THE PHOSPHAZOTRIHALIDES

M. Bermann*

Institut für Anorganische Chemie der Technischen Hochschule, Wien, Austria

I. Introduction 1
II. Nomenclature 2
III. General Remarks Concerning the Synthesis of Phosphonitrile Chlorides 5
IV. Ionic P–N Compounds Containing $-N{=}PX_3$ Groups in the Cation 6
A. Symmetrical Cation (Two P Atoms in the Cation) . . . 6
B. Higher Ionic P–N Compounds (More than Two P Atoms in the Cation) 9
C. Ionic Compounds Containing [P=N=C(R)=N=P] Units . . 12
D. Unsymmetrical Ionic P–N Compounds 16
E. Spectroscopic Investigations 19
V. *N*-Phosphorylated Phosphazotrihalides 24
A. Syntheses 24
B. Reactions 28
C. Spectroscopic Investigations 30
VI. Sulfonylphosphazotrihalides 33
A. Syntheses 33
B. Reactions 37
C. Spectroscopic Investigations 43
VII. Carbonylphosphazotrichlorides 44
A. Syntheses 44
B. Reactions 50
C. Spectroscopic Investigations 54
VIII. Aryl- and Alkylphosphazotrihalides 55
A. Trichlorophosphazoaryls 55
B. Alkylphosphazotrichlorides 59
C. Phosphazotrifluorides 77
D. Physical Investigations 78
IX. Miscellaneous Compounds 81
X. Applications 90
References 92

I. Introduction

A great number of compounds containing the phosphazo group $-N{=}PX_3$ (X = halogen) is known; their reactions and applications have led to very intensive investigations. In the last 7 years (since 1964) over

* *Present address*: Huegelgasse 8/10, Wien 13, Austria.

300 new papers dealing with this subject have been published; yet there is no comprehensive and up-to-date review about these compounds.

The present review does not consider the chemistry of the cyclic phosphonitrilic compounds (phosphazenes) $(PNCl_2)_n$ $(n \geqslant 3)$; many authoritative reviews on this subject have appeared (*182*, *188b*, *220b*, *292*, *355*, *357*, *407*, *418*, *420*, *525*) as well as shorter ones (*3a*, *4*, *55*, *406*, *415–417*). Linear phosphorus–nitrogen compounds have been reviewed lately (*161*, *188*). Also phosphinimines do not fall within the scope of this survey, unless they can be prepared from phosphazotrihalides or are made available through analogous syntheses. There exists an excellent review about phosphinimines (*483*) and another one which is related to them (*392*).

Phosphazotrihalides are, however, sometimes mentioned in reviews (*16*, *19*, *68*, *161*, *188b*, *206a*, *342*, *350*, *389*, *408a*, *411*, *492a*). Kirsanov and co-workers have provided an excellent coverage of these compounds up to early 1964 (*137*), and very recently a Russian review about cyclodiphosphazanes (*180b*) has been published. Otherwise only very short reviews (*224*, *227*, *427b*) from Kirsanov's group have appeared.

The present survey considers the syntheses and reactions, along with physical data, of all compounds containing a $-N{=}PX_3$ group (X = halogen). The abbreviations used are: Me = methyl, Et = ethyl, Pr = *n*-propyl, Bu = *n*-butyl, Am = *n*-amyl, and Ph = phenyl; if not otherwise stated, R = alkyl group, Ar = aryl group, X = halogen, and Y, Z =other substituents.

Original papers (over 80% of the literature references) were consulted whenever and wherever possible. The literature (primary, secondary, and tertiary) has been surveyed up to the end of November 1971. Names of Russian and Japanese authors are given as listed in *Chemical Abstracts*.

II. Nomenclature

No consistent system is available for naming phosphorus–nitrogen compounds. In the particular case of $-N{=}PX_3$ compounds the presence of the monomeric form $-N{=}PX_3$ (as a derivative of the hypothetical phosphinimine $HN{=}PH_3$) and the dimeric form $(-N{=}PX_3)_2$ (cyclodiphosphazane) gives rise to very different nomenclature systems. Table I summarizes the most commonly used nomenclature; nomenclature preferred by *Chemical Abstracts* is set in italics.

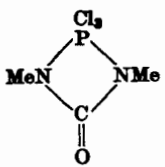
TABLE I

NOMENCLATURE OF PHOSPHORUS COMPOUNDS[a]

Compound	Trivial name	Rational or partly rational nomenclature
$[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$	1,1,1,3,3,3-Hexachlorodiphosphonitrilium hexachlorophosphate	Iminobis(trichlorophosphazyl)hexachlorophosphate
	—	*Trichloro[(trichlorophosphoranylidene)amino]-phosphorus(V) hexachlorophosphate*
	1,1,1,3,3,3-Hexachloro-2,1,3-azadiphosphapropanium[1]hexachlorophosphamethanate	—
$Cl_2OPN{=}PCl_3$	—	Trichlorophosphazophosphorus(V) oxychloride *(Trichlorophosphoranylidene)amidophosphoryldichloride*
$ClSO_2N{=}PCl_3$	—	*Trichlorophosphazosulfonyl (or -sulfuryl) chloride* *Trichlorophosphoranylidenesulfamoyl chloride*
$HN{=}PH_3$	*Phosphinimine*	Monomeric form: Phosphazene Dimeric form: *Diazadiphosphetidine* Diazadiphosphacyclobutane
$RN{=}PCl_3$	*Alkylphosphorimidic trichloride*	Monomeric form: *N-Alkyltrichlorophosphinimine* Dimeric form: Dimeric *N*-alkyltrichlorophosphinimine

(*continued*)

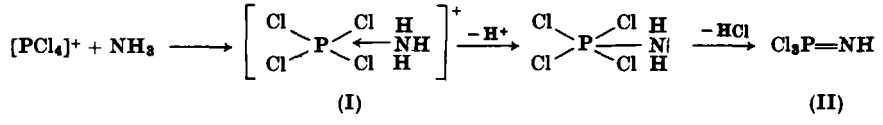
TABLE I—*continued*

Compound	Trivial name	Rational or partly rational nomenclature	
$RN{=}PCl_3$	*Alkylphosphorimidic trichloride*	*N*-Alkyltrichlorophosphazene	Dimeric *N*-alkyltrichlorophosphazene
			1,3-Dialkyl-2,2,4,4-tetrahydro-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetedine
			2,2,2,4,4,4-Hexachloro-1,3-dialkylcyclodiphosphazane
		Trichlorophosphazoalkyl	—
			2,2,2,4,4,4-Hexachloro-1,3-dialkyl-1,3-diaza-2,4-diphosphacyclobutane
	—	*2,2,2-Trichloro-1,3-dimethyl-2,1,3-phospha(V)-diazetidinone-4*	
		2,2,2-Trichloro-1,3-dimethyl-1,3,2-diazaphosphacyclobutanone-4	

[a] Compound names in italics are those preferred by *Chemical Abstracts*.

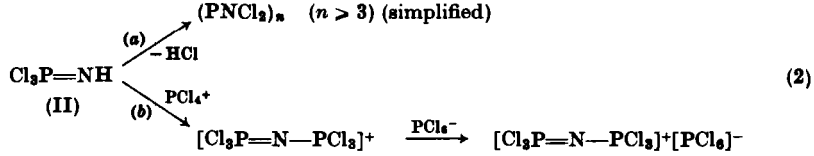
III. General Remarks Concerning the Synthesis of Phosphonitrile Chlorides

The mechanism for the synthesis of phosphonitrile chlorides has been investigated particularly by Becke-Goehring and co-workers (*19*, *30*, *310*). It is suggested that this reaction follows the route of a Kirsanov reaction (*221*): PCl_5 can react in polar solvents by an ionic mechanism, the Lewis acid PCl_4^+ reacts with an amine (for example, ammonia) with formation of (I), which deprotonates and eliminates HCl forming the previously postulated (*357*, *366*) trichlorophosphinimine (II). This compound (II) is not stable;* it polymerizes in the presence of excess NH_3



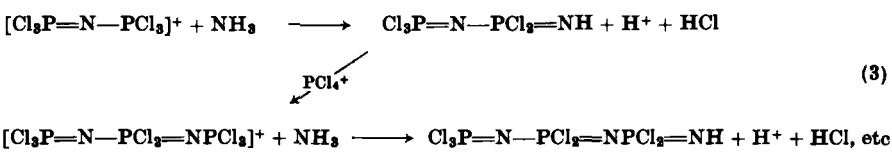
(I) (II) (1)

during the reaction with elimination of HCl to give cyclic phosphonitrilic chlorides $(PNCl_2)_n$ ($n \geqslant 3$) or reacts with excess PCl_5 (in form of PCl_4^+ ion) to give the cation $[Cl_3P{=}N{-}PCl_3]^+$; the latter is stabilized by the PCl_6^- anion. This ionic compound can react with ancther $Cl_3P{=}NH$ unit, etc., so that, in general, linear phosphonitriles with a different number



(2)

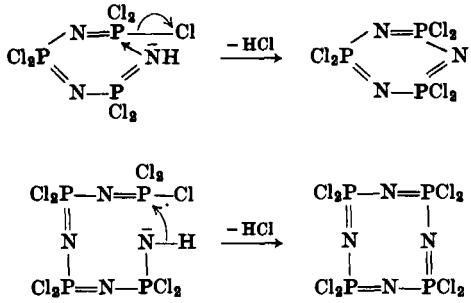
of $-Cl_2P{=}N$ units are obtained (*30*). The different steps are thought to be as follows (NH_4Cl as NH_3 donor):



(3)

* Recently $(CCl_3)_2P(Cl){=}NH$, b.p. 68°–69°/0.03 Torr, f.p. = 41°–42°, has been isolated from the reaction of $(CCl_3)_2PCl_3$ with ammonia (*294a*).

The linear intermediates eliminate HCl in an intramolecular reaction to give the trimeric and tetrameric phosphonitrile chlorides (hexachlorophosphazatriene and octachlorophosphazatetraene). For details, cf. refs.



(4)

(*19*, *30*, *161*, *310*, *521a*). A modern approach to this subject is also given (*406*).

IV. Ionic P-N Compounds Containing —N=PX_3 Groups in the Cation

A. Symmetrical Cation (Two P Atoms in the Cation)

1. Syntheses of the Chlorides

The first isolable compound $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$ (III) from the reaction of PCl_5 with NH_4Cl is formed under controlled conditions (solvent nitrobenzene or a mixture of sym. $C_2H_2Cl_4 + POCl_3$, temperature = 45°–60°) (*15*, *19*, *21*, *24*, *28*, *310*) or from $C_5H_5N \cdot PCl_5 + NH_4Cl$ (*310*); it is also formed from excess PCl_5 and hydroxylamine (*24*, *29*) [with (V) as intermediate], from PCl_3 and NCl_3 (*14*, *19*) and, in minor quantities, from S_4N_4 and PCl_3 (*29*); the latter reaction had previously been interpreted incorrectly (*177*, *183*). Compound (III) is also described in a patent (*10*), but the given structure $PNCl_2 \cdot 2PCl_5$ is erroneous. Other syntheses of (III) include the phosphorylation of $PhCH(NH_2)SO_3H$ with PCl_5 (molar ratios 1:5) or of $PhCHNH_2P(O)(OEt)_2$ (1:6) (*543*), as well as the following reactions (*315*) [Eqs. (5)–(7)]:

$$MeSO(=NPOCl_2)Cl + 4PCl_5 \rightarrow Cl_2 + SCl_2 + MeCl + 2POCl_3 + (III) \quad (5)$$

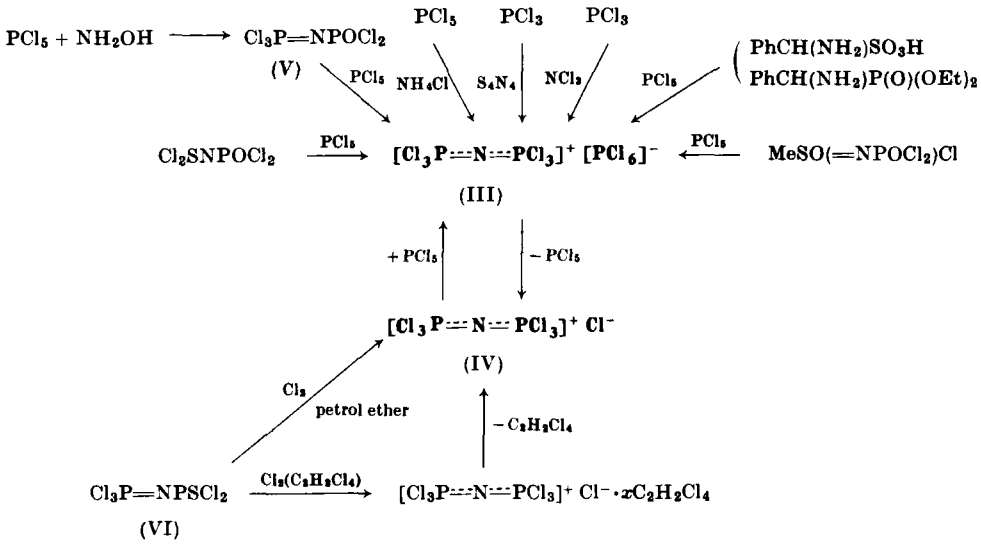
$$Cl_2SNPOCl_2 + 3PCl_5 \rightarrow Cl_2 + SCl_2 + POCl_3 + (III) \quad (6)$$

$$\underset{(V)}{Cl_3P{=}NPOCl_2} + 2PCl_5 \rightarrow POCl_3 + (III) \quad (7)$$

The chloride corresponding to (III), namely, $[Cl_3P{=}N{=}PCl_3]^+Cl^-$ (IV), is formed as a $C_2H_2Cl_4$ adduct from P_2NSCl_5 (VI) with chlorine which loses the solvent by heating (*29*); (IV) is also formed from hydroxylamine hydrochloride and PCl_5 (*11*, *24*). These compounds like all ionic compounds containing at least two $-N{=}PX_3$ groups in the cation, are resonance-stabilized, and are best represented by the formulas (IVa) and (IVb). Other derivatives of (IV), such as the BCl_4^- (*346*) or $SbCl_6^-$

$$\underset{\text{(IVa)}}{[Cl_3P{=}N{-}\overset{+}{P}Cl_3]} \leftrightarrow \underset{\text{(IVb)}}{[Cl_3\overset{+}{P}{-}N{=}PCl_3]}$$

compound (*15*, *29*, *395*) are known. The former compound may also be prepared from $NH_3{\cdot}BF_3$ and 3 moles of PCl_5 (*51e*). The latter can also be prepared directly from NH_4SbCl_6 and PCl_5 (*395*) or from $PCl_4{}^+SbCl_6^-$ and NH_4Cl (*310*) or results from the thermolytic degradation of bis(trichlorophosphazo)benzyl hexachloroantimonate, $[PhC(N{=}PCl_3)_2]^+SbCl_6^-$ with loss of benzonitrile (*402*). Similarly, $[Cl_3P{=}N{=}PCl_3]^+X^-$ ($X^- = AlCl_4^-$, $FeCl_4^-$) have been isolated (*509a*).



SCHEME 1. Syntheses of P_2NCl_7 (IV) and P_3NCl_{12} (III).

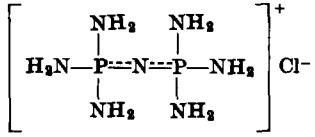
2. *Reactions of the Chlorides*

Reaction of (III) (*15*, *28*, *315*) or (IV) (*29*) with SO_2 or $NH_2OH{\cdot}HCl$ (with addition of PCl_3) (*24*) yields trichlorophosphazophosphorus(V)

oxychloride (V). The same compound can be obtained from (III) with P_4O_{10} (*413*) or formic acid (*192*).

$$[Cl_3P{=}N{=}PCl_3]^+PCl_6^- + 2SO_2 \rightarrow \underset{(V)}{Cl_2(O)PN{=}PCl_3} + POCl_3 + 2SOCl_2 \qquad (8)$$

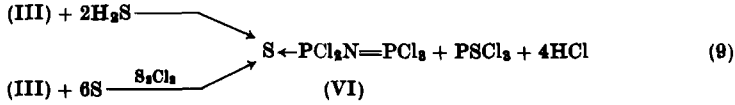
Liquid ammonia and (IV) produce a compound, $P_2N_7H_{12}Cl$, having the following structure:



(*36*), which can also be obtained by thermal condensation of $[P(NH_2)_4]^+Cl^-$ (*287*, *405*) or, as the iodide, from $[P(NH_2)_4]^+I^-$ (*404*). The reaction of (IV) with NH_4Cl yields higher linear polymers (*30*) (cf. Section III).

$[Cl_3P{=}N{=}PCl_3]^+BCl_4^-$ and SO_2 react in a rather complex way, whereas with H_2S the compound (VI) is obtained (*51e*) and with $MeNH_3Cl$ a ring-closure reaction occurs (*51d*). Excess ammonium thiocyanate gives $[(SCN)_3P{=}N{=}P(NCS)_3]^+[B(NCS)_4]^-$ (*51b*) and fluorination (AsF_3) affords the cyclic compound $(NPF_2 \cdot PF_5)_3$ (*51a*).

The thio analog of (V) can be prepared according to Eq. (9) (*13*, *29*);



(9)

it results also as a by-product from the reaction of S_4N_4 with PCl_3 (*29*).

For further details concerning compounds (V) and (VI), cf. Section V,A.

A longer chain polymer $[Cl_3P{=}NPCl_2{=}NPCl_3]^+PCl_6^-$ is obtained from (III) and NH_4Cl (molar ratios 5:2 to 3:2) (*29*) (for details, cf. Section IV,B,1); reaction with H_2NSO_3H gives $NPCl_2(NSOCl)_2$ (*70a*). Compound (III) and red phosphorus do not yield the expected $Cl_2PN{=}PCl_3$ (postulated as an intermediate), but give mainly cyclic phosphazenes (*158*).

$$3[Cl_3P{=}N{=}PCl_3]^+PCl_6^- + 4P \rightarrow (PNCl_2)_{2n} + \text{by-products} \qquad (n = 2, 3, \ldots) \quad (10)$$

The reaction of (IV) with a linear substrate $Ph_4P_2N_3H_4Cl$ gives no characterizable product (*78*), but with $MeNH_3Cl$ in the presence of BCl_3 a six-membered ring containing P, N, and B atoms can be obtained (*16*, *34*; cf. also *512*); an analogous six-membered ring with P, N, and Al

atoms is known (*509a*). (IV) and $MeNH_3Cl$ react only (*169*) according to Eq. (11).

$$2(IV) + 2MeNH_3Cl \rightarrow (PNCl_2)_4 + 2MeCl + 6HCl \quad (11)$$

Various amidinium chlorides react with $[Cl_3P{=}N{=}PCl_3]^+SbCl_6^-$ to give substituted diphospha-1,3,5-triazines (*400*, *402*). Heating $[Cl_3P{=}N{=}PCl_3]^+BCl_4^-$ with $AlCl_3$ in sym. $C_2H_2Cl_4$ is said to give a product $(BP_2N_3Cl_4)_n$ to which a borazine-like structure with four fused six-membered rings was assigned (*346*), but no adequate confirmation was given.

Linear phosphonitrile compounds analogous to (III) and (IV), such as $[Ph_2P(Cl){=}N{=}P(Cl)Ph_2]^+Cl^-$, have been reviewed recently (*161*) and so are not within the scope of this review.

3. *Syntheses and Reactions of the Bromides*

John and Moeller (*205*) obtained only poor yields of $(PNBr_2)_n$ by reacting PBr_3, excess bromine, and NH_4Br at temperatures of 115°–120°, but red crystalline substances of the general formula $PNBr_2 \cdot PBr_{5+n}$

$$\underset{\text{red}}{PNBr_2 \cdot PBr_{5+n}} \underset{Br_2}{\overset{\text{room temp.}}{\rightleftharpoons}} \underset{\text{red}}{PNBr_2 \cdot PBr_7} \underset{Br_2}{\overset{80°\text{–}100°}{\rightleftharpoons}} \underset{\text{yellow}}{PNBr_2 \cdot PBr_5} \quad (12)$$

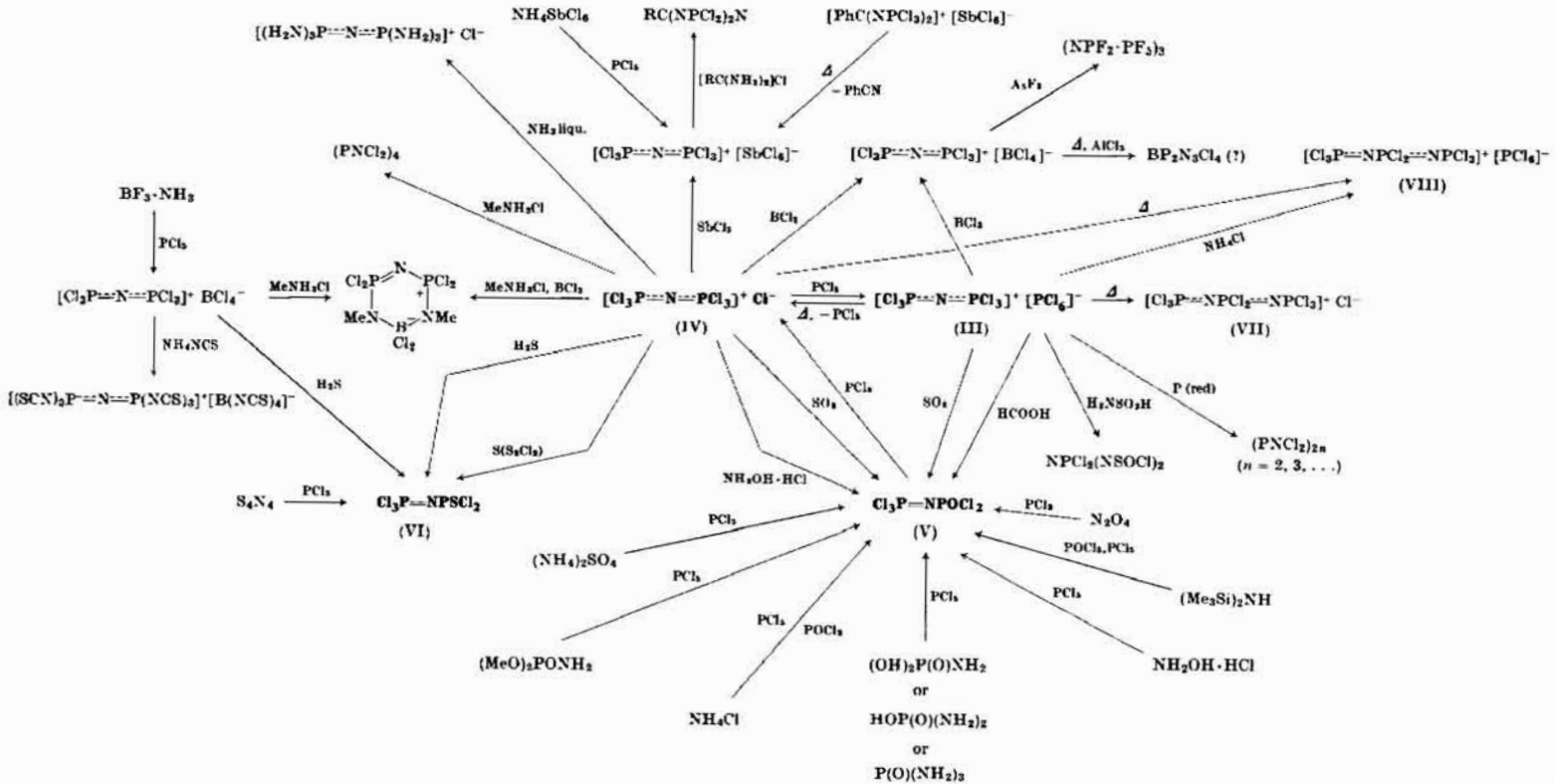
($n \geqslant 0$) (*206*) were formed. These substances can be formulated as $[Br_3P{=}N{=}PBr_3]^+Br_3^-$ and $[Br_3P{=}N{=}PBr_3]^+Br^-$, respectively. Easy addition of bromine with probable formation of polybromides $PNBr_2 \cdot PBr_{5+n}$ ($n \geqslant 0$) with varying bromine content occurs (*206*). On raising the temperature to 85°, $[Br_3P{=}N{=}PBr_3]^+Br_3^-$ slowly loses bromine (*75*); above 120° polymerization to smaller amounts of $(PNBr_2)_3$ and $(PNBr_2)_4$, as well as larger amounts of higher polymers, was observed. A short discussion concerning the ionic structure of these substances is given in the literature (*75*).

B. Higher Ionic P–N Compounds (More than Two P Atoms in the Cation)

1. *Syntheses*

As already mentioned in Section IV, A, 2 the reaction of P_3NCl_{12} (III) with NH_4Cl (ratios 5:2 to 3:2) gives $P_3N_2Cl_9$ (VII) (*29*); the same

$$[Cl_3P{=}NPCl_2{=}NPCl_3]^+Cl^-$$
(VII)



SCHEME 2. Reactions of (III) and (IV) and syntheses of (V) and (VI).

compound had already been described earlier in a patent (*51*) but was not characterized properly. Compound (VII) is also obtained by heating the corresponding hexachlorophosphate (VIII) (*29*). Compound (VIII)

$$[Cl_3P{=}NPCl_2{=}NPCl_3]^+PCl_6^-$$
(VIII)

also results from PCl_5 and NH_4Cl (2:1) along with (IV) (*16a*, *23*), as well as from the thermolysis of (IV) at 150° (2 hr) in 82% yield (*30*). It is also a by-product from the reaction of S_4N_4 with PCl_3 (*23*, *29*) and a major product from that of $(PNCl_2)_3$ with PCl_5 (*156*) at elevated temperatures (200°–220°) (cf. Scheme 3).

A higher homolog of (VIII), $P_5N_3Cl_{16}$, $[Cl_3P{=}NPCl_2{=}NPCl_2{=}NPCl_3]^+PCl_6^-$, is formed in poor yields in the synthesis of (VIII) (*30*). The same compound is formed in the reaction of $(PNCl_2)_3$ with PCl_5 (1:2, 250°, 11 hr) (*339*). The next higher homolog, $[Cl_3PN{-}(PCl_2N)_3{-}PCl_3]^+PCl_6^-$, is formed from $(PNCl_2)_4$ and PCl_5 (1:2, 250°, 100 hr) (*339*). Higher polymers, $[Cl_3PN{-}(PCl_2N)_n{-}PCl_3]^+PCl_6^-$ ($n = 4$ or 5), have been identified by ^{31}P NMR (*339*); a cationic mechanism for the formation of these compounds is suggested.

Long-chain polymers of the probable structure $Cl_3P{=}N{-}(PCl_2N)_n{-}PCl_2{=}NH$ ($n = 8$–13) have been reported (*27*). Related high polymers with terminal $-N{=}PCl_3$ groups were isolated by Paddock (*356*) and Lund *et al.* (*323*) from the reaction of $(PNCl_2)_n$ ($n = 3, 4$) with PCl_5 (molar ratios 100:1).

Recently Schmidpeter and Weingand (*405*) synthesized the compounds $[P(N{=}PCl_3)_4]^+X^-$ ($X^- = Cl^-$, $SbCl_6^-$, Cl_2I^-, HgI_3^-).

$$[P(NH_2)_4]^+Cl^- + 4PCl_5 \rightarrow [P(N{=}PCl_3)_4]^+Cl^- + 8HCl \quad (13)$$

$P_3N_3F_6$ and alkali metal fluorides in the presence of Ph_4AsCl undergo ring cleavage forming the compounds $[F_3P{=}NPF_2{=}NPF_2{=}N]^-[AsPh_4]^+$ (*376*) and $[F_3P{=}NPF_2{=}N]^-AsPh_4^+$ (identified spectroscopically) [see also (*140a*)].

2. *Reactions*

Compounds (VII) and (VIII) react with SO_2 giving $Cl_3P{=}NPCl_2{=}NPOCl_2$ (*23*, *28*, *29*, *524a*), the corresponding thio analog is obtained from (VIII) and H_2S (*13a*, *29*). Ammonolysis of (VIII) yields $(PNCl_2)_3$ (*19*); with H_2NSO_3H the compound $NPCl_2(NSOCl)_2$ is obtained (*70a*). This compound can also be obtained on other ways (cf. Section VI,B).

When $[Cl_3PN{=}(PNCl_2)_2{=}PCl_3]^+PCl_6^-$ is heated to 300°–350°, it yields different linear polymers, among them (III) (*339*). The tetrachloroaluminate and tetrachloroborate of the $[Cl_3PN{=}(PCl_2N)_2{=}PCl_3]^+$ ion are

thermally stable substances up to 700° (*339*); analogous compounds with other anions have been described [(*344*, *345*), cf. also (*407*)]. The compounds $[Cl_3PN{=}(PCl_2N)_n{=}PCl_3]^+Cl^-$ ($n = 2$, 3) react with metal halides such as $NbCl_5$, $MoCl_5$, $TaCl_5$, $PtCl_4$, WCl_6, or $RuCl_4$ to give viscous oils of probable composition $[Cl_3PN{=}(PCl_2N)_nPCl_3]^+M^mCl_{m+1}$ (m = valency state of the metal ion) (*341*); reactions with $NbOCl_3$ and WO_2Cl_2 (*341*) and with phenol (*192c*, *374*), aniline, $MeNH_2$, and EtOH (*374*) have also been reported.

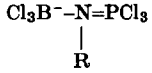
The higher polymers $[Cl_3P(=NPCl_2)_nNPCl_3]^+Cl^-$ ($n = 3$–15) lose PCl_5 when heated in an inert atmosphere to 240°–260°, forming longer P–N chains with an average molecular weight of 3000 to 10000 (*50c*). The ammonolysis product of only one higher linear polymer has been described (*509c*).

Finally, $[P(N{=}PCl_3)_4]^+Cl^-$ reacts with SO_2 to give $Cl_2OPN{=}P(N{=}PCl_3)_3$ (*403*).

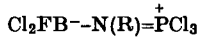
C. Ionic Compounds Containing [P=N=C(R)=N=P] Units

1. Syntheses

The first member of this series is $[Me_2NPCl_3]^+SbCl_6^-$, which can be isolated from the reaction of $[Me_2NH_2]^+SbCl_6^-$ and PCl_5 (*395*). The corresponding hexachlorophosphates $[R_2NPCl_3]^+PCl_6^-$ have previously been described by Michaelis (*334*), but have been formulated as $R_2NPCl_4 \cdot PCl_5$. The tetrachloroborates result from $R_2NH \cdot BF_3$ and PCl_5 (*51g*). Reaction of $RNH_2 \cdot BF_3$ (R = Me, Ph) and 2 moles of PCl_5 gives rise to the compounds

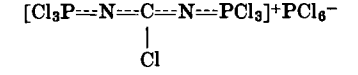


(*51f*);

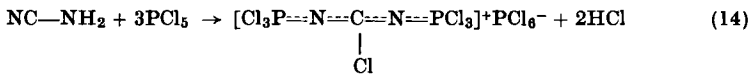


may also be obtained (*51f*).

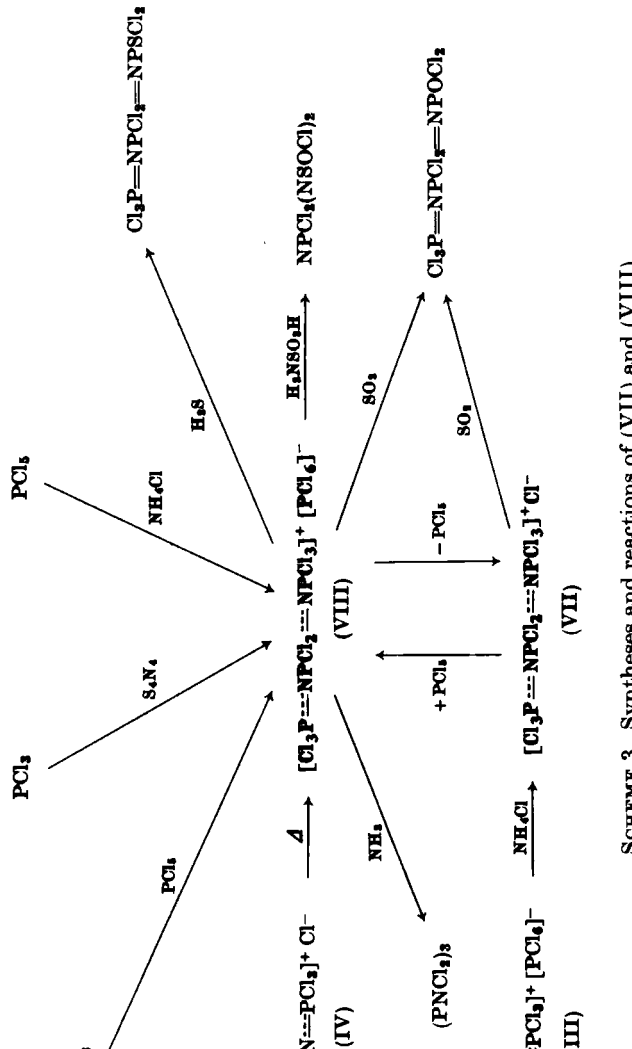
Cyanamide and PCl_5 give



(*26b*, *207*); the same compound is isolable in poor yield from the reaction



(14)



SCHEME 3. Syntheses and reactions of (VII) and (VIII).

of urea and PCl_5 (*207*). The mechanism involved in the first step is thought to be a Kirsanov reaction on the amino group (introducing a $-N{=}PCl_3$ group), followed by attack of a PCl_5 molecule on the $C{\equiv}N$ triple bond with chlorination and formation of a second trichlorophosphazo group (*16*).

Similar compounds

$$[Cl_3P{=}N{=}C(R){=}N{=}PCl_3]^+SbCl_6^-$$

were obtained by Schmidpeter *et al.* (*396*, *397*) as condensation products of amidinium hexachloroantimonates and PCl_5.

$$H_2N{-}C(R){=}NH_2^+ \xrightarrow{2PCl_5} [Cl_3P{=}N{=}C(R){=}N{=}PCl_3]^+ \qquad (15)$$

R = Me, Ph, NMe_2, CCl_3 (the latter by using an excess of PCl_5 during the reaction of the methyl compound)

Stepwise phosphorylation of guanidine with PCl_5 has been accomplished; all intermediates could be isolated (*422*).

$$H_2N{-}C(=NH){-}NH_2\cdot HCl \xrightarrow[-2HCl]{PCl_5} Cl_3P{=}N{-}C(=NH){-}NH_2\cdot HCl \xrightarrow[-3HCl]{PCl_5}$$

$$Cl_3P{=}N{-}C(=NH){-}N{=}PCl_3 \xrightarrow[-HCl]{PCl_5} \left[\begin{matrix} Cl_3P{=}N \\ Cl_3P{=}N \end{matrix}\!\!>\!C{=}NPCl_3\right]^+ Cl^- \qquad (16)$$

The latter compound has also been described independently (*26b*); the hexachloroantimonate salt had been described earlier (*396*, *397*).

The analogous condensation of Ph_2PSCl with dimethylguanidinium sulfate yields $Ph_2P(S){-}N{=}C(NMe_2)NH_2$ (*398*) which reacts with PCl_5

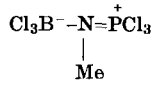
$$Ph_2P(S){-}N{=}C(NMe_2){-}NH_2 + 2PCl_5 \longrightarrow$$

$$\left[Ph_2P(Cl){=}N{-}C(NMe_2){=}NPCl_3\right]^+ Cl^- + 2HCl + PSCl_3 \qquad (17)$$

(*399*) as shown in Eq. (17). The corresponding hexachloroantimonates could also be obtained (*399*).

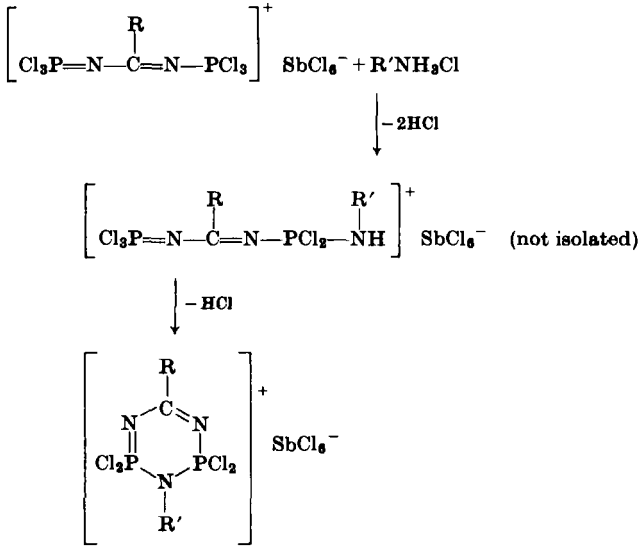
2. *Reactions*

Arsenic trifluoride fluorinates



to BF_3 and $(MeN{=}PF_3)_2$ (*51h*) and $[Me_2NPCl_3]^+BCl_4^-$ to Me_2NPF_4.

A ring-closure reaction occurs with bis(trichlorophosphazyl)methyl- (*393*, *402*) or -phenylhexachloroantimonates (*393*, *394*, *402*) and excess ammonium chloride to give the corresponding diphosphatriazines $RC(NPCl_2)_2N$ in good yields. The same cyclocondensation with $MeNH_3Cl$ or $PhNH_3Cl$ stops at the hexachloroantimonate salt of these triazines (*394*, *396*).



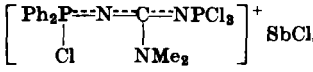
(18)

R = Me, Ph

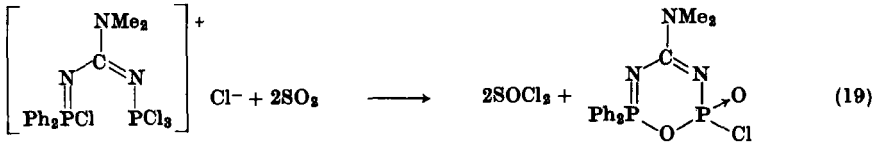
R′ = Me, Ph

The thermolytic behavior of $[RC(NPCl_2)_2]^+SbCl_6^-$ depends strongly on the nature of R. With R = Ph, elimination of benzonitrile occurs giving $[N(PCl_3)_2]^+SbCl_6^-$; with R = Me, only tars are formed and with R = Me_2N no condensation occurs (*402*).

The reaction of the saltlike compound



with SO_2 results in the formation of a six-membered ring (*393*).

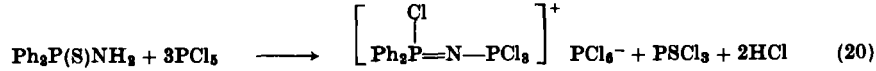


(19)

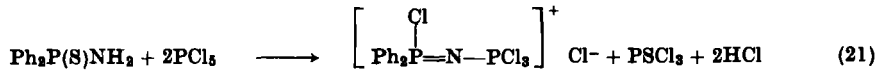
D. Unsymmetrical Ionic P–N Compounds

1. Syntheses

The reaction of $Ph_2P(S)NH_2$ with PCl_5 proceeds in the following manner (*26*):



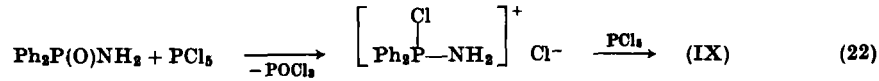
(20)



(21)

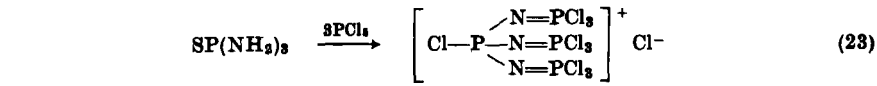
(IX)

Compound (IX) results also (*25*) as shown in Eq. (22).



(22)

Thiophosphoryl triamide reacts with PCl_5 to give the ionic compound (X) (*33*, *155*) in contrast to the reaction of $OP(NH_2)_3$ (cf. Section V,A).

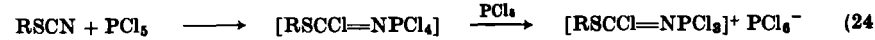


(23)

(X)

Excess PCl_5 produces the hexachlorophosphate salt of (X), $P_5N_3Cl_{16}$ (XI) (isolated as the $C_2H_2Cl_4$ adduct) (*302*).

Other $-N{=}PCl_3$-containing unsymmetrical ionic compounds are formed in the first step of the phosphorylation of aliphatic (*297f*, *442*) or aromatic (*443*) thiocyanates and of aryl cyanates (*443a*).



(24)

$$ArOCN + PCl_5 \longrightarrow [ArOCCl{=}NPCl_4] \xrightarrow{PCl_5} [ArOCCl{=}NPCl_3]^+ PCl_6^- \quad (25)$$

$$\downarrow ArOCN$$

$$[(ArOCCl{=}N)_2PCl_3]^+ PCl_6^-$$

Ar = Ph; *o*-, *m*-, *p*-MeC_6H_4; *p*-ClC_6H_4; *o*-, *p*-BrC_6H_4; 3,5-$Me_2C_6H_3$, 1-$C_{10}H_7$

Derkach and co-workers prepared compounds of the type $[RC(=NPCl_3)OR']^+Cl^-$ (R = Ph, *p*-BrC_6H_4; R′ = Et) by reacting $RC(=NCl)OR'$ and PCl_3 (or PCl_5), as well as $[(RO)_2C{=}NPCl_3]^+Cl^-$ (R = Me, Et) from $(RO)_2C{=}NCl$ and PCl_3 (*127*) (see also Section VII,A).

Addition of PX_3 to *N*-bromotriphenylphosphinimine results in the formation of ionic compounds $[X_3P{=}N{=}PPh_3]^+Br^-$ (*7*).

$$PX_3 + BrN{=}PPh_3 \rightarrow [X_3P{=}N{=}PPh_3]^+Br^- \quad (26)$$

X = Cl, Br

The phosphorylation of various cyanides (for details see Section VIII,B,1, phosphorylation of nitriles) at room temperature results in the formation of ionic compounds (*16*, *239*, *307*, *423*, *425*, *445*). These

$$MeCN + 3PCl_5 \longrightarrow \left[\begin{array}{l} H \\ Cl \end{array}\!\!>\!C{=}C\!<\!\begin{array}{l} N{=}PCl_3 \\ PCl_3 \end{array}\right]^+ PCl_6^- + 2HCl \quad (27)$$

$$CH_2ClCN + 3PCl_5 \longrightarrow \left[\begin{array}{l} Cl \\ Cl \end{array}\!\!>\!C{=}C\!<\!\begin{array}{l} N{=}PCl_3 \\ PCl_3 \end{array}\right]^+ PCl_6^- + 2HCl \quad (28)$$

$$EtCN + 3PCl_5 \longrightarrow \left[\begin{array}{l} Me \\ Cl \end{array}\!\!>\!C{=}C\!<\!\begin{array}{l} N{=}PCl_3 \\ PCl_3 \end{array}\right]^+ PCl_6^- + 2HCl \quad (29)$$

compounds were formulated earlier as $H_2C{=}CNPCl_4 \cdot PCl_5$ and $ClCH{=}CNPCl_4 \cdot PCl_5$, respectively (*239*, *425*).

Higher nitriles yield

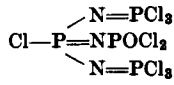
$$[Cl_3P{=}NCCl{=}C(R){-}PCl_3]^+PCl_6^-$$

(R = Me, $ClCH_2$, Et, Pr, Bu, *i*-Bu, Am) (*445*).

The compounds $[R_2C(CN)CCl{=}NPCl_3]^+PCl_6^-$ (R = Cl, Me, Et, Pr) result as intermediates in the phosphorylation of dinitriles (*290c*) (cf. Section VIII,B,1).

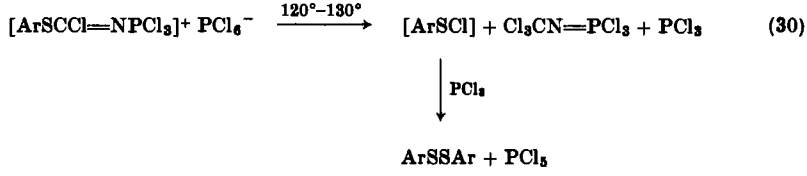
2. Reactions

Reaction of $[Ph_2P(Cl)NPCl_3]^+PCl_6^-$ with SO_2 (*26*) or DMSO (*192*) gives $Ph_2P(Cl)NPOCl_2$. Analogously, (X) reacts with SO_2 giving



(*155*) and with H_2S to give the corresponding thio compound.

Interaction of $[RSCCl{=}NPCl_3]^+PCl_6^-$ (R = Et, Ph, *p*-MeC_6H_4, *p*-$O_2NC_6H_4$) (*442*, *443*) with excess PCl_5 yields $CCl_3N{=}PCl_3$, which can also be obtained on other ways (cf. Section VIII,B,1). Heating the above-mentioned ionic compounds (120°–130°) results also in formation of $CCl_3N{=}PCl_3$, as well as HCl, PCl_3, and MeCHClSCl (in case of R = Et) (*442*), whereas with R = aryl groups, PCl_5 and ArSSAr are obtained as by-products (*443*).



$$[ArSCCl{=}NPCl_3]^+\,PCl_6^- \xrightarrow{120°-130°} [ArSCl] + Cl_3CN{=}PCl_3 + PCl_3 \qquad (30)$$

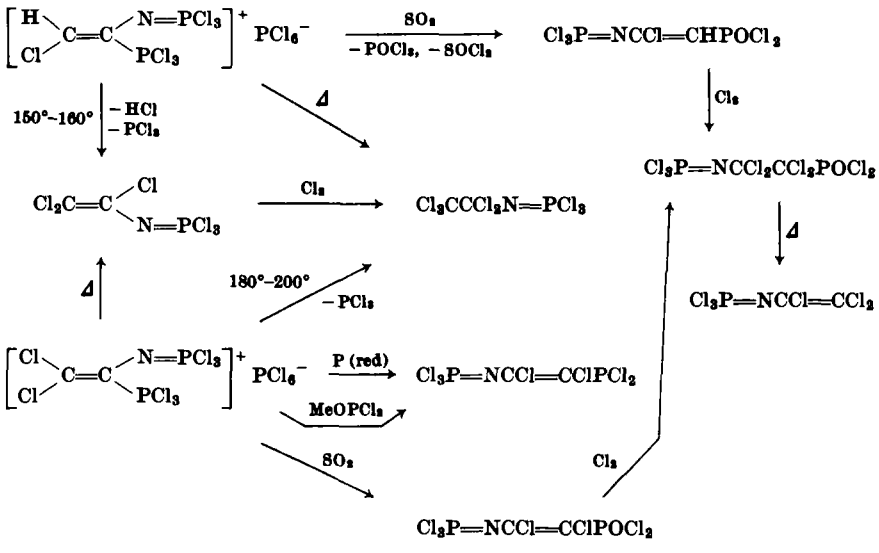
$$[ArSCl] \xrightarrow{PCl_3} ArSSAr + PCl_5$$

Sulfur dioxide reacts with $[ArXCCl{=}NPCl_3]^+PCl_6^-$ [X = S (*443*); X = O (*443a*)] to give $ArXCCl{=}NPOCl_2$.

The thermal decomposition of $[Cl_3P{=}NCCl{=}CRPCl_3]^+PCl_6^-$ (R = Me, $CHCl_2$, Et, Pr, Bu, *i*-Bu, Am) at 150°–200° results in formation of HCl, PCl_5, PCl_3, and $RCCl_2CCl_2N{=}PCl_3$ (*445*) (for details cf. Section VIII,B,1), and compounds with the formula $[RC(=NPCl_3)OR']^+Cl^-$ (R = Ph, *p*-BrC_6H_4; R′ = Et) at 130° give R′Cl and $RCON{=}PCl_3$ (*127*) (see also Section VII,A).

The ionic compounds $[Ph_3P{=}N{=}PX_3]^+Br^-$ (X = Cl, Br) hydrolyze with HX elimination to yield $Ph_3PNP(O)X_2$ (*5*, *7*); in the case of X = Cl the corresponding product results also from the reaction of Ph_3P, PCl_5, and hydroxylamine hydrochloride (*7*).

The reactions of the ionic intermediates obtained by the phosphorylation of nitriles are represented by the following scheme (*16*, *307*, *423*).



(*307*).

Compounds $[R_2C(CN)CCl{=}NPCl_3]^+PCl_6^-$ react with SO_2 to give $R_2C(CN)CCl{=}NPOCl_2$, $SOCl_2$, and $POCl_3$ (*290c*).

E. Spectroscopic Investigations

1. Infrared Spectroscopy

A normal coordinate analysis of $[Cl_3P{=}N{=}PCl_3]^+Cl^-$ (IV) and $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$ (III) has been carried out (*12*); the most probable value of ∢PNP is 140°* giving a force constant of 6.97 mdynes/Å and a bond order of $b = 2.0$ (*12, 180*). As characteristic frequencies of these compounds the following have been assigned (*12*): ν_s NP_2 at 833 cm^{-1}, ν_{as} NP_2 at 1298 cm^{-1}, ν_s PCl_3 at 468 cm^{-1} and ν_{as} PCl_3 at 653 cm^{-1} for compound (III) and 778 cm^{-1} for ν_s NP_2, 1338 cm^{-1} for ν_{as} NP_2, 421 cm^{-1} for ν_s PCl_3, and 592 cm^{-1} for ν_{as} PCl_3 for compound (IV).

Three characteristic bands for compounds of the type $[RC(NPCl_3)_2]^+$-$SbCl_6^-$ are assigned between 700 and 1100 cm^{-1} (*397*); ν_s PN lies between 670 (R = CCl_3) and 727 cm^{-1} (R = Me).

* The X-ray structure investigation of the related compound $[Ph_2P(NH_2){=}N{=}P(NH_2)Ph_2]^+Cl^-$ gives a value of ∢PNP of 136° (*74*).

2. Nuclear Magnetic Resonance

Phosphorus-31 NMR has proved very successful in elucidating the structures of the compounds described in Sections IV,A,1 to IV,D,1. Mention of this subject is made in a few reviews [(*159*, *160*), see also (*19*)].

a. Symmetrical Cations. The cations of (III) and (IV) show only one peak ($\delta_P = -21.4$ ppm) in the ^{31}P NMR (*15*, *23*, *155*), thus showing magnetic equivalence of the two phosphorus atoms. The PCl_6^- anion in (III) gives the peak at ~305 ppm (Fig. 1).

