or b.p., °C. (mm.)	Configuration	References
$N_3P_3Cl_5NH_2$	>140	2,2,4,4,6:6	(107)
$N_3P_3Cl_5NMe_2$	12–14	2,2,4,4,6:6	(281)
	70–72 (0.01)		
$N_3P_3Cl_5NEt_2$	81–83 (0.01)	2,2,4,4,6:6	(281)
	$n^{22}D$ 1.5310		
$N_3P_3Cl_5NHCH_2CO_2Et$	74–75	2,2,4,4,6:6	(203)
$N_3P_3Cl_5NH(CH_2)_2CO_2Me$	58–59.5	2,2,4,4,6:6	(203)
$N_3P_3Cl_5NC_5H_{10}$	68–69	2,2,4,4,6:6	(203)
$N_3P_3Cl_4(NH_2)_2$	163–165	2,2,4,6:4,6	(107, 221, 351)
$N_3P_3Br_4(NH_2)_2$			(147)
$N_3P_3Cl_4(NHMe)_2$	100–100.5	2,2,4,6:4,6	(30, 51, 281)
	85	2,2,4,6:4,6	(28, 30)
$N_3P_3Cl_4(NMe_2)_2$	103	2,2,4,6:4,6	(28, 30, 280, 281)
$N_3P_3Cl_4(NEt_2)_2$	134		(280, 281)
$N_3P_3Cl_4(NBu\text{-}i_2)_2$	73		(281)
$N_3P_3Cl_4[N(C_5H_{11})_2]_2$	200		(280, 281)
$N_3P_3Cl_4(NHCH_2CH_2NH_2)_2$	188		(51)
$N_3P_3Cl_4(NHCH_2CO_2Et)_2$	83–84		(203)
$N_3P_3Cl_4[NH(CH_2)_2CO_2Me]_2$	59–60		(203)
$N_3P_3Cl_4(NHC_6H_4NH)$	>350	2,2,4,4:6,6	(51)
$N_3P_3Cl_4(NHC_6H_3MeNH)$	211	2,2,4,4:6,6	(51)
$N_3P_3Cl_4(NC_5H_{10})_2$	104–105	2,2,4,4:6,6	(203)
$N_3P_3Cl_3(NMe_2)_3$	104.5–105.5	2,4,6:2,4,6	(281)
	107		(28, 30)
$N_3P_3Cl_3(NEt_2)_3$	102 (2)		(280, 281)
	$n^{25}D$ 1.5100		
	162		(61, 281)
$N_3P_3Cl_3(NBu\text{-}n_2)_3$	170 (0.01)		(281)
$N_3P_3Cl_3(NC_5H_{10})_3$	113.5–114.5		(203)
$N_3P_3Cl_3(NH_2)_2(NMe_2)$	87	2,4,6:2,4:6	(28, 30)
$N_3P_3Cl_3(NHMe)(NMe_2)_2$	82	2,4,6:2:4,6	(28, 30)
$N_3P_3Cl_2(NH_2)_3(NHMe)_2$	140	2,4:6,6:2,4	(28, 30)
$N_3P_3Cl_2(NMe_2)_4$	103.5–104	2,4:2,4,6,6	(280, 281)
	101–101.5		(281)
$N_3P_3Cl_2(NEt_2)_4$	125 (0.02)		(281)
	$n^{22}D$ 1.5103		
$N_3P_3Cl_2(NHPr\text{-}n)_4$	93		(281)
$N_3P_3Cl_2(NHPr\text{-}i)_4$	126		(281)
$N_3P_3Cl_2(NHBu\text{-}s)_4$	71		(281)
$N_3P_3Cl_2(NHBu\text{-}t)_4$	155.5		(281)
$N_3P_3Cl_2(NHPh)_4$	191	2,4:2,4,6,6	(51)
$N_3P_3Cl_2(NH\text{-}p\text{-}C_6H_4Me)_4$	174		(51, 281)
$N_3P_3Cl_2(NHCH_2CO_2Et)_4$	73–74		(203)
$N_3P_3Cl_2[NH(CH_2)_2CO_2Me]_4$	42		(203)
$N_3P_3Cl_2(NC_5H_{10})_4$	111–112		(203)
$N_3P_3Cl(NC_5H_{10})_5$	121–123.5		(203)
$N_4P_4Cl_6(NHMe)_2$	143		(187)
$N_4P_4Cl_6(NMe_2)_2$	171		(187)
$N_4P_4Cl_6(NEt_2)_2$	113		(187)
$N_4P_4Cl_6(NHBu\text{-}t)_2$	124		(187)
	169		(283)
$N_4P_4Cl_6(NHPh)_2$	166	2,2,4,6,6,8:4,8	(187)
$N_4P_4Cl_6(NMePh)_2$	146		(187)
$N_4P_4Cl_6(o\text{-}NHC_6H_4Me)_2$	172	2,2,4,6,6,8:4,8	(187)
$N_4P_4Cl_6(m\text{-}NHC_6H_4Me)_2$	204	2,2,4,6,6,8:4,8	(187)
$N_4P_4Cl_6(p\text{-}NHC_6H_4Me)_2$	196		(187)
$N_4P_4Cl_6(NC_5H_{10})_2$	194		(187)
$N_4P_4Cl_6(NC_4H_8O)_2$	205		(187)
$N_4P_4Cl_4(NHPr\text{-}i)_4$	187		(283)
$N_4P_4Cl_4(NC_5H_{10})_4$	204		(188)
$N_4P_4Cl_4(NMePh)_4$	146		(188)

corded in the reviewers' laboratory refer to samples in melting point tubes. Some of these compounds exist in several solid modifications possessing different melting points which can be observed with a polarizing microscope. Compounds of the same formula, for which different physical constants are reported, may be isomers or different crystalline modifications of the same substance.

TABLE 14

ALKYL AND ARYL AMINOCHLOROPHOSPHAZENES AND AMINOPHOSPHAZENES

Compound	M.p., °C., or b.p., °C. (mm.)	Configuration	References
$N_3P_3Ph_4ClNHMe$	166	2,2,4,4:6:6	(165)
$N_3P_3Ph_4ClNMe_2$	166	2,2,4,4:6:6	(165)
$N_3P_3Ph_4ClNEt_2$	148	2,2,4,4:6:6	(165)
$N_3P_3Ph_4ClNC_5H_{10}$	175	2,2,4,4:6:6	(2)
$N_3P_3Ph_4(NHMe)_2$	190	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NMe_2)_2$	145	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NHEt)_2$	165	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NHBu\text{-}t)_2$	163	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NHC_6H_{11})_2$	122–123	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NHPh)_2$	224	2,2,4,4:6,6	(165)
$N_3P_3Ph_4(NC_5H_{10})_2$	181	2,2,4,4:6,6	(165)
$N_3P_3Me_3(NMe_2)_3$	146–147 (3)	2,4,6:2,4,6	(368)
$N_3P_3Ph_3Cl_3$	188	2,4,6:2,4,6	(328)
$N_3P_3Ph_3(NHMe)_3$	167	2,4,6:2,4,6	(328)
$N_3P_3Ph_3(NC_5H_{10})_3$	185–187	2,4,6:2,4,6	(328)
$N_3P_3Ph_2Cl_3NHMe$	151	2,2:4,4,6:6	(165)
$N_3P_3Ph_2Cl_3NMe_2$	110	2,2:4,4,6:6	(165)
$N_3P_3Ph_2Cl_3NHEt$	97	2,2:4,4,6:6	(165)
$N_3P_3Ph_2Cl_3NHC_6H_{11}$	111–112	2,2:4,4,6:6	(165)
$N_3P_3Ph_2Cl_3NC_5H_{10}$	125	2,2:4,4,6:6	(2)
$N_3P_3Ph_2Cl_2(NH_2)_2$	162–163	2,2:4,6:4,6	(51)
$N_3P_3Ph_2Cl_2(NHMe)_2$	170–171	2,2:	(165)
$N_3P_3Ph_2Cl_2(NMe_2)_2$	143–144	2,2:	(165)
$N_3P_3Ph_2Cl_2(NEt_2)_2$	64.5–66	2,2:	(165)
$N_3P_3Ph_2Cl_2(NHC_6H_{11})_2$	144	2,2:	(165)
$N_3P_3Ph_2Cl_2(NHPh)_2$	193	2,2:4,6:4,6	(51)
$N_3P_3Ph_2Cl_2(NC_5H_{10})_2$	144–145	2,2:	(165)
	131	2,2:	(165)
$N_3P_3Ph_3(NH_2)_4$	275 and 106	2,2:4,4,6,6	(28, 29)
$N_3P_3Ph_2(NH_2)_2(NHMe)_2$	140	2,2:4,6:4,6	(28, 29)
$N_3P_3Ph_2(NH_2)_2(NMe_2)_2$	137	2,2:4,6:4,6	(28, 29)
$N_3P_3Ph_2(NH_2)_2(NHPh)_2$	218	2,2:4,6:4,6	(51)
$N_3P_3Ph_2(NHMe)_4$	174	2,2:4,4,6,6	(28, 29, 165)
$N_3P_3Ph_2(NMe_2)_4$	120	2,2:4,4,6,6	(28, 29, 165)
$N_3P_3Ph_2(NHEt)_4$	122	2,2:4,4,6,6	(165)
$N_3P_3Ph_2(NHC_6H_{11})_4$	136.5	2,2:4,4,6,6	(165)
$N_3P_3Ph_2(NHPh)_4$	198–199	2,2:4,4,6,6	(51)
$N_3P_3Ph_2(NHCH_2Ph)_4$	92.5	2,2:4,4,6,6	(165)
$N_3P_3Ph_2(NC_5H_{10})_4$	195–197	2,2:4,4,6,6	(165)
$N_4P_4Ph_4Cl_4$	248	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NH_2)_4$	228–229	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHMe)_4$	130 and 151	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NMe_2)_4$	178–180	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHEt)_4$	99.5–101.5	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NEt_2)_4$	310–320 dec.	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHPr\text{-}n)_4$	97–98	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHPr\text{-}i)_4$	139.5–140	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHBu\text{-}t)_4$	250–252	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHC_6H_{11})_4$	131.5–132	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NC_5H_{10})_4$	258–259	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHPh)_4$	241.5–242.5	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHNHPh)_4$	173–175	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4Cl_4$	202	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHMe)_4$	130–131	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NMe_2)_4$	154	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHEt)_4$	121–122	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHPr\text{-}i)_4$	133–133.5	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NC_5H_{10})_4$	224	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4Cl_4$	148	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NHMe)_4$	112–113	2,4,6,8:2,4,6,8	(328)
$N_4P_4Ph_4(NC_5H_{10})_4$	239–240	2,4,6,8:2,4,6,8	(328)