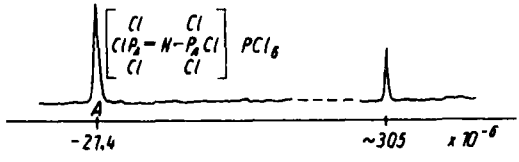


FIG. 1. ^{31}P NMR spectrum of $[Cl_3P{=}N{=}PCl_3]^+[PCl_6]^-$. From reference (*155*).

A spin-spin coupling is observed in compound (VIII) with the characteristic AB_2C pattern (*153*, *155*) (Fig. 2).

The compound $[Cl_3P{=}N(PNCl_2)_xPCl_3]^+PCl_6^-$ ($x = 2$) has been shown to be linear (*30*, *157*). Higher homologs ($x = 2$, 3) have been synthesized

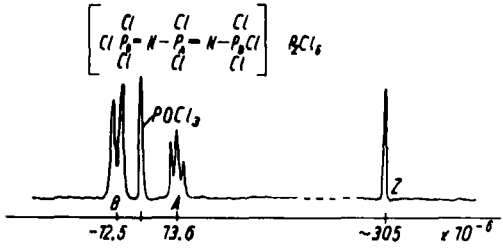


FIG. 2. ^{31}P NMR spectrum of $[Cl_3P{=}NPCl_2{=}NPCl_3]^+[PCl_6]^-$. From reference (*155*).

recently (*339*), but has been postulated earlier on the basis of ^{31}P NMR results (*156*). Figures 3a–c and 4 give the appropriate spectra. In general, a $Cl_3P{=}N$ group (terminal group) gives a chemical shift around −12 ppm (*39*, *156*, *310*), a $-NPCl_2$ group (in the chain) is centered around 14 ppm (*155*, *156*), and the PCl_6^--anion at ~300 ppm (*155*, *156*, *160*). Furthermore, increasing the value of x results in shifting the cationic phosphorus atoms to higher field and, in addition to this, the band width of the most shifted cationic phosphorus atom decreases. It can be concluded that

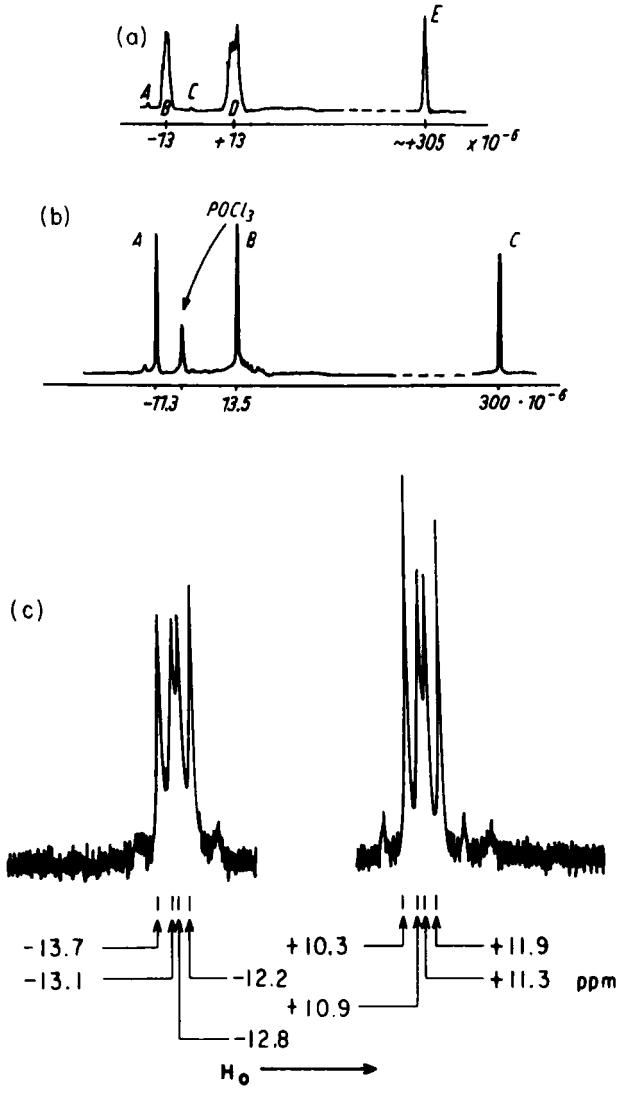


FIG. 3. (a) ^{31}P NMR spectrum of $[Cl_3PN(PCl_2N)_2PCl_3]^+[PCl_6]^-$ (from the reaction of $PCl_5/(PNCl_2)_3$. From reference (*156*). (b) ^{31}P NMR spectrum of $[Cl_3PN(PCl_2N)_2PCl_3]^+[PCl_6]^-$ neat. From reference (*157*). (c) ^{31}P NMR spectrum of $[Cl_3PN(PCl_2N)_2PCl_3]^+[BCl_4]^-$ (from the reaction of PCl_5 and $(PNCl_2)_3$. From reference (*339*).

with higher values of x (4 or 5) the cationic peak shifts to 15 ppm (*339*) or with $x \sim 10$ to 18 ppm (*323*).

The compound $[P_A(N{=}P_BCl_3)_4]^+X^-$ (*405*) gives a characteristic AB_4 spectrum with $\delta_{P_B} = 38.5$–39.3 ppm (depending on the nature of X^-) and with $\delta_{P_A} = 3.4$–4.1 ppm ($J_{PNP} = 28.7 - 29.9$ Hz).

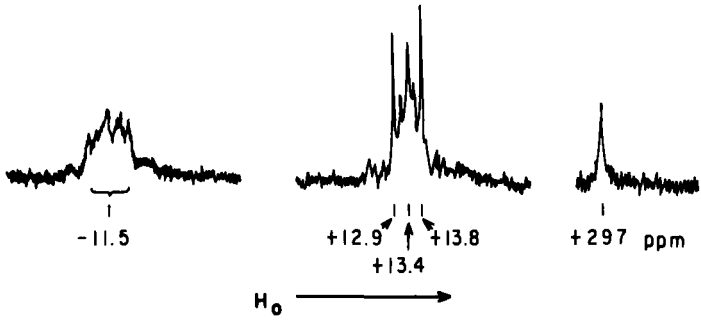
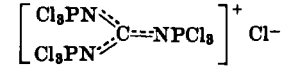


FIG. 4. ^{31}P NMR spectrum of $[Cl_3PN(PCl_2N)_3PCl_3]^+[PCl_6]^-$. From reference (*339*).

b. Cations with (*P=N=C(R)=N=P*) *Units.* The resonance in cations of the type $[Cl_3P{=}N{=}C(R){=}N{=}PCl_3]^+X^-$ ($R = Cl$; $X^- = PCl_6^-$) is shown by the fact that only one peak ($\delta_P = -38.5$ ppm) for the cation is obtained (*16*). Similar results occur with R = Me, Me_2N, $Cl_3P{=}N{-}$, and $X^- = SbCl_6^-$, but a strong dependence of the chemical shift of the cationic phosphorus atoms on the nature of R is observed (*396*, *397*). An obviously erroneous result for



with two peaks (−13.2 and −32.9 ppm, ratio 2:1, respectively) was recently reported (*422*).

The equivalence of the two phosphorus atoms is also shown in the ^1H NMR spectrum (*396*, *397*) of $[MeC(NPCl_3)_2]^+SbCl_6^-$ consisting of a triplet. The proton nuclear magnetic resonance spectrum of $[Me_2NC(NPCl_3)_2]^+SbCl_6^-$ (at 40°) shows a quartet of nonequidistant lines (part of an A_2X_2 system) (*396*, *397*), which turns to a triplet (AX_2) at 90° (Fig. 5).

c. Unsymmetrical Cations. The compound $[Ph_2P_A(Cl){=}NP_BCl_3]^+Cl^-$ gives two peaks ($\delta_{P_A} = -42.3$ and $\delta_{P_B} = -14.3$ ppm), both showing tetracoordinate phosphorus (*26*); $[ClP_A(N{=}P_BCl_3)_3]^+X^-$ [$X^- = Cl^- = (X)$; $X^- = PCl_6^- = (XI)$] similarly show two cationic peaks ($\delta_{P_A} = 26.8$ and $\delta_{P_B} = -6.5$ ppm) (*302*).

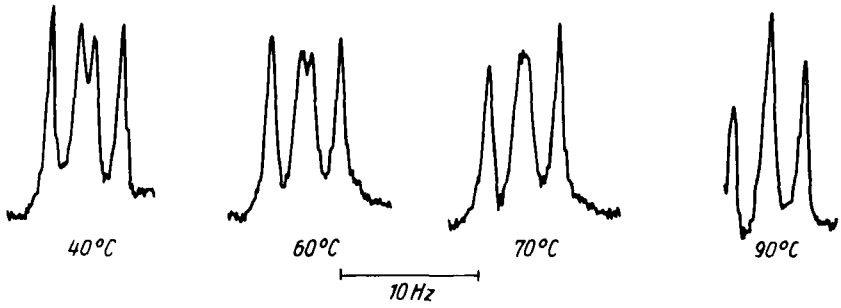
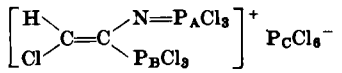
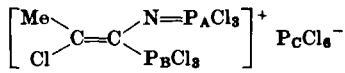


FIG. 5. ^1H NMR spectrum of $[Me_2NC(NPCl_3)_2]^+[SbCl_6]^-$. From reference (*397*).

The structures of the ionic compounds resulting from the phosphorylation of nitriles have been elucidated mainly by ^{31}P NMR spectroscopy (*16*, *307*). Cis-trans isomerism was shown for the following substances.

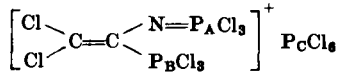


$\delta_{P_A} = -15.9$ ppm $\delta_{P_B} = -83.1$ and -80.7 ppm $\delta_{P_C} = 297$ ppm



$\delta_{P_A} = -7.8$ ppm $\delta_{P_B} = -84.0$ and -86.0 ppm $\delta_{P_C} = 292$ ppm

The compound



gives only the three expected peaks ($\delta_{P_A} = -14.2$, $\delta_{P_B} = -85.0$, $\delta_{P_C} = 296$ ppm) (*16*, *307*).

Finally, the chemical shift of $[(EtO_2)C{=}NPCl_3]^+Cl^-$ ($\delta_P = -20.4$ ppm) is reported (*475*).

3. Other Physical Investigations

X-Ray powder patterns of compounds (III), (IV), (VII), and (VIII) are reported in the literature (*29*) and discussed in detail, especially in view of the earlier published data for (III) and (VIII) (*183*). Powder diagrams of $[Br_3P{=}N{=}PBr_3]^+Br^-$ and $[Br_3P{=}N{=}PBr_3]^+Br_3^-$ are also available (*206*).

Electric conductance studies of (III) (*28*), (IV) (*34*), (VIII) (*23*, *29*), and (IX) (*26*), as well as (X) and (XI) (*302*) show these substances to be 1 : 1 electrolytes in the specified solvents.

Chlorine-35 NQR work on (III)* and (VIII) was recently published (*215*), but no positive results could be obtained.

V. *N*-Phosphorylated Phosphazotrihalides

A. Syntheses

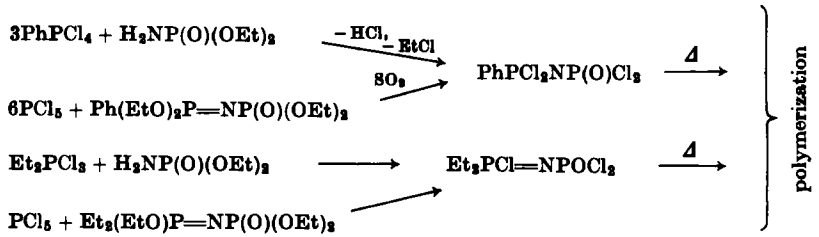
The synthesis of the simplest *N*-phosphorylated phosphazotrichloride, Cl_2PNPCl_3, was attempted (*158*) by reaction of $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$ (III) with red phosphorus, but the compound could not be isolated. Recently, a derivative $(C_3F_7)_2PN{=}PCl_3$ has been described (*366a*). Trifluorophosphazodifluorophosphine is also known (*180c*).

The corresponding oxygen-containing substance (V), $Cl_2(O)PNPCl_3$, is formed (cf. Scheme 2) in the reaction of PCl_5 and hydroxylamine hydrochloride (*24*, *214*) or with phosphoric acid amides (*33*, *214*) or ammonium diamidophosphate (*33*) or other ammonium salts (*146a*). The same compound is synthesized from SO_2 and (III) (*15*, *20*, *28*, *315*, *543*) or (IV) (*29*), by acidolysis (HCOOH) of (III) (*192*), or from PCl_3 and N_2O_4 (*15*, *18*). The last synthesis had already been carried out earlier [(*286*), see also (*11*)], but the compound was characterized erroneously. Interaction of hexamethyldisilazane and $POCl_3$ results first in a white material having the approximate composition $(HNOPCl)_n$ [(*173*), see also (*42*)], which with PCl_5 at 120° gives compound (V) (*173*). The compound $Cl_2P(O)NPCl_3$ is also (*548*) formed by reaction (31).

$$(MeO)_2PONH_2 + 3PCl_5 \rightarrow 2HCl + 2MeCl + 2POCl_3 + (V) \qquad (31)$$

The same compound is formed from PCl_5 and NH_4Cl in $POCl_3$–solvent using P_4O_{10} as oxidizing agent [with (III) as intermediate] (*413*).

Compounds similar to (V) are obtained in the following ways [(*524*), see also (*366a*)].



* However, a recent ^{35}Cl NQR paper (*191a*) of the same authors reports affirmative results on compound (III).

$$Ph_2PCl_3 + H_2NP(O)(OEt)_2 \longrightarrow Ph_2PCl{=}NPOCl_2$$
$$MePCl_4 + H_2NP(O)(OEt)_2 \longrightarrow MePCl_2{=}NPOCl_2 \xrightarrow{\Delta} \text{polymerization} \quad (32)$$

Compounds $Ph_3P{=}NP(O)X_2$ (X = Cl, Br) result by hydrolysis of $[Ph_3P{=}NPX_3]^+Br^-$ (*5*).

The series $F_nCl_{2-n}P(O)NPCl_3$ ($n = 0$, 1, 2) are obtained from $F_nCl_{2-n}P(O)NH_2$ and PCl_5 (*387*) [for $n = 2$, cf. also (*176, 290*]; $F_2P(O)N{=}PCl_3$ is formed also from the Si–N cleavage of $Me_3SiNHPOF_2$ with PCl_5 (*173*).

$$Me_3SiNHPOF_2 + PCl_5 \rightarrow F_2P(O)N{=}PCl_3 + HCl + Me_3SiCl \quad (33)$$

Hexamethyldisilazane and $POFCl_2$ react in two ways (*347*):

$$(Me_3Si)_2NH + POFCl_2 \longrightarrow Me_3SiCl + [Me_3SiNHPOFCl]$$
$$\swarrow \Delta \qquad \downarrow PCl_5 \quad (34)$$
$$Me_3SiCl + \text{polymeric material} \qquad FClP(O)N{=}PCl_3 + HCl + Me_3SiCl$$

The compound $Cl_2P(S)N{=}PCl_3$ (VI), representing the thio analog of (V), is formed from (III) and H_2S or sulfur (requiring S_2Cl_2 addition) (*13, 29*), as well as from S_4N_4 and PCl_3 in poor yield (*29*). The syntheses of (V) and (VI) are summarized in Scheme 2.

The analogous compounds $(PhO)_2P(X)N{=}PCl_3$ (X = O, S) are formed by the Kirsanov reaction of $(PhO)_2P(X)NH_2$ (*283*); $Ph_2P(O)N{=}PCl_3$, which should be formed from $Ph_2P(O)NH_2$ and PCl_5, could not be isolated. Only $[Ph_2P(Cl)NH_2]^+Cl^-$ (*25*) is formed in the first step (cf. Sections IV,D,1 and 2); the corresponding tautomer $Ph_2PClNPOCl_2$ is described (Section IV,D,2).*

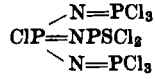
Derkach and co-workers described compounds* such as $RR'P(O)N{=}PCl_3$(?) (R = Me, R′ = Cl, OPh, *p*-ClC_6H_4O, *p*-MeC_6H_4O; R = CH_2Cl, R′ = Cl, OPh, *p*-$O_2NC_6H_4O$, *p*-MeC_6H_4O) (*473*). Recently $EtP(S)FN{=}PCl_3$ was isolated (*385*), but the analogous reaction of $PhP(S)FNH_2$ did not give concrete results.

The compound $Cl_3P{=}NPCl_2{=}NPOCl_2$ is obtained from (VII) or (VIII) with SO_2 (*23, 28, 29*), the thio analog by treating (VIII) with H_2S (*23, 29*). Similarly, (X) with SO_2 yields

$$ClP\begin{matrix}=NPOCl_2\\ \diagup N{=}PCl_3\\ \diagdown N{=}PCl_3\end{matrix}$$

* $Et_2P(O)N{=}PCl_3$ cannot be isolated from $Et_2P(O)NCl_2$ and PCl_3 nor from $Et_2P(O)NH_2$ and PCl_5, but its tautomer $Et_2PCl{=}NPOCl_2$ can (*523a*); the same applies to $MeP(O)ClN{=}PCl_3$ which should rather be considered as $MePCl_2{=}NPOCl_2$ (*473a*).

(*155*), and with H_2S



The compound $F_2P(O)N{=}PF_3$ results from $F_2P(O)NH_2$ and PF_3Cl_2 (*324*), analogous compounds $FX(S)PN{=}PF_3$ (X = Cl, F) from the corresponding amine and PF_3Cl_2 (*324*, *383*).

Compounds OPX_2NH_2 and SPX_2NH_2 (X = F, Cl) with $MePCl_4$ or CCl_3PCl_4 give the corresponding phosphazo compounds (*378a*); $SP(X,Y)NH_2$ (X = Cl, F) and $PhPF_4$ react similarly to $SP(X,Y)N{=}PF_2Ph$ (*379a*).

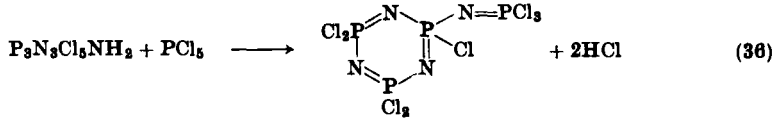
The series $F_nCl_{2-n}P(S)N{=}PF_{3-m}Cl_m$ ($n = 0, 1, 2$; $m = 0, 1$) has been described recently (*382*); $F_2P(S)N{=}PCl_3$ and $FClP(S)N{=}PCl_3$ are also formed from $Me_3SiNHPSF_2$ or $Me_3SiNHPSFCl$ and PCl_5 (*174*), as well as from $Cl_nF_{2-n}P(S)NH_2$ ($n = 0, 1, 2$) and PCl_5 (*378*). A higher *N*-phosphorylated phosphazotrichloride $Cl_2(O)PN{=}P(N{=}PCl_3)_3$ results from $[P(N{=}PCl_3)_4]^+Cl^-$ and sulfur dioxide (*403*).

Longer chains are also obtained (*381d*) according to Eq. (35).

$$FXP(S)NPF_2NHSiMe_3 + PCl_5 \rightarrow FXP(S)NPF_2NPCl_3 + HCl + Me_3SiCl \quad (35)$$
X = F, Cl

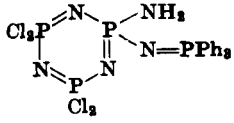
Compounds SPX_2NPF_2Br (X = Cl, F) have also been prepared (*382a*).

The reaction of the monoamide of $(PNCl_2)_3$, namely, $P_3N_3Cl_5NH_2$, with PCl_5 (*149*) proceeds in a normal Kirsanov reaction to give (XII).



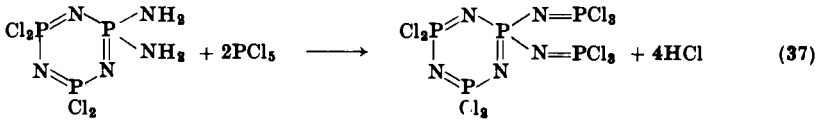
(XII)

The compound



(*218*), also obtained by other ways [(*150*), Section V, B] on phosphorylation with PCl_5 probably gives the trichlorophosphazo compound (*309*).

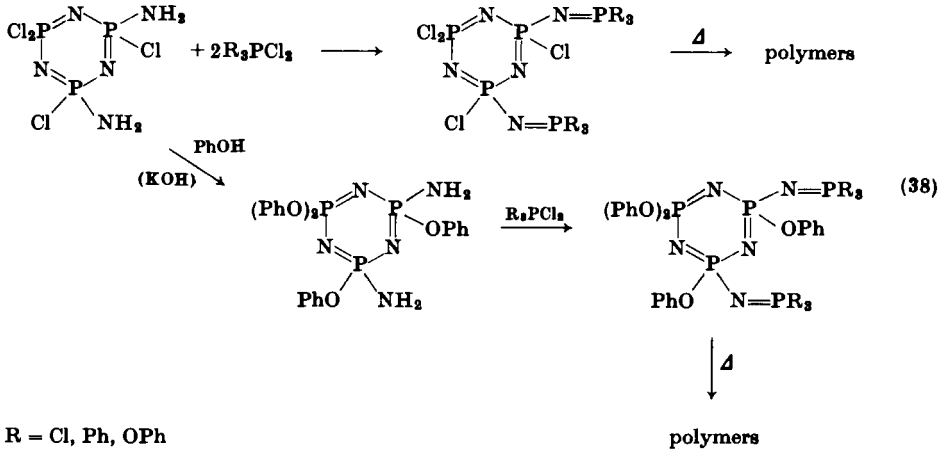
The geminal diamide of hexachlorophosphazatriene, $P_3N_3Cl_4(NH_2)_2$, and PCl_5 give (XIII) (*149*, *308*, *309*). For the similar reaction with Ph_3PBr_2, Ph_3PCl_2, and Ph_2PCl_3 cf. (*217*, *218*).



(37)

(XIII)

The reactions of a nongeminal diamide of $(PNCl_2)_3$ [the existence of which is questioned by other authors (*309*)] with PCl_5 and Ph_3PCl_2 were recently described (*204*).



(38)

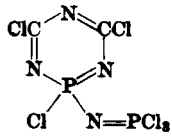
R = Cl, Ph, OPh

Interaction of $P_3N_3F_5NH_2$ and PCl_5 (*386*) gives $P_3N_3F_5N{=}PCl_3$, with PF_3Cl_2 $P_3N_3F_5N{=}PF_3$ (*385*, *385d*), and with $PhPF_4$ the compound $P_3N_3F_5N{=}PPhF_2$ (*379a*) is obtained. $P_4N_4F_7N{=}PX_3$ (X = Cl, F) are obtained similarly from $P_4N_4F_7NH_2$ and PCl_5 or PF_3Cl_2, respectively (*385d*). Analogous compounds $P_3N_3F_5N{=}PPh_nCl_{3-n}$ (n = 0, 1, 2) result from $P_3N_3F_5NH_2$ and Ph_nPCl_{5-n} (*347a*).

The reactions of some geminal and nongeminal amido derivatives of $(PNCl_2)_4$ has been investigated (*309a*).

$P_3N_3F_5NPX_2N{=}PCl_3$ and $P_3N_3F_5NPX_2NPCl_2N{=}PCl_3$ (X = F, Cl) as well as $P_5N_5F_9N{=}PCl_3$ and $P_6N_6F_{11}N{=}PCl_3$ were recently prepared (*385a*).

Finally, dicyandiamide and excess PCl_5 give



(*26b*, *110*, *207*) (cf. also Section VIII,B,1).

B. Reactions

Heating (V) to ~200° results in decomposition to $POCl_3$ and $(PNCl_2)$ units (*164*, *524*) [see also the thermal degradation of $RPCl_2N{=}POCl_2$ (R = Me, Ph) and $Et_2PCl{=}NPOCl_2$ to long-chain phosphazene units (*524*)]. Acidolysis yields amidophosphoric acid; at lower pH values $(NH_4)_3PO_4$ and H_3PO_4 (*33*) results. The hydrolysis with DMSO does not give the expected $Cl_2P(O)NHPOCl_2$, but white solids (P:N = 2:1) with no definite structure (*192*). Interaction with chlorosulfonic acid leads to $POCl_3$, SO_2Cl_2, and uncharacterized products (*192*). However, careful hydrolysis of (V) with HCOOH gives $Cl_2OP{-}NH{-}POCl_2$ (*374a*).

The reaction of $Cl_2(O)PNPCl_3$ (V) with aniline (*33*) or dimethylamine (*13*, *18*) results in replacement of the chlorine atoms; the product of the latter reaction has also been obtained by a phosphine–azide reaction (*509*). The reaction of (V) with BuONa and various alcohols is described (*220c*). Compound (V) and *p*-$O_2NC_6H_4ONa$ give $(p\text{-}O_2NC_6H_4O)_3PNP(O)(OC_6H_4NO_2\text{-}p)_2$ (*315*). Analogous compounds such as $(RO)_2P(O)N{=}P(OR')_3$ (R = Me, Et, *i*-Pr; R′ = Me, Et, *i*-Pr, Ph, *p*-MeC_6H_4) (*476*), as well as $(MeO)_2PON{=}P(NC_2H_4)_3$ (*234*), have been prepared in other ways [cf. also (*10*, *209*, *211*)]. With $TiCl_4$ (V) gives the compound $TiCl_4 \cdot 2P_2NOCl_5$ (*35*, *203*) [erroneously reported in (*164*)]; the coordination is by the oxygen atoms. Other crystalline adducts of this type are $2P_2NCl_5O \cdot SnCl_4$, $P_2NCl_5O \cdot SbCl_5$, and the liquid 1:1 adduct $P_2NCl_5O \cdot AlCl_3$ (*203*). Finally (V) with 2 moles of PCl_5 gives $[Cl_3P{=}N{=}PCl_3]^+PCl_6^-$ (*315*).

The compound $F_2(O)PN{=}PCl_3$ decomposes analogously to (V) at 200° with elimination of POF_2Cl and $POCl_3$ to give a mixture of $(PNCl_2)_n$ and $(PNF_2)_n$ (*290*). No reaction occurs with difluorophosphoric acid at room temperature. $POF_2NHPOCl_2$ and POF_2Cl result at 65° and polymerization takes place at 130° (*176*); $POF_2NHPOCl_2$ is also formed by reaction of $F_2(O)PN{=}PCl_3$ with formic acid. The reaction with FSO_3H is complex and is thought to proceed (*176*) as outlined in Eq. (39).

$$2POF_2N{=}PCl_3 + 2FSO_3H \rightarrow \underset{\text{(not isolable)}}{2(POF_2NHSOF)_2} + 2POCl_3$$
$$\downarrow$$
$$FSO_2NHSO_2F + \underset{\text{(polymerizes)}}{POF_2NHPOF_2} \qquad (39)$$

Compound (VI) and NaOPh give the corresponding pentaphenoxy compound (*29*), also obtained in other ways (*283*).

Aminolysis of $(PhO)_2PON{=}PCl_3$ with aniline gives $(PhO)_2PON{=}P(NHPh)_3$ (*283*); $(PhO)_2PXN{=}PCl_3$ (X = O, S) react with NaOAr

(Ar = Ph, p-ClC_6H_4, p-$O_2NC_6H_4$) giving the appropriate esters (*283*, *534*), which can also be obtained from $(PhO)_5P$ and $(PhO)_2PONH_2$ or $(PhO)_2PSNH_2$. Attempts to prepare $Ph_2PSN{=}PPh_3$ by an azide–phosphine reaction failed (*9*), only polymerization products being obtained.

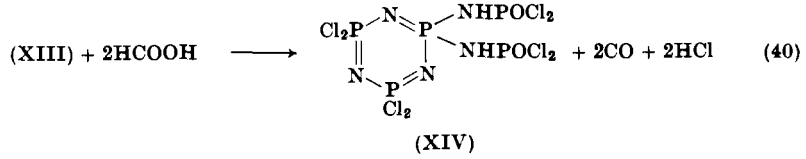
Hydrolysis (HCOOH) of $(PhO)_2P(X)N{=}PCl_3$ (X = O, S) gives rise to $(PhO)_2P(X)NHPOCl_2$ (*283*). Other $(RO)_2PON{=}P(OR')_3$ compounds (R = R′ = Et, Bu) are formed from $(RO)_2PONSO$ and $P(OR')_3$ (*518*); $RP(O)(OAr)N{=}PCl_3$ (R = Me, $ClCH_2$, Ar = p-MeC_6H_4, p-ClC_6H_4; R = $ClCH_2$, Ar = Ph) and ethylenimine give the triamides (*369*).

Compounds $X_2P(S)N{=}PF_3$ (X = Cl, F) and Me_3SiNMe_2 form $X_2P(S)NPF_2NMe_2$ (*382a*); with HCOOH or NH_3, $SX_2PNHPOF_2$ and $SPX_2NPF_2NH_2$ are obtained (*382b*). The compounds $SPX_2N{=}PF_2Cl$ (X = F, Cl) and methanol react to the *S*-methyl derivatives $MeSPX_2{=}NP(O)F_2$ (*382c*). The reaction of the compounds $SPF_nCl_{2-n}N{=}PF_mCl_{3-m}$ (n = 0, 1, 2; m = 0, 1) with hexamethyldisilazane and subsequent chain elongation is described (*383a*).

Alcoholysis of $Cl_3P{=}NPCl_2{=}NPOCl_2$ gives the corresponding esters (*509b*).

The interaction of 2,2,6,6-tetrakis(trichlorophosphazo)-4,4,8,8-tetrachlorophosphazatetraene with $VOCl_3$ is reported (*483a*).

Partial hydrolysis of (XIII) with formic acid (*309*) leads to (XIV).



$$\text{(XIII)} + 2\text{HCOOH} \longrightarrow \text{(XIV)} + 2\text{NHPOCl}_2 + 2\text{CO} + 2\text{HCl} \qquad (40)$$

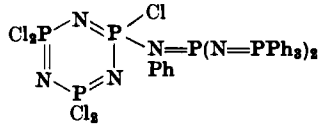
A ring-closure reaction of (XIII) with heptamethyldisilazane yields a spiro compound (*308*).

Arylation of (XII) and (XIII) has been described (*150*). Geminal $N_3P_3Cl_4Ph(N{=}PPh_3)$ could also be obtained in other ways (*48*, *140*, *217*).

$$\begin{aligned}
&\text{(XII)} + 3\text{PhMgBr} \xrightarrow{\Delta,\ Et_2O} N_3P_3Cl_5(N{=}PPh_3) + 3\text{MgClBr} \\
&\text{(XII)} + 4\text{PhMgBr} \xrightarrow{\Delta,\ Et_2O} \textit{gem}\text{-}N_3P_3Cl_4Ph(N{=}PPh_3) + 4\text{MgClBr} \qquad (41) \\
&\text{(XIII)} + 6\text{ArMgBr} \xrightarrow{\Delta,\ Et_2O} N_3P_3Cl_4(N{=}PAr_3)_2 + 6\text{MgClBr} \\
&\text{Ar} = \text{Ph},\ p\text{-}MeC_6H_4
\end{aligned}$$

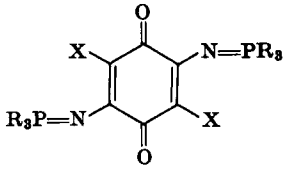
Geminal $N_3P_3Cl_4(NH_2)(N{=}PPh_3)$ results from geminal $N_3P_3Cl_4(NH_2)_2$ and Ph_3PBr_2 (*150*).

Another compound belonging to this group results from $(PNCl_2)_3$ and diphenylmagnesium (*49*). This is



A chain elongation results by the reaction of heptamethyldisilazane on $P_3N_3F_5N{=}PX_3$ (X = Cl, F) (*385a*); with Me_3SiNMe_2 or Me_3SiNCS stepwise replacement of the halogens occurs (*383c*).

Analogous compounds



X = Cl, Br, I; R = Ph, *p*-ClC_6H_4, *o*-BrC_6H_4, *p*-MeC_6H_4, *p*-BuC_6H_4, *p*-$BuOC_6H_4$, 2,4-$F_2C_6H_3$, substituted naphthalenes

(*340*) are also described. Finally, the $-N{=}PCl_3$ group of 2-(trichlorophosphazo)-2,4,6-trichloro-2-phospha-1,3,5-triazine is converted by SO_2 or HCOOH into the $-NHPOCl_2$ group (*26b*).

C. Spectroscopic Investigations

The IR spectrum of (V) is reported (*18, 35*); Glemser and co-workers assigned the $\nu_{P=N}$ at 1320 (*173*) or 1332 cm^{-1} (*387*) and ν_{P-N} at 776 cm^{-1}. The P=N vibration in $F_2(O)PN{=}PCl_3$ is found at 1350 (*290*), 1355 (*173*) or 1360 cm^{-1} (*387*) and ν_{P-N} at 768 cm^{-1} (*173, 387*). For $FCl(O)PN{=}PCl_3$ $\nu_{P=N}$ is at 1347–1350 cm^{-1} and ν_{P-N} at 780 cm^{-1} (*173, 387*). The infrared spectrum of $FCl(S)PN{=}PCl_3$ is given in the literature (*378*); the $\nu_{P=N}$ in the series $F_nCl_{2-n}(S)PN{=}PCl_3$ decreases from 1340 cm^{-1} ($n = 2$) to 1328 ($n = 1$) and 1305 cm^{-1} ($n = 0$) (*378*). Recently, the compounds $F_nCl_{2-n}(S)PN{=}PF_{3-m}Cl_m$ ($n = 0, 1, 2$; $m = 0, 1$) were investigated (*382*), showing absorption for $\nu_{P=N}$ between 1365 and 1430 cm^{-1}.

The IR spectra of $FX(S)PN{=}PF_3$, reported for X = F (*324*), show the P=N vibration at 1415 (X = Cl) and 1430 cm^{-1} (X = F) (*383*).

The compounds (XII) and (XIII) also show (*149*) the P=N vibration in the usual range (1190–1335 cm^{-1}).

More attention was given to the nuclear magnetic resonance investigations of the compounds listed in Section V, A. The compound $F_2P_BN{=}P_AF_3$ shows δ_{P_B} at −129 ppm and δ_{P_A} at 43.6 ppm, thus proving the

structure (*180c*). The compound $Cl_2P_B(O)N{=}P_ACl_3$ (V) (AB type) shows coupling of the phosphorus nuclei ($\delta_{P_A} = 0.1 \pm 0.5$ ppm; $\delta_{P_B} = 14.2 \pm 0.5$ ppm; $J_{P_AP_B} = 15.4 \pm 0.3$ Hz) (*154*) (see also (*153, 371*)). Other authors (*2*) reported $\delta_{P_A} = 1.1$ ppm, $\delta_{P_B} = 12.7$ ppm, and $J_{P_AP_B} = 19.5$ Hz.

The analogous compound $F_{X_2}(O)P_BN{=}P_ACl_3$ represents a simple ABX_2 spectrum [$\delta_{P_A} = -8$ ppm, $\delta_{P_B} = 26$ ppm, $\delta_{F_X} = 70$ ppm (*176*); $\delta_{P_A} = -6.5$ ppm, $\delta_{P_B} = 25$ ppm, and $\delta_{F_X} = 70.3$ ppm, $J_{F-P_B} = 973.5$ Hz, $J_{P_AP_B} = 70$ Hz, and J_{F-P_A} 21.5 Hz (*173*)]; $FCl(O)PN{=}PCl_3$ is of an ABX type (*173*).

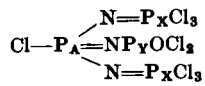
Compound (VI), like (V), is of an AB type, but no coupling of the two phosphorus nuclei could be observed (*2*, *157*). $(PhO)_2P(O)N{=}PCl_3$ gives only one peak in the ^{31}P NMR spectrum [with a half-band width of 3 Hz (*349*)], the chemical shift is $\delta_P = 11.2$ ppm (*349a*).

Phosphorus-31 NMR results of $(R'O)_3P{=}N{=}P(O)R_2$ were recently reported (*421*).

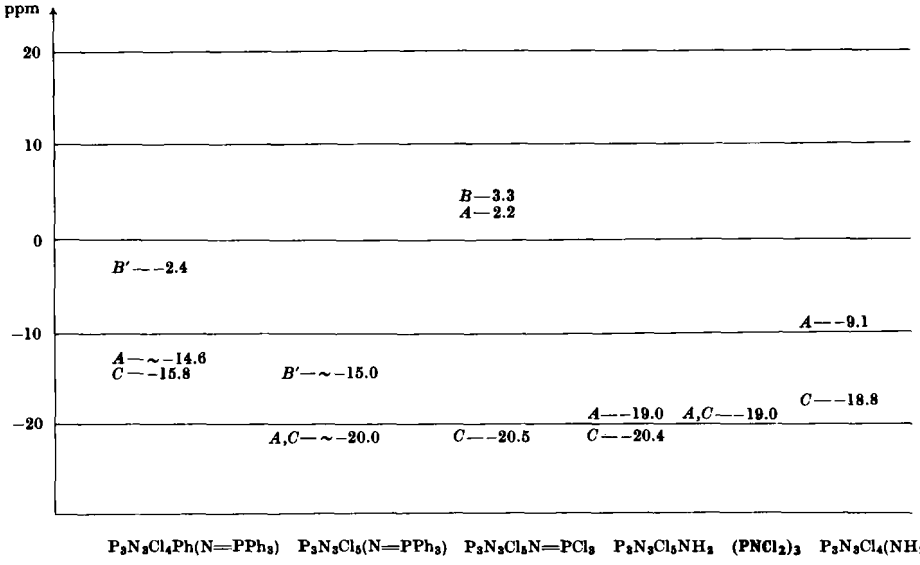
Fluorine-19 spectra of the series $F_nCl_{2-n}(S)PN{=}PF_{3-m}Cl_m$ ($n = 0, 1, 2$; $m = 0, 1$) have been recorded [(*382*), see also (*383*)]; the two compounds $F_2(S)P_BN{=}P_ACl_3$ ($\delta_{P_A} = -4.4$ ppm, $\delta_{P_B} = -40.7$ ppm, $\delta_F = +33.7$ ppm, $J_{P_AP_B} = 70$ Hz, $J_{P_AF} = \pm 22$ Hz, $J_{P_BF} = \pm 1085$ Hz) and $FCl(S)P_BN{=}P_ACl_3$ ($\delta_{P_A} = -0.8$ ppm, $\delta_{P_B} = -42.3$ ppm, $\delta_F = 33.5$ ppm, $|J_{P_AP_B}| = 40$ Hz, $J_{P_AF} = \pm 21.5$ Hz, $J_{P_BF} = +1115$ Hz) have been examined in detail (*378*).

Fluorine and phosphorus spectra of $Cl_2(S)PN{=}PF_2Cl$ and $F_nCl_{2-n}(S)$-$PN{=}PF_3$ ($n = 0, 1, 2$) are reported (*163*); only data from the ^{19}F NMR spectrum are given for $EtP(S)FN{=}PCl_3$ (*385*). The compound $Cl_3P_B{=}NP_ACl_2{=}NP_XOCl_2$ gives a spectrum of the ABX type (*155*) with $\delta_{P_A} = 20.0 \pm 0.5$ ppm, $\delta_{P_B} = 13.4 \pm 0.5$ ppm, and $\delta_{P_X} = -7.1 \pm 0.5$ ppm, spin-spin coupling occurs ($J_{P_XP_A} = 29.5 \pm 1$ Hz, $J_{P_AP_B} = 26.7 \pm 1$ Hz) analogously to (V). $Cl_3P{=}NPCl_2{=}NPSCl_2$ (ABX-type) has also linear structure according to NMR results (*157*), and a more detailed investigation of this compound has been carried out (2). NMR work (^{19}F, ^{31}P) on higher linear diphosphazenes is available (*383a*).

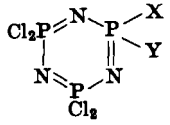
The compound



gives a spectrum of the type AX_2Y with $\delta_{P_X} = 1.9 \pm 0.5$ ppm, $\delta_{P_Y} = 13.6 \pm 0.5$ ppm, and $\delta_{P_A} = 29.6 \pm 0.5$ ppm (*155*); the corresponding thio compound has the same structure, but no spin-spin coupling between P_A–P_Y could be observed (*157*). Some discussion (*159*, *160*) of the ^{31}P NMR spectra of the above-mentioned compounds has been given. An



SCHEME 4. Graphical plot of the chemical shifts of the phosphorus nuclei in compounds of the structure

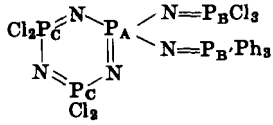


X = N=PPh3, N=PCl3, NH2, Cl, NHPOCl2
Y = Ph, Cl, NH2, N=PCl3, NHPOCl2, N=PPh3

* Ref. (*49*) gives for $A = -8.6 \pm 0.2$ ppm and for $C = -17.5 \pm 0.2$ ppm.

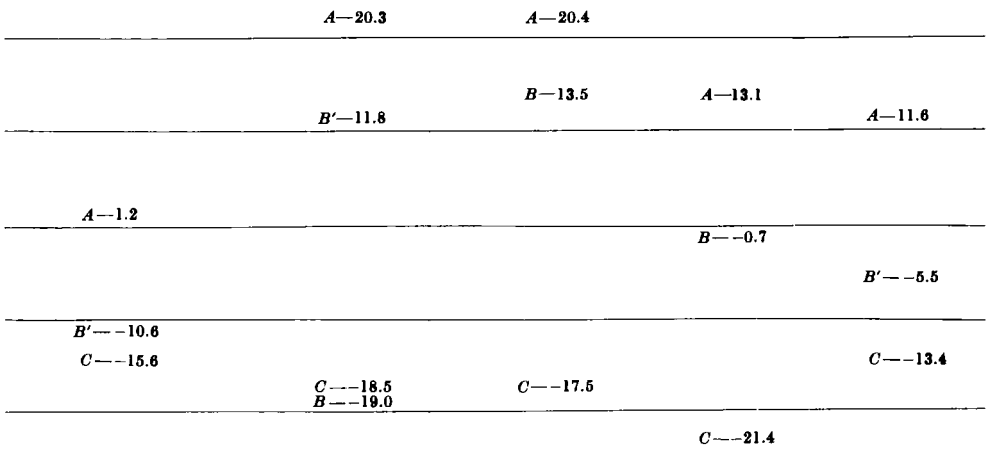
† Ref. (*150*) lists the following values: −17.0 ppm (*C*), −12.1 ppm (*B′*) and 1.8–4.1 ppm (*A*).

The phosphorus nuclei mentioned in the text and in this scheme are denoted as outlined on the following example:



Compilation with values of the refs. (*49*, *149*, *150*, *309*).

ABC_3 spectrum (*403*) is observed for $Cl_2(O)PN{=}P(N{=}PCl_3)_3$; $P_3N_3Cl_5(N{=}PCl_3)$ (XII) has an ABC_2 spectrum (in fact, an approximate ABX_2 spectrum) (*149*); $P_3N_3Cl_4(N{=}PCl_3)_2$ (XIV), an AB_2C_2 (approximate AB_2X_2) spectrum (*149*, *309*). A more detailed interpretation of the ^{31}P NMR spectra of these two compounds is given in detail [(*149*), see also (*140*)].



For $P_3N_3F_5N{=}PF_3$ only ^{19}F NMR data have been reported so far (*385*).

Scheme 4 gives the variation of the chemical shifts of the phosphorus nuclei of these cyclic phosphazatriene derivatives.

Only a few other physical data of compounds listed in Section V,A have been reported: P_2NOCl_5 (V) is diamagnetic, with a molecular susceptibility of -115.7×10^{-6} (*18*). The ^{35}Cl NQR spectrum of (V) shows two nonequivalent groups of chlorines (*215*), whereas no results were obtained on the thio analog. The molecular refractivity of (V) is $M_D^{38} = 46.02$ (*214*).

Mass spectra of $F_2(O)PN{=}PF_3$ (*324*) and $F_2(S)PN{=}PF_3$ (*324, 382*), as well as of $FCl(S)PN{=}PF_3$, $Cl_2(S)PN{=}PF_3$, $F_2(S)PN{=}PF_2Cl$, $FCl(S)PN{=}PF_2Cl$, $Cl_2(S)PN{=}PF_2Cl$ (*382*), and $P_3N_3F_5N{=}PF_3$ (*385*), are reported.

VI. Sulfonylphosphazotrihalides

A. Syntheses

Fittig (*151*), in 1858, and later Gerhardt (*170*) investigated the reaction of arylsulfonamides with PCl_5 and formulated the products erroneously as imidochlorides $-SO(=NH)Cl$. Wichelhaus (*517*) gave the formulation $ArSO_2NHPCl_2$ and so did later workers in the field (*514*).

The simplest species of a sulfonylphosphazotrichloride is $ClSO_2N{=}PCl_3$ (XV); erroneously reported earlier (*148*), it can be obtained by phosphorylation of amidosulfuric acid (*22, 221, 225a, 229, 508*).

$$HOSO_2NH_2 + 2PCl_5 \rightarrow \underset{(XV)}{ClSO_2N{=}PCl_3} + 3HCl + POCl_3 \quad (42)$$

The fluoro analog $FSO_2N{=}PCl_3$ is obtained from H_2NSO_2F and PCl_5 (*289*) and in ways listed in Section VI,B; $ClSO_2N{=}PF_3$ (*384*) and $FSO_2N{=}PF_3$ (*324*) result from $ClSO_2NH_2$ or FSO_2NH_2 with PCl_5, respectively. Similarly, fluorosulfonylamide and $PhPF_4$ yield $FSO_2N{=}PF_2Ph$ (*379a*).

Other sulfonylphosphazotrichlorides, $RSO_2N{=}PCl_3$, obtained analogously to Eq. (42) are known having the following R: $ClCH_2$ (*317*); Me, Et (*248*); CF_3 (*385c*); Pr (*317*); *i*-Pr, Bu (*248*); C_4F_9 (*378c*); *i*-Bu, Am, *i*-Am, *n*-C_6H_{13} (*317*); cyclohexyl, $PhCH_2$ (*248*); $PhCH_2CH_2$ (*317*); Ph (*221, 225b, 230, 354*); *o*-MeC_6H_4 (*221, 225b, 230*); *p*-MeC_6H_4 (*221, 225b, 230, 354*); *o*-, *m*-, *p*-$O_2NC_6H_4$ (*252*); *p*-FC_6H_4, *m*-$CF_3C_6H_4$ (*522*); *o*-ClC_6H_4 (*225b, 316*); *p*-ClC_6H_4 (*312, 354*); *p*-BrC_6H_4 (*225b, 316*); *p*-$MeOC_6H_4$ (*225b, 316, 354*); Me_2N, Et_2N (*272, 506*); Pr_2N, Bu_2N (*337, 506*);  (*310a, 337, 506*); $(CH_2)_5N$ (*310a*); *p*-$ClOC_6H_4$ (*72, 372, 375*); *p*-$Me_2NC_6H_4N{=}NC_6H_4$ (*255*); 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*275*); *p*-$(PhO)O_2SC_6H_4$ (*320*); PhNH (*510*); and other substituents (*71*).

Analogously $ArSO_2N{=}PPhCl_2$ compounds (*444*) are obtained with Ar = Ph, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$; interaction with Ph_2PCl_3 yields $RSO_2N{=}PPh_2Cl$ (R = Cl (*192a*), Ph, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*456*), *p*-MeC_6H_4 (*56, 456*)); with *p*-$MeC_6H_4PPhCl_3$ the compounds $ArSO_2N{=}PPh(C_6H_4Me\text{-}p)Cl$ (Ar = Ph, *o*-, *p*-MeC_6H_4, *m*-$O_2NC_6H_4$, 2-$C_{10}H_7$) are obtained [(*458*), see also (*446*)]. Ph_3PCl_2 gives $ArSO_2N{=}PPh_3$ (Ar = Ph, *o*-, *p*-MeC_6H_4, *o*-$O_2NC_6H_4$, 1-$C_{10}H_7$) (*457*), $(PhO)_3PCl_2$ yields $ArSO_2N{=}P(OPh)_3$ (*487*); $CF_3SO_2N{=}PPhCl_2$ has been described (*385b*).

Another way to sulfonylphosphazotrichlorides (and bromides) is a variation of the chloramine-T method; the use of carefully dried reagents and solvents is essential, otherwise the reaction may be explosive.

$$ArSO_2NNaCl + PX_3 \rightarrow ArSO_2N{=}PX_3 + NaCl \quad (43)$$

X = Cl; Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$ (*222, 226*), 2-$C_{10}H_7$ (*226*)
X = Br; Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$ (*222, 284*), 2-$C_{10}H_7$ (*284*)

The compound $FSO_2N{=}PBr_3$ has recently been prepared (*379*) according to Eq. (44), as well as some homologs $RSO_2N{=}PBr_3$ [R = Me, CF_3, *p*-ClC_6H_4 (*387a*)].

$$FSO_2NSO + PBr_5 \rightarrow FSO_2N{=}PBr_3 + SOBr_2 \quad (44)$$

Variation of the method used in Eq. (43) is described. Thus, $ROPCl_2$ (R = Ph, Me, Et) instead of PX_3 gives $PhSO_2N{=}P(OR)Cl_2$ (*279*); with

$(RO)(R'O)PCl$ (R = Ph; R′ = Ph, *o*-, *m*-, *p*-MeC_6H_4) and $PhSO_2N{\cdot}NaCl$ the products $PhSO_2N{=}P(OR)(OR')Cl$ are obtained (*279*). Phosphorous esters $P(OR)(OR')(OR'')$ give $ArSO_2N{=}P(OR)(OR')(OR'')$ (R = Ph; R′ = Ph, *o*-, *m*-, *p*-MeC_6H_4; R, R′, R″ = Ph, *o*-, *m*-, *p*-MeC_6H_4; Ar = Ph or 2-$C_{10}H_7$) (*67*, *278*). $ArSO_2N{\cdot}NaCl$ and $PhPCl_2$ give $ArSO_2N{=}PPhCl_2$ (Ar = Ph, *o*-, *p*-MeC_6H_4, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$) (*444*); with PR_3, sulfonylphosphinimines $ArSO_2N{=}PR_3$ result (*329*, *487*).

The sodium salts of *N*-chloroarylsulfonamides or the *N*,*N*-dichloroarylsulfonamides (dichloroamines)* and PCl_5 react with elimination of elemental chlorine and give nearly quantitative yields of arylsulfonylphosphazotrichlorides (*313*).

$$\begin{gathered} ArSO_2N{\cdot}NaCl + PCl_5 \rightarrow ArSO_2N{=}PCl_3 + NaCl + Cl_2 \\ ArSO_2NCl_2 + PCl_5 \rightarrow ArSO_2N{=}PCl_3 + 2Cl_2 \\ Ar = Ph,\ p\text{-}MeC_6H_4,\ p\text{-}ClC_6H_4,\ m\text{-}O_2NC_6H_4 \end{gathered} \qquad (45)$$

Compounds $ArSO_2N{=}PAr_2'Cl$ can be obtained from $ArSO_2NCl_2$ and $Ar_2'PCl$ (*446*); compounds like $ArSO_2N{=}P(Et)(Ph)CH_2Ph$ (Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$) from $ArSO_2N{\cdot}NaCl$ and $PhCH_2PPhEt$ (*459*). Further variation of this method is described (*202*, *412*, *447*, *478*).

The action of PCl_5 on arylsulfonyldichlorophosphoramidates, $ArSO_2NHPOCl_2$, also yields sulfonylphosphazotrichlorides (*320*).

$$\begin{gathered} ArSO_2NHPOCl_2 + PCl_5 \rightarrow HCl + ArSO_2N{=}PCl_3 + POCl_3 \\ Ar = o\text{-},\ m\text{-},\ p\text{-}O_2NC_6H_4,\ p\text{-}PhOSO_2C_6H_4 \end{gathered} \qquad (46)$$

Analogous derivatives may be synthesized (*320*).

$$ArSO_2NHPO(OPh)_2 + PCl_5 \rightarrow POCl_3 + ArSO_2N{=}P(OPh)_2Cl + HCl \qquad (47)$$

The reaction outlined in Eq. (46) is strongly dependent on the nature of Ar. Only if electronegative groups are present in Ar does this reaction occur; thus, no reaction occurs with Ar = Ph, MeC_6H_4, or ClC_6H_4 (*320*), but the tautomers of the formula $ArSO(=NPOCl_2)Cl$ are obtained (*310a*, *314*).

$$\begin{gathered} ArSO_2NHPOCl_2 + PCl_5 \rightarrow ArSO(=NPOCl_2)Cl + POCl_3 + HCl \\ Ar = Ph,\ o\text{-},\ p\text{-}MeC_6H_4,\ o\text{-},\ p\text{-}ClC_6H_4,\ p\text{-}BrC_6H_4,\ p\text{-}FC_6H_4,\ p\text{-}MeOC_6H_4,\ m\text{-}CF_3C_6H_4 \end{gathered} \qquad (48)$$

The same results are obtained with aliphatic substituents (*317*).

The compound $PhCH_2SO_2NHPOCl_2$ and PCl_5 (1 : 2) react in a different way (*315*).

$$PhCH_2SO_2NHPOCl_2 + 2PCl_5 \rightarrow PhCH_2Cl + 2POCl_3 + HCl + Cl_2S{=}NPOCl_2 \qquad (49)$$

* $ArSO_2NCl_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$O_2NC_6H_4$) and elemental selenium give $ArSO_2N{=}SeCl_2$ (*60*).

$PhSO_2N{=}SCl_2$ and PCl_3 give $PhSO_2N{=}PCl_3$ in quantitative yield (*315*).

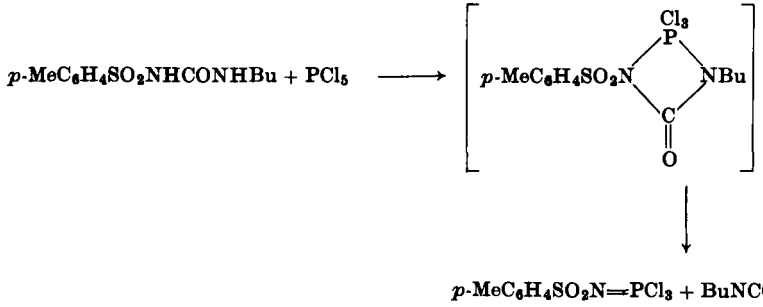
$$3PCl_3 + PhSO_2N{=}SCl_2 \xrightarrow{100°} PSCl_3 + PCl_5 + PhSO_2N{=}PCl_3 \qquad (50)$$

Iminobis(sulfonaryls) and PCl_5 react in two ways, the product depending on the electronegativity of Ar (*311*).

$$HN(SO_2Ar)_2 + PCl_5 \begin{cases} \nearrow ArSO_2Cl + HCl + ArSO_2N{=}PCl_3 \\ \searrow POCl_3 + HCl + ArSO(=NSO_2Ar)Cl \end{cases} \qquad (51)$$

Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, *p*-$O_2NC_6H_4$

The compound *p*-$MeC_6H_4SO_2N{=}PCl_3$ results also from the decomposition of a 1,3,2-diazaphosphetidinone (see also Sections VIII,B,1 and IX), formed by interaction of 1-*p*-toluenesulfonyl-3-butylurea and PCl_5 (*498*).



In contrast to hexachlorodialkyldiazadiphosphetidines, *p*-MeC_6H_4-$SO_2N{=}PCl_3$ gives no further reaction with isocyanates (see also Section VIII,A,2).

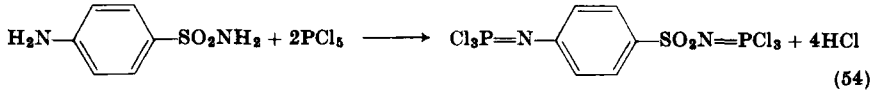
Only few compounds with two $-SO_2N{=}PCl_3$ groups in the molecule are known. Sulfamide reacts with 2 moles of PCl_5 forming bis(trichlorophosphazo)sulfone $Cl_3P{=}NSO_2N{=}PCl_3$ (*232*, *507*). Extension of this reaction to disubstituted benzenes has been described (*256*).

$$A(SO_2NH_2)_2 + 2PCl_5 \rightarrow A(SO_2N{=}PCl_3)_2 + 4HCl \qquad (53)$$
$$A = m\text{-}, p\text{-}C_6H_4 \ (256)$$

Correspondingly, $(PhCl_2P{=}N)_2SO_2$ has been prepared from sulfamide and $PhPCl_4$ (*50a*).

The compounds $(Cl_3P{=}NSO_2)_2NMe$ and $(Cl_3P{=}NSO_2NMe)_2SO_2$ have also been prepared (*343*).

Compounds with one $-SO_2N{=}PCl_3$ and one $-N{=}PCl_3$ group such as compound (XVI) result from *p*-sulfonamidoaniline and PCl_5 (*354*, *458*, *488*). Similarly, $Cl_3P{=}N(CH_2)_2SO_2N{=}PCl_3$ (*542*) is known. These compounds can also be considered as aryl- or alkylphosphazotrichlorides (Sections VIII, A and B).



(54)

(XVI)

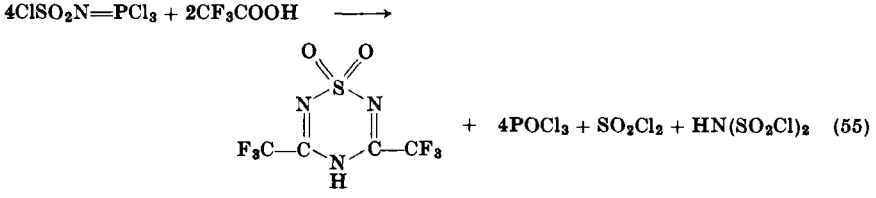
The dimeric ortho and meta isomers of (XVI) are also described (*549*).

The compound *p*-$Cl_3P{=}NSO_2C_6H_4CON{=}PCl_3$ (*367*) represents a type with one $-SO_2N{=}PCl_3$ group and one carbonylphosphazo group (cf. also Section VII, A).

Finally, 4,5-bis(trichlorophosphazosulfone)-1,8-naphthalene has been claimed without any preparative details being given (*71*).

B. Reactions

Thermolysis (118°–120°/2.5–5 Torr) of $ClSO_2N{=}PCl_3$ (XV) gives mainly $POCl_3$ and a mixture of α- and β-sulfanuric chlorides (*228*, *508*), as well as minor amounts of $NPCl_2(NSOCl)_2$ (*70a*, *180a*). Hydrolysis with water leads to phosphoric and amidosulfonic acids; with formic acid an undefined substance is obtained (*192*). Ammonia or NH_4Cl gives $(H_2N)_3P{=}NSO_2NH_2$ (*293*), and amines yield $(RNH)_3P{=}NSO_2NHR$; whereas with diamines such as diethylenediamine cross-linked polymers are formed; silylation with heptamethyldisilazane affords $Me_3SiN(Me)$-$PCl_2{=}NSO_2Cl$ (*50b*). Compound (XV) and chlorosulfonic acid yield $HN(SO_2Cl)_2$, also obtained from chlorosulfonic acid and urea (*6*, *22*). Trifluoracetic acid and $ClSO_2N{=}PCl_3$ react in a rather complex manner (*377*):



(55)

Reaction of (XV) with SO_2 eliminates $POCl_3$ and minor quantities of $OSNSO_2Cl$ (*388*). Fission of the P=N bond occurs on the reaction of $ClSO_2N{=}PCl_3$ with anhydrous hydrogen fluoride in presence of BF_3 (*200*),

whereas fluorination of (XV) with AsF_3 gives $FSO_2N{=}PCl_3$ (*388*), also obtained in other ways (*289*). The halogen atoms may be successively

$$ClSO_2N{=}PCl_3 + xHF \xrightarrow{BF_3} H_2NSO_2F + P(Cl,F)_5 + nHCl \quad (n = 1\text{–}4) \qquad (56)$$

replaced in the reaction of $ClSO_2N{=}PX_3$ or $FSO_2N{=}PX_3$ (X = Cl, F) with Me_3SiNMe_2 or Me_3SiNCS, respectively (*383c*).

Fluorosulfonylphosphazotrichloride, $FSO_2N{=}PCl_3$, which on hydrolysis gives FSO_2NH_2 (*388*), reacts with fluorosulfonic acid (*388*) and difluorophosphoric acid (*176*) to form $(FSO_2)_2NH$ and $POCl_3$; with CF_3COOH (*381c*) and C_2F_5COOH (*381b*) compounds FSO_2NHCOR_f are obtained, whereas with CF_3SO_3H the compound $FSO_2NHPOCl_2$ is formed (*381a*). In the reaction between $ClSO_2N{=}PF_3$ and PF_3Cl_2 phosphorus(V) fluoride is eliminated and $ClSO_2N{=}PF_2Cl$ formed (*384*); $FSO_2N{=}PF_3$ reacts similarly with PF_3Cl_2 to form $FSO_2N{=}PF_2Cl$ (*385*). Formic acid hydrolyzes $CF_3SO_2N{=}PCl_3$ to $CF_3SO_2NHPOCl_2$, whereas XSO_3H (X = F, Cl) yields $CF_3SO_2NHSO_2X$ (*381a*).

The reaction of $ArSO_2N{=}PCl_3$ [Ar = Ph (*222*, *225c*, *236*); *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$ (*222*, *236*); *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-ClC_6H_4 (*354*); *o*-, *m*-, *p*-$O_2NC_6H_4$ (*252*); PhNH (*510*)] with HCOOH gives all possible intermediates, i.e., $ArSO_2NHPOCl_2$, $ArSO_2NHP(O)(OH)Cl$, $ArSO_2NHP(O)(OH)_2$, and $ArSO_2NH_2$ (*222*, *236*). Hydrolysis with water [early work (*170*, *517*)], benzoic acid, or other carboxylic acids leads only to the isolation of the first step (*222*, *236*). Complex mixtures are obtained with acetone, ether, or esters (*222*). No definite product could be isolated from $PhSO_2N{=}PCl_3$ and $ClSO_3H$; with DMSO, $PhSO_2NHPOCl_2$ is formed (*192*). In contrast, this latter reaction ($ArSO_2N{=}PCl_3$ + DMSO) has been described as giving sulfylimines in 44% yield (*353*).

$$ArSO_2N{=}PCl_3 + Me_2SO \xrightarrow{\text{pyridine}} ArN{=}SMe_2 + SO_2 + POCl_3 \qquad (57)$$

Alkylsulfonylphosphazotrichlorides, $RSO_2N{=}PCl_3$ (R = Me, Et, *i*-Pr, Bu, $PhCH_2$, *n*-C_6H_{13}), and HCOOH yield the dichlorides (*249*). $R_2NSO_2N{=}PCl_3$ (R = Me, Et) and formic acid give all three hydrolysis steps (*272*), whereas their reaction with CF_3COOH proceeds with elimination of CF_3COCl and formation of $R_2NSO_2NHPOCl_2$ (*378b*).

The interaction of $ArSO_2N{=}PCl_3$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *m*-$O_2NC_6H_4$) with Cl_2O is interesting owing to the formation of $ArSO(OCl){=}NPOCl_2$ (*290b*).

$$ArSO_2N{=}PCl_3 + Cl_2O \rightarrow Cl_2 + ArSO(OCl){=}NPOCl_2 \qquad (58)$$

Several sulfonylphosphazotrichlorides, $ArSO_2N{=}PCl_3$ (Ar = Ph, p-ClC_6H_4, p-MeC_6H_4, p-$O_2NC_6H_4$) form stable adducts with DMF; these decompose upon heating (*297d*).

Ammonolysis of arylsulfonylphosphazotrichlorides gives $ArSO_2N{=}P(NH_2)_3$ (*222*, *237*); aqueous ammonia yields $ArSO_2NHPO(NH_2)OH$ (*237*). Reaction with aniline or p-toluidine gives first the monochlorides $ArSO_2N{=}P(NHAr')_2Cl$ (*238*, *426*), the triamides being obtained only with excess of amine (*238*). Alkylsulfonylphosphazotrichlorides (R = Et, Bu) give analogous results (*251*).

Hydrolysis of the dianilides gives $ArSO_2NHPO(NHPh)_2$ which cannot be obtained by the simple action of $ArSO_2NHPOCl_2$ and aniline; in the latter case saltlike compounds result (*312*).

$$ArSO_2NHPOCl_2 + PhNH_2 \begin{cases} \not\rightarrow\ ArSO_2NHP(O)(NHPh)_2 \\ \rightarrow\ [PhSO_2NPOCl_2]^-\,[PhNH_3]^+ \end{cases} \qquad (59)$$

Aminolysis of $ArSO_2N{=}PCl_3$ with secondary amines such as Me_2NH (*254*), ethylenimine (*296*, *354*, *489*), or methylaziridine (*373*) gives the corresponding triamides.

$$ArSO_2N{=}PCl_3 + 3HNC_2H_4 \xrightarrow{3Et_3N} ArSO_2N{=}P(NC_2H_4)_3 + 3Et_3NHCl \qquad (60)$$

With ethylenimine: Ar = Ph, p-MeC_6H_4, p-ClC_6H_4 (*296*, *354*, *489*); p-$O_2NC_6H_4$ (*296*); p-$MeOC_6H_4$ (*354*, *489*)
With dimethylamine: Ar = o-, m-, p-$O_2NC_6H_4$ (*254*)
With methylaziridine: Ar = Ph, Me, MeC_6H_4, 3,4-$(O_2N)(PhNH)C_6H_3$ (*373*)

The reaction with diethylamine stops at the diamides, o-, m-, p-$O_2NC_6H_4SO_2N{=}P(NEt_2)_2Cl$ (*254*).

The analogous ammonolysis of $ArSO_2N{=}PPhCl_2$ gives $ArSO_2N{=}PPh(NH_2)_2$ (Ar = Ph, o-, p-MeC_6H_4, p-ClC_6H_4, 1-$C_{10}H_7$) (*453*), the reaction with aniline yields $ArSO_2N{=}PPh(NHPh)_2$ (Ar = Ph, o-, m-, p-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$) (*452*). The compound $PhNHSO_2N{=}PCl_3$ reacts with PCl_5 at 80° to form p-$ClC_6H_4NHSO_2N{=}PCl_3$, as well as $ClSO_2N{=}PCl_3$ (XV) and p-$ClC_6H_4N{=}PCl_3$ (*510*).

Compounds of the type $XSO_2NRPOCl_2$ (X = F, Cl) are formed by the alcoholysis (R = Me, Et, Pr, Bu) of $XSO_2N{=}PCl_3$ (*383b*). The compounds $MeSO_2N{=}PCl_3$ and $ClSO_2N{=}PF_3$ react with alcohols to give the monoesters which rearrange with catalytic amounts of ether to $MeSO_2N(Me)POCl_2$ and $ClSO_2N(Et)POF_2$, respectively (*384a*). Reaction

of $ArSO_2N{=}PCl_3$ with anhydrous* alcohols, ROH (R = Me, Et, Bu), yields $ArSO_2N{=}P(OR)_3$ (Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$) as relatively stable substances,† which give on hydrolysis the diesters $ArSO_2NHPO(OR)_2$ (*275*), also obtainable from $ArSO_2NHPOCl_2$ and sodium alcoholates (*276*). The interaction of *o*-, *m*-, *p*-$O_2NC_6H_4SO_2N{=}PCl_3$ with various alcohols (R = Me, Ph, *p*-ClC_6H_4, *o*-, *p*-$O_2NC_6H_4$) is described in detail (*253*). Isolation of the monoesters (Ar = Ph, *o*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$) is only possible at low temperatures (2°–5°) (*280*). Some esters may also be obtained by the chloramine-T method (*278*). The substances $ArSO_2N{=}PPhCl_2$ (Ar = Ph, *o*-, *p*-MeC_6H_4, *o*-, *m*-$O_2NC_6H_4$, *p*-ClC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$) (*454*) and $ArSO_2N{=}PPh_2Cl$ (Ar = Ph, *o*-, *p*-MeC_6H_4, *p*-$O_2NC_6H_4$, 2-$C_{10}H_7$) (*455*) show analogous behavior with RONa (R = Me, Et, Ph). Bis-*t*-butyl peroxides of $ArSO_2N{=}PPhCl_2$ (*524b*) as well as the compounds $ArSO_2N{=}PPh_2$(OO*tert.* Bu) (*524c*) have been described recently.

Unsaturated esters such as $ArSO_2N{=}P(OCH_2CH{=}CH_2)_3$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$) (*460*) and $ArSO_2N{=}PPh(OCH_2CH{=}CH_2)_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$) (*461*) are described; they may also be prepared from $ArSO_2N{\cdot}NaCl$ and phosphorous triallyl ester (*460*).

Esterification of $ArSO_2N{=}PCl_3$ (Ar = Ph, *o*-MeC_6H_4, *o*-, *p*-ClC_6H_4, *o*-, *p*-$O_2NC_6H_4$, *p*-FC_6H_4, *p*-$CF_3C_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$) with aromatic alcohols (Ar′ = Ph, *o*-, *m*-, *p*-MeC_6H_4, *p*-FC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$) yields the triesters $ArSO_2N{=}P(OAr')_3$ (*261*, *277*, *320*, *522*), which on alkaline hydrolysis give $ArSO_2NHPO(OAr')_2$. The above triesters can also be obtained from the corresponding sulfamide and $(PhO)_3PCl_2$ or pentaphenoxyphosphorus(V) (*534*).

$$PhSO_2NH_2 + Cl_2P(OPh)_3 \rightarrow PhSO_2N{=}P(OPh)_3 + 2HCl \quad (61)$$

$$PhSO_2NH_2 + P(OPh)_5 \rightarrow PhSO_2N{=}P(OPh)_3 + 2PhOH \quad (62)$$

The aliphatic sulfonylphosphazotrichlorides, $R_2NSO_2N{=}PCl_3$ (R = Me, Et), and Ar′ONa (Ar′ = Ph, *o*-, *p*-ClC_6H_4, *o*-, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$) (*273*), as well as $RSO_2N{=}PCl_3$ (R = Me, Et, *i*-Pr, Bu, $PhCH_2$; Ar = Ph, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$) (*250*) give the triesters.

Diesters $ArSO_2N{=}PCl(OPh)_2$ may not be obtained in this way. They

* $ArSO_2N{=}PCl_3$ and alcohols in the presence of NaOH give water-soluble compounds $ArSO_2NNaPO(OR)_2$ (Ar = Ph, *p*-MeC_6H_4; R = Bu, *n*-C_6H_{13} to *n*-$C_{10}H_{21}$) (*468*) (see also Section X).

† The triesters $ArSO_2N{=}P(OR)_3$ isomerize on heating at 200°–210° to give $ArSO_2NRPO(OR)_2$ (*462*), in contrast to the results of other authors (*178*) (see also Section VI, C).

are synthesized (*320*) following Eq. (63) or from $PhSO_2N{\cdot}NaCl$ and $(PhO)_2PCl$ (*279*) (Section VI,A).

$$ArSO_2NHPO(OPh)_2 + PCl_5 \rightarrow ArSO_2N{=}PCl(OPh)_2 + POCl_3 + HCl \quad (63)$$

Arylation of sulfonylphosphazotrichlorides with Grignard reagents leads to phosphinimines.

$$ArSO_2N{=}PCl_3 + 3PhMgBr \rightarrow 3MgBrCl + ArSO_2N{=}PPh_3 \quad (64)$$

Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*271*)

$$R_2NSO_2N{=}PCl_3 + 3Ar'MgBr \rightarrow 3MgClBr + R_2NSO_2N{=}PAr'_3 \quad (65)$$

R = Me, Et, Pr, Bu, C_4H_8O

Ar′ = Ph, *m*-, *p*-MeC_6H_4 (*337*, *505*)

The compound *p*-$MeC_6H_4SO_2N{=}PPh_3$ was obtained earlier in another way (*329*); $PhSO_2N{=}PR_3$ (R = Me, Et, Bu, $PhCH_2$, Ph) compounds are also prepared (*318*) by the following procedures; see also (*139*):

$$PhSO_2NSO + R_3PO \rightarrow PhSO_2N{=}PR_3 + SO_2 \quad (66)$$

$$(PhSO_2N)_2S + 2R_3PO \rightarrow 2PhSO_2N{=}PR_3 + SO_2 \quad (67)$$

Analogous compounds $RSO_2N{=}PY_3$ (Y = R, Ar, OAr) were isolated from the reactions of RSO_2NSO with PY_3, POY_3 or PSY_3 (*224*, *319*, *414*).

$$p\text{-}MeC_6H_4SO_2NSO + PhN{=}PPh_3 \rightarrow p\text{-}MeC_6H_4SO_2N{=}PPh_3 + PhNSO \quad (68)$$

$$RSO_2NSO + POY_3 \rightarrow SO_2 + RSO_2N{=}PY_3 \quad (69)$$

$$RSO_2NSO + PSY_3 \rightarrow RSO_2N{=}PY_3 \quad (70)$$

$$RSO_2NSO + 3PY_3 \rightarrow SPY_3 + OPY_3 + RSO_2N{=}PY_3 \quad (71)$$

$$RSO_2N{=}S{=}NO_2SR + 2POY_3 \rightarrow SO_2 + 2RSO_2N{=}PY_3 \quad (72)$$

Fluorination (KF) of $ArSO_2N{=}PCl_3$ in aqueous solution gives the salts $K^+(ArSO_2NPOCl_2)^-$ and $K^+(ArSO_2NPOF_2)^-$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-FC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$), also obtained from $ArSO_2NHPOCl_2$ and $KF{\cdot}2H_2O$ (*258*). The salts $K_2^+(ArSO_2NPOF_2)^{2-}$ have also been described (*258*).

Formation of nitriles occurs on the attempted distillation of *p*-$ClCOC_6H_4SO_2N{=}PCl_3$ (*221*, *231*, *372*, *375*), sometimes with the use of catalysts (*71*, *72*).

$$\begin{array}{ccc} 2p\text{-}ClCOC_6H_4SO_2N{=}PCl_3 & & 2POCl_3 + 2NCC_6H_4SO_2Cl \\ & \searrow^{\Delta} \quad \nearrow & \\ & ClCOC_6H_4SO_2Cl + Cl_3P{=}NCOC_6H_4SO_2N{=}PCl_3 & \end{array} \quad (73)$$

Extension of this method, i.e., the reaction of sulfonylphosphazotrichlorides with acyl chlorides, is described in detail [(*221*, *231*), see also (*222*)].

$$ArSO_2N{=}PCl_3 + Ar'COCl \rightarrow ArSO_2Cl + Ar'CON{=}PCl_3 \downarrow \quad Ar'CN + POCl_3 \qquad (74)$$

Ar = Ph, *o*-, *p*-MeC_6H_4
Ar′ = Ph, *o*-, *m*-, *p*-MeC_6H_4, *p*-ClC_6H_4, *o*-, *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$

The production of the nitriles is thought to proceed through the intermediate formation of carbonylphosphazotrichlorides (cf. Section VII,B).

Dinitriles are formed in a similar way using dicarbonyl dichlorides.

$$2PhSO_2N{=}PCl_3 + A(COCl)_2 \longrightarrow 2POCl_3 + 2PhSO_2Cl + A(CN)_2 \qquad (75)$$

A = *o*-C_6H_4 (*231*, *235*); *m*-C_6H_4, $(CH_2CH_2)_2$, $CH_2\langle^{CH_2-}_{CH_2-}$, $-CH_2CH_2-$, $-CH_2-$; trimesitylchloride (*235*)

The hydrolytic behavior (HCOOH) of some sulfonylphosphazotribromides $ArSO_2N{=}PBr_3$ (Ar = Ph, *o*-, *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$) is described; all possible intermediates can be isolated (*285*).

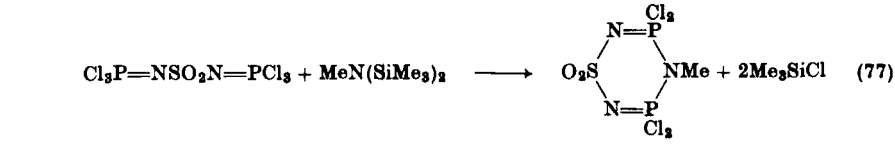
$$ArSO_2N{=}PBr_3 \xrightarrow[-HBr,\,-CO]{HCOOH} ArSO_2NHPOBr_2 \xrightarrow[-HBr,\,-CO]{HCOOH}$$

$$ArSO_2NHPO(OH)Br \xrightarrow[-HBr,\,-CO]{HCOOH} ArSO_2NHPO(OH)_2 \xrightarrow[-CO]{HCOOH} H_3PO_4 + ArSO_2NH_2 \qquad (76)$$

Sulfonylphosphazotribromides $RSO_2N{=}PBr_3$ (R = Me, CF_3, Ph, *p*-MeC_6H_4) react readily with Me_3SiNMe_2 or $(Me_3Si)_2NH$ to give $RSO_2N{=}PBr_2NMe_2$ or $RSO_2N{=}PBr_2NH(SiMe_3)_2$, respectively (*378a*).

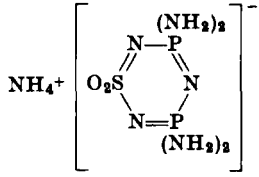
The compound $SO_2(N{=}PCl_3)_2$ reacts violently with water, amines, NH_3, ROH, PhOH, and organometallics (*232*), but no details are given. Excess water gives HCl, phosphoric acid, and sulfamide (*192*). Molar quantities of HCOOH yields $Cl_3P{=}NSO_2NHPOCl_2$; excess of formic acid results in the formation of minor quantities of $Cl_2OPNHSO_2NHPOCl_2$ and large amounts of uncharacterized compounds (*192*). ArONa gives bis(triesters) $SO_2[N{=}P(OAr)_3]_2$ (Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$) (*267*); the bis(triphenylester) can also be prepared on another way (*534*). Interaction of $SO_2(N{=}PCl_3)_2$ with ArMgBr [Ar = Ph (*337*, *505*), *m*-, *p*-MeC_6H_4 (*337*)] gives $SO_2(N{=}PAr_3)_2$. With *o*-tolylmagnesium bromide no reaction occurs, probably owing to steric factors.

A ring-closure reaction [(*17*), see also (*286a*)] between heptamethyldisilazane and $SO_2(N{=}PCl_3)_2$ proceeds according to Eq. (77). With



(77)

ammonia instead of the silazane an ionic compound



is formed, whereas amines such as dimethylamine, aniline (*17*), or ethylenimine (*367*) only give the hexamides. With silylamines Me_3SiNR_2 (R = Me, Et) (*286a*) a partial replacement of the chlorine atoms occurs.

Arylation (PhMgBr) of $(Cl_3P{=}NSO_2)_2NMe$ leads to $(Ph_3P{=}NSO_2)_2$-NMe, and the bis(triesters) of $(Cl_3P{=}NSO_2)_2NMe$ or $(Cl_3P{=}NSO_2NMe)_2$-SO_2 are obtained with PhONa (*343*).

The acidolysis (HCOOH) of *m*- and *p*-$C_6H_4(SO_2N{=}PCl_3)_2$ results in *m*- and *p*-$C_6H_4(SO_2NHPOCl_2)_2$; the reaction with RONa (R = Me, Et, Ph) gives *m*- or *p*-$C_6H_4[SO_2NHPO(OR)_2]_2$ (*256*). Analogous esters $(CH_2)_n[SO_2N{=}P(XR)_3]_2$ ($n = 3$, 4; R = Et, Ph; X = O, S) may be obtained by a Staudinger reaction (*178*).

The interaction of 1,4-$Cl_3P{=}NC_6H_4SO_2N{=}PCl_3$ (XVI) (*354*, *488*) and *m*- and *p*-$C_6H_4(SO_2N{=}PCl_3)_2$ (*367*) with ethylenimine giving the hexamides is described. Both $-N{=}PCl_3$ groups are hydrolyzed in the reaction of $Cl_3P{=}NC_6H_4SO_2N{=}PCl_3$ (*o*-, *m*-, *p*-) with HCOOH giving $Cl_2P(O)$-$NHC_6H_4SO_2NHP(O)Cl_2$ and subsequently $(OH)_2P(O)NHC_6H_4SO_2$-$NHP(O)(OH)_2$ (*549*), in sharp contrast to the difficult hydrolysis of $SO_2(N{=}PCl_3)_2$.

C. Spectroscopic Investigations

In general, only a few spectroscopic data of sulfonylphosphazotrihalides are available.

Goerdeler and Ullmann (*178*) assign the P=N vibration at 1260–1290 cm^{-1} in compounds of the type $RSO_2N{=}P(OR')_3$; other authors (*337*,

343) give 1255–1300 cm^{-1}, mentioning that the asymmetric SO_2 stretching vibration is also involved and that coupling cannot be ruled out. Kirsanov and co-workers (*462*) point out that distillation (in the course of isolation) of the above esters leads to a rearrangement to $RSO_2NR'P(O)(OR')_2$, and that therefore the assignments cannot be sustained. A detailed investigation concerning the P=N vibration in such compounds is available (*520*).

The $\nu_{P=N}$ of p-$MeC_6H_4SO_2N{=}PCl_3$ is given at 1199 cm^{-1} (*521*). A band at 1357 cm^{-1} is assigned (*324*) to the P=N vibration in $FSO_2N{=}PF_3$, and at 1190 cm^{-1} a band is tentatively assigned for $FSO_2N{=}PBr_3$ (*379*). Infrared tables for $ClSO_2N{=}PF_3$ and $ClSO_2N{=}PF_2Cl$ are given (*384*).

Only a few chemical shifts (^{31}P) from sulfonylphosphazotrichlorides have been measured so far: $ClSO_2N{=}PCl_3$ ($\delta_P = -20.5 \pm 0.5$ ppm) (*510*), $PhSO_2N{=}PCl_3$ ($\delta_P = -4$ ppm) (*192*), $PhNHSO_2N{=}PCl_3$ ($\delta_P = -3.5 \pm 0.3$ ppm) and p-$ClC_6H_4NHSO_2N{=}PCl_3$ ($\delta_P = -4.2 \pm 0.3$ ppm) (*510*), showing tetracoordinate phosphorus and thus proving their structure. It is interesting to note that the compounds $RSO_2N{=}PBr_3$ show ^{31}P NMR chemical shifts as follows: R = Me ($\delta_P = 105.1$ ppm), R = CF_3 ($\delta_P = 85.1$ ppm), R = Ph ($\delta_P = 101.4$ ppm), R = p-MeC_6H_4 ($\delta_P = 108.9$ ppm), and R = p-ClC_6H_4 ($\delta_P = 99.5$ ppm), thus showing the great influence of R (*387a*).

Fluorine-19 NMR measurements have been made on $FSO_2N{=}PF_3$ ($\delta_F = -59.6$ ppm, $J_{PF} = 4$ Hz) (*388*), $ClSO_2N{=}PF_3$ ($\delta_F = 84.6$ ppm, $J_{PF} = 1078$ Hz), $ClSO_2N{=}PF_2Cl$ ($\delta_F = 50.4$ ppm, $J_{PF} = 1120$ Hz) (*384*), and $FSO_2N{=}PBr_3$ ($\delta_F = -61.4$ ppm, $J_{PF} = 2$ Hz) (*379*).

Mass spectral data of $ClSO_2N{=}PF_3$, $ClSO_2N{=}PF_2Cl$ (*384*), and $FSO_2N{=}PF_3$ (*385*) are mentioned in the literature.

A ^{35}Cl NQR study of $ClSO_2N{=}PCl_3$ (XV) has been reported recently (*191b*).

VII. Carbonylphosphazotrichlorides

A. Syntheses

As for the reaction of sulfamides with phosphorus(V) chloride, the interaction of amides of carboxylic acids with PCl_5 attracted attention more than 110 years ago (*170*). Wallach (*511–513*) described reaction products $RCCl_2NH_2$ (imidochlorides) resulting from various oxamides and PCl_5; later workers (*61, 70, 165, 321, 360, 485, 491*), including quite recent ones (*361*), still assigned the formula $RCClNPOCl_2$ to the reaction products.

Kirsanov, in 1954, showed in the first of a series of outstanding papers that in this reaction carbonylphosphazotrichlorides $RCON{=}PCl_3$, and not the isomers $RCCl{=}NPOCl_2$, are formed (*233*).

$$RCONH_2 + PCl_5 \rightarrow RCON{=}PCl_3 + 2HCl \qquad (78)$$

Compounds following Eq. (78) are known with R = Ph (*223*, *260*); *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-, *p*-ClC_6H_4, *p*-BrC_6H_4, 2,4-$(O_2N)_2C_6H_3$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl_2C_6H_3$ (*260*); 2,4-$Cl(O_2N)C_6H_3$ (*244*, *260*); *o*-, *m*-, *p*-FC_6H_4 (*136*); Ph_2CCl, Ph_3C (*243*); CCl_3 (*240*); CF_3 (*210*, *370*); *o*-BrC_6H_4 (*246*); *o*-MeC_6H_4 (*244*); *p*-$MeOC_6H_4$ (*133*); PhO (*265*); EtO (*223*, *233*, *264*); MeO, PrO, *i*-PrO, BuO, *i*-BuO (*264*); 2,3,6-$Cl_3C_6H_2$ (*484*); 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*244*); CHF_2CF_2 (*147*); $MeCHCl$ (*387h*); $ClCH_2CCl_2$, $ClCH_2CHCl$ (*117*); $MeCCl_2$ (*119*); CBr_3 (*295*); $NCCH_2$ (*450*); Ph_2N (*274*); $Me_2C(CN)$, $Et_2C(CN)$, $Pr_2C(CN)$, $Bu_2C(CN)$, $Am_2C(CN)$, $(Me_2CHCH_2CH_2)_2C(CN)$ (*427*); $(EtO)_2P(O)CCl_2$ (*59*); see also (*225*, *234*). These carbonylphosphazotrichlorides are also obtained from acylamides and PCl_3 plus Cl_2 (*135*).

Not mentioned above are earlier papers (*61*, *170*, *485*, *512*, *513*) which assign to these products the formulas of imidochlorides $RCCl{=}NPOCl_2$.

Analogous compounds, $RCON{=}PR'Cl_2$ (R = $CHCl_2$, CCl_3, CF_3; R' = CH_2Cl, $CHCl_2$), result from $RCONH_2$ and $R'PCl_4$ (*471b*). The use of $PhPCl_4$ gives $RCON{=}PPhCl_2$ (R = CCl_3) (*466*), with CCl_3PCl_4 is obtained $RCON{=}P(CCl_3)Cl_2$ (R = $CHCl_2$, CCl_3, CF_3, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$) (*469*). $MePCl_4$ yields $RCON{=}PMeCl_2$ (R = CCl_3, CF_3, *p*-$O_2NC_6H_4$, Ph) (*471*). The interaction of carboxylic amides and Ph_2PCl_3 in a fairly smooth reaction gives $RCON{=}PPh_2Cl$ with elimination of the HCl formed. Ph_3PCl_2 gives only phosphonium salts, except if electronegative substituents (R = CCl_3) are present [(*466*), see also (*137*)]. Interaction of $R_2C(CN)CONH_2$ and $PhPCl_4$ yield $R_2C(CN)CON{=}PPhCl_2$ (R = Me, Et, Pr, Bu, Am) (*427a*).

The similar reaction of $ArCSNH_2$ and PCl_5 does not give $ArCSN{=}PCl_3$, but, as stated in the example with $PhCSNH_2$, a rather complex reaction producing HCl, $PSCl_3$, PCl_3, PhCN, and 3,5-diphenyl-1,2,4-thiadiazole and other products (*282*).

The distinction between $RCON{=}PCl_3$ and $RCCl{=}NPOCl_2$ was effected by the characterization of the reaction products and by synthesis of ^{18}O-labeled $PhC^{18}ON{=}PCl_3$ (*298*) and $Et^{18}OC^{18}ON{=}PCl_3$ (*3*) (see Section VII,B).

Excess PCl_5 partially chlorinates 2-cyanacetamide to give $NCCCl_2CON{=}PCl_3$ (*450*), not attacking the CO group (cf. in the following) nor the nitrile group (see Section VIII,B).

Oxalic ester amides $ROOCCONH_2$ react with PCl_5 in an initial step to form $ROCCl_2CONH_2$* and then with excess PCl_5 to form $ROCCl_2CON{=}PCl_3$.

$$ROOCCONH_2 + PCl_5 \rightarrow POCl_3 + ROCCl_2CONH_2 \quad (79)$$

$$ROCCl_2CONH_2 + PCl_5 \rightarrow 2HCl + ROCCl_2CON{=}PCl_3 \quad (80)$$

R = Et (*223*, *268*); Me, Bu, *i*-Bu, C_6H_{11} (*268*); Ph (*270*); *p*-ClC_6H_4, *o*-, *m*-, *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*269*, *270*); see also (*225*)

The reaction of $PhPCl_4$ and alkoxyureas under normal condition follows Eq. (81) up to 80% yield [(*448*), see also (*137*)]. If the reaction is carried out *in vacuo* reasonable yields of $ROCON{=}PPhCl_2$ are obtained

$$ROCONH_2 + PhPCl_4 \rightarrow \underset{R = Me, Et}{HCl + RCl + PhPOCl_2 + \tfrac{1}{n}(HNCO)_n} \quad (81)$$

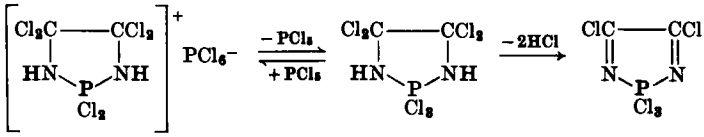
(*474*). These latter compounds may also be obtained from *N*,*N*-dichlorocarbamates and $PhPCl_4$ (*449*). The isocyanate $CCl_3PO(NCO)Cl$ is obtained without formation of the phosphazo compound by reaction of

$$ROCONCl_2 + PhPCl_4 \rightarrow 2Cl_2 + ROCON{=}PPhCl_2 \quad (82)$$

$MeOCONH_2$ with CCl_3PCl_4 (*472*). Similarly $MeOP(O)(Cl)NCO$ is obtained using $MePCl_4$ (*470*), and a mixture of $ClCH_2PO(NCO)Cl$ and $ClCH_2POCl_2$ is formed using $ClCH_2PCl_4$ (*471a*).

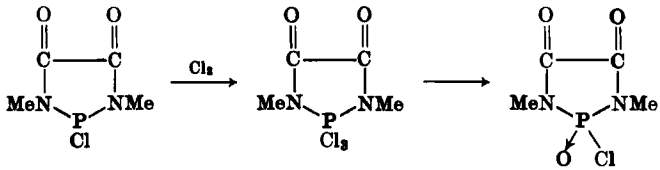
* Chlorination and ring-closure reaction to 1,3,2-diazaphospholanes occurs with PCl_5 and oxamide (*451*):

$$H_2NCOCONH_2 + 4PCl_5 \xrightarrow[-2HCl]{-2POCl_3,}$$



(80a)

Other authors (*41*) obtained in this reaction four- and five-membered fused ring systems. *N*,*N'*-Dimethyloxamide and PCl_3, followed by chlorination and intermolecular reaction, give the product shown in Eq. (80b) (*41*).



(80b)

Alkoxyureas and Ph_2PCl_3 (*in vacuo*) give only 3% yield of ROCON=PPh_2Cl; with Ph_3PCl_2 instead, only isocyanuric acid and triphenylphosphine oxide are obtained (*449*).

$$ROCONH_2 + Ph_nPCl_{5-n} \rightarrow HCl + RCl + \tfrac{1}{x}(HNCO)_x + Ph_nPOCl_{3-n} \quad (83)$$
$$n = 2, 3$$

In an analogous manner only Ph_3PO and unidentified products result from $PhNHCONH_2$ and Ph_3PCl_2 (*544*), instead of the expected PhNHCON=PPh_3; this latter compound is obtained from Ph_3P=NH and PhNCO (*544*). In contrast, PhNHCSN=PPh_3 is synthesized from $PhNHCSNH_2$ and Ph_3PCl_2 (*545*). Compounds $RNHCONH_2$ (R = Me, Et, Ph, *p*-$MeOC_6H_4$, *p*-BrC_6H_4) and PCl_5 react with intramolecular rearrangement to give phosphorylated diazetidines (*343a*).

$$2RNHCONH_2 + 2PCl_5 \rightarrow 6HCl + (RN{=}C{=}NPOCl_2)_2 \quad (84)$$

In order to obtain phosphazo compounds, the HCl formed during the reaction has to be removed; for example, ROCON=PPh_2Cl reacts with HCl in the following way:

$$ROCON{=}PPh_2Cl + HCl \rightarrow [ROCONHPPh_2Cl]^+Cl^- \rightarrow RCl + Ph_2POCl + \tfrac{1}{n}(HNCO)_n \quad (85)$$

Similar results are obtained with $(PhO)_3PCl_2$ (*96*).

Finally, alkyltetrachlorophosphoranes and perfluorinated carbonyl amides give $R_fCON{=}PRCl_2$ (*327*).

Imidoalkylcarbamates RC(=NH)OR′ or their hydrochlorides react with PCl_5 to form an ionic compound and then to give carbonylphosphazotrichlorides (*129*, *134*, *247*).

$$RC(NH_2Cl)OR' + PCl_5 \rightarrow [RC(=NHPCl_4)OR']^+Cl^- \rightarrow 2HCl + R'Cl + RCON{=}PCl_3 \quad (86)$$
$$R = Ph\ (in\ vacuo),\ p\text{-}MeC_6H_4,\ p\text{-}BrC_6H_4,\ m\text{-},\ p\text{-}O_2NC_6H_4,$$
$$R' = Et;\ R = CCl_3,\ R' = Me\ (129)$$

With R = Me, decomposition giving EtCl, HCl, $POCl_3$ and MeCN occurs; with R = R′ = Et no reaction takes place.

Analogous behavior is observed with $PhPCl_4$ [R = Ph, *p*-ClC_6H_4, *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$ (*132*), $CHCl_2$, CCl_3 (*466*)] and Ph_2PCl_3 (R = $CHCl_2$, CCl_3) (*466*). Compounds RCON=PPh_2Cl may alternatively be prepared by the phosphine–azide reaction (*90*).

Another route toward carbonylphosphazotrichlorides consists in the action of phosphorus(III) halides on *N*-chloroiminocarbamates, involving an ionic intermediate (*96*).

$$(RO)_2C{=}NCl + PX_2Cl \longrightarrow [(RO)_2C{=}NPX_2Cl]^+ Cl^- \longrightarrow$$

$$RCl + ROCON{=}PX_2Cl \quad (131, 481) \quad (87)$$

$$\begin{matrix} RC(=NCl)OR' + PCl_3 \\ \\ RC(=NCl)OR' + PCl_5 \end{matrix} \searrow\nearrow [RC(=NPCl_3)OR']^+ Cl^- \xrightarrow{\Delta} R'Cl + RCON{=}PCl_3 \quad (88)$$

R = Ph, *p*-BrC_6H_4; R′ = Et (*127*)

The following reactions are known in detail:

$$RC(=NCl)OR' + (ArO)_2PCl \rightarrow RCON{=}P(OAr)_2Cl + R'Cl \quad (89)$$

R = Me, Ph, MeO, *p*-BrC_6H_4, *p*-$O_2NC_6H_4$

Ar = Ph, *p*-MeC_6H_4 (*490*)

$$RC(=NCl)OR' + PhOPCl_2 \rightarrow R'Cl + RCON{=}P(OPh)Cl_2 \quad (90)$$

R = Ph, *p*-$O_2NC_6H_4$ (*127*)

$$RC(=NCl)OR' + (ArX)_3P \rightarrow RCON{=}P(XAr)_3 + R'Cl \quad (91)$$

R = Me, Et, Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, X = O, S (*94*)

R = Me, Et, *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$, Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, X = O (*96*) [see also (*103*, *106*)]

Interaction of NCC(=NCl)OEt and $(ArO)_3P$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4) gives NCCON=$P(OAr)_3$. With trialkylphosphites and at 75°–80° a Michaelis–Arbuzov rearrangement, giving NCC[=$NPO(OR)_2$]OEt, takes place (*91*).

$$RC(=NCl)OR + Ph_nPCl_{3-n} \rightarrow RCON{=}PPh_nCl_{3-n} + RCl \quad (92)$$

n = 1, 2, 3 (*97*)

$$(RO)_2C{=}NCl + R''R_2'P \rightarrow ROCON{=}PR_2'R'' + RCl \quad (93)$$

R = Me, Et, Ph

R′, R″ = various substituents (*88*)

$$(RO)_2C{=}NCl + R_n'PCl_{3-n} \rightarrow ROCON{=}PR_n'Cl_{3-n} + (n+1)RCl \quad (94)$$

n = 0; R = Me, Et; Ar = Ph

n = 1; R = Me, Et; Ar = Ph, PhO

n = 2; R = Me, Et; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4

R = Et; Ar = PhO [(*131*), see also (*89*, *128*)]

With PCl_3, instead, the reaction stops at $[(RO)_2C{=}NPCl_3]^+Cl^-$ (R = Me, Et) (*127*).

The analogous reaction (100°–120°) of $(EtO)_2C{=}NCl$ with PR_2Cl [R = Ph (*100*, *126*), *p*-ClC_6H_4 (*126*)] or $PRCl_2$ [R = *p*-ClC_6H_4, Ph_2PN (*126*), Ph (*100*, *126*)] gives via the (assumed) intermediate phosphazo compound the appropriate isocyanates RP(O)ClNCO or $R_2P(O)NCO$ with elimination of EtCl; see also (*79*, *82*, *124*, *257*).

In a similar way carbonylphosphazotrichlorides are obtained (*130*).

$$RCONHCl + PCl_3 \longrightarrow HCl + RCON{=}PCl_3 \quad (95)$$

$$ArC(=NH)OR + PCl_3 \xrightarrow{Et_3N} ArC(=NPCl_2)OR \xrightarrow{Cl_2}$$

$$[ArC(=NPCl_3)OR]^+ Cl^- \longrightarrow RCl + ArCON{=}PCl_3 \quad (96)$$

Finally, compounds $RCON{=}PCl_3$ are formed, as listed in Section VI,B, as intermediates in the interaction of sulfonylphosphazotrichlorides with acyl chlorides [(*231*), cf. also (*71*, *72*, *221*, *222*, *235*, *372*, *375*)].

$CCl_3CON{=}PCl_3$ may also be obtained from $CCl_2{=}CClN{=}PCl_3$ (obtained itself from dichloroacetonitrile and PCl_5, Section VIII,B,1) and $POCl_3$ (*307*).

$$CCl_2{=}CClN{=}PCl_3 + POCl_3 \rightarrow CCl_3CON{=}PCl_3 + PCl_3 \quad (97)$$

For the reactions of substituted ureas with PCl_5, see Section IX.

Only few bis(trichlorophosphazoacyls) are known. Urea reacts with 2 moles of PCl_5 on both amide groups,* giving $CO(N{=}PCl_3)_2$ (*233*); the analogous compounds *m*-$C_6H_4(CON{=}PCl_3)_2$ (*244*), *p*-$C_6H_4(CON{=}PCl_3)_2$ (*367*), $(F_2C)_n(CON{=}PCl_3)_2$ [*n* = 3 (*122*, *387e*), 4 (*387e*)], and $(F_2C)_n$(*p*-$C_6H_4CON{=}PCl_3)_2$ (*n* = 1, 2) (*123*, *387e*) are known. Similarly, the compounds $A(CON{=}PCl_3)_2$ [A = CCl_2, $(CCl_2CH_2)_2$, $(CH_2)_6(CCl_2)_2$] have been prepared (*387e*). As for the compounds with one $-CON{=}PCl_3$ group, bis(carbonylphosphazotrichlorides) may be postulated as intermediates in the action of dicarbonyldichlorides on sulfonylphosphazotrichlorides (*235*, *367*). The compound $Cl_2PPh{=}NCOCON{=}PPhCl_2$ is formed from $PhPCl_2$ and EtOC(=NCl)C(=NCl)OEt (*91*).

A mixed carbonyl- and sulfonylphosphazotrichloride *p*-$Cl_3P{=}NSO_2C_6H_4CON{=}PCl_3$ is obtained (*367*) from *p*-sulfonamidobenzamide and phosphorus(V) chloride.

Substituted malonic acid diamides and PCl_5 yield bis(carbonylphosphazotrichlorides) (*450*) without chlorination of the CO group as in the case of the oxalic ester amides.