TABLE 15

ADDITION COMPOUNDS OF AMINOPHOSPHAZENES

Compound	M.p., °C.	Reference
$N_3P_3Cl_2(NH_2)_2(NHC_6H_4NH)\cdot 0.5HCl$	160–161	(51)
$N_3P_3Cl_2(NHPh)_4\cdot 0.5HCl$	217	(51)
$N_3P_3(NHEt)_6\cdot HCl$	197	(282)
$N_3P_3(NHPr\text{-}n)_6\cdot HCl$	184	(282)
$N_3P_3(NHPr\text{-}i)_6\cdot HCl$	203	(282)
$N_3P_3(NHBu\text{-}n)_6\cdot HCl$	132	(282)
$N_3P_3(NHBu\text{-}i)_6\cdot HCl$	211	(282)
$N_3P_3(NHPh)_6\cdot HCl$	221	(51)

TABLE 16

OPEN-CHAIN AMINOPHOSPHAZENES

Compound	M.p., °C.	B.p., °C. (mm.)	Reference
$NP_2O(NMe_2)_5$	*ca.* 26	152 (2.2) $n^{25}D$ 1.4830	(27)
$NP_2O(NHPh)_5$	228–229		(33)

Using non-geminal assignments of amino groups in the compounds $N_3P_3Cl_4(NH_2)_2$ and $N_3P_3Ph_2Cl_2(NH_2)_2$ (28, 29, 30) it is possible to assign configurations to compounds prepared previously (47, 51). The configuration of 2,4-bisamino-2,4,6,6-tetrakisanilinocyclotriphosphazene (XIV) was discussed in Section III-A.

C. REACTION WITH TERTIARY AMINES

The suggestion that chlorophosphazenes react with tertiary bases to form addition compounds of formula $NPX_2 \cdot 2NR_3$ (306) appears unlikely (64, 195), and reported addition compounds of hexachlorocyclotriphosphazene (147) remain unconfirmed (64, 195).

Trimethylamine reacts with hexachlorocyclotriphosphazene to give tetramethylammonium chloride and a mixture of partially substituted dimethylamino derivatives, $N_3P_3Cl_{6-n}(NMe_2)_n$. No reaction was observed with pyridine or triethylamine, or between trimethylamine and hexafluorocyclotriphosphazene (64). Dealkylation of dimethylaniline to form hexa-N-methylanilinocyclotriphosphazene (45) and a similar reaction of cyanuric chloride with diethylaniline have been observed (145a). Hexachlorocyclotriphosphazene, like other acid halides, gives a red crystalline dye with pyridine and aniline. The reaction involves opening of the pyridine ring (147).

D. REACTION WITH HYDRAZINES

Hexaphenylhydrazinocyclotriphosphazene (80, 307, 308) and hexahydrazinocyclotriphosphazene, which forms crystalline derivatives with six molecules of benzaldehyde or salicylaldehyde (252), have been prepared. A phenylhydrazine derivative, $N_4P_4Ph_4(NHNHPh)_4$, prepared from one of the isomeric 2,4,6,8:-2,4,6,8-tetrachlorotetraphenylcyclotetraphosphazenes, forms an addition compound with benzene (328).

E. PHOSPHAMS

Phosphams are insoluble, gray-white solids, formed by reaction of phosphorus pentachloride with ammonia (121, 122, 132, 226, 330).

$$PCl_5 + 2NH_3 \rightarrow (NPNH)_x$$

Similar products have been formed by reaction of ammonia or ammonium chloride with molten hexachlorocyclotriphosphazene (80, 224), or liquid ammonia with chlorophosphazenes followed by thermal decomposition of the resulting amides (17, 40, 221, 230, 334). It has been reported that the reaction is not reversible (349).

Similar compounds are obtained by the thermal decomposition of tetra-aminotetrachlorocyclotetraphosphazene or octa-aminocyclotetraphosphazene (101). These reactions have been investigated in some detail, and thermogravimetric and differential thermal analysis of the pyrolysis of hexa-aminocyclotriphosphazene and octa-aminocyclotetraphosphazene to corresponding phosphams show that the reaction path and thermal stability depend markedly on the material of the pyrolysis crucible (221).

$$N_3P_3(NH_2)_6 \xrightarrow{-NH_3} (NPNH)_x$$
$$N_4P_4Cl_4(NH_2)_4 \xrightarrow{-HCl} (NPNH)_x$$
$$N_4P_4(NH_2)_8 \xrightarrow{-NH_3} (NHNH)_x$$

Some of the early work has been summarized by Steger (346), who suggests that P=N—P and P—NH—P groups occur in an irregular spatial array (334, 344, 345, 346, 348).

Cyclotriphosphazenes and cyclotetraphosphazenes are distinguished readily by their infrared spectra (88, 321), but phosphams obtained by pyrolysis of different aminophosphazenes give broad diffuse absorption areas with little indication of original ring structures (221, 347). Cyclotetraphosphazenes have higher densities than analogous cyclotriphosphazenes, and density measurements provide a method of distinguishing between phosphams (Table 17), which suggests that six- and eight-membered ring structures are retained under some conditions (221).

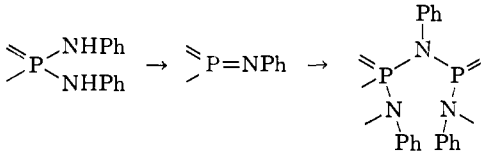
TABLE 17

DENSITY OF AMIDES AND DERIVED PHOSPHAMS

Compound	*d*	Compound	*d*	Method displacement	Ref.
$N_3P_3(NH_2)_6$	1.68 ± 0.04	$N_4P_4(NH_2)_8$	1.77 ± 0.04	Toluene	(221)
$[N_3P_3(NH)_3]_x$	2.17 ± 0.04	$[N_4P_4(NH)_4]_x$	2.43 ± 0.04	Toluene	(221)
	2.21 ± 0.02		2.49 ± 0.02	Hydrogen	(118)

Further thermal decomposition of phosphams gives successively $(N_5P_3)_x$ and $(NP)_x$ (107, 227); the former has been obtained by heating $N_3P_3Cl_4(NH_2)_2$ (224).

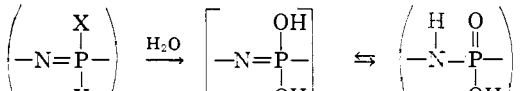
Phosphams containing phenyl groups have been prepared by the thermal decomposition of anilinophosphazenes (52, 168). Initial products were slightly soluble in nitrobenzene and nitromethane, but it was concluded that polymerization increased on further heating, as insoluble final products were formed without further weight loss. Reaction with aniline in sealed tubes gave back the starting materials without change in ring size (52).



VIII. COMPOUNDS CONTAINING PHOSPHORUS–OXYGEN BONDS

A. ACIDS AND SALTS

Hydrolysis of halogenophosphazenes under acidic, neutral, or alkaline conditions gives hydroxyoxophosphazanes (imidophosphates) as suggested by Stokes (353) rather than hydroxyphosphazenes (79); *cf.* cyanuric acid (333a). The acids contain one replaceable hydrogen atom per phosphazane unit, and the hexasilver salt prepared by Stokes is considered to contain nitrogen–silver bonds, $N_3Ag_3P_3(O_2Ag)_3$ (279, 353).



Phosphazane structures have been confirmed by the infrared spectra of a number of anhydrous salts (269). The spectrum of the hydroxyoxotetraphosphazane provides evidence of O—H. . .O and N—H. . .N (or O) hydrogen bonding. Bands due to the former do not appear in the spectrum of the tetrasilver salt, and in the octasilver salt this region of the spectrum is transparent (348). Conductometric titration of tri- and tetraphosphazane acids has established that neutralization occurs in three and four distinct steps, respectively (103).