* By-products of this reaction are described (*207*) in Section IV,C,1.

$$XYC(CONH_2)_2 + 2PCl_5 \longrightarrow XYC(CON{=}PCl_3)_2 + 4HCl \qquad (98)$$

X = Y = Cl, Br
X = H, Y = Cl
X = Br, Y = NO_2

Analogous compounds $R(CON{=}PCl_3)_2$ ($R = -CCl_2-$, $-CCl_2(CH_2)_nCCl_2-$, $n = 2, 5, 6$) have been described recently (*387f*).

B. Reactions

Nitriles and $POCl_3$ result from the pyrolysis of carbonylphosphazotrichlorides.

$$RCON{=}PCl_3 \rightarrow RCN + POCl_3 \qquad (99)$$

R = Ph [(*223*, *260*), cf. also (*298*)], *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-, *p*-ClC_6H_4, *p*-BrC_6H_4, 2,4-$(O_2N)_2C_6H_3$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl(O_2N)C_6H_3$, 2,4-$Cl_2C_6H_3$ (*260*), CCl_3 (*240*), Ph_2CCl (*243*), *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*244*)

Hydrogen chloride acts catalytically in the same way at lower temperatures (*240*).

^{18}O-Labeling in $PhC^{18}ON{=}PCl_3$ showed that ^{18}O migration from the CO group to the phosphorus atom is involved [via a cyclic mechanism (*298*)]; the same results apply to $Et^{18}OC^{18}ON{=}PCl_3$ (*3*).

$$PhC^{18}ON{=}PCl_3 \xrightarrow{\Delta} \left[Ph{-}C(=N{-}\overset{+}{P}Cl_3)({}^{18}O^-) \right] \longrightarrow PhCN + P^{18}OCl_3 \qquad (100)$$

Alkoxycarbonylphosphazotrichlorides $ROCON{=}PCl_3$ give alkyl chlorides and dichlorophosphorylisocyanates on heating.

$$ROCON{=}PCl_3 \xrightarrow{\Delta} Cl_2(O)PNCO + RCl \qquad (101)$$

R = Et (*3*, *223*), Me (*135*, *264*)

The compound $PhOCON{=}PCl_3$ decomposes *in vacuo* (80°) to $POCl_3$, triphenylcyanurate, cyanuric chloride and $PhOPOCl_2$ (*265*).

Similarly, $ROCON{=}PX_2Cl$ compounds decompose (*131*, *448*) as shown in Eq. (102). Several other papers [(*100*, *124*, *126*, *266*, *481*), see

$$ROCON{=}PX_2Cl \xrightarrow{\Delta} X_2P(O)NCO + RCl \qquad (102)$$

also (*79*)] dealing with this formation of isocyanates without isolation of the corresponding carbonylphosphazotrichloride have been published.

Hydrolysis of carbonylphosphazotrichlorides with HCOOH or moist air leads to $RCONHPOCl_2$. This reaction has been carried out with the

$$RCON{=}PCl_3 + HCOOH \rightarrow RCONHPOCl_2 + HCl + CO \quad (103)$$

following R: $EtOCCl_2$, $BuOCCl_2$ (*268*); Ph [(*223, 259*); cf. also (*368*) and earlier (*491*)]; *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-, *p*-ClC_6H_4, 2,4-$(O_2N)_2C_6H_3$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl(O_2N)C_6H_3$, 2,4-$Cl_2C_6H_3$ (*259*); CCl_3 (*240*); Ph_2CCl, Ph_3C (*243*); $PhOCCl_2$, *o*-, *m*-, *p*-$MeC_6H_4OCCl_2$, 1-$C_{10}H_7OCCl_2$, 2-$C_{10}H_7OCCl_2$ (*270*); Ph_2N (*274*); *p*-MeC_6H_4, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*244*); CHF_2CF_2, $CHClFCF_2$, $CHCl_2CF_2$ (*147*); CF_3 (*210, 330*); $CNCH_2$ (*450*); C_3F_7 (*330*); $ClCH_2CCl_2$, $ClCH_2CHCl$ (*117*); $MeCCl_2$ (*119*); $Me_2C(CN)$, $Et_2C(CN)$, $Pr_2C(CN)$, $Bu_2C(CN)$, $Am_2C(CN)$, and $(Me_2CHCH_2CH_2)_2C(CN)$ (*427*).

Similarly $RCONHP(O)(CCl_3)Cl$ (R = $CHCl_2$, CCl_3, CF_3, *p*-$O_2NC_6H_4$) (*469*) and $MeOCONHP(O)PhCl$ (*482*) have been prepared; $EtCCl{=}NPOCl_2$ and $PhCCl{=}NPOCl_2$ are synthesized from nitriles and PCl_3 in presence of oxygen (*66*).

Further hydrolysis [(*262*), see also (*491*)] of $RCONHPOCl_2$ gives the free amides $RCONHPO(OH)_2$ [R = Ph, *o*-, *m*-, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$(O_2N)_2C_6H_3$, *o*-, *p*-ClC_6H_4, 2,4-$Cl_2C_6H_3$ (*262, 454*), 2,4-$Cl(O_2N)C_6H_3$ (*262*), Ph_2N (*274*)].

Thermolysis of $PhCONHPOCl_2$ (1 hr/150°) results in a quantitative yield of PhCN, $POCl_3$, and HCl (*259*); $Ph_3CONHPOCl_2$ shows analogous behavior (*243*).

Interaction of $RCONHPOCl_2$ and PCl_5 gives, in addition to $POCl_3$, the compounds $RCCl{=}NPOCl_2$ (XVII) ["isophosphazo compounds," *N*-(dichlorophosphoryl)acylimidochlorides] [R = CCl_3 (*240*); CF_3 (*122*); $MeCCl_2$ (*119*); *p*-$O_2NC_6H_4$ (*243*); Ph, *p*-MeC_6H_4, *o*-, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl(O_2N)C_6H_3$, 2,4-$Cl_2C_6H_3$, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*244*); *p*-BrC_6H_4 (*296*)]. The compound *p*-$C_6H_4(CONHPOCl_2)_2$ gives similar reactions (*367*).

The fluorides $ArNHCONHPOF_2$ (Ar = *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *m*-, *p*-$O_2NC_6H_4$, 2-$C_{10}H_7$) and $ArNHCONHPOClF$ (Ar = Ph, *p*-$O_2NC_6H_4$) react similarly to $ArNHC(=NPOF_2)Cl$ and $ArNHC(=NPOFCl)Cl$, respectively (*114*).

The former compounds (XVII) ($RCCl{=}NPOCl_2$) [R = CCl_3 (*240*); Ph, *p*-MeC_6H_4, *o*-, *p*-ClC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl(O_2N)C_6H_3$, 2,4-$Cl_2C_6H_3$, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*244*)] give on thermolysis RCN and $POCl_3$; with ArONa the corresponding esters are obtained (*245*).

Compounds $ArNHCON{=}PCl_3$ (formed from $ArNHCONH_2$ plus PCl_5) (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-BrC_6H_4) rearrange after some time

to *N*-phosphorylchloroformamidines $ArNHC(=NPOCl_2)Cl$ (*115*). The latter compounds may also be obtained from $ArNHCONHPOCl_2$ and PCl_5 [Ar = Ph, *o*-, *p*-MeC_6H_4, *m*-, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-IC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, *p*-$F_3CC_6H_4$, 4,3(Me)$O_2NC_6H_3$] (*138*) and in the aliphatic series from $RNHCONH_2$ (R = Me, Et) and phosphorus(V) chloride (*113*). Analogies (*243*) are described.

$$Ph_2CClCONHPOCl_2 + PCl_5 \rightarrow POCl_3 + Ph_2CClC(=NPOCl_2)Cl + HCl \quad (104)$$

The reaction of phenol with $RCON{=}PCl_3$ [R = Ph, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$] gives $RCON{=}P(OPh)Cl_2$ or $RCON{=}P(OPh)_3$ (*105*). The synthesis of triesters, i.e., without the isolation of partially chlorinated products, has been described with the following R and Ar substituents: R = CCl_3, Ar = Ph, *p*-ClC_6H_4, Et, Me (*241*); 1-$C_{10}H_7$, 4-$ClC_{10}H_6$ (*242*); R = Ph_2CCl, *p*-$O_2NC_6H_4$, Ar = 1-$C_{10}H_7$ (*243*); R = Ph, Ar = Ph (*96*, *223*, *246*); R = 1-$C_{10}H_7$, *p*-ClC_6H_4, 3,5-$(O_2N)_2C_6H_3$, 2,4-$Cl(O_2N)C_6H_3$, Ar = Ph; R = Me, *p*-BrC_6H_4, *m*-$O_2NC_6H_4$, Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4 (*96*); R = *p*-$O_2NC_6H_4$, Ar = Ph (*96*, *246*); R = Ph_2N, Ar = Ph, *o*-, *p*-ClC_6H_4, *o*-, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$ (*274*); R = Ph_2CCl, Ar = 1-$C_{10}H_7$ (*243*); R = *p*-FC_6H_4, *m*-$CF_3C_6H_4$, Ar = Me, Et, Ph, *p*-FC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$ (*522*). Reaction of several carbonylphosphazotrichlorides $RCON{=}PCl_3$ (R = Ph, *p*-ClC_6H_4, alkyls) with various alcohols, phenol, thiophenol, and amines have been described recently (*368a*, *387c*, *387g*).

Some triesters $CF_3CON{=}P(OAr)_3$ are claimed to have been obtained from the reaction of $CF_3CONHPOCl_2$ with 3 moles of ArOH (Ar = Ph, *p*-BrC_6H_4) (*122*); $CF_3CON{=}P(OEt)_3$ is prepared from an azide–phosphine reaction [(*210*); see also (*478a*)].

Diesters $RCONHP(O)(OMe)_2$ [R = CCl_3, Ph, *p*-ClC_6H_4, *m*-, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$] can be prepared by direct action of alcohols, e.g., methanol (*133*, *263*); extension to higher alcohols is mentioned in the literature (*464*).

$$RCON{=}PCl_3 + 3MeOH \rightarrow 2HCl + MeCl + RCONHPO(OMe)_2 \quad (105)$$

The analogous reactions of $RCON{=}P(Ar)Cl_2$ (*466*), $RCON{=}P(CCl_3)Cl_2$ (*469*), $RCON{=}P(OPh)Cl_2$ (*105*), and $ArCON{=}P(Ar')Cl_2$ (*95*) are described.

Alcoholysis in presence of triethylamine yields the free dichlorides (*465*); the use of sodium alcoholates (*241*) or excess alcohol (*264*) gives the triesters, some of which, however, have been obtained on another way (*210*).

The compounds $ArNHCON{=}P(OR)_3$ are only obtained by a phosphine–azide reaction (*112*).

Finally, it must be mentioned that esters of the type $ROCON{=}P(OR')_3$ isomerize to $ROCONR'P(O)(OR')_2$ on heating (*477*).

Excess of aromatic amines with carbonylphosphazotrichlorides (6:1) readily give the amides $ArCON{=}P(NHAr')_3$ [Ar = *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$, Ar' = *p*-MeC_6H_4 (*93*); Ar = Ar' = Ph [(*93, 104*), see also (*288a*)] in contrast to the very increased difficulty with sulfonylphosphazotrichlorides; $ArCON{=}P(NHAr')_3$ compounds hydrolyze to $ArCONHPO(NHAr')_2$.

The compound $CCl_3CON{=}PCl_3$ forms 1:1 complexes with DMF or DMA (*297d*).

Molar ratios of aniline and $ArCON{=}PCl_3$ lead to the monoanilides (ionic form) (XVIII) (*107*); these salts give,

$$PhNH_2 + ArCON{=}PCl_3 \xrightarrow{Et_3N} \underset{\text{(XVIII)}}{[ArCON{=}P(NHPh)Cl_3]^-\ Et_3NH^+} \qquad (106)$$

Ar = Ph, *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$, 3,5-$(O_2N)_2C_6H_3$

on hydrolysis (HCOOH, H_2O), $ArCONHPO(NHPh)Cl$ and subsequently $ArCONHPO(NHPh)OH$; diesters $ArCON{=}P(NHPh)(OPh)_2$ are formed from (XVIII) and PhONa.

Trisaziridines $ArCON{=}P(NC_2H_4)_3$ (Ar = Ph, *o*-, *p*-ClC_6H_4, *o*-, *p*-BrC_6H_4, *m*-, *p*-$O_2NC_6H_4$) are obtained from $ArCON{=}PCl_3$ and ethylenimine at 3°–7° (*296*); $PhNHCON{=}P(NC_2H_4)_3$ and $MeOCON{=}P(NC_2H_4)_3$, among others, have been obtained by a phosphine–azide reaction (*109*).

The compound *p*-$FC_6H_4CON{=}PCl_3$ gives with ethylenimine, in the presence of alcohols ROH (R = Me, Et, Pr, *i*-Pr, Bu, *n*-C_6H_{13}), compounds of the type *p*-$FC_6H_4CON{=}P(OR)(NC_2H_4)_2$ (*369a*).

Excess phenylhydrazine and $RCON{=}PCl_3$ (R = CCl_3, $MeCCl_2$, $ClCH_2CHCl$, $ClCH_2CCl_2$, *m*-, *p*-FC_6H_4, *p*-BrC_6H_4) give the corresponding hydrazides (*387b*).

The arylation of arylcarbonylphosphazotrichlorides yields $ArCON{=}PPh_3$ (Ar = Ph, *p*-ClC_6H_4, *p*-BrC_6H_4) (*92*). $NCCON{=}PPh_3$ may be prepared from PPh_3 and $NCC(=NCl)OEt$ (*91*).

The fluorination of $R_fCON{=}PCl_3$ ($R_f = CF_3$, CF_3CF_2, $CF_3CF_2CF_2$, $CF_3CF_2CF_2CF_2$) with AgF results in elimination of POF_3 and a ring closure (*370*) to 2,4,6-tris(perfluoroalkyl)-1,3,5-triazine (XIX).

$$3R_fCON{=}PCl_3 + 9AgF \longrightarrow \underset{\text{(XIX)}}{\text{2,4,6-tris(perfluoroalkyl)-1,3,5-triazine}} + 3POF_3 + 9AgCl \qquad (107)$$

Chlorination of $CCl_3CON{=}PCl_3$ with PCl_5 or Cl_2 yields $CCl_3CCl_2N{=}PCl_3$ (*424*).

$$CCl_3CON{=}PCl_3 + PCl_5 \rightarrow CCl_3CCl_2N{=}PCl_3 + POCl_3 \quad (108)$$

The compounds $(CF_2)_3(CON{=}PCl_3)_2$ and $(CF_2)_n(p\text{-}C_6H_4CON{=}PCl_3)_2$ ($n = 1$, 2) react with HCOOH to give $(CF_2)_3(CONHPOCl_2)_2$ and $(CF_2)_n(p\text{-}C_6H_4CONHPOCl_2)_2$, respectively. Reaction of these compounds with sodium alcoholates and amines has been mentioned (*123*). The interaction of $R(CON{=}PCl_3)_2$ with various alcohols, amines, etc., is described (*387d*, *387f*); *m*- and *p*-$C_6H_4(CON{=}PCl_3)_2$ and ethylenimine give the corresponding hexamides *m*- and *p*-$C_6H_4[CON{=}P(NC_2H_4)_3]_2$ (*367*). Thermolysis of *m*-$C_6H_4(CON{=}PCl_3)_2$ gives $POCl_3$ and isophthalic dinitrile; its hydrolysis (HCOOH) leads to *m*-$C_6H_4(CONHPOCl_2)_2$ (*244*).

A compound $Et_2C(Br)CONHP(O)(NHPOCl_2)_2$ has been reported in in the literature (*168*). Finally, $Ph_3P{=}NCOCON{=}PPh_3$ is formed from PPh_3 and $EtOC(=NCl)C(=NCl)OEt$ (*91*).

C. Spectroscopic Investigations

Only a few spectroscopic data for carbonylphosphazotrichlorides are available.

The $\nu_{P=N}$ of $RCON{=}PCl_3$ (R = CCl_3, CF_3, Ph, *p*-ClC_6H_4) is found in the range 1290–1360 cm^{-1} (*98*); for $CF_3CON{=}PCl_3$ the assignment has been made at 1381 cm^{-1} (*210*).

An infrared investigation of $^{14}N/^{15}N$-labeled compounds $RCON{=}PCl_3$ (R = CF_3, CCl_3, Ph, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, *p*-FC_6H_4, *p*-MeC_6H_4, MeO, EtO) has been made recently (*475*).

The P=N band in the esters $ArCON{=}P(OR)_3$ (Ar = Ph, *m*-, *p*-$O_2NC_6H_4$; R = Me, Et, Pr, *i*-Pr; Ar = Ph, R′ = Me, Ph) has been found (*90*) to be typical at 1340–1360 cm^{-1}; another paper (*210*) gives a wider range of 1317–1415 cm^{-1}. The $\nu_{P=N}$ for $MeCON{=}P(OEt)_3$ lies at 1350–1385 cm^{-1} (*212*). Infrared spectra of $CCl_3CON{=}PPh(OPh)_2$ (*467*), $MeOCON{=}P(OPh)_2(NHPh)$, and $MeOCON{=}P(OPh)_2NH_2$ (*102*) have been reported.

Matrosov (*331*) carried out a calculation of the IR spectra of $CCl_3CON{=}PCl_3$ and $(EtO)_3P{=}NP(O)(OEt)_2$ and assigns the $\nu_{P=N}$ to a range of 1290–1415 cm^{-1}, in accordance with experimental results. It is mentioned that the $\nu_{P=N}$ is strongly dependent on the substituents at the nitrogen atoms and to a lesser extent on those at the phosphorus atom [see also (*295*)]. The compounds $PhCON{=}PR_3$ exhibit the $\nu_{P=N}$ at 1332 cm^{-1} (R = Ph) and at 1341 cm^{-1} (R = Bu), $PhCON{=}PPh_2Et$ at 1337 cm^{-1}, and $EtOCON{=}PPh_3$ at 1268 and 1281 cm^{-1}, respectively (*520*).

Only a few ^{31}P NMR chemical shifts have been measured (*475*): $CCl_3CON{=}PCl_3$ ($\delta_P = -25.1$ ppm), $PhCON{=}PCl_3$ ($\delta_P = -13.2$ ppm), $p\text{-}O_2NC_6H_4CON{=}PCl_3$ ($\delta_P = -18.7$ ppm), $p\text{-}FC_6H_4CON{=}PCl_3$ ($\delta_P = -15.0$ ppm), $p\text{-}MeC_6H_4CON{=}PCl_3$ ($\delta_P = -12.2$ ppm), $MeOCON{=}PCl_3$ ($\delta_P = -8.9$ ppm), and $EtOCON{=}PCl_3$ ($\delta_P = -7.3$ ppm).

VIII. Aryl- and Alkylphosphazotrihalides

A. Trichlorophosphazoaryls

1. Syntheses

Gilpin (*172*) described the reaction of equimolar amounts of PCl_5 and aniline hydrochloride at 170°, but the resulting compound $C_6H_5NPCl_3$ was not further characterized. The same compound is mentioned without further specification in some patents (*322*). Recent work uses PCl_5 and primary aromatic amines (or their hydrochlorides) in CCl_4 (*535*) or a twice molar ratio of the amine in CCl_4 (*538*).

As found from infrared spectra and molecular weight measurements, dimerization of the resulting compounds occurs when the amine used has a basicity constant K_B (in aqueous solution) greater than 10^{-10}. If $K_B = 10^{-10}$–10^{-13}, the compounds are dimeric in the solid state, but monomeric in benzene solution; with amines of $K_B = 10^{-14}$–10^{-19}, only monomeric compounds are obtained (*535*).

The following steps for this reaction have been proposed:

$$\begin{array}{l} ArNH_2 + [PCl_4]^+ \longrightarrow [ArNH_2PCl_4]^+ \xrightarrow{-H^+} (ArNHPCl_4) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow -HCl \qquad (109) \\ [PCl_6]^- + H^+ \longrightarrow PCl_5 + HCl \qquad\qquad\qquad\qquad (ArN{=}PCl_3)_n \\ n = 1, 2 \end{array}$$

The following $(ArN{=}PCl_3)_2$ ($n = 1$ or 2) have been obtained: Ar = Ph, *o*-, *p*-MeC_6H_4, *o*-, *m*-, *p*-ClC_6H_4 (*535*, *538*),* *m*-MeC_6H_4, *o*-, *m*-, *p*-BrC_6H_4, 2,4-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$, 3,5-$Me_2C_6H_3$, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$, 3,5-$Cl_2C_6H_3$, *o*-, *m*-, *p*-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_2C_6H_2$, 2,4,6-$Cl_2(O_2N)C_6H_2$ (*535*), *o*-, *m*-, *p*-FC_6H_4, 2,4-$F_2C_6H_3$, 2,5-$F_2C_6H_3$, 2,3,4,5-F_4C_6H, 2,3,5,6-F_4C_6H [(*502*), see also (*500*)], $ClSO_2C_6H_4$ (*50*, *354*), *o*-, *m*-, *p*-$CF_3C_6H_4$, 2-F,5-$CF_3C_6H_3$ (*46*), *o*-, *m*-, *p*-$Me_2NSO_2C_6H_4$ (*549*), 5-Me, 2-NCC_6H_3 (*401*).

* *p*-$ClC_6H_4N{=}PCl_3$ has also been isolated (*510*) as a by-product of $PhNHSO_2N{=}PCl_3$ and PCl_5 (Section VI,B) and from another reaction (*361a*) (Section VIII,B,1).

Arylphosphazotrichlorides can also be obtained by phosphorylation (PCl_5) of $ArNHPOCl_2$, $ArNHPO(OPh)_2$, $ArNHPO(OPh)Cl$, $(ArNH)_2POCl_2$, and $(ArNH)_3PO$ (*535*, *536*) or of $ArNHPO(Cl)NArPOCl_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-BrC_6H_4, 3,5-$Me_2C_6H_3$) (*536*).

$$(ArNH)_2POCl + 2PCl_5 \rightarrow POCl_3 + 2HCl + (ArN{=}PCl_3)_2 \quad (110)$$

$$2ArNHPOCl_2 + 2PCl_5 \rightarrow 2POCl_3 + 2HCl + (ArN{=}PCl_3)_2 \quad (111)$$

$$ArNHPO(Cl)NArPOCl_2 + 2PCl_5 \rightarrow (ArN{=}PCl_3)_2 + 2POCl_3 + HCl \quad (112)$$

Compounds $PhN{=}PPh_nCl_{3-n}$ ($n = 0, 1, 2$) may be generated from an azide–phosphine reaction using Ph_nPCl_{3-n} and phenyl azide (*65*).

$$2PhN_3 + 2Ph_nPCl_{3-n} \rightarrow (PhN{=}PPh_nCl_{3-n})_2 + 2N_2 \quad (113)$$

$(PhN{=}PCl_3)_2$ should be formed as an intermediate in the thermolysis of 2-phospha-1,3-diazetidin-4-ones as well as isocyanate. These two products react further to form a carbodiimide and $POCl_3$ (*495–498*).

Finally, dimeric arylphosphazotrichlorides (1,3,2,4-diaryldiazadiphosphetidines) are obtained on chlorination (Cl_2) of arylaminothiophosphoryldichlorides (*99*).

In an analogous manner $PhPCl_4$ reacts with $ArNH_3Cl$ [Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4, *o*-, *m*-, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$, 2,4-$Cl_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$, *o*-, *m*-, *p*-BrC_6H_4, 2,4-$Br_2C_6H_3$, 2,4,6-$Br_3C_6H_2$, *o*-, *m*-, *p*-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$, 2,4,6-$Cl_2(O_2N)C_6H_2$] to give $ArN{=}PPhCl_2$ (*537*). With Ph_2PCl_3 and only in presence of pyridine the corresponding compounds $ArN{=}PPh_2Cl$ (Ar = Ph, *o*-MeC_6H_4, *o*-, *p*-ClC_6H_4, 2,4-$Cl_2C_6H_3$, *p*-BrC_6H_4, *p*-$EtOC_6H_4$, *m*-, *p*-$O_2NC_6H_4$) are obtained [(*537*, *540*); see also (*192a*)].

$$Ph_2PCl_3 + ArNH_3Cl \longrightarrow [ArNH{=}PPh_2Cl]^+\,Cl^- \xrightarrow{\text{pyridine}} ArN{=}PPh_2Cl \quad (114)$$

Similarly $MePCl_4$ gives $(ArN{=}PCl_2Me)_n$ ($n = 1$, Ar = *p*-ClC_6H_4, *o*-, *p*-BrC_6H_4, *o*-MeC_6H_4, 2,4-$Cl_2C_6H_3$, *p*-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$; $n = 2$, Ar = *o*-, *p*-ClC_6H_4, *o*-BrC_6H_4) (*526*). $C_6F_5N{=}PCl_3$ is obtained from the reaction of PCl_5 with C_6F_5NSO (*188c*).

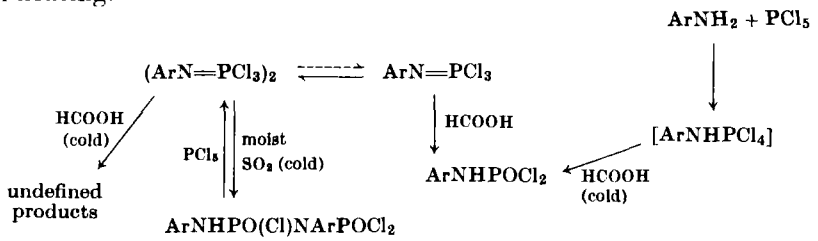
A difluorotetrachlorodiazadiphosphetidine $(FCl_2P{=}NPh)_2$ has been synthesized (*37*) from aniline hydrochloride and PCl_2F_3 (see also Section VIII,C).

Aminobenzenesulfonamides *o*-, *m*-, *p*-$H_2NSO_2C_6H_4NH_2$ react with PCl_5 at both amino groups to form *o*-, *m*-, *p*-$Cl_3P{=}NSO_2C_6H_4N{=}PCl_3$ (*549*) (Section VI,A). The para isomer has also been synthesized independently (*354*, *489*); only the ortho isomer is dimeric, the meta and para isomers are monomeric.

2. Reactions

The monomeric and dimeric forms of $(ArN{=}PCl_3)_n$ ($n = 1, 2$) show different behaviors upon hydrolysis.

$ArN{=}PCl_3$ compounds hydrolyze with HCOOH to form $ArNHPOCl_2$ [Ar = 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$, 2,4-$(O_2N)_2C_6H_3$, 2,4,6-$Cl_2(O_2N)C_6H_2$ (*536*); Ph, *o*-, *p*-MeC_6H_4, *m*-, *p*-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$ (*538*); *o*-ClC_6H_4 (*297a*, *538*); *o*-$Me_2NSO_2C_6H_4$ (*549*)]. In contrast, hydrolysis of the dimers in the cold results in ring opening to yield $ArNHPO(Cl)NArPOCl_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-BrC_6H_4, 3,5-$Me_2C_6H_3$) (*536*). The temperature control of this hydrolysis reaction is probably the most important factor, because the dimeric products monomerize in solution on heating.



Compounds $ArN{=}PPhCl_2$ hydrolyze similarly to ArNHP(O)PhCl (*539*).

Ammonolysis of $(PhN{=}PCl_3)_2$ gives an ionic compound $[PhNHP(NH_2)_2]_2N^+Cl^-$ (*504*). The reaction with methylamine yields only a polymeric substance (*219*) (see also Section VIII,B,2); fluorophenylphosphazotrichlorides also give saltlike compounds with liquid ammonia (*502*).

Polymers with [HN–P(Cl)=N–] units have been obtained by the reaction of $(PhN{=}PCl_3)_2$ with urea or melamine at elevated temperatures (*525a*).

By the action of diethylamine on $(PhN{=}PCl_3)_2$ gradual substitution of the chlorine atoms occurs to monomeric compounds $PhN{=}P(NEt_2)_{3-n}Cl_n$ ($n = 0, 1, 2$) (*184*); analogous substances $PhN{=}P(X)Cl_2$ [X = NMe_2, NBu_2, N(Me)CH_2Ph] have been synthesized (*501*) which give, on ammonolysis, tetraminophosphonium salts $[PhNHP(X)(NH_2)_2]^+Cl^-$ [X = NMe_2, NEt_2, NBu_2, N(Me)CH_2Ph] (*501*). The reaction of $PhN{=}P(NEt_2)Cl_2$ with other secondary amines leads to $PhN{=}P(NEt_2)YCl$ (Y = NMe_2, NEt_2, NPr_2, NBu_2, morpholine, piperidine, pyrrolidine) which hydrolyze to unsymmetrical phosphine oxides $PhNHP(O)(NEt_2)Y$ (*47*).

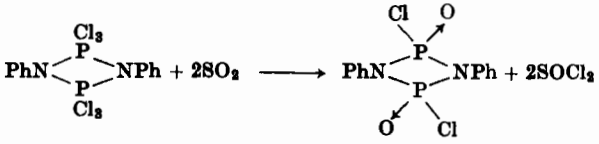
Trisaziridines $ArN{=}P(NC_2H_4)_3$ have only been obtained from the phosphine $P(NC_2H_4)_3$ and the corresponding azide (Ar = Bu, Ph, *p*-PhC_6H_4, *p*-BrC_6H_4, *p*-MeC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$) (*109*).

Trichlorophosphazoaryls give with PhONa the triesters ArN=$P(OPh)_3$ [Ar = Ph, *o*-, *m*-, *p*-MeC_6H_4, *o*-, *m*-, *p*-BrC_6H_4, *o*-, *m*-, *p*-$O_2NC_6H_4$, *o*-, *m*-, *p*-ClC_6H_4, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$, 3,5-$Me_2C_6H_3$, 2,4-$Cl_2C_6H_3$, 2,5-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$, 2,4-$(O_2N)_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$, 2,6,4-$Cl_2(O_2N)C_6H_2$] (*546*), which with water yield the diesters $ArNHPO(OPh)_2$ [see also (*549*)]. Some $ArN{=}P(OPh)_3$ [Ar = Ph, *p*-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$, 3,4-$(O_2N)_2C_6H_3$, 5-O_2N,2-pyridyl-C_6H_3, 2,4,6-$(O_2N)_3C_6H_2$] are also obtained from $(PhO)_5P$ and the corresponding amine; $PhN{=}P(OPh)_3$ is also obtained from $(PhO)_3PCl_2$ and aniline (*534*). Compounds $PhN{=}P(OR)_3$ (R = Me, Et, Pr, Me_2CH) have only been prepared by an azide–phosphine reaction (*208*); $PhN{=}P(OEt)_3$ may also be prepared (*518*) using the method indicated in Eq. (115).

$$PhNSO + 3(EtO)_3P \rightarrow PhN{=}P(OEt)_3 + (EtO)_3PO + (EtO)_3PS \qquad (115)$$

2,2,2,4,4,4-Hexachloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine reacts with phenylisocyanate at 150° (with postulated monomerization) to give diphenylcarbodiimide* (*494–496*, *498*). With CO_2 or CS_2 the corresponding isocyanate and thioisocyanate are obtained (*494*).

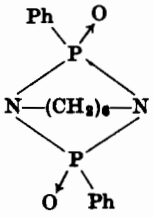
Reaction of $(PhN{=}PCl_3)_2$ with sulfur dioxide yields 2,4-dichloro-2,4-dioxo-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (*181*). This compound



(116)

was made previously by Michaelis (*334*, *335*) from $POCl_3$ and aniline. Action of HCl on it produces a ring opening to $ArNHP(O)ClNArPOCl_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4) (*297a*), also obtained by hydrolysis of $(ArN{=}PCl_3)_2$.

Analogous compounds, such as $(RN{=}P(O)R')_2$ (R = Ph, R' = Et) and



(from $PhPOCl_2$ and hexamethylenediamine), are known (*53*).

* Isocyanates do not react with alkylsulfonylphosphazotrichlorides (*495*, *496*).

The monomeric compound o-$Me_2NSO_2C_6H_4N{=}PCl_3$ gives with HCOOH a quantitative yield of o-$Me_2NSO_2C_6H_4NHPOCl_2$, whereas the (dimeric) meta and para isomers do not react in this way (*549*). Reaction with RONa in absolute alcohol gives the diesters o-, m-, p-Me_2NSO_2-$C_6H_4NHP(O)(OR)_2$ (R = Me; for the ortho isomer also R = Ph) (*549*).

For the reactions of o-, m-, p-$Cl_3P{=}NSO_2C_6H_4N{=}PCl_3$, see Section VI,B.

B. Alkylphosphazotrichlorides

1. Syntheses

2,2,2,4,4,4-Hexachloro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine, $(MeN{=}PCl_3)_2$, was first synthesized independently by Haasemann (*186*) and Chapman and co-workers (*69*) from the reaction of methylamine hydrochloride and PCl_5 in symmetric $C_2H_2Cl_4$. The heat of formation was found to be -217.3 ± 0.5 kcal/mole (*166*); the energy of this P–N bond is 74.3 kcal/mole (*166*) and thus lies between the energy of a single bond (66.8 kcal/mole) and a double bond (98 kcal/mole), so that in some extent delocalization of the nitrogen electron pair can be assumed (*519*) (see also Section VIII,D,3).

Other routes to the synthesis of $(MeN{=}PCl_3)_2$ are the action of PCl_5

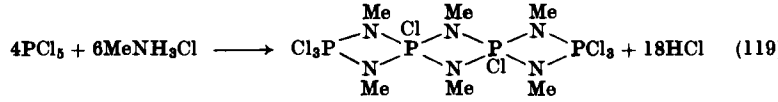
$$2CF_3CONHMe + 2PCl_5 \rightarrow \begin{cases} 2CF_3C(Cl){=}NMe + 2POCl_3 + 2HCl \\ 2CF_3COCl + (MeN{=}PCl_3)_2 + 2HCl \end{cases} \quad (117)$$

on N-methyltrifluoroacetamide (*352*) and the (indirect) synthesis from $[MeNH_3]^+SbCl_6^-$ (*395*).

$$2MeNH_3SbCl_6 + 4PCl_5 \rightarrow (MeN{=}PCl_3)_2 + 2PCl_4SbCl_6 + 6HCl \quad (118)$$

Minor amounts of $(MeN{=}PCl_3)_2$ are formed in the reaction of $MeNH_3Cl$ with PCl_5 in presence of BCl_3 (*34*) or $AlCl_3$ (*509a*) (where six-membered ring compounds are formed, see Section IV,A,2) and by the action of PCl_5 on N,N'-dimethylsulfamide (*36b, 510*), as well as by the reaction of PCl_5 or $PhPCl_4$ with $Me_3SiN(Me)PCl_2{=}NSO_2Cl$ (*50b*). Another way is the chlorination of methylaminothiophosphoryldichloride (*99*).

A by-product (3%) of the normal synthesis of $(MeN{=}PCl_3)_2$ ($MeNH_3Cl + PCl_5$) is formed according to Eq. (119) (*31, 32*).



(119)

Higher alkylphosphazotrichlorides $(RN{=}PCl_3)_n$ ($n = 1, 2$) are known with the following R: Et, Pr, Bu, Am (*185*, *528*); n-C_6H_{13} to n-$C_{10}H_{21}$ (*185*); $ClCMe_2CHCl$, $ClCMe_2CH_2$, Me_3C (*528*); i-Pr (*185*); i-Bu* (*142*); Me_2CClCH_2 (*528*); Me_3C (*527c*, *528*); Me_3CCH_2 (*529*); Et_2CH (*527a*, *529*); $Me_3CCH_2CH_2$, Et_2CH, $PhCH_2$, $PhCH_2CH_2$, Me_3CCCl_2CHCl,† $(ClCH_2)_2$-CH,† $ClCH_2CH_2$† (*529*); $Me_2CHCH_2CH_2$, $EtCH(Me)CH_2$ (*185*); Ph_2CH (*543*); $(CF_3)_2CH$, $(CF_3)_2CCl$, $(CF_3)_3C$ (*295*); $ClSO_2(CH_2)_n$ ($n = 2$–4) (*542*).

It has been shown (*185*) that in the case of isoalkylamines not only the basicity of the amine involved (as for the arylamines), but also the place of branching, influences whether the monomer or the dimer is formed. Thus, α-branched isoamines yield monomeric compounds (with the exception of $(i\text{-PrN}{=}PCl_3)_2$), β-branched amines yield either monomeric or dimeric species, and γ-branched amines yield only the dimeric compounds.

Similarly $(RN{=}PPhCl_2)_2$ compounds (R = Me, Et, Pr, Bu) are prepared from $PhPCl_4$ and alkylammonium chlorides (*527*); $(MeN{=}PPh_2Cl)_2$ has only been synthesized from the azide and Ph_2PCl (*196*), whereas $MeNH_3Cl$ and Ph_2PCl_3 yield only the ionic compound $[MeNHPClPh_2]^+$-Cl^- (*192a*, *519*), which is also obtained from $Ph_2PONHMe$ and PCl_5 (*192a*). Interaction of $(CCl_3)_2PCl_3$ and aliphatic amines gives the monomeric compounds $(CCl_3)_2ClP{=}NR$ (R = Me, Et, Pr, i-Pr, Bu, C_6H_{11}) (*294b*).

Partially or fully halogenated trichlorophosphazohaloalkyls are known: $(CH_2ClN{=}PCl_3)_2$ is formed in 40–63% yield by the reaction of aminomethanesulfonic acid with a 3.5-fold excess of PCl_5 (*338*, *542*); tris(chloromethyl)amine $N(CH_2Cl)_3$ is also formed in the reaction (*338*). $(CH_2ClN{=}PCl_3)_2$ results also on careful chlorination of $(MeN{=}PCl_3)_2$ (*141a*). The attempted synthesis of $(CHCl_2N{=}PCl_3)_n$ ($n = 1$ or 2) by the action of PCl_5 on HCN failed (*44*). The fully chlorinated monomeric compound $CCl_3N{=}PCl_3$ may be prepared by chlorination (UV) of $(MeN{=}PCl_3)_2$ (*142*, *294*), thiophosphoric triisocyanate (*162*), or $MeN{=}PCl(CCl_3)_2$ (*294b*). Smaller yields of $CCl_3N{=}PCl_3$ are formed in the

* i-$BuNH_3Cl$ reacts with excess PCl_5 to give $CCl_2{=}C(CHCl_2)N{=}PCl_3$ (*527b*) or $ClCMe_2CHClN{=}PCl_3$ (*528*):

$$i\text{-}BuNH_3Cl + 3PCl_5 \rightarrow 5HCl + 2PCl_3 + ClCMe_2CHClN{=}PCl_3 \qquad (119a)$$

† Only when excess PCl_5 is used during the reaction (*529*).

$$MeN{=}PCl(CCl_3)_2 + 5Cl_2 \rightarrow 3HCl + 2CCl_4 + CCl_3N{=}PCl_3 \quad (120)$$

thermolysis (120°–130°) of $[EtSCCl{-}NPCl_3]^+PCl_6^-$ along with HCl, MeCHClSCl, and PCl_3 (*442*) and by the action of excess PCl_5 on EtSCN or ArSCN (Ar = Ph, *p*-MeC_6H_4, *p*-$O_2NC_6H_4$) (*442*, *443*). It can also be obtained from the reaction of Cl_2CNCl with PCl_3 (*188a*).

$$EtSCN + 4PCl_5 \rightarrow 2HCl + 3PCl_3 + CCl_3N{=}PCl_3 + MeCCl_2SCl \quad (121)$$

Higher aminoalkanesulfonic acids and excess PCl_5 react with partial chlorination of the SO_3H group and formation of the following $RN{=}PCl_3$ compounds (*542*): R = CCl_3CHCl, Me_2CCl_2CHCl, $EtCCl_2CHCl$, and $Me_2CClCHCl$; see also the phosphorylation of nitriles.

Because of the numerous publications in the field, the phosphorylation of nitriles is considered somewhat in detail.

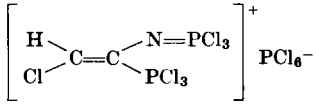
Acetonitrile and chloroacetonitrile give with PCl_5 different products depending on temperature and ratio of the reactants (*425*).

$$MeCN + 2PCl_5 \xrightarrow{20°} HCl + \text{"}NCCH_2PCl_4{\cdot}PCl_5\text{"} \quad (122)$$

$$MeCN + 4PCl_5 \xrightarrow{20°} 3PCl_3 + CCl_3CCl_2N{=}PCl_3 + 3HCl \quad (123)$$

(XX)

Acetonitrile and PCl_5 (2:1) at 80° give an intermediate compound, $CH_2{=}CClN{\cdot}PCl_3$, which may be chlorinated to (XX) (*425*). Other workers (*307*), in contrast, find the action of MeCN and PCl_5 (1:3) at room temperature to give only the ionic compound



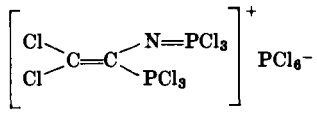
(see Section IV,D,1), which decomposes at 130°–150° to $CCl_2{=}CClN{-}PCl_3$; the same result is found in later work by Shevchenko and Bodnarchuk (*423*).

$$MeCN + 2PCl_5 \xrightarrow{20°} \left[\begin{matrix} H \\ H \end{matrix}\!\!>\!C{=}C<\!\!\begin{matrix} N{=}PCl_3 \\ Cl \end{matrix}\right]^+ PCl_6^- \quad (?) \quad (124)$$

$$MeCN + 3PCl_5 \xrightarrow{20°} \left[\begin{matrix} H \\ Cl \end{matrix}\!\!>\!C{=}C<\!\!\begin{matrix} N{=}PCl_3 \\ PCl_3 \end{matrix}\right]^+ PCl_6^- \xrightarrow[-HCl,\ -PCl_3]{\Delta}$$

$$CCl_2{=}CClN{=}PCl_3 \xleftarrow{\Delta} MeCN + 0.5PCl_5 \quad (125)$$

Chloroacetonitrile and PCl_5 (1:3) react at room temperature to form



which decomposes on heating to give compound (XX) (*307*, *423*). Kirsanov and co-workers describe various products which are obtained by this reaction (*239*, *425*).

$$ClCH_2CN + 0.5PCl_5 \xrightarrow{20°}$$

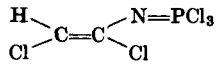
$$ClCH_2CN + PCl_5 \xrightarrow{\Delta} CCl_2{=}CClN{=}PCl_3 \quad (126)$$

$$2ClCH_2CN + 3PCl_5 \xrightarrow{20°}$$

$$ClCH_2CN + 2PCl_5 \xrightarrow{20°} \text{"}ClCH(CN)PCl_4 \cdot PCl_5\text{*"} \quad (127)$$

$$ClCH_2CN + 3PCl_5 \xrightarrow{20°} \text{"}NCCCl_2PCl_4 \cdot PCl_5\text{*"} \xrightarrow[-PCl_3]{\Delta} (XX) \quad (128)$$

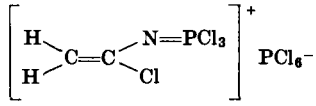
Chloroacetonitrile and PCl_5 (2:1) at elevated temperature give



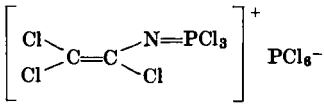
(*307*); fluoroacetonitrile under the same conditions gives $FClCHCCl_2N{=}PCl_3$ (*239*, *280*, *425*).

Phosphorylation of dichloroacetonitrile with PCl_5 (1:0.4) in the cold yields $CCl_2{=}CClN{=}PCl_3$, which upon chlorination with Cl_2 or PCl_5 gives (XX) (*239*, *281*, *307*, *424*); $CCl_2{=}CClN{=}PCl_3$ may also be obtained from

* Rather to be formulated as



and



respectively.

thermolysis of $[Cl_3P{=}NCCl{=}CHPCl_3]^+PCl_6^-$ (Section IV,D,2) (*423*) or by heating $Cl_3P{=}NCCl_2CCl_2POCl_2$ at 150°–170° (*423*).

Compound (XX) is also obtained from $CCl_3CON{=}PCl_3$ and PCl_5 [Eq. (108)] or from $CCl_3CCl{=}NPOCl_2$ and PCl_5 (*424*), as well as from thermo-

$$CCl_3CCl{=}NPOCl_2 + PCl_5 \rightarrow (XX) + POCl_3 \qquad (129)$$

lysis of $[Cl_3P{=}NCCl{=}CClPCl_3]^+PCl_6^-$ besides PCl_3 (*423*). The same compound (XX) is obtained from the interaction of trichloroacetonitrile* and PCl_5 (1:1) at 140°–150° (*291*) and from the chlorination (UV) of $(EtN{=}PCl_3)_2$ (*142*) or $CHCl_2CCl(COCl)N{=}PCl_3$ at 200°–210° (*532*). It results also as a by-product of the reactions of $CHCl(COCl)N{=}PCl_3$ (*532*)

$$CHCl(COCl)N{=}PCl_3 + 2PCl_5 \rightarrow POCl_3 + PCl_3 + HCl + (XX) \qquad (130)$$

and $NCCCl_2CCl_2N{=}PCl_3$ or $CCl_2(CN)_2$ (*290c*) with PCl_5.

The compound $CF_3CCl_2N{=}PCl_3$ is obtained from $CF_3CFClNO$ and PCl_3 (*336*); $(CF_3)_2CClN{=}PCl_3$ results from the chlorination of $(CF_3)_2CHN{=}PCl_3$ (*295*), and $PhCCl{=}CClN{=}PCl_3$ (*239, 281*) and $PhCCl_2CCl_2N{=}PCl_3$ (*239*) have also been described.

Higher nitriles upon reaction with PCl_5 (1:3) at room temperature, give, besides the ionic compounds $[Cl_3P{=}NCCl{=}CRPCl_3]^+PCl_6$ (Section IV,D,1) in 25–45% yield, substances of the formula $RCCl_2N{=}PCl_3$ (R = $MeCCl_2$, $ClCH_2CCl_2$, $EtCCl_2$, $PrCCl_2$, *i*-PrCHCl, $BuCCl_2$, *i*-$BuCCl_2$, $AmCCl_2$) (*445*), which are obtained directly when the reaction is carried out under heating. Contrary to these results other authors (*307*) found only the ionic compound $[MeC(Cl){=}C(PCl_3)N{=}PCl_3]^+PCl_6^-$ in the reaction of propionitrile with PCl_5.

Aromatic-aliphatic cyanides $RC_6H_4CH_2CHClCN$ (R = H, *o*-, *p*-Cl, *p*-Br, *o*-, *p*-NO_2, *m*-, *p*-Me, *p*-MeO) with PCl_5 give $RC_6H_4CH_2CCl_2CCl_2N{=}PCl_3$ directly (*444a*).

$$RC_6H_4CH_2CHClCN + 2PCl_5 \rightarrow HCl + PCl_3 + RC_6H_4CH_2CCl_2CCl_2N{=}PCl_3 \qquad (131)$$

Isopropylcyanide and PCl_5 give, besides HCl, PCl_3, and Me_2CClCN, poor yields of $Me_2C{=}CClN{=}PCl_3$ (*432*); excess of PCl_5 produces $Me_2CClCCl_2N{=}PCl_3$ (*307, 432*).

Other secondary nitriles with PCl_5 (1:2) give $MeRCClCCl_2N{=}PCl_3$ (R = $ClCH_2$, CH_2Br, Et) (*432*) via a postulated ionic compound. Excess PCl_5 and isopropylamine [the equimolar reaction follows the usual route (*185*)] produce various compounds (*530*).

* Trichloroacetonitrile with $SbCl_5$ gives only the adduct $CCl_3CN \cdot SbCl_5$ (*125*).

$$i\text{-PrNH}_3\text{Cl} + 4\text{–}6\text{PCl}_5 \longrightarrow \underset{(9\text{–}60\%)}{\text{CCl}_2{=}\text{C(CHCl}_2\text{)N}{=}\text{PCl}_3} \xrightarrow{\text{Cl}_2} \text{CCl}_3\text{CCl(CHCl}_2\text{)N}{=}\text{PCl}_3$$

$$\downarrow \; 170°\text{–}180°,\ -\text{HCl}$$

$$i\text{-PrNH}_3\text{Cl} + 7\text{PCl}_5 \longrightarrow \underset{(25\%)}{\text{CCl}_2{=}\text{C(CCl}_3\text{)N}{=}\text{PCl}_3} \qquad (132)$$

$$\downarrow \; \text{Cl}_2\ (20°),\ \text{PCl}_5\ (160°\text{–}170°)$$

$$i\text{-PrNH}_3\text{Cl} + 8\text{PCl}_5 \longrightarrow \underset{(18\%)}{(\text{CCl}_3)_2\text{CClN}{=}\text{PCl}_3}$$

The compound $Cl_2P(O)CCl_2CCl_2N{=}PCl_3$ is prepared (*59*) according to Eqs. (133)–(135).

$$(\text{EtO})_2\text{P(O)CCl}_2\text{CN} + 3\text{PCl}_5 \rightarrow \text{Cl}_2\text{P(O)CCl}_2\text{CCl}_2\text{N}{=}\text{PCl}_3 + 2\text{POCl}_3 + 2\text{EtCl} \quad (133)$$

$$\text{Cl}_2\text{P(O)CCl}_2\text{CN} + \text{PCl}_5 \rightarrow \text{Cl}_2\text{P(O)CCl}_2\text{CCl}_2\text{N}{=}\text{PCl}_3 \quad (134)$$

$$(\text{EtO})_2\text{P(O)CH}_2\text{CN} + 5\text{PCl}_5 \rightarrow$$

$$\text{Cl}_2\text{P(O)CCl}_2\text{CCl}_2\text{N}{=}\text{PCl}_3 + 2\text{POCl}_3 + 2\text{PCl}_3 + 2\text{EtCl} + 2\text{HCl} \quad (135)$$

α-Cyanoamine hydrochlorides $RR'C(CN)NH_3Cl$ react with PCl_5 to form either monomeric or dimeric compounds $(RR'C(CN)N{=}PCl_3)_n$ ($n = 1, 2$) [R = Me, Et; R′ = Me, Et; RR′ = $(CH_2)_4$, $(CH_2)_5$] (*362*). The monomeric species may also be prepared from α-*N*,*N*-dichloroaminonitriles (*365*).

$$RR'C(CN)NCl_2 + PCl_5 \rightarrow RR'C(CN)N{=}PCl_3 + 2Cl_2 \quad (136)$$

The reaction of $RR'C(CN)NH_2R''Cl$ and PCl_5 gives a five-membered ring (*364*).

$$\underset{\text{R''NH}_2\text{Cl}}{\overset{\text{RR'CCN}}{|}} + \text{PCl}_5 \longrightarrow \underset{\text{Cl}_3}{\overset{\text{RR'C}\text{——}\text{CCl}}{\underset{\text{R''N}\diagdown\text{P}\diagup\text{N}}{|\quad\quad\|}}} + 2\text{HCl} \quad (137)$$

R = R′ = R″ = Me; R = R′ = Me, R″ = Et, Bu
R = R″ = Me, R′ = Et; R = R′ = $(CH_2)_5$, R″ = Me

The aminonitriles $RArC(CN)NH_2$ (R = Me, Et, Pr, *i*-Pr, Bu, Ar = Ph; R = Me, Ar = *p*-MeC_6H_4, *p*-ClC_6H_4, 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$) with PCl_5 yield the monomeric compounds $R(Ar)C(CN)N{=}PCl_3$ (*363*). With R = Me and Ar = Ph the dimer can also be isolated in small yields (3–5%). $ArCH{=}C(CN)CONH_2$ and PCl_5 yield $ArCH{=}C(CN)CON{=}PCl_3$

(*427b*). The reaction of enamines $XYC=C(R)NH_2$ (X = Y = COOR, CN or X = COOR, Y = CN, COMe; R = $CHCl_2$, CCl_3, CF_3) with $PhPCl_4$, $MePCl_4$, and Ph_2PCl_3 has been described (*57a*).