Studies of hydrolysis have been confined mainly to chlorophosphazenes, but no quantitative data are available. Hydrolysis in the presence of moist pyridine gives pyridine salts which are converted to amorphous powders by loss of pyridine on heating (308).

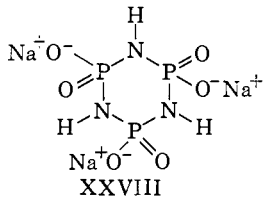
It has been suggested that salts of phosphazane acids give N-chloro derivatives on treatment with hypochlorite (360, 361). Reaction of hexachlorocyclotriphosphazene with sodium benzoate gave benzonitrile, benzoic anhydride, and sodium chloride, and initial formation of a hexabenzoate and subsequent rearrangement with the formation of carbon–nitrogen bonds was suggested (41).

X-Ray powder diffraction patterns of a number of acids and salts have been reported (164).

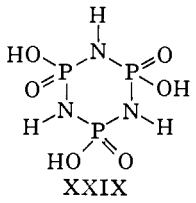
1. Hydrolysis of Cyclotriphosphazenes

Hydrolysis of an ether solution of hexachlorocyclotriphosphazene by aqueous sodium acetate gives the tetrahydrate of a trisodium salt (XXVIII), and the monohydrate has also been obtained. Decomposition to ammonia and phosphoric acid occurs on acidification, and the three intermediates obtained under milder conditions were regarded as di-imidotriphosphoric acid, $N_2P_3O_8H_7$; imidodiphosphoric acid, $NP_2O_6H_5$; and pyrophosphoric acid, $P_2O_7H_4$ (353).

An intermediate, $N_3P_3Cl_4O_2H_2$, has been obtained,



XXVIII

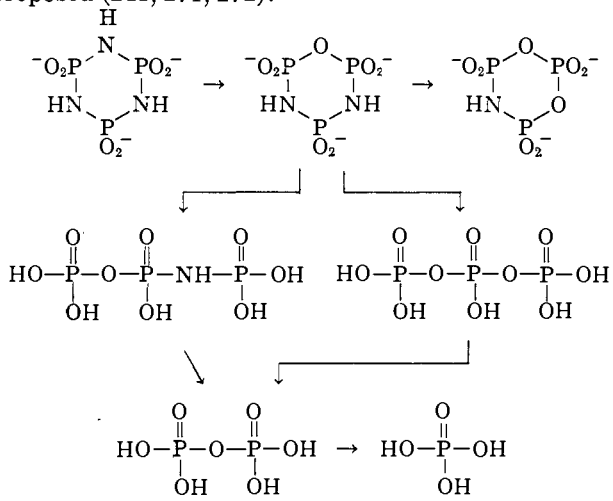


XXIX

but the structure is not known with certainty (273, 351). Hydrolysis of an ether solution of $N_3P_3Cl_4(NH_2)_2$ gave di-imidophosphoric acid rather than the expected hydroxyoxophosphazane (102) and further investigation using modern methods would be informative.

An improvement in technique involves the use of dioxane as solvent. Reaction is more rapid and monohydrates of trisodium or tripotassium salts are obtained directly (45, 247, 248). Acidification of the tripotassium salt with perchloric acid gave a dihydrate of the parent acid, and the anhydrous acid XXIX also could be obtained (245).

Hydrolysis of the acid XXIX has been followed using paper chromatographic and ion-exchange techniques, and it has been shown that the intermediates isolated by Stokes are cyclic compounds. It is believed that water can add to hydroxyoxophosphazane ions to form an intermediate from which ammonium ions are eliminated without ring-opening, and the following scheme was proposed (241, 271, 272).

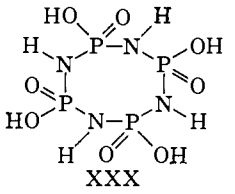


Hexafluorocyclotriphosphazene is decomposed less readily than hexachlorocyclotriphosphazene by methanolic potassium hydroxide (319, 320).

2. Hydrolysis of Cyclotetraphosphazenes

Octahalogenocyclotetraphosphazenes are hydrolyzed more readily than hexahalogenocyclotriphosphazenes (319, 320, 354). Stokes prepared salts containing two, four, and in the case of silver, eight metal atoms. A stable dihydrate of the hydroxyoxophosphazane (XXX) was obtained on acidification (108, 164, 273, 348, 354). The water of crystallization is lost with difficulty (109, 354) and a hydrogen-bonded structure is

indicated by the infrared spectrum. The acid dihydrate is isomorphous with dipotassium, dirubidium, and diammonium salts, and an ionic structure containing H_3O^+ ions has been proposed (78).



XXX

3. *Hydrolysis of Higher Chlorophosphazenes*

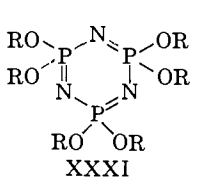
Hydrolysis of the compounds $N_5P_5Cl_{10}$, $N_6P_6Cl_{12}$, and $N_7P_7Cl_{14}$ was studied by Stokes. The metal salts are amorphous, and, on heating with acetic acid, small quantities of the tetraphosphazane acid XXX were obtained (356). It has been established that the hydroxyoxocyclotriphosphazane is an important intermediate (266) and hydrolysis of a polymeric chlorophosphazene has been investigated (129).

B. ESTERS

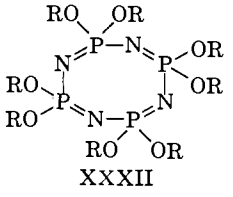
Compounds derived from halogenophosphazenes by replacement of halogen by –OR or –SR groups may be regarded as esters or thio-esters of hypothetical hydroxyphosphazene acids. This replacement is achieved by reaction with a metal alkoxide or thio-alkoxide, an alcohol or thio-alcohol in the presence of a hydrogen-halide acceptor.

1. *Phosphazene Alkyl Esters*

No cyclic phosphazene esters were isolated from the earliest investigations of reactions of alcohols and phenols with chlorophosphazenes (208, 209, 384) and the first successful preparation was reported by Dishon. Methyl and *n*-butyl esters (XXXI, R = Me, *n*-Bu) were prepared from sodium methoxide and 1-butanol–pyridine, respectively, and purified by vacuum distillation, but the yield of the methyl ester was reduced by partial conversion to an undistillable residue. Preparation of the allyl ester XXXI (R = allyl) was attempted, but the product decomposed rapidly to a viscous oil (94). The subsequent preparation of this compound from the sodium alkoxide and by heating the chloride with allyl alcohol was described, but no physical constants were given (397).



XXXI



XXXII

The ethyl ester XXXI (R = Et) was prepared from sodium ethoxide and hexachlorocyclotriphosphazene (279). Satisfactory analyses were obtained, but it is possible that the product, which changed from a viscous oil to a gelatinous solid on standing and decomposed to form ethyl ether on heating to 120°, contained impurities which catalyzed thermal decomposition. The preparation was later re-investigated, and the ester, which can be purified by vacuum distillation (111, 389), is insoluble in water; but the compound described previously was separated from an insoluble compound, $N_3P_3Cl_2(OEt)_4$, by extraction with water.

Alkyl esters (XXXI, R = Et, *n*-Pr, *n*-Bu; XXXII, R = Me, Et, *n*-Pr, *n*-Bu) were prepared from reaction of alcohols with chlorophosphazenes in the presence of pyridine, but the methyl ester XXXI (R = Me) decomposed on removal of excess of solvent, possibly because of nucleophilic attack by pyridine on carbon (111). Hexa-alkyl esters XXXI are liquids whose boiling points increase with increasing carbon chain-length, and octa-alkyl esters XXXII are less volatile. Unidentified products were obtained from alcohol–pyridine reactions, but use of sodium alkoxides was more successful (389). Sodium alkoxides have been used also in the preparation of the methyl ester XXXI (R = Me) (94, 111), a mono-alkoxychlorophosphazene, $N_3P_3Cl_5OMe$ (165), and fluoro-alkylmethylene esters of high thermal stability (277). The infrared spectra of a number of phosphazene esters have been described, but the method of preparation was not stated (89).

2. *Phosphazene Aryl Esters*

Aryl esters (XXXI, XXXII; R = Ph, *p*-C_6H_4OMe, β-$C_{10}H_7$) and some partially phenoxylated derivatives, $N_3P_3Ph_2Cl_2(OPh)_2$, $N_3P_3Cl_5OPh$, $N_3P_3Cl_2(OPh)_4$, and $N_3P_3Cl(OPh)_5$, have been prepared conveniently from metal aryloxides and chlorophosphazenes (90, 111). Phenols did not give well-defined products on heating with hexachlorocyclotriphosphazene in the presence of aqueous sodium hydroxide (60), but a number of aryl esters (XXXI, R = *p*-C_6H_4X, X = H, Cl, NO_2) were prepared when pyridine was used as the condensing agent. An ionic intermediate was postulated (391). Heating hexachlorocyclotriphosphazene with dibenzyl ether yielded benzyl chloride, but no phosphazene derivatives were isolated (384).

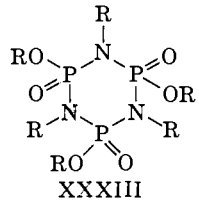
3. *Phosphazane Esters*

Alkylation of the trisilver salt of the phosphazane acid gives the N-alkyl ester XXXIII (R = Et) (279).