β-Cyanoamine hydrochlorides and PCl_5 give the following reactions (*361a*):

$$NCCH_2CH_2NH_3Cl + 4PCl_5 \longrightarrow 5HCl + 2PCl_3 + Cl_3P{=}NCCl_2CCl_2CH_2N{=}PCl_3$$

$$\downarrow \Delta$$

$$PCl_5 + NCCCl_2CH_2N{=}PCl_3 \qquad (138)$$

$$\downarrow Cl_2$$

$$NCCCl_2CCl_2N{=}PCl_3$$

$$NCCH_2CH_2N(Ph)H_2Cl + 4PCl_5 \longrightarrow 5HCl + 2PCl_3 + \left[\begin{array}{c} Cl \\ C{=}N \\ HC \\ C{-}N \\ Cl\ Ph \end{array}\right]^{+} PCl_6^- \qquad (139)$$

$$\downarrow -HCl, -PCl_3,\ 130°$$

$$PhN{=}CClCCl_2CCl_2N{=}PCl_3 \xleftarrow{Cl_2} PhN{=}CCl{-}CCl{=}CClN{=}PCl_3$$

$$NCCH_2CH_2N(C_6H_4Cl\text{-}p)H_2Cl + 4PCl_5 \xrightarrow[-HCl,\ -PCl_3]{}$$

$$x\ p\text{-}ClC_6H_4N{=}CClCCl{=}CClN{=}PCl_3 + y(p\text{-}ClC_6H_4N{=}PCl_3)_2 \qquad (140)$$

The phosphorylation of *N*-alkyl(aryl)-3-aminopropionitriles has been described recently (*292a*).

The CH_2 groups of the alkoxynitriles are partially chlorinated by PCl_5 at elevated temperatures and the amine group shows the normal reaction to form $ROCH_2CCl_2CCl_2N{=}PCl_3$ (R = Pr, Bu, Ph). Heating to 175° gives $ClCH_2CCl_2CCl_2N{=}PCl_3$; the latter compound is also obtained from $MeOCH_2CH_2CN$ and excess of PCl_5 via the intermediate formation of $ClCH_2CH_2CN$ (*439*).

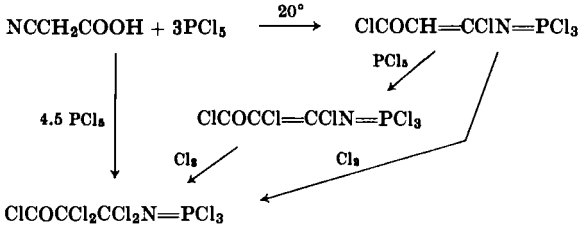
$$ROCH_2CH_2CN + 3PCl_5 \rightarrow ROCH_2CCl_2CCl_2N{=}PCl_3 + 2HCl + PCl_3 \qquad (141)$$

$$MeOCH_2CH_2CN + 4PCl_5 \xrightarrow{\Delta} ClCH_2CCl_2CCl_2N{=}PCl_3 + MeCl + 2PCl_3 + POCl_3 + 2HCl \qquad (142)$$

The similar reaction of $EtOCH_2CH_2CN$ and PCl_5 gives intractable mixtures of $EtOCH_2CCl_2CCl_2N{=}PCl_3$ and $ClCH_2CCl_2CCl_2N\ PCl_3$ (*439*).

Aminoacetic acid reacts with a twofold excess of PCl_5 with chlorination of the carboxyl group and Kirsanov reaction on the amine side to give $(ClCOCH_2N{=}PCl_3)_2$ (*531*, *532*) and $CHCl(COCl)N{=}PCl_3$ (*532*). The former compound with excess PCl_5 gives $ClCOCHClN{=}PCl_3$, which may also be obtained directly from glycine and PCl_5 (1 : 3) (*531*, *532*). Further chlorination at 160°–170° yields $CCl_2(COCl)N{=}PCl_3$ (*532*). α-Amino acids $RCH(NH_2)COOH$ (R = Me, Et) give upon phosphorylation (1 : 4–6 PCl_5) $MeCHClCCl(COCl)N{=}PCl_3$ or $CHCl{=}C(COCl)N{=}PCl_3$ and $CHCl_2CCl(COCl)N{=}PCl_3$, respectively (*530–532*). Higher α-amino acids (α-methylalanine, valine, leucine) give $Me_2C(COCl)N{=}PCl_3$, $Me_2CClCCl(COCl)N{=}PCl_3$, and $i\text{-}PrCCl_2CCl(COCl)N{=}PCl_3$, respectively (*532*).

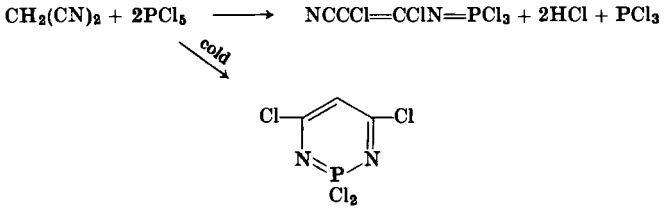
Cyanoacetic acid and PCl_5 at room temperature yield $ClCOCH{=}CClN{=}PCl_3$; on heating or with excess PCl_5 $ClCOCCl{=}CClN{=}PCl_3$ is obtained. The chlorination (PCl_5 or Cl_2) of these two latter compounds gives $ClCOCCl_2CCl_2N{=}PCl_3$ (*429*).



(143)

α-Cyanocarbonic acids $RCH(CN)COOH$ with PCl_5 give in the initial step $RCH(CN)COCl$ and then $RC(COCl){=}CClN{=}PCl_3$ (R = Me), whereas excess PCl_5 produces $RCCl(COCl)CCl_2N{=}PCl_3$ (R = Me, Et, Pr, *i*-Pr) (*431*). The compounds $(EtO)_2P(O)CH_2CN$ and $(EtO)_2P(O)CCl_2CN$ with excess PCl_5 give $Cl_2P(O)CCl_2CCl_2N{=}PCl_3$ (*59*) [Eqs. (133–135)].

Malonic dinitrile and PCl_5 (1 : 1) give 1,1,3,5-tetrachloro-1,2,6-phosphadiazine (*239*), whereas with a 3 : 2 ratio at elevated temperatures besides HCl and small amounts of 1,1,3,4,5-pentachloro-1,2,6-phosphadiazine, the compound $NCCH{=}CClN{=}PCl_3$ is obtained (*239*, *430*). A



(144)

higher ratio of PCl_5 (1:2) at elevated temperatures produces $NCCCl{=}CClN{=}PCl_3$; chlorination (Cl_2 or PCl_5) of both linear compounds leads to $NCCCl_2CCl_2N{=}PCl_3$ (*430*).

Alkylmalonic dinitriles react with PCl_5 (2:1) to form 1,1,3,5-tetrachloro-4-alkyl-1,2,6-phosphadiazines and $RC(CN){=}CClN{=}PCl_3$ (R = Me, Et, Pr, *i*-Pr, Bu) (*428*); chlorination of these phosphazotrichlorides results in $RCCl(CN)CCl_2N{=}PCl_3$. Other substituted malonic dinitriles $R_2C(CN)_2$ (R = Me, Et, Pr, Cl) with PCl_5 give $R_2C(CN)CCl_2N{=}PCl_3$ (*290c*).

$$R_2C(CN)_2 \xrightarrow{PCl_5} [R_2C(CN)CCl{=}NPCl_3]^+ PCl_6^- \xrightarrow{PCl_5} R_2C(CN)CCl_2N{=}PCl_3 \qquad (145)$$

Phosphorylation (PCl_5) of 1,1-dicyano-2-amino-2-arylethylenes, $(NC)_2C{=}CArNH_2$ (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$) also yields cyclic compounds (*290a*).

Succinic acid dinitrile and PCl_5 undergo a ring closure to form (XXI) (*436*); the same compound is obtained starting from fumaric acid dinitrile (1:3) (*436*, *441*) or chloromaleinic acid dinitrile and PCl_5 (1:2) (*436*).

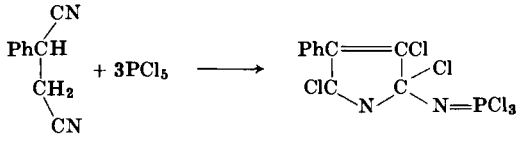
$$(CH_2CN)_2 + 4PCl_5 \longrightarrow 4HCl + \text{(XXI)}^{*} + 3PCl_3 \qquad (146)$$

(XXI)

$$\underset{\text{fumaric acid dinitrile}}{NCCH{=}CHCN} + 3PCl_5 \longrightarrow \text{(XXI)} + 2HCl + 2PCl_3 \qquad (147)$$

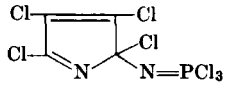
$$\underset{\text{chloromaleinic acid dinitrile}}{NCCCl{=}CHCN} + 2PCl_5 \longrightarrow \text{(XXI)} + HCl + PCl_3 \qquad (148)$$

Phenylsuccinic acid dinitrile (*441*) and other derivatives $RR'C(CN)\text{-}CH_2CN$ [R = Ph, R' = H (*441*); R = Me, R' = Me, Et, Bu, *sec*-Bu, Ph; R = R' = Et, Pr; RR' = $(CH_2)_4$, $(CH_2)_5$ (*441a*)] also give five-membered rings.

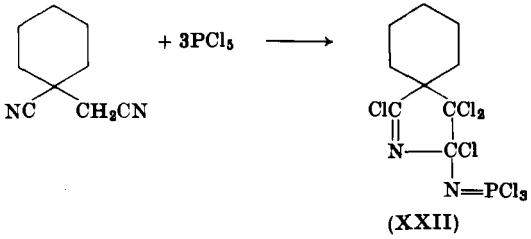


(149)

* Better formulated as



A spiro compound (XXII) is obtained (*441*) from Eq. (150).

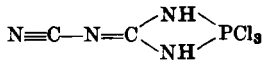


(150)

(XXII)

It is interesting to note that other derivatives of maleinic acid, i.e., $RR'C{=}CR''NH_2$, react with PCl_5 only to give $RR'C{=}CR''NHCl$ (R, R′ = EtOCO, R″ = CCl_3) (*58*).

The reaction of dicyandiamide with PCl_5 (1:2) gives via the postulated intermediates



(*26b*, *207*) and $NCN{=}C(Cl)NHPCl_3N{=}PCl_3$ a compound $C_2H_4P_2Cl_6$ [2-(trichlorophosphazyl)-2,4,6-trichloro-2-phospha-1,3,5-triazine] (Section V,A), also described by other authors (*110*); the corresponding hydrochloride may also be isolated (*26b*).

Other trichlorophosphazoalkyls are obtained from the phosphorylation (PCl_5) of amidines: while only 1:1 adduct formation between trichloroacetamidine $CCl_3(=NH)NH_2$ and PCl_5 occurs, the corresponding *N*-alkyl- or *N*-aryltrichloroacetamidines or their hydrochlorides react with PCl_5 in the expected manner.

$$CCl_3C(=NR)NH_2 + PCl_5 \rightarrow CCl_3C(=NR)N{=}PCl_3 + 2HCl \qquad (151)$$

R = Me, Et, $PhCH_2$ (*118*), Bu, $COCCl_3$, $MeP(O)NMe_2$, $POCl_2$ (*120*), Ph (*116a*, *121*), *p*-MeC_6H_4, *p*-BrC_6H_4, *p*-$MeOC_6H_4$ (*121*)

Compounds $CF_3C(=NPh)N{=}PCl_3$ (*120*) and $PhC[=NP(O)(OPh)_2]N{=}PCl_3$ (*84*) have also been described.

For the reaction of amidinium salts with PCl_5, see Section IV,C,1.

N-Sulfonylarylamidines and PCl_5 yield the phosphazo compounds.

$$ArC(=NSO_2Ar')NH_2 + PCl_5 \rightarrow ArC(=NSO_2Ar')N{=}PCl_3 + 2HCl \qquad (152)$$

Ar = Ph, Ar′ = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*84*)

Ar = *p*-$O_2NC_6H_4$, Ar′ = Ph (*87*)

Contrary to the reactions above, *N*-carbonylarylamidines $ArC(=NCOAr')NH_2$ do not form the phosphazo compound, but (with a

probable intramolecular rearrangement) only phosphorylated amidines $ArC(=NPOCl_2)N{=}CClAr'$ (Ar = Ph, *p*-BrC_6H_4, Ar' = Ph, *p*-MeC_6H_4,

$$ArC(=NCOAr')NH_2 + PCl_5 \rightarrow ArC(=NPOCl_2)N{=}CClAr' + 2HCl \quad (153)$$

p-BrC_6H_4), which decompose upon heating to form $ArC(=NPOCl_2)Cl$ and Ar'CN (*101*).

Kirsanov and co-workers (*115*, *116*) also report the reaction of *N*-arylureas $ArNHCONH_2$ (Ar = Ph, *p*-ClC_6H_4, *p*-MeC_6H_4) with PCl_5 at room temperature to yield, via $ArNHCON{=}PCl_3$ and subsequent rearrangement, phosphorylated formamidines (see also Section VII, A).

$$ArNHCONH_2 + PCl_5 \xrightarrow{18°-20°} ArNHC(=NPOCl_2)Cl + 2HCl \quad (154)$$

Introduction of a sulfonyl group, i.e., with $ArSO_2NHCONH_2$ (Ar = Ph, *p*-$O_2NC_6H_4$), leads to phosphazotrichlorides (*80*).

$$ArSO_2NHCONH_2 + 2PCl_5 \rightarrow ArSO_2N{=}C(Cl)N{=}PCl_3 + POCl_3 + 3HCl \quad (155)$$

An analogous reaction has been described (*81*).

Similarly, *N*-chloroalkylamidines give with $(ArO)_3P$, $(PhO)_2PCl$, $PhOPCl_2$, or PCl_3 the substances $RC(=NH)N{=}P(OAr)_nCl_{3-n}$ (R = Me, CCl_3; Ar = Ph, *p*-ClC_6H_4; *n* = 1, 2, 3) (*103*). Variation of the method leads to $ROC(=NH)N{=}PCl_3$ [(*257*), see also (*114*)].

When dinitriles of higher dicarbonic acids are heated with excess PCl_5, they react at both nitrile groups and with partial chlorination of the methylene groups (*437*).

$$NC(CH_2)_mCN \xrightarrow{\text{excess } PCl_5} Cl_3P{=}NCCl_2(CH_2)_nCCl_2CCl_2N{=}PCl_3 \quad (156)$$

$$m = 2\text{–}6;\ n = 1\text{–}5$$

Other dinitriles *o*-, *m*-, *p*-$C_6H_4(CH_2CN)_2$ give *o*-, *m*-, *p*-$C_6H_4(CCl_2CCl_2N{=}PCl_3)_2$ (*427c*), whereas dinitriles of the type $NCCH(Ph)CH_2CH_2CN$ react only at one cyanide group with PCl_5 (*427b*).

$$NCCH(Ph)CH_2CH_2CN + 4PCl_5 \rightarrow$$
$$3HCl + 3PCl_3 + NCCCl(Ph)CH_2CCl_2CCl_2N{=}PCl_3 \quad (157)$$

Both nitrile groups are attacked in $NCCH_2CH(Ph)CH_2CN$ (*427b*).

$$NCCH_2CH(Ph)CH_2CN + 4PCl_5 \rightarrow$$
$$Cl_3P{=}NCCl_2CHClCH(Ph)CHClCCl_2N{=}PCl_3 + 2HCl + 3PCl_3 \quad (158)$$

Bis(trichlorophosphazo)tetrachloroethane $(CCl_2N{=}PCl_3)_2$ is obtained from isothiocyanic acid and PCl_5 (*41*); 3-aminopropionitrile and PCl_5 give $Cl_3P{=}NCCl_2CCl_2CH_2N{=}PCl_3$ (*297c*).

$$NCCH_2CH_2NH_3Cl + 4PCl_5 \rightarrow Cl_3P{=}NCCl_2CCl_2CH_2N{=}PCl_3 + 4HCl + 2PCl_3 \quad (159)$$

Phenyldichlorophosphazopolychloroalkenes have been obtained recently (*59a*). Only one amino group in $(CF_3)_2C(NH_2)_2$ reacts with $MePF_4$ to give $(CF_3)_2(NH_2)CN{=}PMeF_2$ (*143a*).

Finally, $Cl_3P{=}NSO_2(CH_2)_2N{=}PCl_3$ (*542*) can also be considered as a sulfonylphosphazotrichloride (see Section VI, A).

2. *Reactions*

Heating of $(MeN{=}PCl_3)_2$ should result in monomerization (*186*); this is in accordance with the reaction with phenylisocyanate at 150° producing an unsymmetrical carbodiimide (*494*). Milder conditions give ring enlargement (*305*) to the six-membered ring compound (XXIII), also obtained in other ways (*299*, *300*, *304*) (Section IX). It is interesting to note that $(MeN{=}PPhCl_2)_2$ and $(MeN{=}PPh_2Cl)_2$ with methylisocyanate

$$(MeN{=}PCl_3)_2 + 6MeNCO \longrightarrow \text{(XXIII)} + \text{by-products} \quad (160)$$

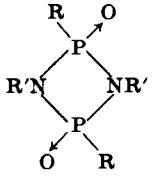
lead only to the formation of $PhPOCl_2$ and Ph_2POCl, respectively (*196*). Reaction of $(MeN{=}PCl_3)_2$ with CO_2 and CS_2 gives the corresponding isocyanates and isothiocyanates, respectively (*494*).

$$\text{(XXIII)} \xrightarrow{SO_2,\ -SOCl_2} \text{(XXIV)} \xrightarrow{H_2S,\ -HCl} \text{(XXV)} \quad (161)$$

The P–N ring system is preserved in the interaction of $(MeN{=}PCl_3)_2$ with SO_2 and H_2S giving (XXIV) (2,4-dioxo-2,4-dichloro-1,3-dimethyl-1,3,2,4-diazadiphosphetidine) and the thio analog (XXV), respectively [(*32*, *181*), cf. also (*297a*)].

The compounds $(EtN{=}PCl_3)_2$ and $(PrN{=}PCl_3)_2$ (*181*) react similarly with liquid SO_2, as does $P_4(NMe)_6Cl_8$ (*32*) with SO_2 or H_2S to give the group $>P\begin{matrix}Cl\\ \diagdown X\end{matrix}$ (X = O, S).

Analogous compounds to (XXIV)



R = PhO, R′ = Me (*52*)

R = $C_6H_{11}O$, R′ = C_6H_{11} (*54*)

R = Bu, R′ = p-ClC_6H_4, $PhCH_2$; R = $Cl(CH_2)_4$, R′ = p-$MeSC_6H_4$, m-, p-ClC_6H_4 (*193*)

R = Me, C_6H_{11}, Ph, $PhCH_2$; R′ = Et, Ph, $PhCH_2$ (*53*)

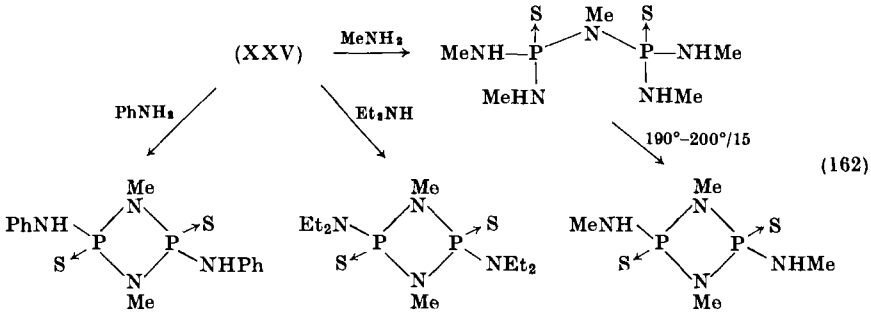
have generally been prepared from the amine and a phosphoric ester dichloride or phosphonic dichloride. Other compounds $[R'NP(O)R]_2$ (R = Me_2N, Et_2N, PhNH; R′ = Ph, p-BrC_6H_4, p-MeC_6H_4, p-$MeOC_6H_4$) are isolated from the thermolysis of phosphoric trianilide or from the reaction of phosphoric trianilide or phenylphosphonic dianilide with phosphoric tris(dialkylamides) [(*216*), cf. also (*359*)]. Chain polymers with four-membered P–N ring units are known (*348*, *358*, *359*).

Similar compounds to (XXV), $[R'NP(S)R]_2$, result from the thermal degradation of R′NHP(S)RCl (R = Me, R′ = Me, Et, Ph, p-MeC_6H_4, m-, p-ClC_6H_4, p-$MeOC_6H_4$, p-$EtOC_6H_4$; R = Ph, R′ = Me, i-Pr, Ph, p-$EtOC_6H_4$) (*333*). Elimination of amine from $PhP(S)(NHR)_2$ [R = $PhCH_2$ (*492*), Me (*201*, *492*), Et,* Pr, Bu (*201*)] results in formation of the corresponding diazadiphosphetidines; with R = H the corresponding $[PhP(S)NH]_2$ can only be isolated as a by-product (*419*).

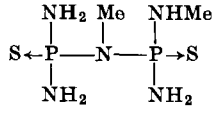
Some of the above-mentioned compounds have previously been described by Michaelis (*334*, *335*) ("phosphazoles") and a monomeric or a dimeric form was assigned to them. Bock and Wiegräbe, however (*57*), showed that only the dimeric form is present [see also (*63*)].

* With R = Et, the *cis*- and *trans*-1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazanes have been observed (*152*).

Of some interest are further reactions of (XXV) with replacement of the two chlorine atoms (*32*).



The interaction of (XXV) with ethanol also gives substitution without affecting the P–N ring system (*391*). Linkage with catechol, resorcinol, hydrochinone, and their derivatives gives chainlike, thermally quite stable polymers which still contain some four-membered rings (*197*). The ammonolysis of (XXV) yields (XXVI) (*391*), the structure of which



has been established (*553*).

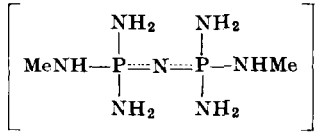
The compounds (XXIV) and (XXV) react with MeNCO to form six-membered ring compounds [analogous to (XXIII) (*305*)]. Dimethylamino or thiomethyl groups are introduced by the action of (XXIV) with Me_3SiNMe_2 or Me_3SiSMe, respectively (*181*); azide groups may also be introduced (*196c*).

The ammonolysis of $(MeN{=}PCl_3)_2$ (and its higher homologs) with liquid ammonia (*185*) gives in the case of the methyl compound an ionic product $C_2H_{16}N_7P_2Cl$ (XXVII), to which a symmetrical structure (XXVIIa) (as for the phenyl compound) was assigned.

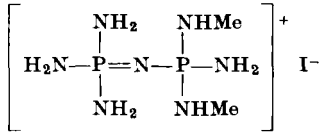
$$(MeN{=}PCl_3)_2 + 10NH_3 \rightarrow (XXVII) + 5NH_4Cl \qquad (163)$$

Ziegler (*550*, *551*) carried out an X-ray investigation of the iodide (*391*) and rather surprisingly found an unsymmetrical structure (XXVIIb). Evidence for both the symmetrical structure (mechanism, ^{31}P NMR spectrum) and the unsymmetrical structure of the iodide (X-ray investigation) is available, and a definitive answer concerning the structure is not yet possible. An ammonolysis mechanism formerly suggested (*185*)

has now been given up in favor of another involving the intermediate formation of a tetraminophosphonium salt (*501*).



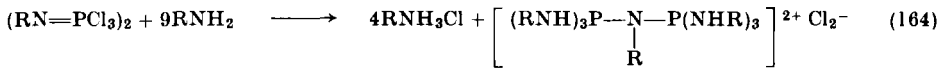
(XXVIIa)



(XXVIIb)

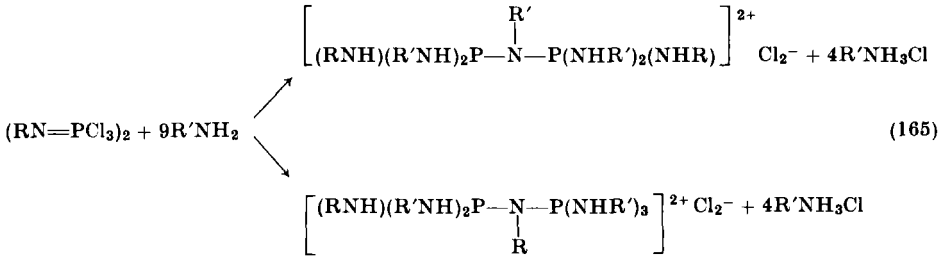
Ammonolysis of $(RN{=}PCl_3)_2$ (R = Me, Ph) with NH_4Cl at 180° yields high polymers of the proposed formulas $[P(=NR)ClNH]_n$ (*525b*).

The similar reactions of $(RN{=}PCl_3)_2$ with primary amines have been described (*143*).



(164)

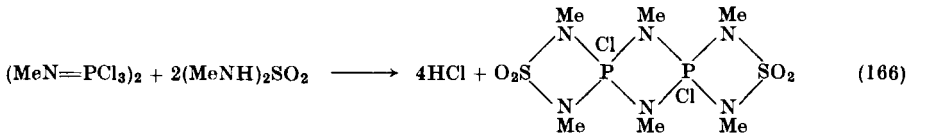
R = Pr, Bu, *i*-Bu



(165)

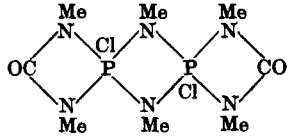
R = Et, Pr, Bu, *i*-Bu; R′ = Et, Bu, *i*-Bu (some salts as iodides)

The attempted isolation of $MeN{=}P(NMe_2)_3$ [by aminolysis of $(MeN{=}PCl_3)_2$ with Me_2NH] failed (*45*, *187*); this compound has only been prepared by an azide–phosphine reaction (*187*). The compound $Et_2CHN{=}PCl_3$ with $MeNH_2$ (1 : 5) gives the salt $(Et_2CHNH)(MeNH)_3PCl$ (*143*). It is found that $(MeN{=}PCl_3)_2$ gives with *N*,*N*′-dimethylsulfamide (*36b*, *37*, *510*) a compound containing three four-membered rings [Eq. (166)].



(166)

With *N,N'*-dimethylurea



is similarly obtained (*36a*). In the reaction between $(MeN{=}PCl_3)_2$ and NaN_3 the hexazide is formed (*196c*); with NH_4NCS correspondingly the hexaisothiocyanate results (*51b*).

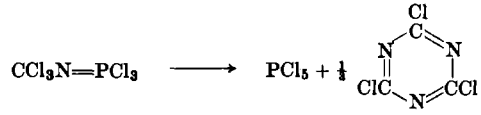
Interaction of $(MeN{=}PCl_3)_2$ and $Cr(CO)_6$ yields a blue-red product $(OC)_4Cr(MeN{=}PCl_3)_2$, which on thermal degradation gives a polymer $(Cr_7P_5N_2)_x$ (*198*).

Chlorination (UV) of $(MeN{=}PCl_3)_2$ gives $CCl_3N{=}PCl_3$ (*142, 294*). Fluorination with Na_2SiF_6 gives both $(MeN{=}PF_3)_2$ and partially fluorinated compounds (for these, see Section VIII,C); with KSO_2F (*187*) $(MeN{=}PF_3)_2$ is obtained. Fluorination of $(RN{=}PCl_3)_2$ [R = Me (*142, 294*), Et, Pr (*142*)] with SbF_3 leads to the corresponding hexafluorodiazadiphosphetidines; $(BuN{=}PCl_3)_2$ and $(i\text{-}BuN{=}PCl_3)_2$ were fluorinated with AsF_3 to the corresponding fluoro compounds (*142*).

Hydrolysis of higher alkylphosphazotrichlorides $RN{=}PCl_3$ [R = Me_3C (*527c, 533*), Me_3CCH_2, Et_2CH, $ClCMe_2CH_2$, $CCl_2{=}C(CHCl_2)$, $CCl_2{=}CCCl_3$, $ClCMe_2CHCl$, Me_3CCCl_2CHCl, ClCOCHCl, $CHCl_2CCl(COCl)$ (*533*)] with moist air, formic acid, or acetic acid leads to the corresponding alkylaminophosphonic acid dichlorides. $ClCMe_2CH{=}NPOCl_2$ is obtained by elimination of HCl from $ClCMe_2CHClNHPOCl_2$; $ClCMe_2CH{=}NPOCl_2$ and $Me_3CCCl_2CH{=}NPOCl_2$ are formed from $ClCMe_2CHClN{=}PCl_3$ and $Me_3CCCl_2CHClN{=}PCl_3$ with SO_2 at 140°–150°, respectively (*533*).

Finally, the compounds $MeN{=}P(OEt)_3$ (*187*) (phosphine–azide reaction) and $(CF_3)_3CN{=}PPh_3$ and $(CF_3)_3CN{=}P(OEt)_3$, prepared from Ph_3P or $(EtO)_3P$ with $(CF_3)_3CNO$ (*336*), are known.

The reactions of the phosphorylation products of nitriles are well studied. $CCl_3N{=}PCl_3$ decomposes at room temperature, at a faster rate at 150° to cyanuric chloride and PCl_5 (*162*):



(167)

With SO_2 at room temperature $CCl_2{=}NPOCl_2$ is obtained (*294, 442*), whereas compound (XX) reacts analogously only at 180°–200° (*442*).

Other perchloroalkylphosphazotrichlorides $RCCl_2N{=}PCl_3$ [R = $MeCCl_2$, $ClCH_2CCl_2$, $EtCCl_2$, $PrCCl_2$, *i*-PrCHCl, $BuCCl_2$, *i*-$BuCCl_2$,

$AmCCl_2$ (*445*), Me_2CCl (*432*)] give (180°–220°) the corresponding chlorinated nitriles, PCl_5, HCl, and PCl_3 on thermolysis (*445*).

ω-Cyanoalkylphosphazotrichlorides (from malonic acid dinitriles and PCl_5) undergo an intermolecular ring closure to form six-membered rings upon heating (*430*).

Hydrolysis of $CCl_2{=}C(CHCl_2)N{=}PCl_3$ or $CCl_2{=}C(CCl_3)N{=}PCl_3$ with excess water produces $(CHCl_2)_2CO$ or $CHCl_2COCCl_3$ (*530*), respectively. A mechanism has been suggested [(*445*), cf. also (*442*)] which involves fission of the P=N bond leading finally to chlorinated nitriles.

A unique feature is observed in the controlled hydrolysis (formic or acetic acid, or, in some cases, SO_2) of perchloroalkylphosphazotrichlorides; no formation of $-CCl_2NHPOCl_2-$ from $-CCl_2N{=}PCl_3$ occurs, but the $\diagdown C{=}NPOCl_2$ group is formed instead, with intermolecular elimination of HCl.

$$RCCl_2CCl_2N{=}PCl_3 \xrightarrow{MeCOOH,\ HCOOH,\ SO_2} RCCl_2CCl{=}NPOCl_2 \qquad (168)$$

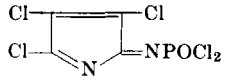
R = Cl (*290c*, *445*), $ClCH_2$, Me, Et, Pr, Bu, *i*-Bu, Am (*445*), COCl (*429*)

It is interesting to note that β-cyanoperchloroalkylphosphazotrichlorides react in the same way (*428*).

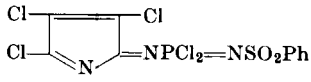
$$RCCl(CN)CCl_2N{=}PCl_3 \xrightarrow{MeCOOH} RCCl(CN)CCl{=}NPOCl_2 \qquad (169)$$

R = Me, Et, Pr, *i*-Pr, Bu

Compound (XXI) gives upon acidolysis (acetic acid) or with SO_2 the compound



(*436*), but compound (XXII) reacts with formation of a $-NHPOCl_2$ group (*441*). Action of $PhSO_2NH_2$ on (XXI) leads to



(*436*).

Alcoholysis of $CCl_3CCl_2N{=}PCl_3$ (XX) with 1 mole of ROH (R = Bu, n-C_8H_{17}) leads to $CCl_3CCl_2N{=}PCl_2OR$; with 3 moles of ROH the diesters $CCl_3CCl{=}NPO(OR)_2$ or $CCl_3C(OR){=}NPO(OR)Cl$ (R = Me, Et, Pr, Bu, *i*-Bu, Am, *i*-Am) are obtained (*433*). The reaction at 80° gives with (XX) only the orthoesters $CCl_3C(OR)_3$ (R = Me, Et, Pr, Bu, Am), not decomposed even upon distillation (*434*). Higher phosphazo compounds $RCCl_2CCl_2N{=}PCl_3$ (R = Et, Pr) with 1 mole of R'OH eliminate R'Cl and

give only $RCCl_2CCl{=}NPOCl_2$; with a molar ratio of 1:3 the diesters $RCCl_2CCl{=}NPO(OR')_2$ (R = R' = Me, Et; R = Et, R' = Pr) (*435*) are obtained. A 1:4 ratio leads at room temperature to $\cdot RCCl_2C(OR'){=}NPO(OR')_2$ (R = Me, Et, Pr; R' = Me, Et, Pr, Bu); a tenfold excess of alcohol gives in addition to NH_4Cl only $RCCl_2COOR'$ (R = R' = Me, Et, Pr) (*435*), also obtained from $RCCl_2C(OR'){=}NPO(OR')_2$ and HCl. However, the reaction of $RCCl_2N{=}PCl_3$ (R = CCl_3, $MeCCl_2$, $EtCCl_2$, $PrCCl_2$) with phenols XC_6H_4OH (X = H, *p*-Cl, *m*-NO_2, *p*-Me) gives $RCCl_2N{=}P(OC_6H_4X)_3$ (*435b*).

α-Cyanoalkylphosphazotrichlorides $RR'C(CN)N{=}PCl_3$ hydrolyze to $RR'C(CN)NHPOCl_2$ [R = R' = Me, Et; RR' = $(CH_2)_4$, $(CH_2)_5$ (*362*); R = Et, Pr, *i*-Pr, Bu, R' = Ph; R = Me, R' = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$ (*363*)]. With excess water the free amines $RR'C(CONH_2)NH_3Cl$ are obtained as salts.

The action of arenesulfonamides on $CCl_3CCl_2N{=}PCl_3$ (XX) leads to $ArSO_2N{=}C(CCl_3)N{=}PCl_3$ (Ar = Ph, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-MeC_6H_4, *m*-, *p*-$O_2NC_6H_4$, 4-Cl,3-$O_2NC_6H_4$, 2-$C_{10}H_7$) (*297e*) which hydrolyze to $ArSO_2N{=}C(CCl_3)NHPOCl_2$; the reaction of (XX) with carboxylic amides was recently described (*297c*). Reaction of (XX) with DMF gives the compound $Me_2NCH{=}NPOCl_2$ (*297d*).

The alcoholysis of 2,4,4,5-tetrachloro-5-(trichlorophosphazo)-3,3-dialkylpyrrolidines is briefly described (*435a*).

Ethylenimino derivatives of substituted phenyldichlorophosphazovinyls have been described recently (*369b*).

The reactions of the phosphorylated amidines follow the usual pattern: hydrolysis with HCOOH (or acetic acid) of $RC(=NR')N{=}PCl_3$ gives $RC(=NR')NHPOCl_2$ [R = CCl_3, R' = Bu, $COCCl_3$, $MeP(O)NMe_2$, $POCl_2$ (*120*); R = CF_3, R' = Ph (*120*); R = CCl_3, R' = Ph, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, *p*-BrC_6H_4 (*121*); R = Ph, R' = $P(O)(OPh)_2$ (*84*)]. The same results are obtained for $PhC(=NSO_2Ar)N{=}PCl_3$ [Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$ (*84*)], but reaction with water leads to phosphoric acid, HCl, and the corresponding amidine. However, $PhC(=NH)N{=}PCl_3$ and acetic acid yield only $PhC(=NPO(OH)Cl)NH_2$ (*103*).

Reaction of $CCl_3C(=NAr)N{=}PCl_3$ with Ar'OH [Ar' = Ph, *p*-ClC_6H_4 (*121*)] gives the triesters; analogously *p*-$O_2NC_6H_4C(=NSO_2Ph)N{=}P(OPh)_3$ has been prepared (*87*), as well as $PhC(=NSO_2Ar)N{=}P(OAr')_3$ (Ar = Ph, *p*-MeC_6H_4; Ar' = Ph, *p*-ClC_6H_4; Ar = *p*-ClC_6H_4, Ar' = Ph) (*85*), which hydrolyze to $PhC(=NSO_2Ar)NHPO(OAr')_2$.

Primary amines react with $PhC(=NSO_2Ar)N{=}PCl_3$ to $PhC(=NSO_2Ar)N{=}P(NHAr')_3$ (Ar = Ph, *p*-MeC_6H_4, *p*-$O_2NC_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$, Ar' = Ph; Ar = *p*-MeC_6H_4, Ar' = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; Ar = Ph,

$Ar' = p\text{-}BrC_6H_4$) (*86*), which upon hydrolysis yield the diamides $PhC(=NSO_2Ar)NHPO(NHAr')_2$ and subsequently $ArSO_2NH_2$ and $PhCONHPO(NHAr')_2$.

Acidolysis of $Cl_3P{=}NCCl_2(CH_2)_nCCl_2CCl_2N{=}PCl_3$ ($n = 2$–4, 6) results in solvolysis of the $-N{=}PCl_3$ group and an intermolecular HCl elimination to form $Cl_2OPN{=}CClCCl_2(CH_2)_nCCl_2CCl{=}NOPCl_2$ (*437*). The latter compounds with water give $H_2NCOCCl_2(CH_2)_nCCl_2CONH_2$, also obtained directly from $CCl_3P{=}NCCl_2(CH_2)_nCCl_2CCl_2N{=}PCl_3$ ($n = 1$–6) (*438*); excess alcohol produces the esters $(CH_2)_n[CCl_2C(OR){=}NPO(OR)_2]_2$ (R = Me, Et; $n = 2$, 4–6) (*297b*). Fluorination with KF or NaF leads only to the dinitriles $NCCCl_2(CH_2)_nCCl_2CN$ ($n = 2$–6) and PF_5 (*440*).

C. Phosphazotrifluorides

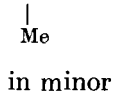
Some compounds of the type $(RN{=}PF_3)_n$ ($n = 1$, 2) have been described; $(MeN{=}PF_3)_2$, for example, may be prepared by several different methods: fission of the Si–N bond with PF_5 (*76*, *77*, *408–410*):

$$PF_5 + (Me_3Si)_2NMe \rightarrow (MeN{=}PF_3)_2 + 2Me_3SiF \qquad (170)$$

direct reaction of PF_5 with methylamine in presence of a tertiary amine (*187*); this reaction has been formulated as proceeding in the steps (*188d*):

$$\begin{aligned} PF_5 + MeNH_2 &\rightarrow MeNH_2 \cdot PF_5 \\ MeNH_2 \cdot PF_5 + MeNH_2 &\rightarrow (MeNH)_2PF_3 \\ (MeNH)_2PF_3 + PF_5 &\rightarrow (MeN{=}PF_3)_2 \end{aligned} \qquad (171)$$

fluorination of $(MeN{=}PCl_3)_2$ with SbF_3 (*142*, *294*), KSO_2F (*187*), Na_2SiF_6 (*503*), and PbF_2 (*142*), and fluorination (AsF_3) of

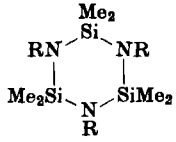


(Section IV,C,1) (*51h*), as well as in minor amounts as a decomposition product of $F_2PNMePF_4$ and $MeNHPF_4$ (*188e*).

Higher dimeric alkylphosphazotrifluorides $(RN{=}PF_3)_2$ with the following R are known: R = Et, Bu, *i*-Bu (*142*); Pr (*142*, *190*); *tert*-Bu (*190*). The aryl compound $(PhN{=}PF_3)_2$ has also been synthesized (*189*, *190*), as well as derivatives with Ar = 2,4-$Me_2C_6H_3$, 2,6-$Me_2C_6H_3$, and 2,6-$Et_2C_6H_3$ (*190*).

The analogous compounds $(RN{=}PF_2R')_2$ [R = Me, R′ = Me, $ClCH_2$, Et, 2,5-$Me_2C_6H_3$, 3-$CF_3C_6H_4$; R = Ph, R′ = Me, Ph; R = Et, R′ = Ph (*409–411*); R = Me, R′ = Ph (*62*, *409*)] are also known.

An interesting synthesis for $(RN{=}PF_2Ph)_2$ (R = Me, Et) has been described (*411*).



$$\xrightarrow[-Me_2SiF_2]{PhPF_4} \tfrac{3}{2}(RN{=}PF_2Ph)_2 \qquad (172)$$

The reaction of heptamethyldisilazane with Ph_2PF_3 gives the monomeric compound $MeN{=}PFPh_2$ (*409*); $PhN{=}PPh_2F$ has been prepared by an azide–phosphine reaction (*62a*). Finally, the compounds $NCN{=}PPhF_2$ and $NCN{=}PPh_2F$ have been obtained from bis(trimethylsilyl)carbodiimide with $PhPF_4$ and Ph_2PF_3, respectively (*175*).

Phosphazotrifluorides have been described (*190*, *410*) as quite stable to water (?). The halogen exchange between $(MeN{=}PCl_3)_2$ and $(MeN{=}PF_3)_2$ yields mixed chlorofluorodiazadiphosphetidines $(MeN{=}P)_2Cl_nF_{6-n}$ (n = 1–5) (*503*). The compound $(MeN{=}PFCl_2)_2$ is also obtained in the reaction of $(MeN{=}PCl_3)_2$ with BF_3 (*51c*). Apart from these, only $(PhN{=}PCl_2F)_2$ (from $PhNH_3Cl$ and PF_3Cl_2) is known (*37*).

D. Physical Investigations

1. Infrared Studies

A band near 850 cm^{-1} is assigned as characteristic of a P–N–P vibration in $(MeN{=}PCl_3)_2$ (*69*, *492*) and is also found in all other dimeric alkylphosphazo compounds (*181*, *185*, *338*, *502*, *519*). A normal coordinate analysis (*523*) of $(MeN{=}PCl_3)_2$, assuming a C_{2h} structure (cf. Section VIII, D, 3), has been carried out.

The monomeric compounds $ArN{=}PCl_3$ [Ar = 2,4-$Br_2C_6H_3$, 2,6,4-$Cl_2(O_2N)C_6H_2$, 2-Br, 2,6-$Cl_2H_6H_2$] have $\nu_{P=N}$ at 1325–1385 cm^{-1} (*541*), in sharp contrast to a former report (*199*). The P=N vibration for $Ph_3P{=}NPh$ has been definitely found at 1344 cm^{-1} [(*521*), cf. also (*520*)].

For the following compounds $\nu_{P=N}$ have been correlated: $CCl_2{=}CClN{=}PCl_3$ and $CCl_3CCl_2N{=}PCl_3$ (XX)* at 1375 cm^{-1} (*123*), $CF_3CCl_2N{=}PCl_3$ at 1388 and 1450 cm^{-1} (^{14}N) and 1364 and 1400 cm^{-1} (^{15}N) (*475*), $(CF_3)_2CHN{=}PCl_3$, $(CF_3)_2CClN{=}PCl_3$, and $(CF_3)_3CN{=}PCl_3$ between 1300 and 1500 cm^{-1} (*295*). More detailed studies were made on $CCl_3N{=}PCl_3$, $CCl_3CCl_2N{=}PCl_3$, and $(CCl_3)_2CClN{=}PCl_3$ (*220*) and the $\nu_{P=N}$ assignments made at 1357, 1372, and 1465 cm^{-1}, respectively. $CF_3CCl_2N{=}PCl_3$,

* The $\nu_{P=N}$ for ^{14}N- and ^{15}N-labeled $CCl_3CCl_2N{=}PCl_3$ are found at 1373 and 1455 cm^{-1} and at 1345 and 1408 cm^{-1}, respectively (*475*).

$(CF_3)_2CClN{=}PCl_3$ and $(CF_3)_3CN{=}PCl_3$ exhibit their $\nu_{P=N}$ at 1390, 1435, and 1500 cm^{-1}, respectively (*220a*).

IR spectra of $ClCOCH{=}CClN{=}PCl_3$, $ClCOCCl{=}CClN{=}PCl_3$, and $ClCOCCl_2CCl_2N{=}PCl_3$ are reported in the literature (*429*). The $\nu_{P=N}$ for $RCCl(COCl)CCl_2N{=}PCl_3$ (R = Me, Et, Pr, *i*-Pr) are found at 1360 cm^{-1} (*431*). In the analogous compounds $ArN{=}PCl_2Me$ (Ar = *o*-ClC_6H_4, *o*-BrC_6H_4) the $\nu_{P=N}$ lies between 1370 and 1380 cm^{-1} (*526*).

The P=N absorptions for the compounds $MeN{=}P(OR)_3$ (R = Et, Pr, Bu) and $PhN{=}PR'(OR)_2$ [R = Et, R′ = Ph; R = Pr, R′ = Et, Pr; R = Bu, R′ = Me, Et, Pr, Bu, $(CH_2)_5$] are found at 1325–1385 cm^{-1} (*212*).

A planar centrosymmetrical molecule (C_{2h}) is attributed to $(MeN{=}PF_3)_2$, according to infrared and Raman studies (*141*, *523*); a discussion of the spectra is also given elsewhere (*187*).

2. *NMR Investigations*

Nuclear magnetic resonance, in particular ^{31}P NMR, has proved to be a very valuable method for the elucidation of structures containing $-N{=}PCl_3$ groups. In general, the chemical shifts for four-coordinate phosphorus in these compounds are between −40 and ~40 ppm, for five-coordinate phosphorus between 55 and 80 ppm (mostly centered around 80 ppm), and for six-coordinate phosphorus (e.g., PCl_6^-) at 290 to 310 ppm (external standard 85% H_3PO_4). Some papers dealing in part with the ^{31}P NMR of some compounds of Section VIII have appeared (*160*, *301*, *411*).

Hexachlorodiazadiphosphetidines $(RN{=}PCl_3)_2$ [R = Me (*157*, *196b*), Et to *n*-$C_{10}H_{21}$, $Et(Me)CHCH_2$, *i*-Am (*185*), Ph (*301*), *o*-, *m*-, *p*-FC_6H_4, 2,4-$F_2C_6H_3$, 2,5-$F_2C_6H_3$ (*502*), *m*-, *p*-$CF_3C_6H_4$ (*46*), CH_2Cl (*338*)] exhibit a chemical shift of the phosphorus nucleus between 77 and 82 ppm (85% H_3PO_4), thus proving the dimeric structure.

The ^1H NMR spectrum of $(MeN{=}PCl_3)_2$ (1 : 2 : 1 triplet) (J_{PH} = 20 Hz) (*492*) is also characteristic of the dimeric form; the same applies to higher diazadiphosphetidines (*185*).

Four-membered P–N rings with tetracoordinate phosphorus atoms (sp^3 hybridization), as in (XXIV) and (XXV) (*32*) or $(MeN{=}P(S)Ph)_2$ (*492*), give shifts somewhat beyond the above limits; thus δ_P = 5.3 ppm for (XXIV) and δ_P = −51.5 ppm for (XXV). It is, however, interesting to note that $(MeN)_6P_4Cl_8$ gives only one signal at δ_P = 74.5 ppm (*32*).

The following chemical shifts for the monomeric phosphazotrichlorides have been found: $CCl_3N{=}PCl_3$ ($\delta_P = 16.3 \pm 0.5$ ppm) (*162*) (17.4 ppm) (*220a*), $Et(Me)CHN{=}PCl_3$ (δ_P = 38.7 ppm) (*185*), 2,3,4,5-$F_4C_6HN{=}PCl_3$ (δ_P = 37.8 ppm), and 2,3,5,6-$F_4C_6HN{=}PCl_3$ (δ_P = 31.6

ppm) (*502*), *o*-$CF_3C_6H_4N{=}PCl_3$ (δ_P = 49.8 ppm) (*46*), (5-Me,2-$NCC_6H_3N{=}PCl_3)_n$ ($n = 1$ in solution) (δ_P = 38.0 ppm) (*401*), $CCl_2{=}CClN{=}PCl_3$ (δ_P = 23.8 ppm) (*307*), $CCl_3CCl_2N{=}PCl_3$ (δ_P = 11 ppm) (*307*) (δ_P = 13 ppm) (*220a*), $(CCl_3)_2CClN{=}PCl_3$ (δ_P = 43.2 ppm), $CF_3CCl_2N{=}PCl_3$ (δ_P = 6.5 ppm), $(CF_3)_2CClN{=}PCl_3$ (21.2 ppm), $(CF_3)_3CN{=}PCl_3$ (44.8 ppm) (*220a*), $ClHC{=}CClN{=}PCl_3$ (δ_P = 24.0; 25.0 ppm; cis-trans isomerism), $Me_2CClCCl_2N{=}PCl_3$ (δ_P = −8.8 ppm) (*307*), and $Cl_3P{=}NCCl_2CCl_2N{=}PCl_3$ (δ_P = 18 ppm) [(*41*), see also (*305a*)]. Only for (2-F,5-$CF_3C_6H_3N{=}PCl_3)_n$ ($n = 1, 2$) has an equilibrium between the monomeric and the dimeric form (two peaks) been observed (*46*).

The compound $(MeN{=}PF_3)_2$ gives a chemical shift δ_P of 71.5 (*409*) or 69.5 ppm (*77*), thus proving pentacoordinate phosphorus, underlined by its ^1H NMR spectrum (*77*, *196b*, *351*, *409*); the coupling constants are J_{PH} = 14.5 Hz (*351*, *409*) and J_{PF} = 880 (*409*) or 894 Hz (*40*), respectively. A careful NMR study of this compound was carried out by Harris and Woodman (*191*); the equivalence of the fluorine atoms was established and explained by positional exchange processes [cf. also (*411*)]. ^1H NMR work of $(MeN{=}PF_2R)_2$ (R = CH_2Cl, Et, Ph, *m*-$CF_3C_6H_4$) is reported (*351*). NMR data of $(MeN{=}PFCl_2)_2$ (δ_P = 59.3 ppm) are reported (*51c*).

3. *X-Ray Studies*

Two independent X-ray investigations of $(MeN{=}PCl_3)_2$ have been published (*194*, *195*); the molecule consists of a four-membered planar ring with nonequivalent P–N distances with trigonal-bipyramidal

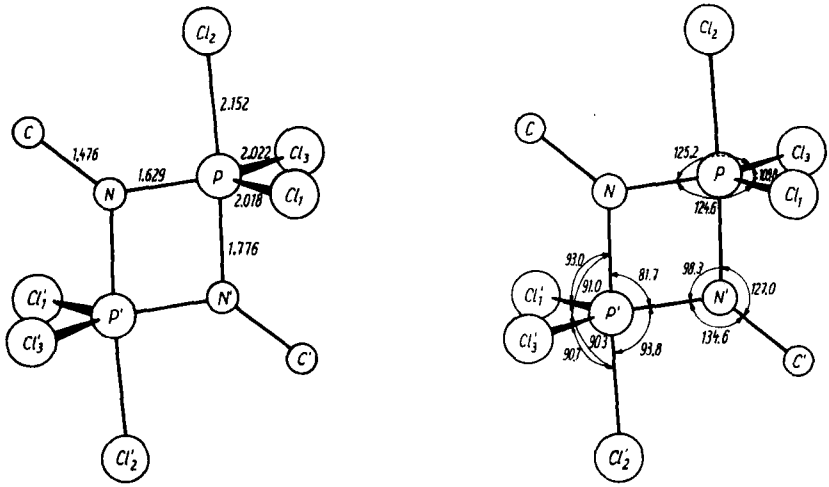


FIG. 6. Bond distances and angles in $(MeN{=}PCl_3)_2$. From reference (*194*).

coordination at the phosphorus atoms; the chlorine atoms have one axial and two equatorial positions. The compound crystallizes in monoclinic form, space group $P_{2_1/n}$, molecular symmetry C_{2h}; $a = 6.013 \pm 0.015$ Å; $b = 14.04 \pm 0.03$ Å; $c = 6.918 \pm 0.015$ Å; $\beta = 98.5 \pm 0.2°$; $V = 579$ Å^3; $Z = 2$; $d = 1.90$ g/cm^3 (*194*) (see Fig. 6).

Equal P–N distances (1.67 Å) are surprisingly found in compound (XXV) (*516*).

The X-ray structure of $(MeN)_6P_4Cl_8$ has been determined (*515*), and it was shown to consist of three planar four-membered rings with nonequivalent P–N distances (delocalized π bonding).

The structure of $(MeN{=}PF_2Ph)_2$ (*73*) is in analogy a parallelogram with the fluorine atoms being in axial and equatorial position.

An electron diffraction study (*4a*) of $(MeN{=}PF_3)_2$ in the vapor phase shows the four-membered ring system.

An examination of $MeN{=}PPh_2F$ proves its monomeric structure (*1*).

4. Other Physical Investigations

The heats of melting, evaporation, and sublimation of $(MeN{=}PCl_3)_2$ are known (*187*). Vapor pressure data for $(MeN{=}PF_3)_2$ have been published (*77*, *187*), as well as its Trouton constant (25.5 cal/mole/deg) (*77*).

Ultraviolet spectra of compounds with phosphazo groups show the P=N bond to give an auxochromic effect (*146*, *547*). The spectra of the compounds RN=PXYZ (R = Ph, *p*-$O_2NC_6H_4$, *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, *p*-$Me_2NC_6H_4$; X, Y, Z = Ph, OPh, *p*-$CF_3C_6H_4$, *p*-$Me_2NC_6H_4$) have also been investigated (*326*), as well as their mass spectral fragmentation (*491a*).

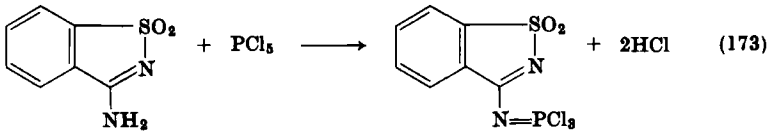
Dipole moments of $RN{=}PCl_3$ [R = CCl_3CCl_2, $MeCCl_2CCl_2$, $ClCH_2$-CCl_2CCl_2, $(CCl_3)_2CCl$, $ClCMe_2CCl_2$, $ClCH_2CMeClCCl_2$, 2,4-$(O_2N)_2C_6H_3$, 2,6,4-$Cl_2(O_2N)C_6H_2$, CCl_3, CF_3CCl_2, $(CF_3)_2CCl$, $(CF_3)_3C$] have been determined (*220a*, *325*).

No signal for $(MeN{=}PCl_3)_2$ is found in the ^{35}Cl NQR spectrum between 20 and 45 MHz (*516a*).

The mass spectra of chlorofluorodiazadiphosphetidines $(MeN{=}P)_2$-Cl_nF_{6-n} ($n = 1$–5) show the presence of all possible isomers (*499*).

IX. Miscellaneous Compounds

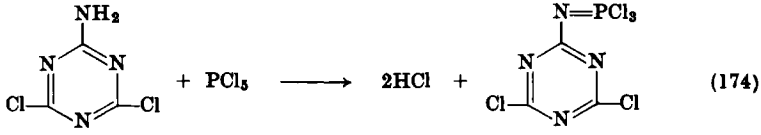
3-Amino-1,2-benzoisosulfonazole reacts with PCl_5 in a normal Kirsanov reaction (*87*).



(173)

Correspondingly, $FSO_2N{=}S(O)FNH_2$ gives $FSO_2N{=}S(O)FN{=}PCl_3$ (*385b*).

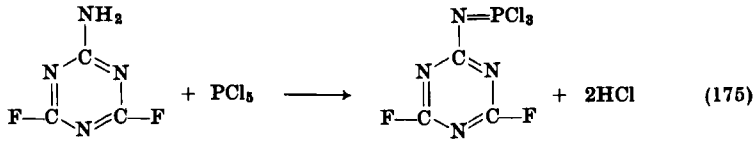
Phosphorus pentachloride and 2-amino-4,6-dichloro-1,3,5-triazine react with introduction of a $-N{=}PCl_3$ group (*83*); with 2,4-diamino-6-chloro-1,3,5-triazine two $-N{=}PCl_3$ groups are introduced, and three with



(174)

melamine (*83*). Tris(trichlorophosphazo)melamine may also be obtained from 2,4,6-tris(chloramino)-1,3,5-triazine and 3 moles of PCl_3 (*179*). Hydrolysis of these compounds with formic acid converts the $-N{=}PCl_3$ groups into $-NHPOCl_2$, $-NHP(O)(OH)Cl$, and finally $-NHP(O)(OH)_2$ groups (*83*). Interaction with NaOPh produces the esters (*64*).

Cyanuric fluoride amide reacts with PCl_5 (*381*), Ph_nPCl_{5-n} ($n = 1, 2, 3$) (*380*) or PF_3Cl_2 (*385*) in the usual way, e.g.,

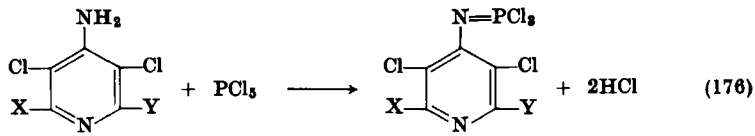


(175)

(XXVIII)

Acidolysis (HCOOH) of (XXVIII) introduces a $-NHPOCl_2$ group (*380*, *381*), whereas substitution to a $-NHSO_2F$ group occurs with fluorosulfonic acid (*380*).

The reaction with several 4-aminopyridines with PCl_5 is described

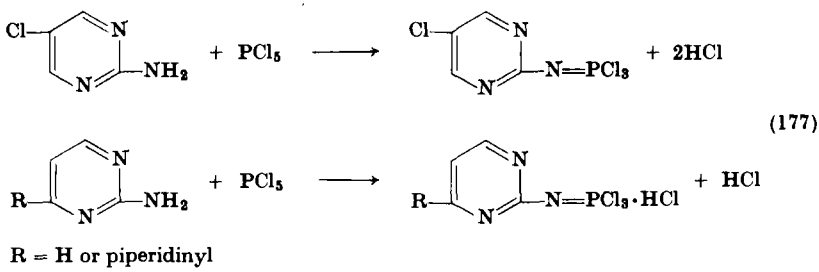


(176)

X = Y = Cl
X = CCl_3, Y = H or Cl

(*359a*); as well as their reactions with alcohols, phenols and formic acid. The similar reaction of 2-aminopyridines and PCl_5 is known (*390a*).

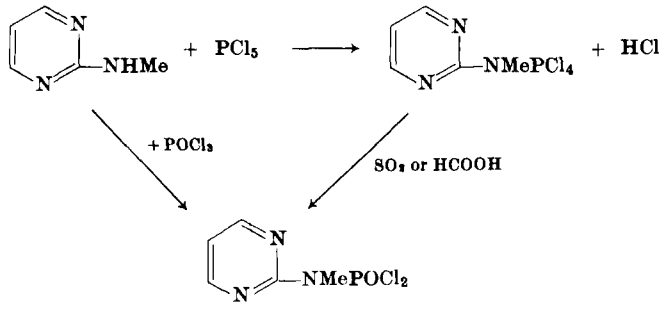
Substituted 2-aminopyrimidines react in an analogous manner (*297*).



(177)

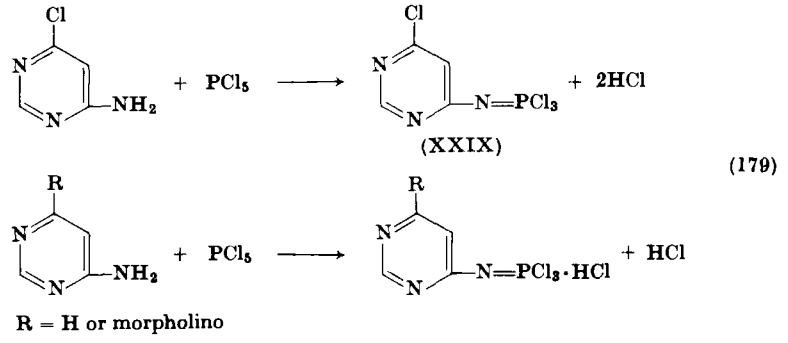
Two of the three chlorine atoms may be replaced by cyclic amines, such as morpholine or piperidine (*297*).

2-Methylaminopyrimidines react as expected with PCl_5 (*297*).



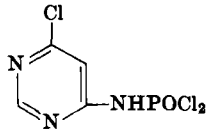
(178)

The behavior of 4-aminopyrimidines and some 4-methylaminopyrimidines with PCl_5 is described (*390*), as well as their subsequent reactions with HCOOH, SO_2, or amines.



(179)

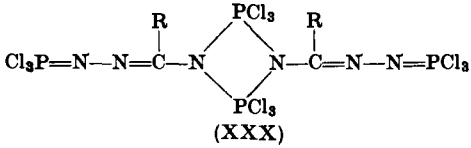
Compound (XXIX) may also be prepared (*390*) as in Eq. (180). The reactions of 5-aminopyrimidines with PCl_5 are similar (*328*).



$$+ PCl_5 \longrightarrow (XXIX) + POCl_3 + HCl \qquad (180)$$

Hydrazine hydrochloride reacts with PCl_5 in $POCl_3$ as solvent to yield $Cl_3P{=}N{-}N{=}PCl_3$, which upon hydrolysis (HCOOH) gives hydrazido-*N*,*N'*-bis(phosphoryldichloride) (*38*). In contrast, Ph_2PCl_3 reacts with hydrazine hydrochloride to give nitrogen, HCl, and $[Ph_2PCl]_2N^+Cl^-$ (*192b*).

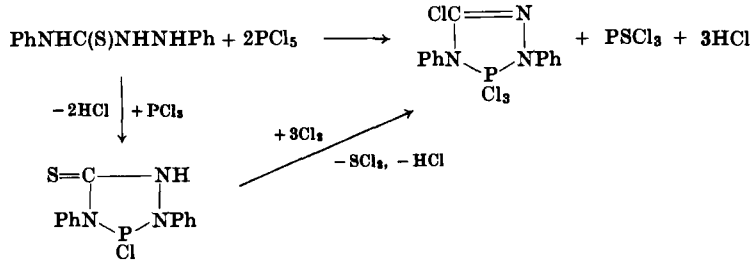
Semicarbazide, $H_2NCONHNH_2$, which possesses a hydrazide and an amide functional group, interacts with PCl_5 (solvent $POCl_3$) to give the interesting compounds (XXX) (*39*); depending on conditions the



(XXX)

substances with R = Cl or R = $OPOCl_2$ may be obtained. Reactions of (XXX) with SO_2 give ill-defined substances.

Diphenylthiosemicarbazide reacts with 2 moles of PCl_5 to produce a five-membered heterocyclic (*195a*) (for analogous systems, see Section VIII,B,1).

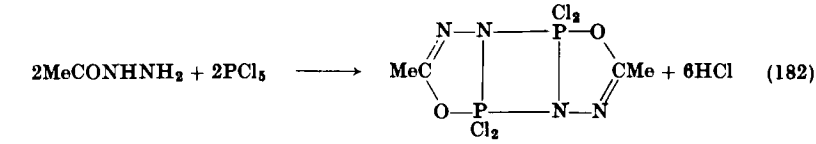


(181)

Interaction of PCl_5 with phenylsulfonylhydrazine (at room temperature or elevated temperature) gives the poorly defined compounds $(C_6H_7N_2O_2S)_2PCl_3$ or $(C_6H_6N_2O_2S{\cdot}PCl_3)_n$, respectively (*510*).

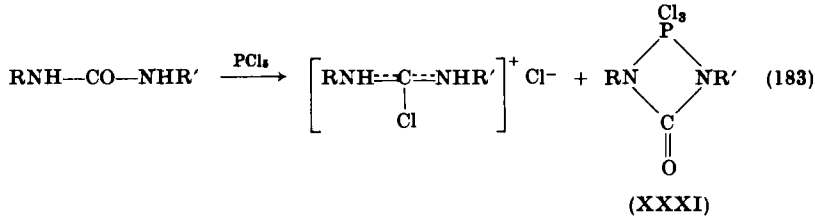
Benzohydrazide, $PhCONHNH_2$, reacts to give $PhCONHN{=}PCl_3$, which on heating reacts further with excess PCl_5, probably via formation of a five-membered heterocyclic and fission of the P=N-bond, to yield

$PhCHCl_2$, HCl, and other products (*332*). Acetohydrazide and equimolar amounts of PCl_5 gives rise to a tricyclic system (*145*).



(182)

1,3-Disubstituted ureas react with PCl_5 giving 1,3,2-diazaphosphetidinones* (XXXI).



(183)

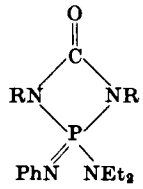
(XXXI)

R = R′ = Me, Bu (*495*, *498*), Ph, 1-$C_{10}H_7$ (*111*)
R = Ph, R′ = Bu (*495*, *498*)

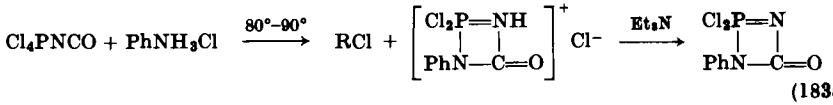
The structure of (XXXI) has been established by means of infrared and ^1H NMR spectra (*498*); $\delta_P = 60.05 \pm 0.5$ ppm (*196*) for (XXXI) (R = R′ = Me), thus proving pentacoordinate phosphorus and the ring structure.

The HCl adduct of (XXXI) (R = R′ = Me) may be obtained from PCl_5 and methyl isocyanate; its hydrolysis gives compound (XXIII), $POCl_3$, and trimethylisocyanuric acid; its interaction with SO_2 (*300*) or with MeNCO (*304*) also gives (XXIII).

Attempts to make a diazaphosphetidinone with tetracoordinated phosphorus atom



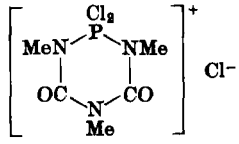
* Formation of a phosphadiazacyclobutenone is found in the reaction of Cl_4PNCO with $PhNH_3Cl$ (*288*).



(183a)

from the reaction of $PhN{=}P(NEt_2)Cl_2$ with *N,N'*-disubstituted ureas failed (*47a*).

Heating (XXXI) (R = R' = Me) to 160°–180°/0.01 Torr produces (XXXII) (*299*); (XXXI) (R = R' = Me) and MeNCO yield (XXIII)

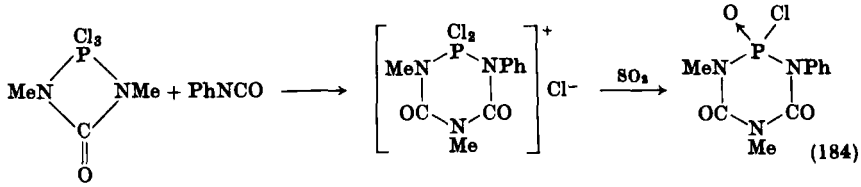


(XXXII)

(*299*); the same compound (XXIII) may also be obtained from $(MeN{=}PCl_3)_2$ and MeNCO (*305*) (cf. Section VIII,B,2).

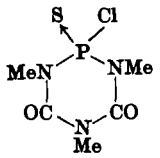
Other authors (*495, 498*) assume that the thermolytic decomposition of 1,3,2-diazaphosphetidinones first produces trichlorophosphazo compounds and isocyanates, which, in turn, react with formation of carbodiimides and $POCl_3$ [(*494*), cf. also (*497*)]. Derkach and Narbut (*111*) observed the same effect upon heating (XXXI) (R = R' = Ph, 1-$C_{10}H_7$) at 100°–200°.

Interaction of (XXXI) and PhNCO proceeds over the following steps (*196*):



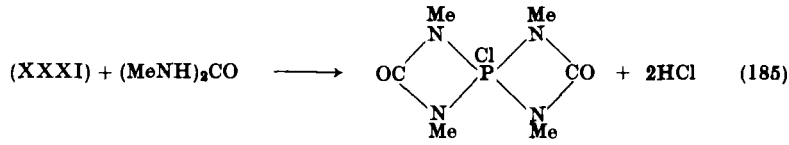
(184)

the mechanism [insertion of a PhNCO molecule between the phosphorus atom in (XXXI) and its adjacent nitrogen atom] has been established. Reaction of (XXXI) with methyl isothiocyanate gives only the thio analog to (XXIII), namely,



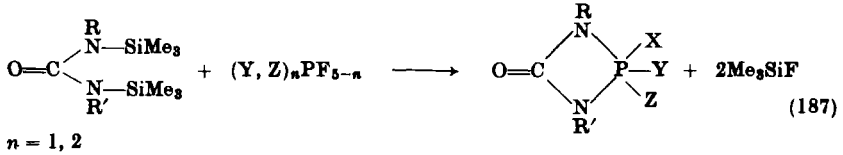
and (XXXIII); with $MeNCCl_2$ only (XXXIII) is obtained (*196a*). A six-membered ring is also obtained from (XXXI) and $ClSO_2NCO$ (*306a*).

Compound (XXXI) (R = R′ = Me) reacts with *N*,*N*′-dimethylurea or *N*,*N*′-dimethylsulfamide forming compounds containing two four-membered rings (*36a*).



The latter compound is the chloro analog of compound (XXXVI).

Replacement of the three chlorine atoms in (XXXI) (R = R′ = Ph, 1-$C_{10}H_7$) with phenol has been described (*111*); its hydrolysis at 100° gives H_3PO_4 and diarylureas, whereas at 15° the compounds ArNHCON-ArPO(OH)$_2$ are obtained. Fluorination of (XXXI) (R = R′ = Me) with SbF_3 gives 2,2,2-trifluoro-2-phospha-1,3-dimethyl-1,3-diazetidine-one [(*144*), cf. also (*342*)]; its structure has been established based on ^{19}F and ^{31}P NMR spectra. A positional exchange of the fluorine atoms has been shown to occur. Other 2-fluoroalkyl(or aryl-)-2-phospha-1,3-dialkyl-1,3-diazetidinones may be prepared from *N*,*N*′-bis(trimethylsilyl)ureas with alkyl- or arylfluorophosphoranes (*144*).



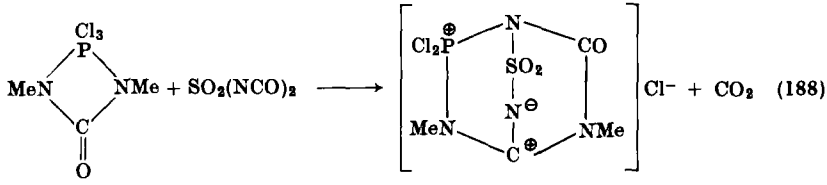
n = 1, 2

R = R′ = Me, X = Y = F, Z = Me, Et, Ph, NMe_2, NEt_2; X = F, Y = Z = Me, Ph

R = Me, R′ = Ph, X = Y = F, Z = Me, Et

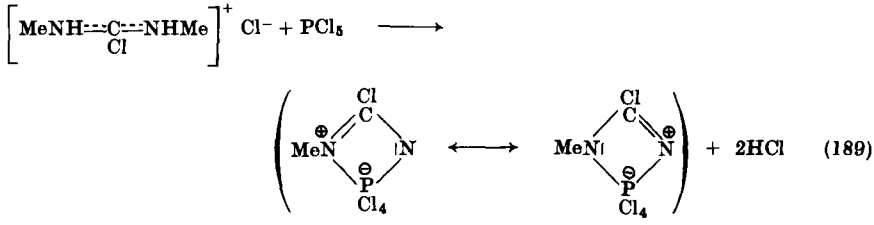
The NMR spectra (^1H, ^{19}F, ^{31}P) of these compounds (*143b*, *144*) are consistent with the proposed structures. The mass spectra of some of these compounds have been recorded (*8*). The similar reaction of *N*,*N*′-bis(trimethylsilyl)ureas with $POCl_3$, $MePOF_2$, etc., failed to yield the desired diazaphosphetidinones (*143c*). The compound $MeNPF_3NMeC(O)$ reacts with methyl isocyanate to give a spiro-phosphonium hexafluorophosphate (*144*).

A six-membered heterocyclic is formed by the reaction of 2,2,2-trichloro-1,3-dimethyl-2,1,3-phosphadiazetidinone (XXXI) with sulfuryldiisocyanate (*306*).



(188)

Interaction of *N,N'*dimethylchloroformamidinium chloride with PCl_5 leads to compound (XXXIII) with hexacoordinate phosphorus



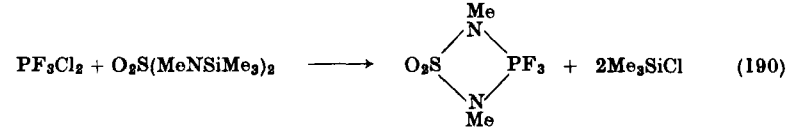
(189)

(XXXIII)

atom (*303*), shown by its ^1H and ^{31}P NMR spectrum ($\delta_P = 202 \pm 1$ ppm, $J_{PH} = 20 \pm 1$ Hz) and later by an X-ray structure determination (*552*).

The reaction of $HN(SO_2Cl)_2$ with PCl_5 (1:1) yields a compound $P_4Cl_6N_2S_2O_4$ (*388*) to which, on the basis of electric conductance studies in nitromethane (1:1 electrolyte) and its ^{31}P NMR spectrum ($\delta_P = -87 \pm 1$ ppm) (*26a*), the ionic structure $[PCl_4]^+[N(SO_2Cl)_2]^-$ is assigned.

N,N'-Bis(trimethylsilyl)-*N,N'*-dimethylsulfamide and PF_3Cl_2 give the four-membered ring system (XXXIV) (*37*, *40*).

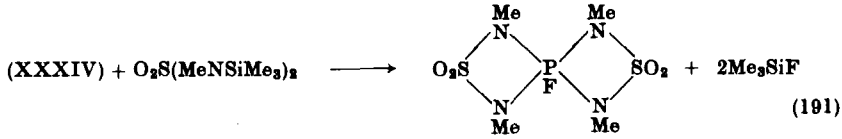


(190)

(XXXIV)

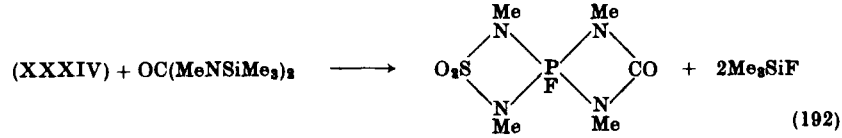
The action of excess $O_2S(MeNSiMe_3)_2$ on (XXXIV) produces (XXXV), whereas *N,N'*-bis(trimethylsilyl)-*N,N'*-dimethylurea and (XXXIV) give (XXXVI) (*37*, *40*).

The ^{31}P NMR spectra of (XXXIV) ($\delta_P = 76.8$ ppm), (XXXV) ($\delta_P = 85.0$ ppm), and (XXXVI) ($\delta_P = 67.0$ ppm) prove the ring structure (*40*)



(191)

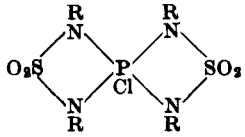
(XXXV)



(192)

(XXXVI)

(pentacoordinated phosphorus atoms with trigonal-bipyramidal arrangement of the ligands); the ^{19}F NMR spectrum of (XXXIV) shows equivalence of the fluorine atoms, thus showing positional exchange of the fluorine atoms [analogous to $(MeN{=}PF_3)_2$, Section VIII, D]. Phosphorus pentachloride reacts in a similar manner with 2 moles of *N,N'*-dimethylsulfamide or *N,N'*-diphenylsulfamide to give

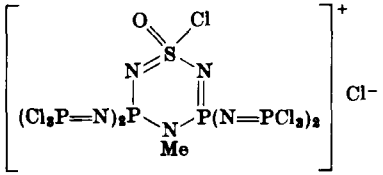


(XXXVII)

R = Me, Ph

(*36b*, *37*, *510*).

Finally, the Kirsanov reaction with a cyclic sulfurylphosphazochloride gives compound (XXXVIII) (*50a*).



(XXXVIII)

X. Applications

$[Cl_3P{=}NPCl_2{=}NPCl_3]^+Cl^-$ (VII) as well as $(MeN{=}PCl_3)_2$, $(PhN{=}PCl_3)_2$, 2,4-$(O_2N)_2C_6H_3N{=}PCl_3$, $PhCON{=}PCl_3$, $MeN{=}P(OPh)Cl_2$, $PhN{=}P(OMe)_2$-Cl, $PhCON{=}P(NMe_2)Cl_2$, $PhCON{=}P(OPh)_3$, and $PhCON{=}P\left[N\begin{smallmatrix}CO\\|\\(CH_2)_5\end{smallmatrix}\right]_3$ are patented for use as cocatalysts in the anionic polymerization of ϵ-caprolactam (*490*). The amido derivative of (VII) has been suggested as a flame-proofing agent for tissues (*51*).

Compounds of the type $[Cl(Cl_2P{=}N)_nPCl_3]^+ZnCl_3^-$ ($n = 1$–10) (Section IV,B,2) have been found useful as high-temperature lubricants (*345*). Compounds of the types $[Cl(Cl_2P{=}N)_nPCl_3]^+M_m{}^+Cl_{m+1}$ (M = Nb, Mo, Ta, $n = 3$–15), $[Cl(Cl_2P{=}N)_nPCl_2]^+M_m{}^+Cl_{m+2}$ (M = Pt, W, Ru; $n =$ 3–15; $m =$ valence state) (*341*), $[Cl(PNCl_2)_nPCl_3]^+Y$, or $[Cl(PNCl_2)_n$-$PCl_2]^{2+}Y_2$ ($n = 3$–15, Y = ArO, RO, RNH, RN=) (*374*) have remarkable thermolytic and hydrolytic stability. Temperature-resistant oils of the formula $[Cl_3P(=NPCl_2)_nN{=}PCl_3]^+Cl^-$ ($n = 10$–15) have been suggested as high-temperature fluids (*50c*). The compound $Cl_3P{=}NPOCl_2$ (V) is an intermediate for lubricant additives, flame-proofing agents, corrosion inhibitors (*214*, *413*), and softeners (*214*); the use of (V) for the polymerization of isobutene and tertiary olefins has been protected by a patent (*213*). Esters of (V), such as $(RO)_3P{=}NP(O)(OR')_2$, have been tested for pharmacological (*43*) and insecticidal (*108*, *214*, *486*) properties.

The pentakis(dimethylamides) of (VI) (*13*) and (VIII) (*16a*) represent effective insecticides.

The compounds $ClSO_2N{=}PCl_3$ (XV) and $SO_2(N{=}PCl_3)_2$ may be used as inhibitors for the polymerization of liquid SO_3 (*171*). Tetramido derivatives of $ClSO_2N{=}PCl_3$ have been suggested for the search of leaks in pipelines (*293*).

Several phosphazotrichlorides, such as $MeSO_2N{=}PCl_3$, $CCl_3CON{=}$ PCl_3, *m*-$Cl_3P{=}NO_2SC_6H_4CON{=}PCl_3$, and their derivatives, stabilize photographic silver halide emulsions (*95a*).

Some sulfonylphosphazo derivatives, such as $ArSO_2N{=}P(NC_2H_4)_3$, have antitumor properties (*108*, *354*, *488*, *489*); some have been patented for their usefulness for coating of textile fibers (*373*).

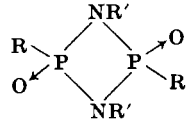
Esters of the type $ArSO_2NNaPO(OR)_2$ (Section VI,B) may be utilized for the extraction of metal ions from neutral or alkaline media (*468*).

A compound $PhSO_2N{=}P(OH)_2(OC_6H_4NO_2$-*p*) has been described to be a good insecticide (*167*).

Arylsulfonylphosphazotriallyl esters have been reported to be intermediates for polymers (*460*).

The physiological properties of 2,3,6-$Cl_3C_6H_2CONHPO(OR)_2$ have been investigated (*484*). The toxicity and cancerostatic behavior of some carbonylphosphazo derivatives, namely, $ArCON{=}P(NC_2H_4)_3$ (Ar = Ph, *o*-, *p*-ClC_6H_4, *m*-, *p*-$O_2NC_6H_4$, *p*-BrC_6H_4) and $ArNHCONHPO(NC_2H_4)_2$ (Ar = Ph, *o*-ClC_6H_4), has been described (*108*, *183a*). The triamides $ArCON{=}P(NHAr')_3$ (Ar = *p*-ClC_6H_4, *p*-BrC_6H_4; Ar′ = Ph, *p*-MeC_6H_4) may be used as fungicides (*480*); several other derivatives of carbonylphosphazotrichlorides are potential insecticides (*387g*) or herbicides (*387b*). The diesters $RCONHPO(OR')_2$ (R = CH_2Cl, $CHCl_2$, MeCHCl, $MeCCl_2$, $ClCH_2CCl_2$, *o*-, *m*-, *p*-ClC_6H_4, *p*-BrC_6H_4, *p*-FC_6H_4; R′ = Me, Et, Pr, Ph) have found application as herbicides (*463*); see (*79*) for general topics. The compound $(PhN{=}PCl_3)_2$, which may also be a cocatalyst for the polymerization of ε-caprolactam (see above), has also been suggested for use as a lubricant additive (*322*) [as has $(MeN{=}PCl_3)_2$] and as an inhibitor for the polymerization of SO_3 (*171*).

The four-membered ring compounds



R = PhO, R′ = Me (*52*)
R = $C_6H_{11}O$, R′ = C_6H_{11} (*54*)
R = Et_2N, Pr_2N, PhNH;
R′ = Et, Pr, Ph (*194a*)

have been described as intermediates for synthetic polymers and as flame retardants (*194a*). Other polymers with P–N four-membered ring units are patented (*348*, *358*, *359*).

The antiblastic properties of *p*-$O_2NC_6H_4N{=}P(NC_2H_4)_3$ have been reported recently (*322a*).

The phosphorylation products of nitriles may be useful starting materials for polymers (*281*).

Phosphorylated trichloroacetamidines have been tested for their herbicidic properties (*493*); they are far more active as fungicides (*479*).

The use of $(MeN{=}PF_3)_2$ and $(MeN{=}PF_2R)_2$ (R = Ph, *m*-$CF_3C_6H_4$) (*62*, *410*) as cocatalysts for the polymerization of ε-caprolactam is also patented.

The trichlorophosphazopyrimidines (*297*, *390*) have been suggested (*297*) for the synthesis of active cytostatics.

ACKNOWLEDGMENTS

The author thanks Prof. Dr. mult. V. Gutmann, Director of the Institut für Anorganische Chemie at the Technische Hochschule, Vienna, Austria for his stimulating interest in this work. He is also grateful to Prof. Dr. H. W. Roesky, Frankfurt/Main, Priv.-Doz. Dr. A. Schmidpeter, Munich, and Prof. Dr. R. Schmutzler, Braunschweig (all W. Germany) for kindly providing unpublished material.

REFERENCES

1. Adamson, G. W., and Bart, J. C. J., *Chem. Commun.* p. 1036 (1969); *J. Chem. Soc.* **A**, p. 1452 (1970).
2. Agahigian, H., Vickers, G. D., Roscoe, J., and Bishop, J., *J. Chem. Phys.* **39**, 1621 (1963).
3. Aleksankin, M. M., Samarai, L. I., and Derkach, G. I., *Zh. Obshch. Khim.* **35**, 923 (1965); *Chem. Abstr.* **63**, 6813 (1965).
3a. Allcock, H. R., "Heteroatom Ring Systems and Polymers," Academic Press, New York, 1967; *Chem. Eng. News* **46**, 68 (1968); *in* "Encyclopedia of Polymer Science and Technology" (N. M. Bikales, ed.), Vol. 10, p. 139, Wiley, New York, 1969.
4. Allen, G., Lewis, C. J., and Todd, S. M., *Polymer* **11**, 31 (1970).
4a. Almenningen, A., Andersen, B., and Astrup, E. E., *Acta Chem. Scand.* **23**, 2179 (1969).
5. Appel, R., U.S. Patent 3,358,021 (1967) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **69**, 10212 (1968).
6. Appel, R., Becke-Goehring, M., Eisenhauer, G., and Hartenstein, J., *Chem. Ber.* **95**, 625 (1962).
7. Appel, R., and Büchler, G., *Z. Anorg. Allg. Chem.* **320**, 3 (1963).
8. Baldwin, M. A., Loudon, A. G., Maccoll, A., Dunmur, R. E., Schmutzler, R., and Gregor, I. K., *Org. Mass Spectrom.* **2**, 765 (1969).
9. Baldwin, R. A., and Washburn, R. M., *J. Amer. Chem. Soc.* **83**, 4466 (1961).
10. Barth-Wehrenalp, G., Park, E., and Kowalski, A., U.S. Patent 2,975,028 (1961) (Pennsalt Chem. Corp.); *Chem. Abstr.* **55**, 20356 (1961); Barth-Wehrenalp, G., and Kowalski, A., *135th Meet., Amer. Chem. Soc., Boston*, Abstr. p. 15M (1959).
11. Baudler, M., *Angew. Chem.* **70**, 376 (1958); Baudler, M., Klement, R., and Rother, E., *Chem. Ber.* **93**, 149 (1960).
12. Baumgärtner, R., Sawodny, W., and Goubeau, J., *Z. Anorg. Allg. Chem.* **340**, 246 (1965).
13. Becke, M., Ger. Patent 1,171,881 (1964) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **61**, 5235 (1964); Brit. Patent 968,167 (1964).
13a. Becke, M., U.S. Patent 3,348,927 (1967) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **67**, 118703 (1967).
14. Becke, M., and Lehr, W., U.S. Patent 3,357,805 (1967) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **68**, 41721 (1968).
15. Becke-Goehring, M., *Angew. Chem.* **73**, 246 (1961).
16. Becke-Goehring, M., *Fortschr. Chem. Forsch.* **10**, 207 (1968); *Chem.-Ztg., Chem. App.* **94**, 179 (1970).

16a. Becke-Goehring, M., U.S. Patent 3,226,181 (1965) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **64**, 7727 (1966).
17. Becke-Goehring, M., Bayer, K., and Mann, T., *Z. Anorg. Allg. Chem.* **346**, 143 (1966).
18. Becke-Goehring, M., Debo, A., Fluck, E., and Goetze, W., *Chem. Ber.* **94**, 1383 (1961).
19. Becke-Goehring, M., and Fluck, E., *Angew. Chem.* **74**, 382 (1962); *Angew. Chem. Int. Ed. Engl.* **1**, 281 (1962).
20. Becke-Goehring, M., and Fluck, E., *Inorg. Syn.* **8**, 92 (1966).
21. Becke-Goehring, M., and Fluck, E., *Inorg. Syn.* **8**, 94 (1966).
22. Becke-Goehring, M., and Fluck, E., *Inorg. Syn.* 8, 105 (1966).
23. Becke-Goehring, M., Fluck, E., and Lehr, W., *Z. Naturforsch. B* **17**, 126 (1962).
24. Becke-Goehring, M., Gehrmann, W., and Goetze, W., *Z. Anorg. Allg. Chem.* **326**, 127 (1963).
25. Becke-Goehring, M., and Haubold, W., *Z. Anorg. Allg. Chem.* **338**, 305 (1965).
26. Becke-Goehring, M., Haubold, W., and Latscha, H. P., *Z. Anorg. Allg. Chem.* **333**, 120 (1964).
26a. Becke-Goehring, M., and Hormuth, P. B., *Z. Anorg. Allg. Chem.* **369**, 105 (1969).
26b. Becke-Goehring, M., and Jung, D., *Z. Anorg. Allg. Chem.* **372**, 233 (1970).
27. Becke-Goehring, M., and Koch, G., *Chem. Ber.* **92**, 1188 (1959).
28. Becke-Goehring, M., and Lehr, W., *Chem. Ber.* **94**, 1591 (1961).
29. Becke-Goehring, M., and Lehr, W., *Z. Anorg. Allg. Chem.* **325**, 287 (1963).
30. Becke-Goehring, M., and Lehr, W., *Z. Anorg. Allg. Chem.* **327**, 128 (1964).
31. Becke-Goehring, M., and Leichner, L., *Angew. Chem.* **76**, 686 (1964); *Angew. Chem. Int. Ed. Engl.* **3**, 590 (1964).
32. Becke-Goehring, M., Leichner, L., and Scharf, B., *Z. Anorg. Allg. Chem.* **343**, 154 (1966).
33. Becke-Goehring, M., Mann, T., and Euler, H. D., *Chem. Ber.* **94**, 193 (1961).
34. Becke-Goehring, M., and Müller, H. J., *Z. Anorg. Allg. Chem.* **362**, 51 (1968).
35. Becke-Goehring, M., and Slawisch, A., *Z. Anorg. Allg. Chem.* **346**, 295 (1966).
36. Becke-Goehring, M., and Scharf, B., *Z. Anorg. Allg. Chem.* **353**, 320 (1967).
36a. Becke-Goehring, M., and Schwind, H., *Z. Anorg. Allg. Chem.* **372**, 285 (1970).
36b. Becke-Goehring, M., and Wald, H. J., *Z. Anorg. Allg. Chem.* **371**, 88 (1969).
37. Becke-Goehring, M., Wald, H. J., and Weber, H., *Naturwissenschaften* **55**, 491 (1968).
38. Becke-Goehring, M., and Weber, W., *Z. Anorg. Allg. Chem.* **333**, 128 (1964).
39. Becke-Goehring, M., and Weber, W., *Z. Anorg. Allg. Chem.* **339**, 281 (1965).
40. Becke-Goehring, M., and Weber, H., *Z. Anorg. Allg. Chem.* **365**, 185 (1969).
41. Becke-Goehring, M., and Wolf, M. R., *Naturwissenschaften* **55**, 543 (1968); *Z. Anorg. Allg. Chem.* **373**, 245 (1970).
42. Becke-Goehring, M., and Wunsch, G., *Chem. Ber.* **93**, 326 (1960).
43. Belonozhko, G. A., Klimova, L. K., Feshchenko, N. G., and Shokol, V. A., *Fiziol. Aktiv. Veshchestva, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb.* p. 67 (1966); *Chem. Abstr.* **67**, 31142 (1967).
44. Bermann, M., Thesis, Technische Hochschule, Vienna, 1968.
45. Bermann, M., and Utvary, K., unpublished observations.
46. Bermann, M., and Utvary, K., *Monatsh. Chem.* **100**, 1041 (1969).
47. Bermann, M., and Utvary, K., *Monatsh. Chem.* **100**, 1280 (1969).

47a. Bermann, M., and Utvary, K., *Synth. Inorg. Metalorg. Chem.* **1**, 171 (1971).
48. Biddlestone, M., and Shaw, R. A., *Chem. Commun.* p. 205 (1965).
49. Biddlestone, M., Shaw, R. A., and Taylor, D., *Chem. Commun.* p. 320 (1969); see also Biddlestone, M., and Shaw, R. A., *J. Chem. Soc.* **A**, p. 1750 (1970); *J. Chem. Soc.* **A**, p. 2715 (1971).
50. Bieber, T. I., and Kane, B., *J. Org. Chem.* **21**, 1198 (1956).
50a. Bieller, U., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **380**, 314 (1971).
50b. Bieller, U., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **381**, 209 (1971).
50c. Bieniek, T., Burnie, G., and Maselli, J. M., U.S. Patent 3,443,913 (1969) (W. R. Grace & Co.); *Chem. Abstr.* **71**, 39655 (1969).
51. Bilger, X., Fr. Patent 1,157,097 (1957) (Compagnie Française des Matières Colorantes); *Chem. Abstr.* **54**, 20236 (1960); see also Fr. Patent 1,225,073 (1960); *Chem. Abstr.* **55**, 17035 (1961); U.S. Patent 3,012,908 (1961).
51a. Binder, H., *Z. Anorg. Allg. Chem.* **383**, 130 (1971).
51b. Binder, H., *Z. Anorg. Allg. Chem.* **383**, 279 (1971).
51c. Binder, H., *Z. Anorg. Allg. Chem.* **384**, 193 (1971).
51d. Binder, H., *Z. Naturforsch. B* **26**, 616 (1971).
51e. Binder, H., and Fluck, E., *Z. Anorg. Allg. Chem.* **381**, 21 (1971).
51f. Binder, H., and Fluck, E., *Z. Anorg. Allg. Chem.* **381**, 116 (1971).
51g. Binder, H., and Fluck, E., *Z. Anorg. Allg. Chem.* **381**, 123 (1971).
51h. Binder, H., and Fluck, E., *Z. Anorg. Allg. Chem.* **382**, 27 (1971).
52. Binder, H., and Heinle, R., Ger. Patent 1,075,611 (1960) (Rottweiler Kunstseidefabrik A. G.); *Chem. Abstr.* **55**, 14383 (1961); Brit. Patent 883,299 (1962).
53. Binder, H., and Heinle, R., Ger. Patent 1,083,818 (1960) (Rottweiler Kunstseidefabrik A. G.); *Chem. Abstr.* **55**, 17543 (1961); U.S. Patent 3,083,222 (1963).
54. Binder, H., and Heinle, R., Ger. Patent 1,139,497 (1962) (Rottweiler Kunstseidefabrik A. G.); *Chem. Abstr.* **60**, 426 (1964).
55. Bissey, J. E., *J. Chem. Educ.* **44**, 95 (1967).
56. Bock, H., and Wiegräbe, W., *Angew. Chem.* **74**, 327 (1962); *Angew. Chem. Int. Ed. Engl.* **1**, 265 (1962).
57. Bock, H., and Wiegräbe, W., *Chem. Ber.* **99**, 377 (1966).
57a. Bodnarchuk, N. D., and Gavrilenko, B. B., *Zh. Obshch. Khim.* **39**, 1961 (1969); *Chem. Abstr.* **72**, 31941 (1970); Bodnarchuk, N. D., Gavrilenko, B. B., and Derkach, G. I., *Zh. Obshch. Khim.* **40**, 1469 (1970).
58. Bodnarchuk, N. D., Gavrilenko, B. B., and Derkach, G. I., *Zh. Org. Khim.* **4**, 1710 (1968); *Chem. Abstr.* **70**, 19532 (1969).
59. Bodnarchuk, N. D., Malovik, V. V., and Derkach, G. I., *Zh. Obshch. Khim.* **39**, 168 (1969); *Chem. Abstr.* **70**, 96857 (1969).
59a. Bodnarchuk, N. D., Semenii, V. Ya., Kukhar, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **41**, 984 (1971); *Chem. Abstr.* **75**, 76924 (1971); see also Rudavskii, V. P., and Zagnibeda, D. M., *Farm. Zh.* **26**, 84 (1971); *Chem. Abstr.* **75**, 88706 (1971).
60. Bol'on, Ya. G., and Levchenko, E. S., *Zh. Org. Khim.* **3**, 777 (1967); *Chem. Abstr.* **67**, 43518 (1967).
61. von Braun, J., *Ber. Deut. Chem. Ges.* **37**, 2812 (1904); von Braun, J., and Rudolph, W., *Ber. Deut. Chem. Ges.* **67**, 1762 (1934).
62. Brouns, H. G., U.S. Patent 3,345,340 (1967) (E. I. du Pont de Nemours & Co.); *Chem. Abstr.* **67**, 117514 (1967).

62a. Brown, C., Murray, M., and Schmutzler, R., *J. Chem. Soc.* **C**, p. 878 (1970).
63. Buck, A. C., and Lankelma, H. P., *J. Amer. Chem. Soc.* **70**, 2398 (1948).
64. Bukovskii, M. I., Solodushenkov, S. N., Kizilova, L. Kh., and Derkach, G. I., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 93 (1967); *Chem. Abstr.* **69**, 36083 (1968).
65. Bunting, R. K., and Schmulbach, C. D., *Inorg. Chem.* **5**, 533 (1966).
65a. Burness, D. M., Silverman, R. A., and Wright, C. J., Brit. Patent 1,198,534 (1970) (Eastman Kodak Co.); *Chem. Abstr.* **73**, 104312 (1970); U.S. Patent 3,567,587 (1971).
66. Bystrova, R. I., Zinov'ev, Yu. M., and Soborovskii, L. Z., *Zh. Obshch. Khim.* **29**, 2088 (1959); *Chem. Abstr.* **54**, 8604 (1960).
67. Cadogan, J. I. G., and Moulden, H. N., *J. Chem. Soc.*, p. 3079 (1961).
68. Carriere, G., *Ned. Chem. Ind.* **10**, 140 (1968); *Chem. Abstr.* **69**, 20733 (1968).
69. Chapman, A. C., Holmes, W. S., Paddock, N. L., and Searle, H. T., *J. Chem. Soc.* p. 1825 (1961).
70. Claus, A., *Ber. Deut. Chem. Ges.* **28**, 2365 (1881).
70a. Clipsham, R., Hart, R. M., and Whitehead, M. A., *Inorg. Chem.* **8**, 2431 (1969).
71. Comte, F., U.S. Patents 2,775,609, 2,775,610, 2,775,611 (1956) (Monsanto Chem. Corp.); *Chem. Abstr.* **51**, 6690 (1957).
72. Comte, F., U.S. Patent 2,775,612 (1956) (Monsanto Chem. Corp.); *Chem. Abstr.* **51**, 6690 (1957).
73. Cox, J. W., and Corey, E. R., *Chem. Commun.* p. 123 (1967).
74. Cox, J. W., and Corey, E. R., *Chem. Commun.* p. 205 (1969).
75. Coxon, G. E., Sowerby, D. B., and Trauter, G. C., *J. Chem. Soc.* p. 5697 (1965).
76. Demitras, G. C., Kent, R. A., and MacDiarmid, A. G., *Chem. Ind. (London)* p. 1712 (1964).
77. Demitras, G. C., and MacDiarmid, A. G., *Inorg. Chem.* **6**, 1903 (1967).
78. Derderian, C., Ph.D. Thesis, Pennsylvania State Univ., University Park, Pennsylvania, 1966.
79. Derkach, G. I., *Angew. Chem.* **81**, 407 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 421 (1969).
80. Derkach, G. I., USSR Patent 158,880 (1963); *Chem. Abstr.* **60**, 14395 (1964).
81. Derkach, G. I., USSR Patent 168,696 (1965); *Chem. Abstr.* **63**, 1700 (1965).
82. Derkach, G. I., *Zh. Obshch. Khim.* **32**, 3107 (1962); *Chem. Abstr.* **58**, 7946 (1963).
83. Derkach, G. I., Bukovskii, M. I., Solodushenkov, S. N., and Mosiichuk, A. I., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 89 (1967); *Chem. Abstr.* **69**, 36082 (1968); see also Kukhar, V. P., Bukovskii, M. I., Kasheva, T. N., Paleichuk, V. S., Petrachenko, A. A., and Solodushenkov, S. N., *Zh. Obshch. Khim.* **40**, 1226 (1970); *Chem. Abstr.* **74**, 141711 (1971).
84. Derkach, G. I., Dregval, G. F., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 3402 (1960); *Chem. Abstr.* **55**, 21029 (1961).
85. Derkach, G. I., Dregval, G. F., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 2385 (1961); *Chem. Abstr.* **56**, 3405 (1962).
86. Derkach, G. I., Dregval, G. F., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 154 (1962); *Chem. Abstr.* **57**, 13668 (1962).
87. Derkach, G. I., Dregval, G. F., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 1878 (1962); *Chem. Abstr.* **58**, 4534 (1963).