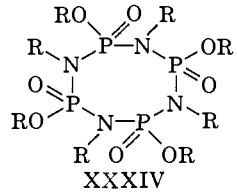
$$N_3H_3P_3(O_2Ag)_3 \xrightarrow[100°]{EtI} N_3Et_3P_3(O_2Et)_3$$

This compound is obtained also by thermal rearrangement at 200° of the phosphazene ester XXXI (R = Et). The tetraphosphazane ester XXXIV (R = Et), which is a crystalline solid, is also prepared by thermal rearrangement (112). Reaction of the tetrasilver salt,

$N_4H_4P_4(O_2Ag)_4$, with ethyl iodide gives an oil (279) which is not identical with the rearranged product, and it is possible that the oil contains a mixture of isomers.



XXXIII



XXXIV

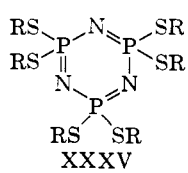
4. Polymeric Esters

Little is known about esters of higher phosphazene and phosphazane acids. A chlorophosphazene polymer of approximate composition $H(NPCl_2)_{11}Cl$ reacts with sodium methoxide to give a methyl ester of the same degree of polymerization, but reaction with sodium *t*-butoxide gives isobutene and the sodium salt of a polymeric acid. With small quantities of water the chlorophosphazene polymer gave a higher polymer containing P–O–P bonds. The methyl ester could be prepared, but reaction with sodium *t*-butoxide gave isobutene and a polymeric acid as before (31).

Alcoholysis of a polymeric chlorophosphazene of degree of polymerization *ca.* 200 has been investigated. With ethanol, isopentyl alcohol, and 2-ethylhexanol, almost complete replacement of chlorine occurred at room temperature in the presence of pyridine. Sodium alkoxide gave products containing a higher proportion of chlorine, but products obtained by both methods were deficient in alkoxyl and presumably contained P=O groups in addition to $P(OR)_2$ groups (145).

5. Thioesters

Alkyl- and aryl-thioesters (XXXV) have been prepared from chlorophosphazenes and thioalcohol–pyridine mixtures (390) or by reaction with sodium mercaptides in tetrahydrofuran (66). Reaction of sodium mercaptides in ether gave compounds of formulas $N_3P_3Cl_4(SAlk)_2$, $N_3P_3Cl_4(SAr)_2$, $N_3P_3(SAr)_6$, $N_4P_4Cl_4(SAlk)_2$, and $N_4P_4Cl_4(SAr)_4$ (66). Densities and refractive indices at 20° have been reported by Yokoyama (390) and other physical constants are reported in Table 20.

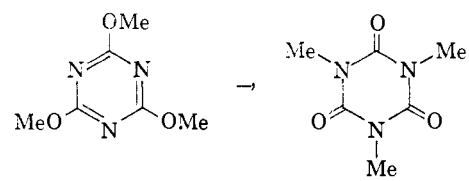


XXXV

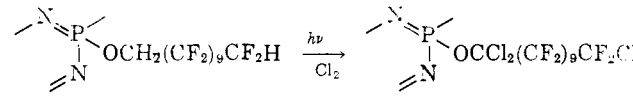
6. Properties

The esters are generally insoluble in water and moderately stable to hydrolysis, but no quantitative hydrolytic studies have been carried out. The N-ethylphosphazane ester XXXIII (R = Et) formed an addition compound with three molecules of hydrogen chloride. One molecule was lost and the dihydrochloride formed on standing in a desiccator for 48 hr. The ester was recovered by treatment with potassium hydroxide. On boiling with 2 *N* hydrochloric acid, ethylammonium chloride and phosphoric acid were obtained, and treatment with 6 *N* potassium hydroxide gave an amorphous solid for which an open-chain structure was proposed (279).

Fitzsimmons and Shaw (112) discovered that phosphazene alkyl esters undergo thermal rearrangement to isomeric N-alkyl phosphazanes on heating at 200°, and the benzyl ester XXXI (R = CH_2Ph) rearranges to the N-benzyl isomer XXXIII (R = CH_2Ph) at a lower temperature of 160°. Phenyl esters (XXXI, XXXII; R = Ph) are stable for prolonged periods at 300°. Aliphatic carbon atoms of P–O–C– groups are often susceptible to nucleophilic attack, and it is suggested that ring nitrogens act as inter- or intra-molecular nucleophiles (112). The phosphazene allyl ester, which contains reactive α-carbon atoms, is known to decompose readily (94), possibly *via* a rearrangement of this type or polymerization of the allyl groups. A formal analogy to this rearrangement involves the conversion of 2,4,6-trimethoxy-*s*-triazine to the N-methyl isomer (167).



The high thermal stability of phosphazene fluoroalkyl esters is of interest (277) since compounds containing α-carbon atoms adjacent to powerful electron-attracting groups might be expected to rearrange more readily than their unfluorinated analogs; but the reported thermal stability probably is greater than that of phenyl esters. Substitution by chlorine of hydrogen attached to α- and ω-carbon atoms occurs under the influence of ultraviolet light (278).



Refractive indices of some phosphazene esters have been measured by Yokoyama (389); other physical constants of phosphazene esters, phosphazane esters, and thioesters are recorded in Tables 18, 19, 20.

IX. Polymerization and Depolymerization

A. Change in Ring Size

Compared with sulfur–nitrogen compounds (142) few examples of change in ring size without intermediate high polymer formation have been reported among

TABLE 18

PHOSPHAZENE ESTERS

Compound	M.p., °C., or b.p. °C. (mm.)	References
$N_3P_3(OMe)_6$	114 (0.1)	(94, 111)
$N_3P_3(OEt)_6$	115–116 (0.1)	(111, 112, 389)
$N_3P_3(OPr\text{-}n)_6$	146–148 (0.1)	(111)
$N_3P_3(OBu\text{-}n)_6$	162–164 (0.01)	(94, 111)
	$n^{26.5}D$ 1.4473	
	$d^{26.5}$ 1.0342	
$N_3P_3(OC_6H_{11})_6$	184	(34)
$N_3P_3(OCH_2Ph)_6$	51.5	(113)
$N_3P_3(OPh)_6$	110–111	(111)
$N_3P_3(p\text{-}OC_6H_4OMe)_6$	103–104	(113)
$N_3P_3(O\text{-}\beta\text{-}C_{10}H_7)_6$	168–169	(113)
$N_3P_3(OCH_2CF_3)_6$	38	(277)
	248 (743)	
$N_3P_3(OCH_2CF_2CF_3)_6$	16–18	(277)
	136.5 (6)	
	$n^{25}D$ 1.3365	
$N_3P_3(OCCl_2CF_2CF_3)_6$	147–148	(278)
	176 (0.5)	
$N_3P_3(OCH_2(CF_2)_2CF_3)_6$	154 (3)	(277)
	$n^{25}D$ 1.3309	
$N_3P_3(OCCl_2(CF_2)_2CF_3)_6$	94	(278)
$N_3P_3(OCH_2(CF_2)_6CF_2H)_6$	32–36	(277)
	258–260 (2)	
$N_3P_3(OCH_2(CF_2)_3CF_2H)_6$	103–105	(277)
	320–324 (2)	
$N_3P_3Cl(OPh)_5$	68–69	(113)
$N_3P_3Cl_2(OPh)_4$	75–76	(90)
$N_3P_3Ph_2Cl_2(OPh)_2$	143–144	(90)
$N_3P_3Cl_5OMe$	30–32	(165)
$N_3P_3Cl_5OPh$	48	(90)
$N_4P_4(OMe)_8$	41	(111, 321)
$N_4P_4(OEt)_8$	45–47	(111, 112)
$N_4P_4(OPr\text{-}n)_8$	38–38.5	(111)
$N_4P_4(OBu\text{-}n)_8$	196–198 (0.005)	(111)
$N_4P_4(OCH_2Ph)_8$	38–39	(113)
$N_4P_4(OPh)_8$	85–86	(111)
$N_4P_4(O\text{-}p\text{-}C_6H_4OMe)_8$	73–74	(113)
$N_4P_4(OCH_2CF_3)_8$	65	(277)
	139–140 (3)	
$N_4P_4(OCH_2CF_2CF_3)_8$	142–144 (3)	(277)
	$n^{27}D$ 1.3530	
$N_4P_4(OCH_2(CF_2)_2CF_3)_8$	84–85	(277)
	169.5–171.5 (3)	
$N_4P_4(OCCl_2(CF_2)_2CF_3)_8$	129–132	(278)
	234 (0.3)	
$N_4P_4(OCH_2(CF_2)_6CF_2H)_8$	398–401 (760)	(277)
$N_4P_4(OCH_2(CF_2)_3CF_2H)_8$	102–105	(277)
	312–320 (0.1)	
$N_4P_4(OCCl_2(CF_2)_3CF_2Cl)_8$	145–150	(278)
$N_4P_4Ph_4(OMe)_4$[a] (2,4,6,8:2,4,6,8)	142–143	(328)
$N_4P_4Ph_4(OEt)_4$[a] (2,4,6,8:2,4,6,8)	103–104	(328)
$N_4P_4Ph_4(OEt)_4$[b] (2,4,6,8:2,4,6,8)	121.5–122	(328)
$N_4P_4Ph_4(OPh)_4$[a] (2,4,6,8:2,4,6,8)	132.5–133.5	(328)

[a] Derived from $N_4P_4Ph_4Cl_4$, m.p. 248°. [b] Derived from $N_4P_4Ph_4Cl_4$, m.p. 202°.