88. Derkach, G. I., Fedorova, G. K., and Gubnitskaya, E. S., *Zh. Obshch. Khim.* **33**, 1017 (1963); *Chem. Abstr.* **59**, 8783 (1963); USSR Patent 154,276 (1963); *Chem. Abstr.* **60**, 5554 (1964).

89. Derkach, G. I., and Gubnitskaya, E. S., USSR Patent 178,373 (1966); *Chem. Abstr.* **65**, 620 (1966).

90. Derkach, G. I., and Gubnitskaya, E. S., *Zh. Obshch. Khim.* **34**, 604 (1964); *Chem. Abstr.* **60**, 13268 (1964).

91. Derkach, G. I., and Gubnitskaya, E. S., *Zh. Obshch. Khim.* **35**, 1009 (1965); *Chem. Abstr.* **63**, 9801 (1965).

92. Derkach, G. I., Gubnitskaya, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3679 (1961); *Chem. Abstr.* **57**, 9876 (1962).

93. Derkach, G. I., Gubnitskaya, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3746 (1961); *Chem. Abstr.* **57**, 9735 (1962).

94. Derkach, G. I., Gubnitskaya, E. S., Samarai, L. I., and Shokol, V. A., *Zh. Obshch. Khim.* **33**, 557 (1963); *Chem. Abstr.* **59**, 2684 (1963).

95. Derkach, G. I., Gubnitskaya, E. S., and Shokol, V. A., *Zh. Obshch. Khim.* **35**, 1014 (1965); *Chem. Abstr.* **63**, 9981 (1965).

96. Derkach, G. I., Gubnitskaya, E. S., Shokol, V. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 1201 (1962); *Chem. Abstr.* **58**, 5721 (1963); Kirsanov, A. V., Gubnitskaya, E. S., Shokol, V. A., and Derkach, G. I., USSR Patent 148,363 (1962); *Chem. Abstr.* **58**, 8974 (1963).

97. Derkach, G. I., Gubnitskaya, E. S., Shokol, V. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 1874 (1962); *Chem. Abstr.* **58**, 6857 (1963).

98. Derkach, G. I., Gubnitskaya, E. S., Shokol, V. A., and Kisilenko, A. A., *Zh. Obshch. Khim.* **34**, 82 (1964); *Chem. Abstr.* **60**, 11502 (1964).

99. Derkach, G. I., Ivanova, Zh. M., and Stukalo, E. A., USSR Patent 239,327 (1969); *Chem. Abstr.* **71**, 50211 (1969).

100. Derkach, G. I., and Kirsanov, A. V., USSR Patent 150,834 (1962); *Chem. Abstr.* **59**, 5198 (1963).

101. Derkach, G. I., Kirsanov, A. V., and Dregval, G. F., USSR Patent 165,715 (1964); *Chem. Abstr.* **62**, 7699 (1965).

102. Derkach, G. I., and Kisilenko, A. A., *Zh. Obshch. Khim.* **34**, 3060 (1964); *Chem. Abstr.* **62**, 2692 (1965).

103. Derkach, G. I., and Kolotilo, M. V., *Zh. Obshch. Khim.* **36**, 1437 (1966); *Chem. Abstr.* **66**, 2292 (1967); see also Shtepanek, A. S., Tkachenko, E. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **40**, 766 (1970); *Chem. Abstr.* **73**, 25584 (1970).

104. Derkach, G. I., Kruzement-Prikhod'ko, V. V., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 2391 (1961); *Chem. Abstr.* **56**, 2374 (1962).

105. Derkach, G. I., and Lepesa, A. M., *Zh. Obshch. Khim.* **34**, 525 (1964); *Chem. Abstr.* **60**, 13179 (1964).

106. Derkach, G. I., Lepesa, A. M., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 171 (1962); *Chem. Abstr.* **57**, 16472 (1962); Petrov, K. A., Neimysheva, A. A., Fomenko, M. G., Chernushevich, L. M., and Kuntsevich, A. D., *Zh. Obshch. Khim.* **31**, 516 (1961); *Chem. Abstr.* **55**, 22111 (1961).

107. Derkach, G. I., Lepesa, A. M., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 2600 (1962); *Chem. Abstr.* **58**, 7864 (1963).

108. Derkach, G. I., and Loseva, I. M., *Fiziol. Aktiv. Veshchestva, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb.* p. 57 (1966); *Chem. Abstr.* **67**, 98715 (1967).

109. Derkach, G. I., and Mikhailik, S. K., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 59 (1967); *Chem. Abstr.* **69**, 2757 (1968).
110. Derkach, G. I., and Narbut, A. V., USSR Patent 181,107 (1966); *Chem. Abstr.* **65**, 8769 (1966).
111. Derkach, G. I., and Narbut, A. V., *Zh. Obshch. Khim.* **35**, 932 (1965); *Chem. Abstr.* **63**, 6984 (1965).
112. Derkach, G. I., and Narbut, A. V., *Zh. Obshch. Khim.* **35**, 1006 (1965); *Chem. Abstr.* **63**, 9857 (1965).
113. Derkach, G. I., and Narbut, A. V., *Zh. Obshch. Khim.* **36**, 322 (1966); *Chem. Abstr.* **64**, 15738 (1966).
114. Derkach, G. I., and Narbut, A. V., *Zh. Obshch. Khim.* **37**, 1364 (1967); *Chem. Abstr.* **67**, 108401 (1967).
115. Derkach, G. I., Narbut, A. V., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 1584 (1963); *Chem. Abstr.* **59**, 12669 (1963).
116. Derkach, G. I., Narbut, A. V., Kirsanov, A. V., and Shokol, V. A., USSR Patent 151,337 (1963); *Chem. Abstr.* **60**, 6787 (1964).
116a. Derkach, G. I., and Rudavskii, V. P., *Metody Poluch. Khim. Reaktoviv Prep.* **19**, 23 (1969); *Chem. Abstr.* **74**, 141207 (1971).
117. Derkach, G. I., and Rudavskii, V. P., *Probl. Org. Sin., Akad. Nauk SSSR Otd. Obshch. Tekh. Khim.* p. 268 (1965); *Chem. Abstr.* **64**, 12577 (1966).
118. Derkach, G. I., and Rudavskii, V. P., *Zh. Obshch. Khim.* **35**, 1202 (1965); *Chem. Abstr.* **63**, 11398 (1965).
119. Derkach, G. I., and Rudavskii, V. P., *Zh. Obshch. Khim.* **35**, 2200 (1965); *Chem. Abstr.* **64**, 12580 (1966).
120. Derkach, G. I., and Rudavskii, V. P., *Zh. Obshch. Khim.* **37**, 1893 (1967); *Chem. Abstr.* **68**, 21489 (1968).
121. Derkach, G. I., Rudavskii, V. P., and Dregval, G. F., *Zh. Obshch. Khim.* **34**, 3959 (1964); *Chem. Abstr.* **62**, 9046 (1965).
122. Derkach, G. I., Rudavskii, V. P., Koval, A. A., and Shevchenko, V. I., *Zh. Obshch. Khim.* **37**, 445 (1967); *Chem. Abstr.* **67**, 32742 (1967).
123. Derkach, G. I., Rudavskii, V. P., and Malichenko, B. F., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 75 (1967); *Chem. Abstr.* **69**, 10169 (1968).
124. Derkach, G. I., and Samarai, L. I., USSR Patent 168,699 (1962).
125. Derkach, G. I., and Samarai, L. I., *Zh. Obshch. Khim.* **32**, 2058 (1962); *Chem. Abstr.* **58**, 3311 (1963).
126. Derkach, G. I., and Samarai, L. I., *Zh. Obshch. Khim.* **33**, 1587 (1963); *Chem. Abstr.* **59**, 12669 (1963).
127. Derkach, G. I., and Samarai, L. I., *Zh. Obshch. Khim.* **34**, 1161 (1964); *Chem. Abstr.* **61**, 1784 (1964).
128. Derkach, G. I., Samarai, L. I., and Kirsanov, A. V., USSR Patent 151,333 (1963); *Chem. Abstr.* **60**, 15778 (1964).
129. Derkach, G. I., Samarai, L. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 3761 (1962); *Chem. Abstr.* **58**, 12461 (1963).
130. Derkach, G. I., Samarai, L. I., and Shokol, V. A., *Zh. Obshch. Khim.* **32**, 2059 (1962).
131. Derkach, G. I., Samarai, L. I., Shtepanek, A. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 3759 (1962); *Chem. Abstr.* **58**, 13985 (1963).
132. Derkach, G. I., Shokol, V. A., and Gubnitskaya, E. S., *Zh. Obshch. Khim.* **33**, 553 (1963); *Chem. Abstr.* **59**, 2854 (1963).

133. Derkach, G. I., Shokol, V. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 3393 (1960); *Chem. Abstr.* **55**, 22220 (1961).
134. Derkach, G. I., Shokol, V. A., Samarai, L. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 159 (1962); *Chem. Abstr.* **57**, 12379 (1962).
135. Derkach, G. I., Shtepanek, A. S., Shokol, V. A., and Kirsanov, A. V., USSR Patent 159,840 (1964); *Chem. Abstr.* **60**, 11955 (1964).
136. Derkach, G. I., and Slyusarenko, E. I., *Zh. Obshch. Khim.* **35**, 532 (1965); *Chem. Abstr.* **63**, 531 (1965).
137. Derkach, G. I., Zhmurova, I. N., Kirsanov, A. V., Shevchenko, V. I., and Shtepanek, A. S., "Fosfazo Soedineniya." Izd. Nauk. Dumka, Kiev, 1965.
138. Derkach, G. I., Zhuravleva, L. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 879 (1962); *Chem. Abstr.* **58**, 2388 (1963).
139. Derkach, N. Ya., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 331 (1968); *Chem. Abstr.* **69**, 96832 (1968).
140. Desai, V. B., Shaw, R. A., and Smith, B. C., *Angew. Chem.* **80**, 910 (1968); *Angew. Chem. Int. Ed. Engl.* **7**, 887 (1968).
140a. Douglas, W. M., Cooke, M., Lustig, M., and Ruff, J. K., *Inorg. Nucl. Chem. Lett.* **6**, 409 (1970).
141. Downs, A. J., *Chem. Commun.* p. 628 (1967).
141a. Drach, B. S., and Zhmurova, I. N., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 63 (1969); *Chem. Abstr.* **75**, 5144 (1971).
142. Drach, B. S., and Zhmurova, I. N., *Zh. Obshch. Khim.* **37**, 892 (1967); *Chem. Abstr.* **68**, 2533 (1968); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 65 (1969); *Chem. Abstr.* **75**, 140164 (1971).
143. Drach, B. S., Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **37**, 2524 (1967); *Chem. Abstr.* **69**, 26691 (1968).
143a. Drozd, G. I., Ivin, S. Z., and Varshavskii, A. D., *Zh. Obshch. Khim.* **39**, 1178 (1969); *Chem. Abstr.* **71**, 61496 (1969).
143b. Dunmur, R. E., Murray, M., and Schmutzler, R., *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 1.12 (1970); Dunmur, R. E., Murray, M., Schmutzler, R., and Gagnaire, D., *Z. Naturforsch. B* **25**, 903 (1970).
143c. Dunmur, R. E., and Schmutzler, R., personal communication.
144. Dunmur, R. E., and Schmutzler, R., *J. Chem. Soc.* **A**, p. 1289 (1971).
145. Ebeling, J., and Schmidpeter, A., *Angew. Chem.* **81**, 707 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 674 (1969); Schmidpeter, A., and Ebeling, J., Ger. Patent Appl. 1,943,158 (1971) (Farbenfabriken Bayer A. G.); *Chem. Abstr.* **74**, 142064 (1971).
146. Edel'man, T. G., and Stepanov, B. I., *Zh. Obshch. Khim.* **39**, 713 (1969); *Chem. Abstr.* **71**, 49101 (1969); *Zh. Obshch. Khim.* **39**, 712 (1969); *Chem. Abstr.* **71**, 49105 (1969); Stepanov, B. I., and Edel'man, T. G., *Zh. Obshch. Khim.* **39**, 1549 (1969); *Chem. Abstr.* **71**, 112204 (1969).
146a. Emsley, J., Moore, J., and Udy, P. B., *J. Chem. Soc.* **A**, p. 2863 (1971).
147. England, D. C., Lindsay, R. V., Jr., and Melby, L. R., *J. Amer. Chem. Soc.* **80**, 6442 (1958).
148. Ephraim, F., and Gurewitsch, M., *Ber. Deut. Chem. Ges.* **43**, 138 (1910).
149. Feistel, G. R., and Moeller, T., *J. Inorg. Nucl. Chem.* **29**, 2731 (1967).
150. Feldt, M. K., and Moeller, T., *J. Inorg. Nucl. Chem.* **30**, 2351 (1968).
151. Fittig, R., *Ann. Chem. Pharm.* **106**, 277 (1858).
152. Flint, C. D., Ibrahim, E. H. M., Shaw, R. A., Smith, B. C., and Thakur, C. P., *Tetrahedron Lett.* p. 3061 (1969); *J. Chem. Soc.* **A** p. 3513 (1971);

Ibrahim, E. H. M., Shaw, R. A., Smith, B. C., Thakur, C. P., Woods, M., Bullen, G. J., Rutherford, J. S., Tucker, P. A., Cameron, T. S., Howlett, K. D., and Prout, C. K., *Phosphorus* **1**, 153 (1971); see also Granzhan, V. A., Grapov, A. F., Razvodovskaya, A. V., and Mel'nikov, N. N., *Zh. Obshch. Khim.* **39**, 1501 (1969); *Chem. Abstr.* **71**, 112283 (1969).

153. Fluck, E., *Angew. Chem.* **75**, 348 (1963).

154. Fluck, E., *Chem. Ber.* **94**, 1388 (1961).

155. Fluck, E., *Z. Anorg. Allg. Chem.* **315**, 181 (1962).

156. Fluck, E., *Z. Anorg. Allg. Chem.* **315**, 191 (1962).

157. Fluck, E., *Z. Anorg. Allg. Chem.* **320**, 64 (1963).

158. Fluck, E., *Z. Naturforsch. B* **18**, 664 (1963); Ger. Patent 1,186,035 (1965) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **62**, 8713 (1965); U.S. Patent 3,384,462 (1968).

159. Fluck, E., *Z. Naturforsch. B* **20**, 505 (1965).

160. Fluck, E., "Die kernmagnetische Resonanz und ihre Anwendung in der anorganischen Chemie." Springer-Verlag, Berlin and New York, 1963.

161. Fluck, E., *in* "Topics in Phosphorus Chemistry" (M. Grayson and E. J. Griffith, eds.), Vol. 4, p. 291. Wiley, New York, 1967.

162. Fluck, E., and Goldmann, F. L., *Z. Anorg. Allg. Chem.* **356**, 307 (1968).

163. Fluck, E., and Heckmann, G., *Z. Naturforsch. B* **24**, 953 (1969).

164. Fluck, E., and Reinisch, R. M., *Z. Anorg. Allg. Chem.* **328**, 172 (1964).

165. Folin, O., *Amer. Chem. J.* **19**, 323 (1897).

166. Fowell, P. A., and Mortimer, C. T., *Chem. Ind. (London)* p. 444 (1960); see also Fleig, H., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **376**, 215 (1970).

167. Fujii, K., Hattori, J., and Yoshioka, H., Jap. Patent 13,947 (1960) (Sumitomo Chem. Ind. Co. Ltd.); *Chem. Abstr.* **55**, 16900 (1961).

168. Gadekar, S. M., and Ross, E., *J. Org. Chem.* **26**, 606 (1961).

169. Geierhaas, H., Thesis, Univ. of Heidelberg, Heidelberg, 1966; quoted in references (*16*, p. 223) and (*34*, p. 56).

170. Gerhardt, G., *Ann. Chem. Pharm.* **108**, 214 (1858).

171. Gilbert, E. E., and Yodis, A. W., Fr. Patent 1,349,057 (1964) (Allied Chemical Corp.); *Chem. Abstr.* **61**, 7984 (1964); Ger. Patent 1,178,833 (1965); Brit. Patent 979,563 (1965); U.S. Patent 3,188,176 (1965).

172. Gilpin, E., *Amer. Chem. J.* **19**, 352 (1897).

173. Glemser, O., Biermann, U., and von Halasz, S. P., *Inorg. Nucl. Chem. Lett.* **5**, 501 (1969).

174. Glemser, O., Biermann, U., and von Halasz, S. P., *Inorg. Nucl. Chem. Lett.* **5**, 643 (1969).

175. Glemser, O., Niecke, E., and Stenzel, J., *Angew. Chem.* **79**, 723 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 710 (1967).

176. Glemser, O., Roesky, H. W., and Heinze, P. R., *Inorg. Nucl. Chem. Lett.* **4**, 179 (1968).

177. Glemser, O., and Wyszomirski, E., *Naturwissenschaften* **28**, 25 (1961).

178. Goerdeler, J., and Ullmann, H., *Chem. Ber.* **94**, 1067 (1961).

179. Gotsmann, G., and Schwarzmann, M., *Justus Liebigs Ann. Chem.* **729**, 106 (1969); Fr. Patent 2,001,704 (1969) (BASF); *Chem. Abstr.* **72**, 66992 (1970); Ger. Patent 1,670,316 (1971).

180. Goubeau, J., *Angew. Chem.* **78**, 565 (1966); *Angew. Chem. Int. Ed. Engl.* **5**, 567 (1966).

180a. van de Grampel, J. C., and Vos, A., *Rec. Trav. Chim. Pays-Bas* **82**, 246 (1963).
180b. Grapov, A. F., Mel'nikov, N. N., and Razvodovskaya, A. V., *Usp. Khim.* **39**, 39 (1970); *Chem. Abstr.* **72**, 110393 (1970).
180c. Graves, G. E., McKennon, D. W., and Lustig, M., *Inorg. Chem.* **10**, 2083 (1971).
181. Green, M., Haszeldine, R. N., and Hopkins, G. S. A., *J. Chem. Soc.* **A**, p. 1766 (1966); Brit. Patent 1,185,462 (1970) (National Research Development Corp.); *Chem. Abstr.* **72**, 122182 (1970); U.S. Patent 3,531,422 (1970).
182. Gribova, I. A., and Ban-Yuan, U., *Usp. Khim.* **30**, 3 (1961); *Chem. Abstr.* **55**, 15321 (1961).
183. Groeneveld, W. L., Visser, J. H., and Seuter, A. M. J. H., *J. Inorg. Nucl. Chem.* **8**, 245 (1958).
183a. Gubnitskaya, E. S., Kropacheva, A. A., and Derkach, G. I., *Puti Sin. Izyskaniya Protivoopukholevykh Prep., Tr. Simp. Khim. Protivoopukholevykh Veshchestva, 3rd, Moscow, 1968*, p. 319 (1970); *Chem. Abstr.* **75**, 140572 (1971).
184. Gutmann, V., Kemenater, C., and Utvary, K., *Monatsh. Chem.* **96**, 836 (1965).
185. Gutmann, V., Utvary, K., and Bermann, M., *Monatsh. Chem.* **97**, 1745 (1966).
186. Haasemann, P., Diplomarbeit, Technische Hochschule, Stuttgart, 1959; quoted in references (*187*) and (*194*, p. 240).
187. Haasemann, P., Thesis, Technische Hochschule, Stuttgart, 1963.
188. Haber, C. P., *Chem. Soc., Spec. Publ.* **15**, 115 (1961).
188a. Hagemann, H., Ger. Patent Appl. (DOS) 1,803,784 (1970) (Farbenfabriken Bayer A.G.); *Chem. Abstr.* **73**, 34838 (1970).
188b. Haiduc, I., "The Chemistry of Inorganic Ring Systems." Wiley (Interscience), New York, 1970.
188c. von Halasz, S. P., Thesis, Göttingen (1969); quoted in Niecke, E., Glemser, O., and Thamm, H., *Chem. Ber.* **103**, 2864 (1970).
188d. Harman, J. S., and Sharp, D. W. A., *J. Chem. Soc.* **A**, p. 1138 (1970).
188e. Harman, J. S., McCartney, M. E., and Sharp, D. W. A., *J. Chem. Soc.* **A**, p. 1547 (1971); Harman, J. S., and Sharp, D. W. A., *Inorg. Chem.* **10**, 1538 (1971).
189. Harris, J. J., U.S. Patent 3,304,160 (1967) (Koppers Co. Inc.); *Chem. Abstr.* **66**, 85852 (1967).
190. Harris, J. J., and Rudner, B., *147th Amer. Chem. Soc. Meet., Philadelphia*, Abstr. p. 25L (1964); *J. Org. Chem.* **33**, 1392 (1968).
191. Harris, R. K., and Woodman, C. M., *Mol. Phys.* **10**, 437 (1966).
191a. Hart, R. M., and Whitehead, M. A., *J. Chem. Soc.* **A**, p. 1738 (1971).
191b. Hart, R. M., and Whitehead, M. A., *Mol. Phys.* **19**, 383 (1970).
192. Haubold, W., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **352**, 113 (1967).
192a. Haubold, W., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **372**, 273 (1970).
192b. Haubold, W., Kammel, D., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **380**, 23 (1971).
192c. Hayashi, T., and Saito, H., *Kogyo Kagaku Zasshi* **74**, 22 (1971); *Chem. Abstr.* **75**, 5385 (1971).
193. Helferich, B., and Schroeder, L., *Justus Liebigs Ann. Chem.* **670**, 48 (1963).
194. Hess, H., and Forst, D., *Z. Anorg. Allg. Chem.* **342**, 240 (1966).
194a. Hindersinn, R. R., and Witschard, G., U.S. Patent 3,449,161 (1969) (Hooker Chem. Corp.); *Chem. Abstr.* **71**, 40354 (1969).

195. Hoard, L. G., and Jacobson, R. A., *J. Chem. Soc.* **A**, p. 1203 (1966).
195a. Hormuth, P. B., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **372**, 280 (1970).
196. Hormuth, P. B., and Latscha, H. P., *Z. Anorg. Allg. Chem.* **365**, 26 (1969).
196a. Hormuth, P. B., and Latscha, H. P., *Z. Anorg. Allg. Chem.* **369**, 59 (1969).
196b. Horn, H. G., *Chem.-Ztg., Chem. App.* **95**, 849 (1971).
196c. Horn, H. G., *Makromol. Chem.* **138**, 163 (1970).
197. Horn, H. G., and Becke-Goehring, M., *J. Polym. Sci., Part A-1* **7**, 959 (1969).
198. Horn, H. G., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **367**, 165 (1969).
199. Horner, L., and Oediger, H., *Justus Liebigs Ann. Chem.* **627**, 142 (1959).
200. Huber, L. K., and Mandell, H. C., Jr., *Inorg. Chem.* **4**, 919 (1965).
201. Ibrahim, E. H. M., and Shaw, R. A., *Chem. Commun.* p. 244 (1967).
202. Ivanova, Zh. M., Levchenko, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1607 (1965); *Chem. Abstr.* **63**, 17949 (1965); Kirsanov, A. V., and Ivanova, Zh. M., USSR Patent 169,525 (1965); *Chem. Abstr.* **63**, 8373 (1965).
203. Jakob, A., Thesis, Munich, 1961; quoted in reference (*350*, p. 358).
204. Jaszka, D. J., U.S. Patent 3,392,214 (1968) (Hooker Chem. Corp.); *Chem. Abstr.* **69**, 59945 (1968).
205. John, K., and Moeller, T., *J. Amer. Chem. Soc.* **82**, 2647 (1960).
206. John, K., and Moeller, T., *J. Inorg. Nucl. Chem.* **22**, 199 (1961).
206a. Johnson, A. W., "Ylid Chemistry." Academic Press, New York, 1966.
207. Jung, D., unpublished observations, quoted in reference (*16*, p. 213); see also (*26b*).
208. Kabachnik, M. I., and Gilyarov, V. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 790 (1956); *Chem. Abstr.* **51**, 1823 (1957).
209. Kabachnik, M. I., and Gilyarov, V. A., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 819 (1961); *Chem. Abstr.* **55**, 27014 (1961); Kabachnik, M. I., Gilyarov, V. A., and Popov, E. M., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 1022 (1961); *Chem. Abstr.* **55**, 27014 (1961).
210. Kabachnik, M. I., Gilyarov, V. A., Cheng-Te Chang, and Matrosov, E. I. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 1589 (1962); *Chem. Abstr.* **58**, 6673 (1963).
211. Kabachnik, M. I., Gilyarov, V. A., and Popov, E. M., *Zh. Obshch. Khim.* **32**, 1598 (1962); *Chem. Abstr.* **58**, 4401 (1963).
212. Kabachnik, M. I., Gilyarov, V. A., and Tsvetkov, E. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 2135 (1959); *Chem. Abstr.* **54**, 10918 (1960).
213. Kahler, E. J., U.S. Patent 2,837,588 (1958) (Pennsalt Chem. Corp.); *Chem. Abstr.* **52**, 15892 (1958).
214. Kahler, E. J., U.S. Patent 2,925,320 (1960) (Pennsalt Chem. Corp.); *Chem. Abstr.* **54**, 17820 (1960).
215. Kaplansky, M., Clipsham, R., and Whitehead, M. A., *J. Chem. Soc.* **A**, p. 584 (1969).
216. Karle, D. W., and Washburn, R. M., *151st Meet., Amer. Chem. Soc., Pittsburgh,* Abstr. p. H20 (1966); Washburn, R. M., and Karle, D. W., *West. Reg. Conf., Soc. Plastics Ind., Palm Springs, Calif., 1966*; NASA Accession No. N66-34009 (1966); *Chem. Abstr.* **67**, 22203 (1967).
217. Keat, R., Miller, M. C., and Shaw, R. A., *J. Chem. Soc.* **A**, p. 1404 (1967).
218. Keat, R., Miller, M. C., and Shaw, R. A., *Proc. Chem. Soc., London* p. 137 (1964).
219. Kemenater, C., Thesis, Technische Hochschule, Vienna, 1965.

220. Khomenko, D. P., Dyadyusha, G. G., and Kozlov, E. S., *Spectrosc. Lett.* **1**, 245 (1968); *Zh. Strukt. Khim.* **11**, 660 (1970); *Chem. Abstr.* **74**, 8002 (1971).

220a. Khomenko, D. P., Kozlov, E. S., and Dyadyusha, G. G., *Spectrosc. Lett.* **3**, 129 (1970).

220b. Kireev, V. V., Kolesnikov, G. S., and Raigorodskii, I. M., *Usp. Khim.* **38**, 1504 (1969); *Chem. Abstr.* **71**, 102235 (1969).

220c. Kireev, V. V., Kolesnikov, G. S., and Titov, S. S., *Zh. Obshch. Khim.* **40**, 2015 (1970); *Chem. Abstr.* **74**, 52966 (1971).

221. Kirsanov, A. V., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 426 (1950); *Chem. Abstr.* **45**, 1503 (1951).

222. Kirsanov, A. V., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 710 (1952); *Chem. Abstr.* **47**, 9904 (1953).

223. Kirsanov, A. V., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 646 (1954); *Chem. Abstr.* **49**, 13161 (1955).

224. Kirsanov, A. V., *Izv. Inst. Org. Khim., Bulg. Akad. Nauk* **3**, 129 (1967); *Chem. Abstr.* **69**, 2961 (1968).

225. Kirsanov, A. V., *Khim. Primen. Fosforog. Soedin., Tr. Konf. 1st, Kazan, 1955* p. 99 (1957); *Chem. Abstr.* **52**, 251 (1958).

225a. Kirsanov, A. V., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 5 (1969); *Chem. Abstr.* **74**, 106704 (1971).

225b. Kirsanov, A. V., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 7 (1969); *Chem. Abstr.* **74**, 141165 (1971).

225c. Kirsanov, A. V., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 11 (1969); *Chem. Abstr.* **74**, 141170 (1971).

226. Kirsanov, A. V., *Sb. Statei Obshch. Khim.* **2**, 1046 (1953); *Chem. Abstr.* **49**, 3051 (1955).

227. Kirsanov, A. V., *Ukr. Khim. Zh.* **33**, 1181 (1967); *Coll. Int. Cent. Nat. Rech. Sci.* **182**, 241 (1969); Derkach, G. I., *Visn. Akad. Nauk Ukr. RSR*, p. 31 (1969); *Chem. Abstr.* **72**, 55536 (1970).

228. Kirsanov, A. V., *Zh. Obshch. Khim.* **22**, 81 (1952); *Chem. Abstr.* **46**, 6984 (1952).

229. Kirsanov, A. V., *Zh. Obshch. Khim.* **22**, 88 (1952); *Chem. Abstr.* **46**, 6984 (1952).

230. Kirsanov, A. V., *Zh. Obshch. Khim.* **22**, 269 (1952); *Chem. Abstr.* **46**, 11135 (1952).

231. Kirsanov, A. V., *Zh. Obshch. Khim.* **22**, 274 (1952); *Chem. Abstr.* **46**, 11135 (1952).

232. Kirsanov, A. V., *Zh. Obshch. Khim.* **22**, 1346 (1952); *Chem. Abstr.* **47**, 5836 (1953); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 9 (1969); *Chem. Abstr.* **74**, 106703 (1971).

233. Kirsanov, A. V., *Zh. Obshch. Khim.* **24**, 1033 (1954); *Chem. Abstr.* **49**, 8787 (1955).

234. Kirsanov, A. V., *Zh. Obshch. Khim.* **26**, 2082 (1956); *Chem. Abstr.* **51**, 1821 (1957).

235. Kirsanov, A. V., and Abrazhanova, E. A., *Sb. Statei Obshch. Khim.* **2**, 865 (1953); *Chem. Abstr.* **49**, 6820 (1955).

236. Kirsanov, A. V., and Abrazhanova, E. A., *Sb. Statei Obshch. Khim.* **2**, 1048 (1953); *Chem. Abstr.* **49**, 3052 (1955).

237. Kirsanov, A. V., and Abrazhanova, E. A., *Sb. Statei Obshch. Khim.* **2**, 1059 (1953); *Chem. Abstr.* **49**, 5405 (1955).

238. Kirsanov, A. V., and Abrazhanova, E. A., *Sb. Statei Obshch. Khim.* **2**, 1370 (1953); *Chem. Abstr.* **49**, 4600 (1955).
239. Kirsanov, A. V., Bodnarchuk, N. D., and Shevchenko, V. I., *Dopov. Akad. Nauk Ukr. RSR* p. 221 (1963); *Chem. Abstr.* **59**, 12666 (1963); see also Shevchenko, V. I., Kornuta, P. P., and Bodnarchuk, N. D., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 96, 98 (1969); *Chem. Abstr.* **74**, 140793, 141989 (1971); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 91 (1969); *Chem. Abstr.* **75**, 110292 (1971).
240. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **26**, 2009 (1956); *Chem. Abstr.* **51**, 1821 (1957); Derkach, G. I., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 15 (1969); *Chem. Abstr.* **74**, 140784 (1971).
241. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **26**, 2631 (1956); *Chem. Abstr.* **51**, 1821 (1957).
242. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **27**, 1080 (1957); *Chem. Abstr.* **52**, 3715 (1958).
243. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **27**, 3248 (1957); *Chem. Abstr.* **52**, 8997 (1958).
244. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **28**, 1887 (1958); *Chem. Abstr.* **53**, 1208 (1959).
245. Kirsanov, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **28**, 2247 (1958); *Chem. Abstr.* **53**, 2134 (1959).
246. Kirsanov, A. V., Derkach, G. I., and Makitra, R. G., *Zh. Obshch. Khim.* **28**, 1227 (1958); *Chem. Abstr.* **52**, 20002 (1958).
247. Kirsanov, A. V., Derkach, G. I., Shokol, V. A., and Samarai, L. I., USSR Patent 148,387 (1962); *Chem. Abstr.* **58**, 6699 (1963).
248. Kirsanov, A. V., and Egorova, N. L., *Zh. Obshch. Khim.* **25**, 187 (1955); *Chem. Abstr.* **50**, 1647 (1956).
249. Kirsanov, A. V., and Egorova, N. L., *Zh. Obshch. Khim.* **25**, 1140 (1955); *Chem. Abstr.* **50**, 3215 (1956).
250. Kirsanov, A. V., and Egorova, N. L., *Zh. Obshch. Khim.* **28**, 1052 (1958); *Chem. Abstr.* **52**, 18290 (1958).
251. Kirsanov, A. V., and Egorova, N. L., *Zh. Obshch. Khim.* **28**, 1587 (1958); *Chem. Abstr.* **53**, 1203 (1959).
252. Kirsanov, A. V., and Feshchenko, N. G., *Zh. Obshch. Khim.* **27**, 2817 (1957); *Chem. Abstr.* **52**, 8069 (1958).
253. Kirsanov, A. V., and Feshchenko, N. G., *Zh. Obshch. Khim.* **28**, 339 (1958); *Chem. Abstr.* **52**, 13663 (1958).
254. Kirsanov, A. V., and Feshchenko, N. G., *Zh. Obshch. Khim.* **29**, 4085 (1959); *Chem. Abstr.* **54**, 20948 (1960).
255. Kirsanov, A. V., and Feshchenko, N. G., *Zh. Obshch. Khim.* **30**, 3389 (1960); *Chem. Abstr.* **55**, 18112 (1961).
256. Kirsanov, A. V., and Kirsanova, N. A., *Zh. Obshch. Khim.* **29**, 1802 (1959); *Chem. Abstr.* **54**, 8693 (1960).
257. Kirsanov, A. V., Kolotilo, M. V., and Derkach, G. I., *Dopov. Akad. Nauk Ukr. RSR* p. 480 (1966); *Chem. Abstr.* **65**, 3902 (1966).
258. Kirsanov, A. V., and Levchenko, E. S., *Zh. Obshch. Khim.* **28**, 1589 (1958); *Chem. Abstr.* **53**, 1219 (1959).
259. Kirsanov, A. V., and Makitra, R. G., *Zh. Obshch. Khim.* **26**, 905 (1956); *Chem. Abstr.* **50**, 14600 (1956).
260. Kirsanov, A. V., and Makitra, R. G., *Zh. Obshch. Khim.* **26**, 907 (1956); *Chem. Abstr.* **50**, 14633 (1956).

261. Kirsanov, A. V., and Makitra, R. G., *Zh. Obshch. Khim.* **27**, 245 (1957); *Chem. Abstr.* **51**, 12844 (1957).
262. Kirsanov, A. V., and Makitra, R. G., *Zh. Obshch. Khim.* **27**, 450 (1957); *Chem. Abstr.* **51**, 15443 (1957).
263. Kirsanov, A. V., and Makitra, R. G., *Zh. Obshch. Khim.* **28**, 35 (1958); *Chem. Abstr.* **52**, 12787 (1958).
264. Kirsanov, A. V., and Marenets, M. S., *Zh. Obshch. Khim.* **29**, 2256 (1959); *Chem. Abstr.* **54**, 10855 (1960).
265. Kirsanov, A. V., and Marenets, M. S., *Zh. Obshch. Khim.* **31**, 1605 (1961); *Chem. Abstr.* **55**, 23339 (1961).
266. Kirsanov, A. V., and Marenets, M. S., *Zh. Obshch. Khim.* **31**, 1607 (1961); *Chem. Abstr.* **55**, 25752 (1961).
267. Kirsanov, A. V., and Matveenko, L. L., *Zh. Obshch. Khim.* **28**, 1892 (1958); *Chem. Abstr.* **53**, 1265 (1959).
268. Kirsanov, A. V., and Molosnova, V. P., *Zh. Obshch. Khim.* **25**, 772 (1955); *Chem. Abstr.* **50**, 2416 (1956).
269. Kirsanov, A. V., and Molosnova, V. P., *Zh. Obshch. Khim.* **28**, 30 (1958); *Chem. Abstr.* **52**, 12760 (1958).
270. Kirsanov, A. V., and Molosnova, V. P., *Zh. Obshch. Khim.* **28**, 347 (1958); *Chem. Abstr.* **52**, 13663 (1958).
271. Kirsanov, A. V., and Nekrasova, Z. D., *Zh. Obshch. Khim.* **26**, 903 (1956); *Chem. Abstr.* **50**, 14631 (1956).
272. Kirsanov, A. V., and Nekrasova, Z. D., *Zh. Obshch. Khim.* **27**, 1253 (1957); *Chem. Abstr.* **52**, 3666 (1958).
273. Kirsanov, A. V., and Nekrasova, Z. D., *Zh. Obshch. Khim.* **27**, 3241 (1957); *Chem. Abstr.* **52**, 8996 (1958).
274. Kirsanov, A. V., and Nekrasova, Z. D., *Zh. Obshch. Khim.* **28**, 1595 (1958); *Chem. Abstr.* **53**, 1206 (1959).
275. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **24**, 474 (1954); *Chem. Abstr.* **49**, 6164 (1955).
276. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **24**, 882 (1954); *Chem. Abstr.* **49**, 8168 (1955).
277. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **24**, 1980 (1954); *Chem. Abstr.* **49**, 13927 (1955).
278. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **26**, 74 (1956); *Chem. Abstr.* **50**, 13786 (1956).
279. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **26**, 250 (1956); *Chem. Abstr.* **50**, 13783 (1956).
280. Kirsanov, A. V., and Shevchenko, V. I., *Zh. Obshch. Khim.* **26**, 504 (1956); *Chem. Abstr.* **50**, 13785 (1956).
281. Kirsanov, A. V., Shevchenko, V. I., and Bodnarchuk, N. D., USSR Patent 162,843 (1964); *Chem. Abstr.* **61**, 10592 (1964).
282. Kirsanov, A. V., and Shokol, V. A., *Zh. Obshch. Khim.* **30**, 3031 (1960); *Chem. Abstr.* **55**, 18636 (1961).
283. Kirsanov, A. V., and Zhmurova, I. N., *Zh. Obshch. Khim.* **28**, 2478 (1958); *Chem. Abstr.* **53**, 3118 (1959).
284. Kirsanov, A. V., and Zolotov, Yu. M., *Zh. Obshch. Khim.* **24**, 122 (1954); *Chem. Abstr.* **49**, 3052 (1955).
285. Kirsanov, A. V., and Zolotov, Yu. M., *Zh. Obshch. Khim.* **25**, 571 (1955); *Chem. Abstr.* **50**, 2521 (1956).

286. Klement, R., Koch, O. and Wolf, K. H., *Naturwissenschaften* **41**, 139 (1954); Klement, R., and Wolf, K. H., *Z. Anorg. Allg. Chem.* **282**, 149 (1955); see also Klement, R., and Rother, E., *Naturwissenschaften* **45**, 489 (1958).

286a. Klingebiel, U., and Glemser, O., *Chem. Ber.* **104**, 3804 (1971).

287. Köhnlein, G., Thesis, Univ. of Heidelberg, Heidelberg, 1963; Appel, R., personal communication.

288. Kolotilo, M. V., and Derkach, G. I., *Zh. Obshch. Khim.* **39**, 463 (1969); *Chem. Abstr.* **70**, 115261 (1969).

288a. Kondratenko, V. I., Rudavskii, V. P., Kucherova, M. N., and Babin, E. P., USSR Patent 252,336 (1969); *Chem. Abstr.* **72**, 54806 (1970).

289. Kongpricha, S., and Preusse, W. C., *148th Meet., Amer. Chem. Soc., Chicago* Abstr. p. 3K (1964); Kongpricha, S., U.S. Patent 3,445,513 (1969) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **71**, 50218 (1969).

290. Kongpricha, S., and Preusse, W. C., *Inorg. Chem.* **6**, 1915 (1967).

290a. Kornuta, P. P., Kalenskaya, A. I., and Shevchenko, V. I., *Zh. Obshch. Khim.* **41**, 988 (1971); *Chem. Abstr.* **75**, 140805 (1971).

290b. Kornuta, P. P., and Shevchenko, V. I., *Zh. Obshch. Khim.* **40**, 551 (1970); *Chem. Abstr.* **73**, 35461 (1970).

290c. Kornuta, P. P., and Shevchenko, V. I., *Zh. Obshch. Khim.* **40**, 788 (1970); *Chem. Abstr.* **73**, 34707 (1970).

291. Kornuta, P. P., Shevchenko, V. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **37**, 2788 (1967); *Chem. Abstr.* **68**, 113971 (1968).

292. Korshak, V. V., Gribova, I. A., Artamonova, T. V., and Bushmarina, A. N., *Vysokomol. Soedin.* **2**, 377 (1960); *Chem. Abstr.* **54**, 24479 (1960).

292a. Kosinskaya, I. M., Pinchuk, A. M., and Shevchenko, V. I., *Zh. Obshch. Khim.* **41**, 105 (1971); *Chem. Abstr.* **75**, 35088 (1971).

293. Kowalski, A., U.S. Patent 3,023,194 (1962) (Pennsalt Chem. Corp.); *Chem. Abstr.* **57**, 10037 (1962).

294. Kozlov, E. S., and Drach, B. S., *Zh. Obshch. Khim.* **36**, 760 (1966); *Chem. Abstr.* **65**, 8742 (1966); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 70 (1969); *Chem. Abstr.* **75**, 88033 (1971).

294a. Kozlov, E. S., Gaidamaka, S. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **39**, 1648 (1969); *Chem. Abstr.* **71**, 91593 (1969).

294b. Kozlov, E. S., Gaidamaka, S. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **40**, 991 (1970); *Chem. Abstr.* **73**, 77332 (1970); see also Kozlov, E. S., Gaidamaka, S. N., Borovikov, Yu. Ya., Tsyba, V. T., and Kirsanov, A. V. *Zh. Obshch. Khim.* **40**, 2549 (1970); *Chem. Abstr.* **75**, 12714 (1971).

295. Kozlov, E. S., Kisilenko, A. A., Sedlov, A. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **37**, 1611 (1967); *Chem. Abstr.* **68**, 48835 (1968).

296. Kropacheva, A. A., Derkach, G. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 1601 (1961); *Chem. Abstr.* **55**, 22274 (1961).

297. Kropacheva, A. A., and Sazonov, N. V., *Puti Sin. Izyskaniya Protivoopukholevykh Prep., Tr. Simp. Khim. Protivoopukholevykh Veshchestva, 2nd, Moscow, 1965* p. 94 (1967); *Chem. Abstr.* **70**, 11660 (1969); *Khim. Geterosikl. Soedin.*, Sb. 1: Azotsoderzhashchie Geterosikly p. 372 (1967); *Chem. Abstr.* **70**, 106453 (1969); see also Noell, C. W., and Cheng, C. C., *J. Med. Chem.* **11**, 63 (1968).

297a. Kukhar, V. P., *Zh. Obshch. Khim.* **40**, 785 (1970); *Chem. Abstr.* **73**, 34708 (1970).

297b. Kukhar, V. P., and Koval, A. A., *Zh. Obshch. Khim.* **40**, 776 (1970); *Chem. Abstr.* **73**, 34711 (1970).
297c. Kukhar, V. P., Semenii, V. Ya., and Kirsanov, A. V., *Zh. Obshch. Khim.* **40**, 2382 (1970); *Chem. Abstr.* **74**, 140869 (1971).
297d. Kukhar, V. P., Semenii, V. Ya., and Kirsanov, A. V., *Zh. Obshch. Khim.* **41**, 1459 (1971); *Chem. Abstr.* **75**, 140418 (1971).
297e. Kukhar, V. P., Semenii, V. Ya., and Pisanenko, N. P., *Zh. Obshch. Khim.* **40**, 557 (1970); *Chem. Abstr.* **73**, 14368 (1970).
297f. Kulibaba, N. K., Shevchenko, V. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **41**, 2105 (1971); *Chem. Abstr.* **76**, 24605 (1972).
298. Lapidot, A., and Samuel, D., *J. Chem. Soc.*, p. 2110 (1962).
299. Latscha, H. P., *Z. Anorg. Allg. Chem.* **346**, 166 (1966).
300. Latscha, H. P., *Z. Anorg. Allg. Chem.* **355**, 73 (1967).
301. Latscha, H. P., *Z. Naturforsch. B* **23**, 139 (1968).
302. Latscha, H. P., Haubold, W., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **339**, 82 (1965).
303. Latscha, H. P., and Hormuth, P. B., *Angew. Chem.* **80**, 281 (1968); *Angew. Chem. Int. Ed. Engl.* **7**, 299 (1968).
304. Latscha, H. P., and Hormuth, P. B., *Z. Anorg. Allg. Chem.* **359**, 78 (1968).
305. Latscha, H. P., and Hormuth, P. B., *Z. Anorg. Allg. Chem.* **359**, 81 (1968).
305a. Latscha, H. P., Hormuth, P. B., and Vollmer, H., *Z. Naturforsch. B* **24**, 1237 (1969).
306. Latscha, H. P., and Klein, W., *Angew. Chem.* **81**, 291 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 278 (1969).
306a. Latscha, H. P., and Klein, W., *Z. Anorg. Allg. Chem.* **377**, 285 (1970).
307. Latscha, H. P., Weber, W., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **367**, 40 (1969).
308. Lehr, W., *Angew. Chem.* **79**, 1002 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 982 (1967); *Z. Anorg. Allg. Chem.* **371**, 225 (1969).
309. Lehr, W., *Z. Anorg. Allg. Chem.* **350**, 18 (1967).
309a. Lehr, W., and Pietschmann, J., *Chem.-Ztg., Chem. App.* **94**, 362 (1970).
310. Lehr, W., and Schwarz, M., *Z. Anorg. Allg. Chem.* **363**, 43 (1968); see also Zhivukhin, S. M., Kireev, V. V., Popilin, V. P., and Kolesnikov, G. S., *Zh. Neorg. Khim.* **15**, 1229 (1970); *Chem. Abstr.* **73**, 51833 (1970).
310a. Levchenko, E. S., and Budnik, L. V., *Zh. Org. Khim.* **6**, 2239 (1970); *Chem. Abstr.* **74**, 42065 (1971).
311. Levchenko, E. S., Derkach, N. Ya., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 1212 (1962); *Chem. Abstr.* **58**, 4456 (1963).
312. Levchenko, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **27**, 3078 (1957); *Chem. Abstr.* **52**, 8070 (1958).
313. Levchenko, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **29**, 1813 (1959); *Chem. Abstr.* **54**, 8694 (1960).
314. Levchenko, E. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 1553 (1960); *Chem. Abstr.* **55**, 3484 (1961).
315. Levchenko, E. S., and Sheinkman, I. E., *Zh. Obshch. Khim.* **34**, 1145 (1964); *Chem. Abstr.* **61**, 1787 (1964).
316. Levchenko, E. S., Sheinkman, I. E., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 1941 (1960); *Chem. Abstr.* **55**, 6426 (1961).

317. Levchenko, E. S., Sheinkman, I. E., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 3315 (1963); *Chem. Abstr.* **60**, 4043 (1964).
318. Levchenko, E. S., and Ugarov, B. N., *Zh. Obshch. Khim.* **35**, 2080 (1965); *Chem. Abstr.* **64**, 6683 (1966).
319. Levchenko, E. S., and Ugarov, B. N., *Zh. Org. Khim.* **4**, 1413 (1968); *Chem. Abstr.* **69**, 86538 (1968).
320. Levchenko, E. S., Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **29**, 2262 (1959); *Chem. Abstr.* **54**, 10926 (1960).
321. Ley, H., *Ber. Deut. Chem. Ges.* **31**, 240 (1898); Ley, H., and Holzweissig, E., *Ber. Deut. Chem. Ges.* **36**, 19 (1903).
322. Lincoln, B. H., and Byrkit, G. D., U.S. Patent 2,380,454 (1945) (Lubri-Zol Co.); *Chem. Abstr.* **40**, 723 (1946); U.S. Patent 2,460,301 (1949); *Chem. Abstr.* **43**, 2765 (1949).
322a. Loseva, I. M., Gubnitskaya, E. S., and Derkach, G. I., *Fiziol. Aktiv. Veshchestva* p. 3 (1969); *Chem. Abstr.* **73**, 3713 (1970); see also Bilich, B. E., Dyachenko, S. S., Koval, A. A., and Rudavskii, V. P., *Fiziol. Aktiv. Veshchestva* p. 40 (1969); *Chem. Abstr.* **73**, 24190 (1970).
323. Lund, L. G., Paddock, N. L., Proctor, J. E., and Searle, H. T., *J. Chem. Soc.* p. 2542 (1960).
324. Lustig, M., *Inorg. Chem.* **8**, 443 (1969).
325. Lutskii, A. E., Samarai, L. I., Kochergina, L. A., Shepel, A. V., Shevchenko, Z. A., Derkach, G. I., Kozlov, E. S., and Drach, B. S., *Zh. Obshch. Khim.* **37**, 2042 (1967); *Chem. Abstr.* **68**, 34387 (1968).
326. Lutskii, A. E., Shevchenko, Z. A., Samarai, L. I., and Pinchuk, A. M., *Zh. Obshch. Khim.* **37**, 2034 (1967); *Chem. Abstr.* **68**, 34386 (1968).
327. Lysenko, V. V., Karavanov, K. V., and Ivin, S. Z., USSR Patent 182,152 (1966); *Chem. Abstr.* **65**, 17003 (1966).
328. Mamaeva, I. E., Sazonov, N. V., and Kropacheva, A. A., *Khim. Geterosikl. Soedin.* p. 521 (1969); *Chem. Abstr.* **72**, 3457 (1970); Sazonov, N. V., Mamaeva, I. E., Kropacheva, A. A., Safonova, T. S., Minakova, S. M., and Chernov, V. A., *Puti Sin. Izyskaniya Protivoopukholevykh Prep., Tr. Simp. Protivoopukholevykh Veshchestva, 3rd, Moscow, 1968*; p. 331 (1970); *Chem. Abstr.* **75**, 49015 (1971).
329. Mann, F. G., and Chaplin, E. J., *J. Chem. Soc.* p. 527 (1937).
330. Mao, T. J., Dresdner, R. D., and Young, J. A., *J. Inorg. Nucl. Chem.* **24**, 53 (1962).
331. Matrosov, E. I., *Zh. Strukt. Khim.* **7**, 708 (1966); *Chem. Abstr.* **66**, 23974 (1967).
332. Matyushecheva, G. I., Narbut, A. V., Derkach, G. I., and Yagupol'skii, L. M., *Zh. Org. Khim.* **3**, 2254 (1967); *Chem. Abstr.* **68**, 59236 (1968); Mikhailov, V. S., Matyushecheva, G. I., Derkach, G. I., and Yagupol'skii, L. M., *Zh. Org. Khim.* **6**, 149 (1970); *Chem. Abstr.* **72**, 90373 (1970); see also Yagupol'skii, L. M., Mikhailov, V. S., and Matyushecheva, G. I., *Zh. Org. Khim.* **6**, 1648 (1970); *Chem. Abstr.* **73**, 109124 (1970).
333. Mel'nikov, N. N., Grapov, A. F., Razvodovskaya, A. V., and Ivanova, T. M., *Zh. Obshch. Khim.* **37**, 239 (1967); *Chem. Abstr.* **66**, 85714 (1967).
334. Michaelis, A., *Justus Liebigs Ann. Chem.* **326**, 129 (1903).
335. Michaelis, A., *Justus Liebigs Ann. Chem.* **407**, 290 (1915).
336. Mochalina, E. P., Dyatkin, B. L., and Knunyants, I. L., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 2247 (1966); *Chem. Abstr.* **66**, 76089 (1967).