TABLE 19

PHOSPHAZANE ESTERS

Compound	M.p., °C.	References
$N_3Et_3P_3(O_2Et)_6$	74.5	(112, 279)
$N_3(CH_2Ph)_3P_3(O_2CH_2Ph)_3$	88–89	(113)
$N_4Et_4P_4(O_2Et)_4$	208–210	(112)

TABLE 20

THIOESTERS

Compound	M.p., °C.	B.p., °C. (mm.)	Reference
$N_3P_3Cl_4(SEt)_2$		128 (0.2)	(66)
$N_3P_3Cl_4(SPr\text{-}n)_2$		124 (0.1)	(66)
$N_3P_3Cl_4(SPr\text{-}i)_2$	53–54	117 (0.03)	(66)
$N_3P_3Cl_4(SBu\text{-}n)_2$		150 (0.08)	(66)
$N_3P_3Cl_4(SBu\text{-}i)_2$		138 (0.08)	(66)
$N_3P_3Cl_4(SPh)_2$	107		(66)
$N_3P_3(SEt)_6$	35.5	196 (0.06)	(66)
$N_3P_3(SPr\text{-}n)_6$		209 (0.02)	(66)
$N_3P_3(SBu\text{-}n)_6$		238 (0.04)	(66)
$N_3P_3(SC_6H_{11})_6$	80–81		(66)
$N_3P_3(SCH_2Ph)_6$	77.5–78.5		(66)
$N_3P_3(SPh)_6$	153.5		(66)
$N_4P_4Cl_4(SEt)_4$	105–106.5		(66)
$N_4P_4Cl_4(SPr\text{-}n)_4$	74.5–75		(66)
$N_4P_4Cl_4(SBu\text{-}n)_4$		148–150 (0.2)	(66)
$N_4P_4Cl_4(SPh)_4$	156		(66)

phosphazenes. Partially phenylated tetraphosphazenes are reported to depolymerize and repolymerize in the presence of dioxane and aqueous alkali (54, 369). It is reported that two chlorofluorocyclotetraphosphazenes dissociate into diphosphazene fragments, but there is no evidence of whether symmetrical cleavage occurs with the formation of identical fragments. It was considered that the tetraphosphazenes, obtained by fluorination of hexachlorocyclotriphosphazene, were cracking products of an intermediate high polymer (310, 313, 314).

B. HIGH POLYMERS

Inorganic polymers (317, 323, 325) and phosphazene polymers (259, 322, 324, 336) have been reviewed, and phosphazene polymers have been classified into addition and condensation polymers (324). Condensation polymers were discussed in Section VII-E.

Lower cyclic chlorophosphazenes are converted on heating to a high molecular weight, insoluble elastomer, which is colorless and transparent when pure. There is a resemblance to unvulcanized rubber, and it was discovered by Stokes that depolymerization to lower cyclic oligomers occurred at higher temperatures, particularly under vacuum (355). Similar observations of polymerization have been recorded (385, 392), but further heating did not lead always to depolymerization, and porous horny materials have been obtained (105, 308), possibly because of the presence of impurities. At lower temperatures the gums and rubbers have a glass-like appearance (299, 300, 383). It was considered that phenomena such as hardening on standing at room temperature are due to crystallization of enmeshed lower cyclic oligomers, which could be extracted by suitable organic solvents (297, 298, 299, 300). The mechanism of polymerization was discussed (105) and it was shown by Schmitz–DuMont that equilibrium in the gas phase is achieved without formation of an inorganic rubber. When 1 g. of hexachlorocyclotriphosphazene was heated in a 100-cc. quartz ampoule at 600°, a mixture of crystalline and liquid oligomers was obtained,

but no rubber. Similar results were obtained when the starting material was octachlorocyclotetraphosphazene or the inorganic rubber, and the effects of temperature and pressure on the equilibrium were discussed. Inorganic rubber was among the products only when excess of starting material was used (311, 312).

Bromophosphazenes (23, 147, 186) and fluorophosphazenes (69, 319, 320) polymerize similarly to elastomers. Isothiocyanatophosphazenes also polymerize at *ca.* 150° (367) and it is possible that ring opening and/or polymerization of isothiocyanate groups may occur. The azide method of polymerization has been discussed (Section VI-D). All high-polymeric halogenophosphazenes hydrolyze easily. Alcoholysis also has been studied (Section VIII-B) (31, 145, 387).

Irradiation of liquid hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene by ultraviolet light did not cause polymerization, although volatile and resinous products were obtained in the presence of hydrocarbons (Section VI-E) (96). Polymerization of chlorophosphazenes did not occur on irradiation with γ-rays or electron beams (313, 337) although in the presence of oxygen open-chain compounds containing pyrophosphate links were formed (337). Graft copolymers with styrene also have been prepared by irradiation (338). Irradiation with high energy electrons of chlorophosphazenes in 1-butanol or dioxane at room temperature in the presence of air gave viscous polymers (339).

Alkyl- and aryl-phosphazenes are not easily polymerized, and thermal decomposition occurs with evolution of hydrocarbons and formation of insoluble residues (43, 152, 197, 318, 324). The higher-melting octaphenylcyclotetraphosphazene and the lower-melting geminal tetraphenyltetrachlorocyclotetraphosphazene were converted to non-elastic products on heating for several hours at 300° (54, 369). Heating of octaphenylcyclotetraphosphazene gave mixtures of cyclic tri-, tetra-, penta-, and hexaphosphazenes, whose relative proportions depended on the reaction temperature. It was suggested that at high temperatures phenylcyclotriphosphazenes are more stable than phenylcyclotetraphosphazenes. At the highest temperatures investigated, evolution of benzene and formation of an intractable residue was observed.

The physical properties of polymeric chlorophosphazene were first observed by Stokes (355) and investigated by Meyer and his co-workers (217, 218, 219, 220). It was concluded that the elastomers consist of chains which are not cross-linked and which have been compared with plastic sulfur and natural rubber (174, 217, 219, 220). Molecular weights of 37,000 to 78,000 (x = 320 to 700) (335) and 38,000 to 173,000 (x = 330 to 1500) (390) were estimated from elastic moduli. Molecular weights of 12,000 to 130,000 for products obtained by polymerization in carbon tetrachloride solutions were measured by viscometry (262) and molecular weights of *ca.* 300,000 were observed in chloroform and toluene solution (193). It has been suggested that the structure consists of phosphazene rings (α = 30 to 150) which are statistically interlocked to form chains whose particle weight is of the order of one million (262).

It is reported that bulk polymerization of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene is initiated thermally and inhibited by small quantities of carbon tetrachloride. Polymerization in carbon tetrachloride solution requires the presence of oxygen. Equilibrium was not achieved at 300°, but depolymerization and repolymerization of pure materials could be carried out any number of times without residue. The kinetics have been discussed in terms of a free radical mechanism, and a resonance contribution of a polar structure has been considered (1, 261, 262, 263, 264). Traces of impurities caused erratic results, and the effect of catalysts such as ether and benzoic acid was investigated, and polymerization was studied at 210°. Octachlorocyclotetraphosphazene reacted more slowly than hexachlorocyclotriphosphazene, and solution polymerization in benzene was slower than bulk polymerization. An ionic intermediate was regarded as the reactive species (195, 196). Different reaction rates were noted in different reaction vessels (130). Branched chains were postulated to account for the formation of chlorine-deficient insoluble products in the presence of benzoic acid (128), but it is possible that reaction was similar to that observed between hexachlorocyclotriphosphazene and sodium benzoate (Section VIII-A) (41). Commercial samples of cyclic chlorophosphazenes do not polymerize under the influence of γ-rays (213) or electrons from a linear accelerator (337) which suggests that a free-radical mechanism is unlikely.

An investigation of floor and ceiling temperatures below which or above which polymerization would not occur has been suggested for a number of inorganic systems, including the chlorophosphazenes. The necessity of distinguishing between kinetic and thermodynamic control of the reaction products has been discussed (120).

X. SPECTROSCOPY

A. ULTRAVIOLET AND VISIBLE SPECTRA

Phosphazenes do not absorb in the visible region of the spectrum. The ultraviolet spectra of different chlorocyclophosphazenes are similar, and appear to be almost independent of ring size. Absorption begins near 250 mμ and rises toward shorter wave lengths in the vacuum ultraviolet region (45, 115, 329). Maxima have been reported between 190 and 225 mμ (92, 193, 199, 200, 372), but these observations have been

questioned (115, 212, 259). Bromophosphazenes absorb at longer wave lengths from about 310 mμ and there are signs of a shoulder near 260 mμ. There is little change in the spectra of solutions of bromides or chlorides on changing the solvent from *n*-hexane to sulfuric acid, and it is considered that absorption is caused by the excitation of unshared electrons on halogen atoms (259).

Open-chain chlorophosphazenes, $Cl(NPCl_2)_nPCl_4$, absorb quite strongly in the near ultraviolet, and exhibit maxima near 320 and 370 mμ (259).

Fluorophosphazenes show no appreciable absorption in the visible or near ultraviolet regions of the spectrum (69, 320) and continuous absorption begins near 170–180 mμ (115). The far ultraviolet spectra of hexafluorocyclotriphosphazene and octafluorocyclotetraphosphazene exhibit maxima of high intensity (log $\epsilon \simeq 4.0$) at 149 ± 0.5 mμ and 147.5 ± 0.5, respectively, and both compounds absorb more strongly beyond minima near 141 mμ. No further minima occur until beyond 110 mμ (115).

Absorption near 260 mμ in the spectra of phenylphosphazenes (330) is characteristic of unconjugated phenyl groups, and resembles the absorption of other phenyl derivatives of four-coördinate phosphorus (181, 182, 183). Fluorescence has been observed in solutions of some phosphazene derivatives (54, 96, 369).

B. INFRARED AND RAMAN SPECTRA

Raman and infrared spectra of hexafluorocyclotriphosphazene, hexachlorocyclotriphosphazene, octafluorocyclotetraphosphazene, and octachlorocyclotetraphosphazene have been investigated in detail.

The Raman spectrum of hexachlorocyclotriphosphazene was the first to receive attention and the number and nature of observed lines supported the existing evidence for a planar molecule of symmetry D_{3h} (108). Numerical values were given for force constants of P–Cl and P–N bonds (178, 179). Raman and infrared spectra of both chlorophosphazenes were examined by Daasch (88). Bands in the spectrum of hexachlorocyclotriphosphazene agreed closely with those expected from a molecule of symmetry D_{3h}. Bands in the spectrum of octachlorocyclotetraphosphazene corresponded to those expected from a planar ring of symmetry D_{4h}, although symmetry D_{2d} was not eliminated. Fewer bands were observed than would be expected from a puckered ring of symmetry S_4. The infrared spectra of solid samples were similar to those of samples dissolved in conventional solvents (88) and therefore assumption of a higher symmetry by the eight-membered ring in solution is unlikely. Investigation of the infrared and Raman spectra of hexafluorocyclotriphosphazene and octafluorocyclotetraphosphazene suggested D_{3h} and C_{2h} symmetry, respectively (24).

The infrared and Raman spectra of cyclotriphosphazenes and cyclotetraphosphazenes are dominated by strong P–N stretching bands in the region 1150–1450 cm.$^{-1}$; these bands are useful in determination of ring size (88, 301, 321). The positions depend on the nature of the attached groups, and P–N stretching frequency plotted against electronegativity gives a smooth curve for cyclotriphosphazenes (257). A selection of P–N stretching frequencies of compounds $N_3P_3X_6$ and $N_4P_4X_8$ is recorded in Table 21. The infrared spectra of acids (79), polymeric perfluoroalkyl- (365), chloro-, and alkoxy (89) phosphazenes have been examined; P–N stretching bands occur at lower frequencies, 116–1180 cm.$^{-1}$, in the spectra of monophosphazenes, $p\text{-}XC_6H_4N{=}PPh_3$ (172).

TABLE 21

P–N STRETCHING FREQUENCIES

X	$N_3P_3X_6$, cm.$^{-1}$	$N_4P_4X_8$, cm.$^{-1}$	References
F	1297–1305	1419–1425	(24, 69, 320)
		1438–1445	
Cl	1218–1220	1310–1315	(88, 212, 321)
Br	1170–1184	1277	(259, 321)
Me	1180	1220	(318)
CF_3	1205	1216	(365)
Et	1157	1231	(43)
		1280	
Ph	1190	1213	(43)
		1170	
OMe	1239	1337	(113)
OEt	1225	1320	(112)
NH_2	1170–1177	1235–1240	(17, 221, 334, 337)
N_2H_3	1218		(252)

The P–N stretching frequency in the compounds $(NPF_2)_n$ increased from 1297 to 1439 cm.$^{-1}$ (n = 3–5) and decreased to 1357 cm.$^{-1}$ (n = 11). Gradations in a PF_2 symmetrical stretching band near 900 cm.$^{-1}$ were also observed, and it was suggested that these changes were consistent with flexible cyclic structures (69).

A comparison of the spectra of several chlorophosphazenes $(NPCl_2)_n$ (n = 3–7) (199, 200, 212) showed increased intensity of a band near 750 cm.$^{-1}$ with increasing values of n (259). This was considered to be caused by a gradual decrease in the phosphorus–nitrogen bond order and an increase in absorption of the P–N stretching frequency of bond order one (259). The infrared spectrum of the supposedly tricyclic compound $N_7P_6Cl_9$ has been investigated (199, 200).

C. NUCLEAR MAGNETIC RESONANCE SPECTRA

Nuclear magnetic resonance spectra of a considerable number of phosphorus compounds have been observed, including hexachlorocyclotriphosphazene, polymeric chlorophosphazenes, and the sodium salt, $N_3H_3P_3(O_2Na)_3$ (376).

Nuclear magnetic resonance spectra were used to investigate the substitution of hexachlorocyclotri-

phosphazene and tetrachlorodiphenylcyclotriphosphazene by ammonia, methylamine, and dimethylamine. Evidence of non-geminal replacement (scheme 2, Section IV) was obtained, but only one line was observed for some compounds when phosphorus atoms were in different chemical environments (30). It may be seen from Van Wazer's tables (375a) that replacement of chlorine by nitrogen when attached to four-coördinate phosphorus is unfavorable for phosphorus nuclear magnetic resonance studies. Of eleven bis-aminocyclotetraphosphazenes, three aromatic amino derivatives showed two triplet bands indicating 2,6-disubstitution. Only one line was observed in the spectra of aliphatic and heterocyclic amino derivatives (187). One line was observed in the spectra of two tetra-aminocyclotetraphosphazenes (188).

Proton magnetic resonance spectra of a series of dimethylaminocyclotriphosphazenes, $N_3P_3Cl_{6-n}(NMe_2)_n$ (n = 1–4, 6), established conclusively a non-geminal reaction pattern (379). A band was observed in the spectrum of the monodimethylamide, and a band in the same position was obtained for the bisdimethylamino and trisdimethylamino derivatives. A band in a different position was obtained for hexakisdimethylaminocyclotriphosphazene, and the spectrum of tetrakisdimethylaminodichlorophosphazene exhibited two bands of equal intensity. All the bands exhibited fine structure, and mean values of the chemical shifts on the high field side of water are given in Table 22.

TABLE 22

PROTON MAGNETIC RESONANCE SPECTRA

Reproduced, with permission, from the *J. Chem. Soc.* (281).

Compound	c./sec.
$N_3P_3Cl_5NMe_2$	83
$N_3P_3Cl_4(NMe_2)_2$	84
$N_3P_3Cl_3(NMe_2)_3$	84
$N_3P_3Cl_2(NMe_2)_4$	81 93
$N_3P_3(NMe_2)_6$	91

Nuclear magnetic resonance spectra were used as evidence of the cyclic nature of fluorophosphazenes (69) and in the assignment of structures of chlorofluorocyclotriphosphazenes. Fluorination of chlorophosphazenes occurs predominantly by reaction scheme 1 (Section III) (70). Phosphorus nuclear magnetic resonance spectra of the chlorophosphazenes tend to a constant value with increasing ring size (212).

It has been shown that chemically different phosphorus atoms are present in open-chain chlorophosphazenes, $Cl(NPCl_2)_nPCl_4$ (212) and $H(NPCl_2)_nCl$, but only two peaks were observed in the spectra compared with the expected three bands. Higher soluble elastomers $(NPCl_2)_{90}$, exhibit one broad band (31).

The spectra of the compounds NP_2Cl_7 (139) and NP_3Cl_{12} (32) have been measured and the structures $PCl_4^+PNCl_3^-$ and $Cl_3P{=}NPCl_3^+PCl_6^-$ suggested. Two different lines corresponding to two chemically different phosphorus atoms have been observed for the compound $Cl_3P{=}NPOCl_2$ (27, 114).

D. NUCLEAR QUADRUPOLE RESONANCE SPECTRA

Nuclear quadrupole resonance investigations of solids are capable of distinguishing between chlorine atoms which are crystallographically different, but which need not be chemically different.

The spectra of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene were reported to contain two lines (371), but four closely spaced lines in the former and four wider spaced lines in the latter have been observed (210a, 243, 244). It is possible that the discrepancy is caused by different crystalline modifications. It has been stated that nuclear quadrupole resonance spectra indicate no fundamental differences in the bonding of chlorine atoms in chlorophosphazenes and in phosphorus oxychlorides (92).

E. ELECTRON SPIN RESONANCE SPECTRA

Observations of electron spin resonance have been applied to the study of polymerization of octachlorocyclotetraphosphazene. Free radicals could not be detected either during or after thermal polymerization, and their concentration, if any, must be lower than 10^{15} spins per gram (177).

XI. STRUCTURES

A. ELECTRONIC STRUCTURE

Chlorophosphazenes are derived from tervalent nitrogen and quinquevalent phosphorus. A cyclic structure, with alternate single and double bonds between nitrogen and phosphorus, was proposed for hexachlorocyclotriphosphazene by Stokes (353). The stability was compared with that of aromatic compounds (351) and Kekulé-type resonance structures (119) became accepted.

A molecular orbital description of the aromatic model was developed by Craig and Paddock (81, 82, 83, 84, 85, 87, 259) and an alternative allylic structure involving three-center π-bonds was suggested by Dewar, Lucken, and Whitehead (92). Common features of both theories are a σ-bonded framework of sp^2-hybridized nitrogen and sp^3-hybridized phosphorus with a superimposed π-bonded system derived from $p\pi$-nitrogen orbitals and $d\pi$-phosphorus orbitals. The theories differ in the choice of phosphorus $d\pi$-orbitals.

Taking the xy-plane as the plane of the molecule, Craig and Paddock considered nitrogen pz-orbitals to combine with phosphorus dxz-orbitals directed tangentially to the phosphazene ring in the formation of molecular orbitals covering all the nuclei. A mismatch of atomic orbital signs is inevitable for any cyclic phosphazene containing odd numbers of NP units, *e.g.*, hexachlorocyclotriphosphazene, but not

for those containing even numbers of NP units, *e.g.*, octachlorocyclotetraphosphazene, which should therefore be more stable.

Dewar, Lucken, and Whitehead used phosphorus dyz-orbitals directed normally to the ring, in addition to dxz-orbitals. Each pair of phosphorus d-orbitals was replaced by a pair of linear combinations, both of which could combine efficiently with one adjacent nitrogen pz-orbital giving a system of almost independent three-center π-bonds containing two phosphorus atoms and one nitrogen atom. This does not constitute an aromatic system, and the heat of formation per $NPCl_2$ unit should be independent of ring size.

An attempt to estimate the extent of dyz-orbital participation by measurement of the diamagnetic anisotropy of hexachlorocyclotriphosphazene, $\Delta K = -10.5 \times 10^{-6}$ c.g.s.u., and the average susceptibility of hexachlorocyclotriphosphazene and higher chlorophosphazenes, was inconclusive (86).

B. THERMOCHEMISTRY

The heats of combustion of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (158) and of hexacyclohexyloxycyclotriphosphazene, hexamethylcyclotriphosphazene, and octaphenylcyclotetraphosphazene (34) have been used to calculate heats of formation of the gaseous compounds. Heats of formation of 2,2,2,4,4,4 - hexachloro - 1,3 - dimethylcyclodiphosphazane (XXI) (117) and of 1-ethyl-2,2,2-trimethylphosphazene and 1-ethyl-2,2,2-triphenylphosphazene (76) have been estimated from heats of hydrolysis. The data are recorded in Table 23.

Estimated bond energy terms, $\bar{E}$(N–P), of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene are identical within the limits of experimental error (158) and very similar to the bond energy term, $\bar{E}$(N–P), of the phosphazane XXI (117). Bond dissociation energies of two monophosphazenes show remarkable differences which have been ascribed to differences in nitrogen–phosphorus bond order resulting from different effects of P–methyl and P–phenyl groups (76). Estimated bond energy terms, $\bar{E}$(N–P), and bond dissociation energies, D(N–P), of a variety of phosphorus–nitrogen derivatives are recorded in Table 24. Variations within one type of structure, *e.g.*, monophosphazenes, are greater than variations between apparently different types of structure, *e.g.*, phosphazene and phosphazenes. In view of the different types of chemical bonds involved and the unknown influences of substituents, it would be difficult to make reasonable assignments of phosphorus–nitrogen bond orders in phosphazenes. Additional thermochemical data would be valuable.

C. CRYSTAL STRUCTURES

Early observations of chlorophosphazene crystals (149, 222, 355, 359) were followed in 1932 by investigations of X-ray powder diffraction patterns of hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene (180). Unit cell dimension of a number of phosphazenes, with recent values preferred, are recorded in Table 25. Hexachlorocyclotriphosphazene and hexabromocyclotriphosphazene, but not hexafluorocyclotriphosphazene, are isomorphous. The same holds for octahalogenophosphazenes.

Electron diffraction measurements of hexachlorocyclotriphosphazene (57, 316) were in agreement with the planar model (I) suggested originally by Stokes

TABLE 23

THERMO-CHEMICAL DATA

Compound	Eq.	ΔH^0_c, kcal./mole	ΔH^0_f(c), kcal./mole	ΔH^0_f(g), kcal./mole	Reference
$N_3P_3Cl_6$	1	−345.9	−194.1	−175.9	(158)
$N_4P_4Cl_8$	1	−460.8	−259.2	−236.1	(158)
$N_3P_3Me_6$	2	−1665.1 ± 2.7	−125.1 ± 2.7	−107 ± 5	(34)
$N_3P_3(OC_6H_{11})_6$	3	−5669.6 ± 4	−528.0 ± 4	−564.0 ± 4	(34)
$N_4P_4Ph_8$	4	−6736.5 ± 11.5	40.7 ± 11.5	58 ± 13	(34)
		ΔH, hydrolysis, kcal./mole			
$N_2Me_2P_2Cl_6$	5	−154.8 ± 0.5	−217.3 ± 0.5	−200.0 ± 2	(117)
EtN=PMe_3	6	−51.7 ± 0.5	−36.6 ± 2.5 (liquid)	−103 ± 3	(76)
EtN=PPh_3	7	−11.7 ± 0.5	27.0 ± 3.5	−21.9 ± 2.6	(76)

EQUATIONS

$$N_nP_nCl_{2n}(c) + (5n/4)O_2(g) \rightarrow (n/4)P_4O_{10}(c) + (n/2)N_2(g) + nCl_2(g) \quad (1)$$

$$N_3P_3Me_6(c) + 28.5\ O_2(g) \rightarrow 3H_3PO_4(c) + 6CO_2(g) + 4.5H_2O(l) + 1.5N_2(g) \quad (2)$$

$$N_3P_3(OC_6H_{11})_6(c) + 53.25\ O_2(g) \rightarrow 3H_3PO_4(c) + 36CO_2(g) + 28.5H_2O(l) + 1.5N_2(g) \quad (3)$$

$$N_4P_4Ph_8(c) + 63\ O_2(g) \rightarrow 4H_3PO_4(c) + 48CO_2(g) + 14H_2O(l) + 2N_2(g) \quad (4)$$

$$N_2Me_2P_2Cl_6(c) + 8H_2O(l) \rightarrow 2H_3PO_4(aq) + 2MeNH_3Cl(aq) + 4HCl(aq) \quad (5)$$

$$EtN{=}PMe_3(l) + H_2O(l) + HCl(aq) \rightarrow EtNH_3Cl(aq) + Me_3PO(aq) \quad (6)$$

$$EtN{=}PPh_3(c) + H_2O(l) + HCl(aq) \rightarrow EtNH_3Cl(aq) + Ph_3PO(c) \quad (7)$$

TABLE 24

NITROGEN–PHOSPHORUS BOND STRENGTHS

Compound	D(N-P), kcal.	References
N≡P	163.7	(173)
EtN=PPh$_3$	125.4	(76)
EtN=PMe$_3$	96.7	(76)
	$\bar{E}$(N-P), kcal.	
(PhHN)$_2$P(O)Me	82.0 ± 2.0	(242)
(PhHN)$_2$P(O)Et	82.5 ± 2.0	(242)
$N_3Me_2P_3Cl_6$	74.3	(117)
$N_3P_3Cl_6$	72.3	(158)
$N_4P_4Cl_8$	72.5	(158)
(Et$_2$N)$_3$P	66.8 ± 0.8	(116)

(351). Two complete X-ray structure determinations have been reported. Wilson and Carroll confirmed the existence of an almost planar phosphazene ring with equivalent phosphorus–nitrogen bonds (381, 382), but non-equivalence of phosphorus–nitrogen bonds was reported by Giglio (123). Bond lengths and bond angles are recorded in Table 26.

The structure determination of octachlorocyclotetraphosphazene by Ketelaar and de Vries (190, 191) established the existence of an eight-membered ring of alternating phosphorus and nitrogen atoms, with two chlorine atoms attached to each phosphorus.

TABLE 25

CRYSTAL DATA

Compound	System	Unit cell parameters: a	b	c	D_m	Z	D_c	Space group	References
$N_3P_3F_6$	Orthorhombic	6.95	12.20	8.70	2.34	4	2.26	$Pn2_1a$	(184, 185)
$N_3P_3Cl_6$	Orthorhombic	14.15 ± 0.02	12.99 ± 0.02	6.19 ± 0.01	1.99 ± 0.03	4	2.02	Pnma	(180, 212, 300, 381, 382)
	Orthorhombic	6.17	12.91	14.03					(75, 267)
$N_3P_3Cl_5Br$	Orthorhombic	14.24	6.28	13.00	2.27		2.24		(301)
$N_3P_3Cl_4Br_2$	Orthorhombic	14.27	6.34	13.02	2.44		2.46	$Pna2_1$ or Pnam	(301)
$N_3P_3Cl_2Br_4$	Orthorhombic	14.29	6.48	13.33	2.84		2.83		(301)
$N_3P_3Br_6$	Orthorhombic	14.38	13.35	6.64		4	3.182	Pnma	(46, 48)
$N_4P_4F_8$	Monoclinic	5.15	14.00 β = 111.1°	7.53	2.24	2	2.18	$P2_1/c$	(184, 185)
	Monoclinic	7.40	13.83 β = 109.5°	5.16		2		$P2_1/a$	(215, 216)
$N_4P_4Cl_8$	Tetragonal	10.844 ± 0.002		5.961 ± 0.005	2.18	2	2.20	$P4_2/n$	(119, 159, 180, 190, 191)
(above 60°)	Tetragonal	10.82$\sqrt{2}$		5.95				$P4_2/n$	(212)
$N_4P_4Br_8$	Tetragonal	11.18		6.29		2	3.439	$P4_2/n$	(46)
$N_4P_4(NMe_2)_4$	Tetragonal	13.00		8.59	1.219	2	1.218	I4	(62, 63)
$N_4H_4P_4O_8H_2(H_3O)_2$	Orthorhombic	13.92 ± 0.04	8.34 ± 0.04	5.05 ± 0.02	1.95	2	1.97	$P2_12_12$	(78)
$N_4H_4P_4O_8H_2K_2$	Orthorhombic	13.89	8.07	5.03	2.31	2	2.31	$P2_12_12$	(78)
$N_4H_4P_4O_8H_2Rb_2$	Orthorhombic	14.03	8.23	5.06	2.74	2	2.75	$P2_12_12$	(78)
$N_4H_4P_4O_8H_2(NH_4)_2$	Orthorhombic			5.08		2		$P2_12_12$	(78)
$N_6P_6Cl_{10}$		19.37	15.42	6.23	2.02	4		$P2_12_12_1$	(212)
$N_6P_6Cl_{12}$	Triclinic	10.6 α = 93.5°	10.7 β = 90°	11.4 γ = 117°	1.96	2			(212)
$N_8P_8Cl_{16}$		24.7	6.2	20.4	1.99	4		C2/c or C_c	(212)
$(NPCl_2)_x$	Orthorhombic	11.07 ± 0.1	4.92 ± 0.05	12.72 ± 0.1	1.98	8	2.21	$Pna2_1$	(218, 219)

TABLE 26

MOLECULAR STRUCTURE

Compound	P–N, Å.	P–X, Å.	Angle PNP	Angle NPN	Angle XPX	Remarks	References
$N_3P_3Cl_6$	1.65 ± 0.03	1.97 ± 0.03	120 ± 3°	120 ± 3°	107–110°	Electron diffraction, satisf. agreement with planar model	(57)
	ca. 1.6	2.04	ca. 120°		ca. 100°	Electron diffraction	(316)
	1.531	1.949	124°26′	118°52′	102°50′	Slight chair conform.	(123, 267)
	1.609	1.968	121°07′	118°54′	101°19′	Non-equiv. P–N bonds	
	1.544	1.979 1.989					
	1.61 ± 0.017	1.98 ± 0.013	120.38 ± 0.75°	120.93 ± 1.10°	101.77 ± 0.52°	Almost flat ring,	(381, 382)
	1.57 ± .017	1.97 ± .013	118.48 ± 1.25°	118.33 ± 1.30°	102.05 ± 0.32°	Symmetry m	
	1.60 ± .011	1.98 ± .008 1.97 ± .008					
$N_3P_3Br_6$	1.53 (mean prelim. value)					Slight chair conform.	(124)
	1.58	2.08				Planar ring	(48)
$N_4P_4F_8$	1.507 ± 0.017	1.514 ± 0.015	147.2 ± 1.4°	122.7 ± 1.0°	99.9 ± 0.9°	P–N bond lengths equal, planar ring, symmetry approx. 4/mmm	(185, 215, 216)
$N_4P_4Cl_8$	1.66	1.975	123°	117°	105°30′	P–N bond lengths equal within exptl. error, puckered ring	(190, 191)
	1.69	2.015					
	1.570 ± 0.01	1.989 ± 0.004				Symmetry $\bar{4}$	(159)
$N_4P_4(NMe_2)_8$	1.576 ± .010	1.686 ± .011	133.0 ± 0.6°	120.1 ± 0.5°	103.8 ± 0.5°	Puckered ring	(62, 63)
	1.580 ± .010	1.671 ± .010				Symmetry $\bar{4}$	
$(NPCl_2)_x$	1.60		127°	119°		P–N bond lengths equal	(125)

Phosphorus–nitrogen bond lengths are equivalent, and the structure resembles the tub-like form of cycloöctatetraene (22). The molecular symmetry has been confirmed and more accurate values of phosphorus–nitrogen and phosphorus–chlorine bond lengths are available (159). A complete structure determination by Bullen, of octadimethylaminocyclotetraphosphazene has established the existence of a similarly puckered eight-membered ring with equivalent phosphorus–nitrogen bonds (62, 63). Phosphorus–nitrogen bonds in octafluorocyclotetraphosphazene are equivalent, but much shorter, and the phosphazene ring is approximately planar (215, 216).

Polydichlorophosphazene, $(NPCl_2)_x$, becomes crystalline when stretched (218, 219). Recent investigation of X-ray fiber photographs suggests that the structure is consistent with a twofold helical conformation (125). Stretched polydi-isothiocyanatophosphazene did not exhibit X-ray fiber patterns (367).

Estimates of multiple bond character can be misleading, even in carbon chemistry where the greatest amount of information is available, and discussions of phosphorus–nitrogen bond order have been based on the single bond distance (166) observed in one compound. Recent work has suggested that assumptions of similar covalent radii for carbon atoms in different states of hybridization may be erroneous (93). Details of stereochemistry and hybridization of other elements are understood less well, and complications of different valency states and participation in bonding of *d*-orbitals occur with elements in the second row of the Periodic Table. It is not known whether covalent bond radii in different types of structures are the same in all directions, and, for these reasons, detailed deductions of phosphazene bond order have not been based on relatively small changes in bond angles and bond distances.

XII. APPLICATIONS

Numerous patents are concerned with the synthesis of chlorophosphazenes and derivatives (21, 26, 97, 110, 189, 238, 255, 258, 260, 276, 277, 278, 362). Use as adhesives for glass, ceramics, and metals, and as lubricant additives, biocides, plasticizers, polymers and co-polymers of various types, and modifying agents for resins, have been suggested. Some general articles deal wholly or partly with possible applications (55, 71, 72, 73, 270, 295, 296, 322).

Semi-ceramic materials have been obtained from chlorophosphazenes and various silicates such as asbestos. It is suggested that these might be suitable for high temperature gaskets, brake linings, abrasives, and insulators (284, 285, 286, 287, 289, 290). Glass fibers coated with chlorophosphazenes possess increased resistance to flexing and abrasion (363). Asbestos and other fibrous materials treated similarly are reported to form electrical insulators with improved heat, flame, and moisture resistance (201, 202).

Resins obtained from chlorophosphazenes and polyhydric phenols have been suggested as suitable for heat-stable coatings, laminates, plasticizers, adhesives, moulding compounds, and fireproofing agents (4, 288, 292). Phenolic resins with improved thermal stability are formed from mixtures of chlorophosphazenes, polyhydric phenols, and inorganic chlorides such as boron trichloride or phosphorus oxychloride (291). Resins, made by reaction of chlorophosphazenes with butylamine (210), or organic amides, *e.g.*, urea (58, 59, 74), are suggested as ingredients for rubbers (74). Octachlorocyclotetraphosphazene can be used as a catalyst to make rubbers from diorganosiloxanes (249, 250).

Hexachlorocyclotriphosphazene acts as a chemical polishing agent and provides an increased wear prevention factor in white oil (35). Use of phosphazenes as additives to increase the load bearing capacity of lubricants has been suggested (207, 208, 209). Alkoxyphosphazenes with long alkyl chains are reported to depress the pour-point of mineral oils (251). Polymeric alkoxyphosphazenes are reported to improve the film-forming properties of nitrocellulose (95, 145).

Flameproofing has attracted attention, and chlorophosphazenes have been used in modifying cotton. Allyloxyphosphazenes combined with bromine or bromoform appear to be particularly useful (155, 156, 157). Other compositions of chlorophosphazenes with amino derivatives (176) and partly or completely hydrolyzed or ammonolyzed chlorophosphazene derivatives are reported to be effective (44, 293, 294, 373, 374). Treatment of unsaturated alkyd resins with chlorophosphazenes and styrene is supposed to improve the fire extinguishing properties (3).

It is suggested that N-chloro derivatives of phosphazane acids are useful bleaching and disinfecting agents (360, 361).

XIII. PHYSIOLOGICAL ACTIVITY

Early workers commented on the aromatic odor of chlorophosphazenes and noted that discomfort was caused to eyes, lungs, and mucous membranes (300, 351). The susceptibility varies with the individual and severe eye pain has been reported. Medical examinations show the effects are similar to acid burns and, although painful, recovery appears to be complete. No discomfort from skin contact has been reported, but in view of the potential biological activity of many phosphorus compounds, considerable care should be taken in the handling of phosphazenes and their derivatives.

Chlorophosphazenes and their derivatives have been investigated for cytotoxic (161) and anti-thyroid (13) activity. Several compounds have been screened in cancer chemotherapy investigations (45, 154).

Brief references have been made to pesticide properties of hexachlorocyclotriphosphazene (19) and to the toxicity of polymeric butoxyphosphazenes to aphids (211). Biological properties of phosphazenes appear to have been neglected, and would merit further study in view of the structural and chemical similarity to *s*-triazines and other synthetic and naturally occurring phosphorus compounds which are biologically active.

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