337. Moeller, T., and Vandi, A., *J. Org. Chem.* **27**, 3511 (1962).
338. Moeller, T., and Westlake, A. H., *J. Inorg. Nucl. Chem.* **29**, 957 (1967).
339. Moran, E. F., *J. Inorg. Nucl. Chem.* **30**, 1405 (1968).
340. Mosby, W. L., Gillham, H. C., and Sherr, A. E., U.S. Patent 3,322,860 (1967) (American Cyanamid Co.); *Chem. Abstr.* **67**, 44425 (1967); U.S. Patent 3,439,005 (1969); *Chem. Abstr.* **71**, 22183 (1969).
341. Murch, R. M., and De Vore, D. C., Can. Patent 884,204 (1971) (W. R. Grace & Co.); Ger. Patent Appl. (DOS) 1,802,016 (1969); *Chem. Abstr.* **71**, 50677 (1969); see also E. Kobayashi, Jap. Patent 00,805 (1971) (Bureau of Industrial Technology of Japan); *Chem. Abstr.* **74**, 112659 (1971).
342. Murray, M., and Schmutzler, R., *Z. Chem.* **8**, 241 (1968).
343. Nannelli, P., Failli, A., and Moeller, T., *Inorg. Chem.* **4**, 558 (1965).
343a. Narbut, A. V., and Derkach, G. I., *Zh. Obshch. Khim.* **39**, 1698 (1969); *Chem. Abstr.* **72**, 3188 (1970).
344. Nichols, G. M., ASD Tech. Rep. 61-2, Contract No. AF 33(616)-7158, Project No. 8128 (May 1961); ASD Tech. Rep. 61-2 Part II, Contract No. AF 33(616)-7158, Project No. 1(8-7340) (February 1962); quoted in reference (*407*), *loc. cit.* p. 298 ff.
345. Nichols, G. M., U.S. Patent 3,449,091 (1969) (E. I. du Pont de Nemours & Co.); *Chem. Abstr.* **71**, 31905 (1969); see also U.S. Patent 3,249,397 (1966); *Chem. Abstr.* **65**, 1831 (1966).
346. Niedenzu, K., and Magin, G., *Z. Naturforsch. B* **20**, 604 (1965).
347. Niecke, E., and Glemser, O., unpublished observations, quoted in reference (*173*), *loc. cit.* p. 502.
347a. Niecke, E., Thamm, H., and Glemser, O., *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 1.14 (1970); cf. Fluck, E., *Chem.-Ztg., Chem. App.* **94**, 833 (1970).
348. Nielsen, M. L., and Parts, L. P., U.S. Patent 3,412,065 (1968) (Monsanto Research Corp.); *Chem. Abstr.* **70**, 48229 (1969); Parts, L., Nielsen, M. L., and Miller, J. T., *147th Meet., Amer. Chem. Soc., Philadelphia*, Abstr. p. 30L (1964); *Inorg. Chem.* **3**, 1261 (1964).
349. Nielsen, M. L., and Pustinger, J. V., Jr., *J. Chem. Phys.* **68**, 152 (1964).
349a. Nielsen, M. L., Pustinger, J. V., Jr., and Strobel, J., *J. Chem. Eng. Data* **9**, 169 (1964).
350. Nielsen, M. L., *in* "Developments of Inorganic Nitrogen Chemistry" (C. B. Colburn, ed.), Vol. 1, p. 307. Elsevier, Amsterdam, 1966.
351. Nixon, J. F., and Schmutzler, R., *Spectrochim. Acta* **22**, 565 (1966).
352. Norris, W. P., and Jonassen, H. B., *J. Org. Chem.* **27**, 1449 (1962).
353. O'Brien, J. B., Ph.D. Thesis, Univ. of New Hampshire, Durham, New Hampshire, 1968; *Diss. Abstr. B* **29**, 113 (1968/1969).
354. Oyamada, K., and Morimura, S., *Takamine Kenkyusho Nempo* **12**, 41 (1960); *Chem. Abstr.* **55**, 6459 (1961).
355. Paddock, N. L., *Quart. Rev. Chem. Soc.* **18**, 168 (1964).
356. Paddock, N. L., Brit. Patent 883,587 (1961) (Albright & Wilson Mfg. Ltd.); *Chem. Abstr.* **56**, 13809 (1962); U.S. Patent 3,026,174 (1962); Can. Patent 575,069 (1961).
357. Paddock, N. L., and Searle, H. T., *Advan. Inorg. Chem. Radiochem.* **1**, 347 (1959).
358. Parts, L., and Nielsen, M. L., U.S. Patent 3,290,259 (1966) (Monsanto Research Corp.); *Chem. Abstr.* **66**, 29517 (1967).

359. Parts, L. P., and Nielsen, M. L., U.S. Patent 3,314,899 (1967) (Monsanto Research Corp.); *Chem. Abstr.* **67**, 12106 (1967).

359a. Pavlenko, A. F., Akkerman, V. P., Zalesskii, G. A., and Ivashchenko, Ya. N., *Zh. Obshch. Khim.* **39**, 1516 (1969); *Chem. Abstr.* **71**, 112762 (1969).

360. von Pechmann, H., *Ber. Deut. Chem. Ges.* **28**, 2362 (1895); **30**, 1779 (1897); **33**, 611 (1900); von Pechmann, H., and Heinze, B., *Ber. Deut. Chem. Ges.* **30**, 1783 (1897).

361. Petitcolas, P., and Roe, R., *Bull. Soc. Chim. Fr.* p. 378 (1954).

361a. Pinchuk, A. M., and Kosinskaya, I. M., *Zh. Obshch. Khim.* **40**, 546 (1970); *Chem. Abstr.* **73**, 35295 (1970).

362. Pinchuk, A. M., Kosinskaya, I. M., and Shevchenko, V. I., *Zh. Obshch. Khim.* **37**, 856 (1967); *Chem. Abstr.* **67**, 108169 (1967).

363. Pinchuk, A. M., Kosinskaya, I. M., and Shevchenko, V. I., *Zh. Obshch. Khim.* **37**, 2693 (1967); *Chem. Abstr.* **69**, 67069 (1968).

364. Pinchuk, A. M., Kosinskaya, I. M., and Shevchenko, V. I., *Zh. Obshch. Khim.* **39**, 583 (1969); *Chem. Abstr.* **71**, 61300 (1969).

365. Pinchuk, A. M., Markovskii, L. N., Levchenko, E. S., and Shevchenko, V. I., *Zh. Obshch. Khim.* **37**, 852 (1967); *Chem. Abstr.* **67**, 108407 (1967).

366. Proctor, J. E., Thesis, London Univ., London, 1958; quoted in references (*69*), *loc. cit.* p. 1826 and (*355*), *loc. cit.* p. 171; see also Emsley, J., and Udy, P. B., *Abstr. Joint Annu. Meet., Chem. Soc., Nottingham*, No. 7.16 (1969); *Chem. Commun.* p. 633 (1967); *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 5.4 (1970); *J. Chem. Soc.* **A**, p. 3025 (1970); Brit. Patent 1,222,506 (1971) (Castrol Ltd.); *Chem. Abstr.* **74**, 89273 (1971).

366a. Prons, V. N., Grinblat, M. P., and Klebanskii, A. L., *Zh. Obshch. Khim.* **40**, 589 (1970); *Chem. Abstr.* **73**, 25595 (1970).

367. Protsenko, L. D., Derkach, G. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3433 (1961); *Chem. Abstr.* **57**, 3355 (1962).

368. Protsenko, L. D., and Kornev, K. A., *Ukr. Khim. Zh.* **24**, 636 (1958); *Chem. Abstr.* **53**, 12266 (1959).

368a. Protsenko, L. D., Rapp, L. B., Skul'skaya, N. Ya., Kuz'menko, I. I., Shokol, V. A., Svyatnenko, E. A., and Derkach, G. I., *Puti Sin. Izyskaniya Protivoopukholevykh Prep., Tr. Simp. Khim. Protivoopukholevykh Veshchestva, 3rd, Moscow, 1968*, p. 347 (1970); *Chem. Abstr.* **75**, 98362 (1971).

369. Protsenko, L. D., Shokol, V. A., Golik, G. A., and Koval, S. N., *Zh. Obshch. Khim.* **39**, 370 (1969); *Chem. Abstr.* **70**, 115240 (1969).

369a. Protsenko, L. D., and Skul'skaya, N. Ya., *Khim.-Farm. Zh.* **3**, 17 (1969); *Chem. Abstr.* **71**, 101619 (1969).

369b. Protsenko, L. D., Skul'skaya, N. Ya., and Bodnarchuk, N. D., *Zh. Obshch. Khim.* **41**, 1242 (1971); *Chem. Abstr.* **75**, 88698 (1971).

370. Raetz, R. F. W., and Kober, E. H., U.S. Patent 2, 81,734 (1961) (Olin Mathieson Chem. Corp.); *Chem. Abstr.* **56**, 10170 (1962).

371. Reddy, G. S., and Weis, C. D., *J. Org. Chem.* **28**, 1822 (1963).

372. Remsen, I., Hartmann, R. N., and Muckenfuss, A. M., *Amer. Chem. J.* **18**, 150 (1896).

373. Resnick, P., and Luzzi, J. J. R., U.S. Patent 3,028,377 (1962) (Interchemical Corp.); *Chem. Abstr.* **57**, 8548 (1962).

374. Rice, R. G., Murch, R. M., and De Vore, D. C., U.S. Patent 3,545,942 (1970) (W. R. Grace & Co.); *Chem. Abstr.* **74**, 54398 (1971); Ger. Patent Appl. (DOS) 1,801,945; *Chem. Abstr.* **71**, 39654 (1969).

374a. Riesel, L., Herrmann, E., Pätzmann, H., Somieski, R., Kroschwitz, H., and Lehmann, H. A., *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 1.7 (1970); Riesel, L., Herrmann, E., Pätzmann, H., Somieski, R., Kroschwitz, H., Schröter, D., and Lehmann, H. A., *Z. Chem.* **10**, 466 (1970).
375. Rodionov, V. M., and Yavorskaya, E. V., *Zh. Obshch. Khim.* **18**, 110 (1948); *Chem. Abstr.* **42**, 4976 (1948).
376. Roesky, H. W., personal communication.
377. Roesky, H. W., *Angew. Chem.* **81**, 493 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 510 (1969).
378. Roesky, H. W., *Chem. Ber.* **101**, 3679 (1968).
378a. Roesky, H. W., *Chem. Ber.* **103**, 694 (1970).
378b. Roesky, H. W., *Inorg. Nucl. Chem. Lett.* **6**, 129 (1970).
378c. Roesky, H. W., *Inorg. Nucl. Chem. Lett.* **6**, 807 (1970).
379. Roesky, H. W., *Z. Anorg. Allg. Chem.* **367**, 151 (1969).
379a. Roesky, H. W., *Z. Naturforsch. B* **25**, 777 (1970).
380. Roesky, H. W., and Giere, H. H., *Chem. Ber.* **102**, 2330 (1969).
381. Roesky, H. W., and Giere, H. H., *Inorg. Nucl. Chem. Lett.* **4**, 639 (1968).
381a. Roesky, H. W., and Giere, H. H., *Inorg. Nucl. Chem. Lett.* **7**, 171 (1971).
381b. Roesky, H. W., and Giere, H. H., *Z. Anorg. Allg. Chem.* **378**, 177 (1970).
381c. Roesky, H. W., Giere, H. H., and Babb, D. P., *Inorg. Chem.* **9**, 1076 (1970).
381d. Roesky, H. W., and Grimm, L. F., *Angew. Chem.* **82**, 255 (1970); *Angew. Chem. Int. Ed. Engl.* **9**, 244 (1970); *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 1.11 (1970).
382. Roesky, H. W., and Grimm, L. F., *Chem. Ber.* **102**, 2319 (1969).
382a. Roesky, H. W., and Grimm, L. F., *Chem. Ber.* **103**, 1664 (1970).
382b. Roesky, H. W., and Grimm, L. F., *Chem. Ber.* **103**, 3114 (1970).
382c. Roesky, H. W., and Grimm, L. F., *Chem. Commun.* p. 998 (1971).
383. Roesky, H. W., and Grimm, L. F., *Inorg. Nucl. Chem. Lett.* **5**, 13 (1969).
383a. Roesky, H. W., Grimm, L. F., and Niecke, E., *Z. Anorg. Allg. Chem.* **385**, 102 (1971).
383b. Roesky, H. W., and Grosse Böwing, W., *Angew. Chem.* **83**, 365 (1971); *Angew. Chem. Int. Ed. Engl.* **10**, 344 (1971); *Chem. Ber.* **104**, 3204 (1971).
383c. Roesky, H. W., and Grosse Böwing, W., *Chem. Ber.* **103**, 2281 (1970).
384. Roesky, H. W., and Grosse Böwing, W., *Inorg. Nucl. Chem. Lett.* **5**, 597 (1969).
384a. Roesky, H. W., and Grosse Bowing, W., *Z. Anorg. Allg. Chem.* **386**, 191 (1971).
385. Roesky, H. W., and Grosse Böwing, W., *Z. Naturforsch. B* **24**, 1250 (1969).
385a. Roesky, H. W., Grosse Böwing, W., and Niecke, E., *Chem. Ber.* **104**, 653 (1971).
385b. Roesky, H. W., and Holtschneider, G., *Z. Anorg. Allg. Chem.* **378**, 168 (1970).
385c. Roesky, H. W., Holtschneider, G., and Giere, H. H., *Z. Naturforsch. B* **25**, 252 (1970).
385d. Roesky, H. W., Kloker, W., and Grosse Böwing, W., *Symposium of Inorganic Phosphorus Compounds, Prague*, Abstr. 1.3 (1970); Roesky, H. W., and Grosse Böwing, W., *Inorg. Nucl. Chem. Lett.* **6**, 781 (1970).
386. Roesky, H. W., and Niecke, E., *Inorg. Nucl. Chem. Lett.* **4**, 463 (1968).
387. Roesky, H. W., and Niecke, E., *Z. Naturforsch. B* **24**, 1101 (1969).
387a. Roesky, H. W., and Remmers, G., *Z. Naturforsch. B* **26**, 75 (1971).
387b. Rudavskii, V. P., Kondratenko, V. I., and Kucherova, M. N., *Zh. Obshch. Khim.* **41**, 1456 (1971); *Chem. Abstr.* **75**, 129487 (1971); see also Rudavskii,

V. P., Kucherova, M. N., Shirankov, D. F., and Makovetskii, P. S., *Khim. Sel. Khoz.* **9**, 453 (1971); *Chem. Abstr.* **75**, 108815 (1971).

387c. Rudavskii, V. P., Kucherova, M. N., Kondratenko, V. I., Zagnibeda, D. M., Litoshenko, N. A., and Babin, E. P., USSR Patent 314,757 (1971); *Chem. Abstr.* **76**, 13259 (1972).

387d. Rudavskii, V. P., Litoshenko, N. A., and Babin, E. P., USSR Patent 253,061 (1969); *Chem. Abstr.* **72**, 66590 (1970).

387e. Rudavskii, V. P., Litoshenko, N. A., and Babin, E. P., *Khim. Prom. Ukr.* p. 46 (1970); *Chem. Abstr.* **73**, 14054 (1971).

387f. Rudavskii, V. P., Litoshenko, N. A., and Kukhar, V. P., *Zh. Obshch. Khim.* **40**, 1002 (1970); *Chem. Abstr.* **73**, 76813 (1970); Rudavskii, V. P., and Litoshenko, N. A., *Khim. Prom. Ukr.*, p. 24 (1970); *Chem. Abstr.* **74**, 52965 (1971).

387g. Rudavskii, V. P., Litoshenko, N. A., and Zagnibeda, D. M., *Khim. Tekhnol. (Kiev)* p. 19 (1971); *Chem. Abstr.* **75**, 129895 (1971).

387h. Rudavskii, V. P., Zagnibeda, D. M., and Kondratenko, V. I., *Farm. Zh.* **26**, 14 (1971); *Chem. Abstr.* **76**, 3496 (1972).

388. Ruff, J. K., *Inorg. Chem.* **6**, 2108 (1967).

389. Sasse, K., *in* Houben-Weyl "Methoden der organischen Chemie," 4th Ed., Vol. XII/2. Thieme, Stuttgart, 1964.

390. Sazonov, N. V., and Kropacheva, A. A., *Khim. Geterosikl. Soedin.* Sb. 1: Azotsoderzhashchie Geterosikly, p. 377 (1967); *Chem. Abstr.* **70**, 87725 (1969); *Khim. Geterosikl. Soedin.* p. 97 (1970); *Chem. Abstr.* **72**, 111403 (1970).

390a. Sazonov, N. V., and Kropacheva, A. A., *Khim. Geterosikl. Soedin.* p. 55 (1970); *Chem. Abstr.* **72**, 111393 (1970).

391. Scharf, B., Thesis, Univ. of Heidelberg, Heidelberg, 1967.

392. Scherer, O. J., *Organometal. Chem. Rev., Sect. A* **3**, 281 (1968).

393. Schmidpeter, A., and Böhm, R., *Angew. Chem.* **77**, 1038 (1965); *Angew. Chem. Int. Ed. Engl.* **4**, 990 (1965).

394. Schmidpeter, A., and Böhm, R., *Z. Anorg. Allg. Chem.* **262**, 65 (1968).

395. Schmidpeter, A., and Düll, K., *Chem. Ber.* **100**, 1116 (1967).

396. Schmidpeter, A., Düll, K., and Böhm, R., *Angew. Chem.* **76**, 605 (1964); *Angew. Chem. Int. Ed. Engl.* **3**, 704 (1964).

397. Schmidpeter, A., Düll, K., and Böhm, R., *Z. Anorg. Allg. Chem.* **362**, 58 (1968).

398. Schmidpeter, A., and Ebeling, J., *Angew. Chem.* **79**, 534 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 565 (1967).

399. Schmidpeter, A., Ebeling, J., and Groeger, H., *Chem. Ber.* in preparation.

400. Schmidpeter, A., Ebeling, J., and Schindler, N., *Angew. Chem.* **79**, 1016 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 996 (1967).

401. Schmidpeter, A., and Schindler, N., *Chem. Ber.* **102**, 2201 (1969).

402. Schmidpeter, A., and Schindler, N., *Z. Anorg. Allg. Chem.* **362**, 281 (1968).

403. Schmidpeter, A., and Weingand, C., personal communication; see also Schmidpeter, A., and Schumann, K., *Z. Naturforsch. B* **25**, 1364 (1970).

404. Schmidpeter, A., and Weingand, C., *Angew. Chem.* **80**, 234 (1968); *Angew. Chem. Int. Ed. Engl.* **7**, 210 (1968).

405. Schmidpeter, A., and Weingand, C., *Angew. Chem.* **81**, 573 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 615 (1969).

406. Schmidpeter, A., Weingand, C., and Hafner-Roll, E., *Z. Naturforsch. B* **24**, 799 (1969).

407. Schmulbach, C. D., *Progr. Inorg. Chem.* **4**, 275 (1962).

408. Schmutzler, R., *Angew. Chem.* **76**, 893 (1964); *Angew. Chem. Int. Ed. Engl.* **3**, 753 (1964).
408a. Schmutzler, R., *Angew. Chem.* **77**, 530 (1965); *Angew. Chem. Int. Ed. Engl.* **4**, 494 (1965).
409. Schmutzler, R., *Chem. Commun.* p. 19 (1965).
410. Schmutzler, R., U.S. Patent 3,287,406 (1966) (E. I. du Pont de Nemours & Co.); *Chem. Abstr.* **66**, 85857 (1967).
411. Schmutzler, R., *in* "Halogen Chemistry" (V. Gutmann, ed.), Vol. 2, p. 31. Academic Press, New York, 1967.
412. Schönberg, A., and Singer, E., *Chem. Ber.* **102**, 2557 (1969).
413. Seglin, L., Lutz, M. R., and Stange, H., U.S. Patent 3,231,327 (1966) (FMC Corp.); *Chem. Abstr.* **64**, 10810 (1966).
414. Senning, A., *Angew. Chem.* **77**, 379 (1965); *Angew. Chem. Int. Ed. Engl.* **4**, 357 (1965); *Acta Chem. Scand.* **19**, 1755 (1965).
415. Shaw, R. A., *Chem. Ind.* (*London*) p. 1737 (1967).
416. Shaw, R. A., *Endeavour* **27**, 74 (1968).
417. Shaw, R. A., *Rec. Chem. Progr.* **28**, 243 (1967).
418. Shaw, R. A., Fitzsimmons, B. W., and Smith, B. C., *Chem. Rev.* **62**, 247 (1962).
419. Shaw, R. A., and Ibrahim, E. H. M., *Angew. Chem.* **79**, 575 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 556 (1967).
420. Shaw, R. A., Keat, R., and Hewlett, C., *Prep. Inorg. React.* **2**, 1 (1965).
421. Sheluchenko, V. V., Filatova, I. M., Zaitseva, E. L., and Yakubovich, A. Ya., *Zh. Obshch. Khim.* **39**, 194 (1969); *Chem. Abstr.* **70**, 92124 (1969).
422. Sherif, F. G., *J. Inorg. Nucl. Chem.* **30**, 1707 (1968).
423. Shevchenko, V. I., and Bodnarchuk, N. D., *Zh. Obshch. Khim.* **36**, 1645 (1966); *Chem. Abstr.* **66**, 54962 (1967).
424. Shevchenko, V. I., Bodnarchuk, N. D., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 1342 (1963); *Chem. Abstr.* **59**, 11239 (1963).
425. Shevchenko, V. I., Bodnarchuk, N. D., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 1591 (1963); *Chem. Abstr.* **59**, 12839 (1963).
426. Shevchenko, V. I., and Bondarev, V. V., *Zh. Obshch. Khim.* **26**, 270 (1956); *Chem. Abstr.* **50**, 13787 (1956).
427. Shevchenko, V. I., El'Dik, M., and Pinchuk, A. M., *Zh. Obshch. Khim.* **38**, 1527 (1968); *Chem. Abstr.* **69**, 95848 (1968).
427a. Shevchenko, V. I., El'Dik, M., and Pinchuk, A. M., *Zh. Obshch. Khim.* **39**, 1514 (1969); *Chem. Abstr.* **71**, 113057 (1969).
427b. Shevchenko, V. I., El'Dik, M., and Pinchuk, A. M., *Zh. Obshch. Khim.* **40**, 1949 (1970); *Chem. Abstr.* **74**, 141201 (1971).
427c. Shevchenko, V. I., and Kirsanov, A. V., *Usp. Khim., Fosfororg. Seraorg. Soedin., Izd. Nauk. Dumka, Kiev* No. 1, p. 44 (1969); *Chem. Abstr.* **72**, 110394 (1970).
428. Shevchenko, V. I., and Kornuta, P. P., *Zh. Obshch. Khim.* **36**, 1254 (1966); *Chem. Abstr.* **65**, 15381 (1966).
429. Shevchenko, V. I., and Kornuta, P. P., *Zh. Obshch. Khim.* **36**, 1642 (1966); *Chem. Abstr.* **66**, 65032 (1967).
430. Shevchenko, V. I., Kornuta, P. P., Bodnarchuk, N. D., and Kirsanov, A. V., *Zh. Obshch. Khim.* **36**, 730 (1966); *Chem. Abstr.* **65**, 8912 (1966); see also Bodnarchuk, N. D., and Gavrilenko, B. B., *Zh. Obshch. Khim.* **39**, 1961 (1969); *Chem. Abstr.* **72**, 31941 (1970); Kornuta, P. P., Kalenskaya, A. I., Shevchenko,

V. I., and Kirsanov, A. V., *Dopov. Akad. Nauk Ukr. RSR, Ser. B* **32**, 533 (1970); *Chem. Abstr.* **73**, 98914 (1970); Shevchenko, V. I., Kornuta, P. P., and Bodnarchuk, N. D., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 89 (1969); *Chem. Abstr.* **74**, 140802 (1971); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 93 (1969); *Chem. Abstr.* **75**, 140803 (1971).

431. Shevchenko, V. I., Kornuta, P. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1598 (1965); *Chem. Abstr.* **63**, 17891 (1965).

432. Shevchenko, V. I., Kornuta, P. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1970 (1965); *Chem. Abstr.* **64**, 8027 (1966).

433. Shevchenko, V. I., and Koval, A. A., *Zh. Obshch. Khim.* **37**, 1111 (1967); *Chem. Abstr.* **68**, 12377 (1968).

434. Shevchenko, V. I., and Koval, A. A., *Zh. Obshch. Khim.* **38**, 22 (1968); *Chem. Abstr.* **69**, 18554 (1968).

435. Shevchenko, V. I., Koval, A. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 555 (1968); *Chem. Abstr.* **69**, 26701 (1968).

435a. Shevchenko, V. I., Koval, A. A., and Litovchenko, N. R., *Dopov. Akad. Nauk Ukr. RSR, Ser. B* **31**, 1021 (1969); *Chem. Abstr.* **72**, 55137 (1970); *Zh. Obshch. Khim.* **40**, 2164 (1970); *Chem. Abstr.* **75**, 63527 (1971).

435b. Shevchenko, V. I., Koval, A. A., and Pisanenko, N. P., *Zh. Obshch. Khim.* **40**, 1005 (1970); *Chem. Abstr.* **73**, 76766 (1970).

436. Shevchenko, V. I., and Kukhar, V. P., *Zh. Obshch. Khim.* **36**, 735 (1966); *Chem. Abstr.* **65**, 8858 (1966).

437. Shevchenko, V. I., and Kukhar, V. P., *Zh. Obshch. Khim.* **36**, 1260 (1966); *Chem. Abstr.* **65**, 16845 (1966); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 102 (1969); *Chem. Abstr.* **75**, 76046 (1971).

438. Shevchenko, V. I., and Kukhar, V. P., *Zh. Obshch. Khim.* **38**, 24 (1968); *Chem. Abstr.* **69**, 18572 (1968).

439. Shevchenko, V. I., Kukhar, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **36**, 467 (1966); *Chem. Abstr.* **65**, 615 (1966).

440. Shevchenko, V. I., Kukhar, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **37**, 2361 (1967); *Chem. Abstr.* **68**, 77683 (1968).

441. Shevchenko, V. I., Kukhar, V. P., Koval, A. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 1270 (1968); *Chem. Abstr.* **69**, 106391 (1968).

441a. Shevchenko, V. I., Kukhar, V. P., and Litovchenko, N. R., *Zh. Obshch. Khim.* **39**, 2203 (1969); *Chem. Abstr.* **72**, 55129 (1970); Shevchenko, V. I., Litovchenko, N. R., and Kukhar, V. P., *Zh. Obshch. Khim.* **40**, 1229 (1970); *Chem. Abstr.* **74**, 76249 (1971); Shevchenko, V. I., and Litovchenko, N. R., *Zh. Obshch. Khim.* **41**, 1243 (1971); *Chem. Abstr.* **75**, 88422 (1971).

442. Shevchenko, V. I., Kulibaba, N. K., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 326 (1968); *Chem. Abstr.* **69**, 18498 (1968); see also Kozlov, E. S., and Drach, B. S., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 80 (1969); *Chem. Abstr.* **75**, 129301 (1971).

443. Shevchenko, V. I., Kulibaba, N. K., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 850 (1968); *Chem. Abstr.* **69**, 58906 (1968).

443a. Shevchenko, V. I., Kulibaba, N. K., and Kirsanov, A. V., *Zh. Obshch. Khim.* **39**, 1689 (1969); *Chem. Abstr.* **72**, 3132 (1970).

444. Shevchenko, V. I., and Merkulova, Zh. V., *Zh. Obshch. Khim.* **29**, 1005 (1959); *Chem. Abstr.* **54**, 1371 (1960).

444a. Shevchenko, V. I., and Nizhnikova, E. E., *Zh. Obshch. Khim.* **40**, 1219 (1970); *Chem. Abstr.* **74**, 31632 (1971).

445. Shevchenko, V. I., Nizhnikova, E. E., Bodnarchuk, N. D., and Kornuta, P. P., *Zh. Obshch. Khim.* **37**, 1358 (1967); *Chem. Abstr.* **68**, 39055 (1968); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 82, 100 (1969); *Chem. Abstr.* **74**, 140794, 140801 (1971).

446. Shevchenko, V. I., and Pinchuk, A. M., *Zh. Obshch. Khim.* **35**, 1492 (1965); *Chem. Abstr.* **63**, 14901 (1965).

447. Shevchenko, V. I., Pinchuk, A. M., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1488 (1965); *Chem. Abstr.* **63**, 14899 (1965).

448. Shevchenko, V. I., Shtepanek, A. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3062 (1961); *Chem. Abstr.* **56**, 15541 (1962).

449. Shevchenko, V. I., Shtepanek, A. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 2595 (1962); *Chem. Abstr.* **58**, 9126 (1963).

450. Shevchenko, V. I., and Stadnik, V. I., *Probl. Org. Sin., Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 281 (1965); *Chem. Abstr.* **64**, 4933 (1966).

451. Shevchenko, V. I., Stadnik, V. I., and Kirsanov, A. V., *Probl. Org. Sin., Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 272 (1965); *Chem. Abstr.* **64**, 5071 (1966).

452. Shevchenko, V. I., and Stratienko, V. T., *Zh. Obshch. Khim.* **29**, 3458 (1959); *Chem. Abstr.* **54**, 15284 (1960).

453. Shevchenko, V. I., and Stratienko, V. T., *Zh. Obshch. Khim.* **29**, 3757 (1959); *Chem. Abstr.* **54**, 22447 (1960).

454. Shevchenko, V. I., and Stratienko, V. T., *Zh. Obshch. Khim.* **30**, 1561 (1960); *Chem. Abstr.* **55**, 1496 (1961).

455. Shevchenko, V. I., and Stratienko, V. T., *Zh. Obshch. Khim.* **30**, 1958 (1960); *Chem. Abstr.* **55**, 6425 (1961).

456. Shevchenko, V. I., Stratienko, V. T., and Pinchuk, A. M., *Zh. Obshch. Khim.* **30**, 1566 (1960); *Chem. Abstr.* **55**, 1490 (1961).

457. Shevchenko, V. I., Stratienko, V. T., and Pinchuk, A. M., *Zh. Obshch. Khim.* **34**, 3954 (1964); *Chem. Abstr.* **62**, 9167 (1965).

458. Shevchenko, V. I., Stratienko, V. T., and Pinchuk, A. M., *Zh. Obshch. Khim.* **35**, 363 (1965); *Chem. Abstr.* **62**, 13173 (1965).

459. Shevchenko, V. I., Stratienko, V. T., and Pinchuk, A. M., *Zh. Obshch. Khim.* **35**, 1487 (1965); *Chem. Abstr.* **63**, 14899 (1965).

460. Shevchenko, V. I., Tkach, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 4047 (1962); *Chem. Abstr.* **58**, 13832 (1963); Kirsanov, A. V., Shevchenko, V. I., and Tkach, V. P., USSR Patent 173,227 (1965); *Chem. Abstr.* **64**, 646 (1966).

461. Shevchenko, V. I., Tkach, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 992 (1965); *Chem. Abstr.* **63**, 9981 (1965).

462. Shevchenko, V. I., Tkach, V. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1224 (1965); *Chem. Abstr.* **63**, 11411 (1965).

463. Shirankov, D. F., Rudavskii, V. P., and Derkach, G. I., USSR Patent 217,135 (1968); *Chem. Abstr.* **69**, 66376 (1968); Abramova, K. A., Rudavskii, V. P., Kucherova, M. N., and Shirankov, D. F., USSR Patent 276,621 (1970); *Chem. Abstr.* **74**, 75499 (1971).

464. Shokol, V. A., and Derkach, G. I., *Zh. Obshch. Khim.* **35**, 1468 (1965); *Chem. Abstr.* **63**, 14750 (1965).

465. Shokol, V. A., Derkach, G. I., and Gubnitskaya, E. S., *Zh. Obshch. Khim.* **33**, 3058 (1963); *Chem. Abstr.* **60**, 1638 (1964).

466. Shokol, V. A., Derkach, G. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 166 (1962); *Chem. Abstr.* **57**, 16648 (1962).

467. Shokol, V. A., Derkach, G. I., and Kisilenko, A. A., *Zh. Obshch. Khim.* **33**, 2660 (1963); *Chem. Abstr.* **60**, 2455 (1964).
468. Shokol, V. A., Fedotova, L. I., Frolova, A. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 534 (1965); *Chem. Abstr.* **63**, 524 (1965).
469. Shokol, V. A., Gamaleya, V. F., and Derkach, G. I., *Zh. Obshch. Khim.* **37**, 1147 (1967); *Chem. Abstr.* **68**, 22009 (1968).
470. Shokol, V. A., Gamaleya, V. F., and Derkach, G. I., *Zh. Obshch. Khim.* **38**, 1081 (1968); *Chem. Abstr.* **69**, 59340 (1968).
471. Shokol, V. A., Gamaleya, V. F., and Derkach, G. I., *Zh. Obshch. Khim.* **38**, 1867 (1968); *Chem. Abstr.* **70**, 20174 (1969).
471a. Shokol, V. A., Gamaleya, V. F., and Derkach, G. I., *Zh. Obshch. Khim.* **39**, 1703 (1969); *Chem. Abstr.* **71**, 124593 (1969).
471b. Shokol, V. A., Gamaleya, V. F., and Kukhar, V. P., *Zh. Obshch. Khim.* **40**, 554 (1970); *Chem. Abstr.* **73**, 25572 (1970).
472. Shokol, V. A., Gamaleya, V. F., Molyavko, L. I., and Derkach, G. I., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 109 (1967); *Chem. Abstr.* **69**, 36225 (1968); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 43 (1969); *Chem. Abstr.* **75**, 20503 (1971).
473. Shokol, V. A., Golik, G. A., and Derkach, G. I., *Zh. Obshch. Khim.* **38**, 871 (1968); *Chem. Abstr.* **69**, 52211 (1968).
473a. Shokol, V. A., Golik, G. A., Tsyba, V. T., and Derkach, G. I., *Zh. Obshch. Khim.* **40**, 931 (1970); *Chem. Abstr.* **73**, 35465 (1970).
474. Shokol, V. A., Kirsanov, A. V., Gubnitskaya, E. S., and Derkach, G. I., USSR Patent 179,772 (1966); *Chem. Abstr.* **65**, 7217 (1966).
475. Shokol, V. A., Kisilenko, A. A., and Derkach, G. I., *Zh. Obshch. Khim.* **39**, 874 (1969); *Chem. Abstr.* **71**, 43880 (1969).
476. Shokol, V. A., Mikhailyuchenko, N. K., and Derkach, G. I., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 78 (1967); *Chem. Abstr.* **69**, 10065 (1968).
477. Shokol, V. A., Mikhailyuchenko, N. K., and Derkach, G. I., *Zh. Obshch. Khim.* **38**, 337 (1968); *Chem. Abstr.* **69**, 18499 (1968).
478. Shokol, V. A., Molyavko, L. I., and Derkach, G. I., *Zh. Obshch. Khim.* **36**, 930 (1966); *Chem. Abstr.* **65**, 12229 (1966).
478a. Shokol, V. A., Molyavko, L. I., and Derkach, G. I., *Zh. Obshch. Khim.* **40**, 998 (1970); *Chem. Abstr.* **73**, 77329 (1970).
479. Shomova, E. A., Rudavskii, V. P., and Derkach, G. I., *Fiziol. Aktiv. Veshchestva, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb.* p. 89 (1966); *Chem. Abstr.* **66**, 104344 (1967).
480. Shomova, E. A., Rudavskii, V. P., and Derkach, G. I., USSR Patent 195,785 (1967); *Chem. Abstr.* **68**, 38527 (1968).
481. Shtepanek, A. S., Piven, Yu. V., and Derkach, G. I., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 61 (1967); *Chem. Abstr.* **68**, 114695 (1968).
482. Shtepanek, A. S., Shevchenko, V. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1023 (1965); *Chem. Abstr.* **63**, 9982 (1965).
483. Singh, G., and Zimmer, H., *Organometal. Chem. Rev., Sect. A* **2**, 279 (1967).
483a. Slawisch, A., and Pietschmann, J., *Z. Naturforsch. B* **25**, 321 (1970).
484. Smolina, A. I., Tsybul'skaya, G. N., Rudavskii, V. P., and Derkach, G. I., *Fiziol. Aktiv. Veshchestva, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb.* p. 96 (1966); *Chem. Abstr.* **67**, 53861 (1967).

485. Steinkopf, W., *Ber. Deut. Chem. Ges.* **41**, 3571 (1908); *J. Prakt. Chem.* [2] **81**, 140, 233 (1910).
486. Stopkan, V. V., Lobov, V. P., Shokol, V. A., Mikhailyuchenko, N. K., and Derkach, G. I., *Fiziol. Aktiv. Veshchestva, Akad. Nauk Ukr. SSR, Respub. Mezhvedom. Sb.* p. 86 (1966); *Chem. Abstr.* **67**, 31879 (1967).
487. Stratienko, V. T., Thesis, Dnjepropetrovsk, 1961; quoted in reference (*137*), *loc. cit.* p. 20.
488. Sunagawa, G., and Onoyama, K., Jap. Patent 9,779 (1960) (Sankyo Co.); *Chem. Abstr.* **55**, 9348 (1961).
489. Sunagawa, G., and Oyamada, K., Jap. Patent 9,030 (1960) (Sankyo Co.); *Chem. Abstr.* **55**, 9348 (1961).
490. Teijin Ltd., Jap. Patent 52,321 (1965); Brit. Patent 1,115,558 (1966); Fr. Patent 1,493,154 (1967); Neth. Appl. 6,612,063 (1967); *Chem. Abstr.* **67**, 54598 (1967).
491. Titherley, A. W., and Worrall, E., *J. Chem. Soc.* **95**, 1143 (1909).
491a. Tökés, L., and Wong, S. C. K., *Org. Mass Spectrom.* **4**, 59 (1970).
492. Trippett, S., *J. Chem. Soc.*, p. 4731 (1962).
492a. Trippett, S., Davidson, R. S., Hutchinson, D. W., Keat, R., Shaw, R. A., and Tebby, J. C., "Organophosphorus Chemistry," Vol. 1. Chem. Soc. Specialist Period. Rep., London, 1970 and following volumes.
493. Tsybul'skaya, G. N., Rudavskii, V. P., and Derkach, G. I., *Khim. Sel. Khoz.* **3**, 59 (1965); *Chem. Abstr.* **63**, 4879 (1965).
494. Ulrich, H., and Sayigh, A. A. R., *Angew. Chem.* **74**, 900 (1962); *Angew. Chem. Int. Ed. Engl.* **1**, 595 (1962).
495. Ulrich, H., and Sayigh, A. A. R., *Angew. Chem.* **76**, 647 (1964); *Angew. Chem. Int. Ed. Engl.* **3**, 585 (1964).
496. Ulrich, H., and Sayigh, A. A. R., *Angew. Chem.* **78**, 761 (1966); *Angew. Chem. Int. Ed. Engl.* **5**, 704 (1966).
497. Ulrich, H., and Sayigh, A. A. R., *J. Chem. Soc.*, p. 5558 (1963).
498. Ulrich, H., and Sayigh, A. A. R., *J. Org. Chem.* **30**, 2779 (1965).
499. Utvary, K., personal communication.
500. Utvary, K., *Oesterr. Chem.-Ztg.* **66**, 322 (1965).
501. Utvary, K., and Bermann, M., *Inorg. Chem.* **8**, 1038 (1969).
502. Utvary, K., and Bermann, M., *Monatsh. Chem.* **99**, 2369 (1968).
503. Utvary, K., and Czysch, W., *Monatsh. Chem.* **100**, 681 (1969).
504. Utvary, K., Gutmann, V., and Kemenater, C., *Monatsh. Chem.* **96**, 1751 (1965).
505. Vandi, A. F., and Moeller, T., *Chem. Ind. (London)* p. 221 (1962); *Inorg. Syn.* **9**, 118, 119 (1967).
506. Vandi, A., and Moeller, T., *Inorg. Syn.* **8**, 116 (1966).
507. Vandi, A., and Moeller, T., *Inorg. Syn.* 8, 119 (1966).
508. Vandi, A., Moeller, T., and Brown, T. L., *Inorg. Chem.* **2**, 809 (1963); Moeller, T., Chang, T. H., Ouchi, A., Vandi, A., and Failli, A., *Inorg. Syn.* **13**, 9 (1971).
509. Vetter, H. J., *Z. Naturforsch. B* **19**, 168 (1964).
509a. Vollmer, H., and Becke-Goehring, M., *Z. Anorg. Allg. Chem.* **382**, 281 (1971).
509b. Volodin, A. A., Kireev, V. V., Kolesnikov, G. S., and Titov, S. S., *Zh. Obshch. Khim.* **40**, 2202 (1970); *Chem. Abstr.* **74**, 141955 (1971).
509c. Wakefield, Z. T., Allen, S. E., McCullough, J. F., Sheridan, R. C., and Kohler, J. J., *J. Agr. Food Chem.* **19**, 99 (1971).

510. Wald, H. J., Thesis, Univ. of Heidelberg, Heidelberg, 1968; see also references (*16*, *36b*).
511. Wallach, O., *Ber. Deut. Chem. Ges.* **7**, 326 (1874).
512. Wallach, O., *Ber. Deut. Chem. Ges.* **8**, 299 (1875).
513. Wallach, O., *Justus Liebigs Ann. Chem.* **184**, 1 (1877); and *loc. cit.*
514. Wallach, O., and Huth, T., *Ber. Deut. Chem. Ges.* **8**, 317 (1875).
515. Weiss, J., and Hartmann, G., *Z. Anorg. Allg. Chem.* **351**, 152 (1967).
516. Weiss, J., and Hartmann, G., *Z. Naturforsch. B* **21**, 891 (1966).
516a. Whitehead, M. A., *Can. J. Chem.* **42**, 1212 (1964).
517. Wichelhaus, H., *Ber. Deut. Chem. Ges.* **2**, 502 (1869).
518. Wieczorkowski, J., *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **13**, 155 (1965).
519. Wiegräbe, W., Thesis, Univ. of Munich, Munich, 1963.
520. Wiegräbe, W., and Bock, H., *Chem. Ber.* **101**, 1414 (1968).
521. Wiegräbe, W., Bock, H., and Lüttke, W., *Chem. Ber.* **99**, 3737 (1966); see also Bock, H., and tom Dieck, H., *Z. Naturforsch. B* **21**, 739 (1966).
521a. Wunsch, G., Schiedermaier, R., Kiener, V., Fluck, E., and Heckmann, G., *Chem.-Ztg., Chem. App.* **94**, 832 (1970); Wunsch, G., Schiedermaier, R., and Wintersberger, K., Belg. Patent 748,775 (1970) (BASF); Fr. Patent 2,043,302 (1971); Ger. Patent Appl. (DOS) 1,918,947 (1970); *Chem. Abstr.* **74**, 5150 (1971); see also Schiedermaier, R., Wintersberger, K., and Wunsch, G., Ger. Patent Appl. (DOS) 1,918,697 (BASF); *Chem. Abstr.* **74**, 5144 (1971); Fr. Patent 2,043,129 (1971).
522. Yagupol'skii, L. M., and Troitskaya, V. I., *Zh. Obshch. Khim.* **29**, 552 (1959); *Chem. Abstr.* **54**, 356 (1960).
523. Yagupsky, M. P., *Inorg. Chem.* **6**, 1770 (1967).
523a. Yakubovich, A. Ya., Filatova, I. M., Zaitseva, E. L., and Simonov, A. P., *Zh. Obshch. Khim.* **39**, 2213 (1969); *Chem. Abstr.* **72**, 55579 (1970).
524. Yakubovich, A. Ya., Shvetsov, N. I., Filatova, I. M., Yakubovich, V. S., Lebedeva, I. V., and Kozlova, N. V., *Zh. Neorg. Khim.* **11**, 810 (1966); *Chem. Abstr.* **66**, 11006 (1967); Yakubovich, A. Ya., Shvetsov, N. I., Lebedeva, I. V., and Yakubovich, V. S., *Zh. Neorg. Khim.* **8**, 1863 (1963); Yakubovich, V. S., Lebedeva, I. V., Yakubovich, A. Ya., and Shvetsov, N. I., USSR Patents 176,412 and 176,416 (1965); *Chem. Abstr.* **64**, 11397 (1966); Yakubovich, A. Ya., Filatova, I. M., Zaitseva, E. L., and Yakubovich, V. S., *Vysokomol. Soedin., Ser. A* **12**, 585 (1970); *Chem. Abstr.* **73**, 45893 (1970).
524a. Yakubovich, A. Ya., Shvetsov, N. I., Lebedeva, I. V., and Yakubovich, V. S., *Zh. Neorg. Khim.* **8**, 534 (1963); *Chem. Abstr.* **59**, 211 (1963).
524b. Yurzhenko, T. I., and Babyak, A. G., USSR Patent 271,519 (1970); *Chem. Abstr.* **73**, 120757 (1970); *Zh. Obshch. Khim.* **40**, 1662 (1970); *Chem. Abstr.* **74**, 53922 (1971).
524c. Yurzhenko, T. I., and Babyak, A. G., *Zh. Obshch. Khim.* **41**, 1454 (1971); *Chem. Abstr.* **75**, 129891 (1971).
525. Yvernault, T., and Casteigneau, G., *Bull. Soc. Chim. Fr.* p. 1469 (1966).
525a. Zhivukhin, S. M., Kireev, V. V., Titov, S. S., and Kolesnikov, G. S., *Tr. Mosk. Khim.-Tekhnol. Inst.* **61**, 200 (1969); *Chem. Abstr.* **73**, 15354 (1970).
525b. Zhivukhin, S. M., Kireev, V. V., Titov, S. S., and Kolesnikov, G. S., *Vysokomol. Soedin., Ser. A* **11**, 1610 (1969); *Chem. Abstr.* **71**, 102403 (1969).
526. Zhmurova, I. N., and Dolgushina, I. Yu., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 195 (1967); *Chem. Abstr.* **69**, 76781 (1968).

527. Zhmurova, I. N., Dolgushina, I. Yu., and Kirsanov, A. V., *Zh. Obshch. Khim.* **37**, 1797 (1967); *Chem. Abstr.* **68**, 22007 (1968).

527a. Zhmurova, I. N., and Drach, B. S., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 72 (1969); *Chem. Abstr.* **74**, 140792 (1971).

527b. Zhmurova, I. N., and Drach, B. S., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 76 (1969); *Chem. Abstr.* **74**, 140796 (1971).

527c. Zhmurova, I. N., and Drach, B. S., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 78 (1969); *Chem. Abstr.* **74**, 140800 (1971).

528. Zhmurova, I. N., and Drach, B. S., *Zh. Obshch. Khim.* **34**, 1441 (1964); *Chem. Abstr.* **61**, 5499 (1964); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 60 (1969); *Chem. Abstr.* **75**, 151296 (1971).

529. Zhmurova, I. N., and Drach, B. S., *Zh. Obshch. Khim.* **34**, 3055 (1964); *Chem. Abstr.* **62**, 14480 (1965).

530. Zhmurova, I. N., and Drach, B. S., *Zh. Obshch. Khim.* **35**, 718 (1965); *Chem. Abstr.* **63**, 4149 (1965); *Metody Poluch. Khim. Reaktivov Prep.* **19**, 74 (1969); *Chem. Abstr.* **74**, 140791 (1971).

531. Zhmurova, I. N., Drach, B. S., and Kirsanov, A. V., *Ukr. Khim. Zh.* **31**, 223 (1965); *Chem. Abstr.* **63**, 1689 (1965).

532. Zhmurova, I. N., Drach, B. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 344 (1965); *Chem. Abstr.* **62**, 13030 (1965); Zhmurova, I. N., and Drach, B. S., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 68 (1969); *Chem. Abstr.* **75**, 19668 (1971).

533. Zhmurova, I. N., Drach, B. S., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 1018 (1965); *Chem. Abstr.* **63**, 9796 (1965).

534. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **29**, 1687 (1959); *Chem. Abstr.* **54**, 8688 (1960).

535. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 3044 (1960); *Chem. Abstr.* **55**, 17551 (1961); Zhmurova, I. N., *Metody Poluch. Khim. Reaktivov Prep.* **19**, 57 (1969); *Chem. Abstr.* **75**, 140401 (1971).

536. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **30**, 4048 (1960); *Chem. Abstr.* **55**, 22197 (1961).

537. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3685 (1961); *Chem. Abstr.* **57**, 13795 (1962).

538. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 2576 (1962); *Chem. Abstr.* **58**, 7848 (1963); see also Shokol, V. A., Mikhailyuchenko, N. K., Derkach, G. I., and Kirsanov, A. V., USSR Patent 271,520 (1970); *Chem. Abstr.* **73**, 119810 (1970).

539. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 182 (1963); *Chem. Abstr.* **59**, 657 (1963); Kirsanov, A. V., and Zhmurova, I. N., USSR Patent 151,332 (1962); *Chem. Abstr.* **59**, 11567 (1963).

540. Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **33**, 1015 (1963); *Chem. Abstr.* **59**, 8782 (1963).

541. Zhmurova, I. N., Kisilenko, A. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 2580 (1962); *Chem. Abstr.* **58**, 10877 (1963).

542. Zhmurova, I. N., and Martynyuk, A. P., *Khim. Org. Soedin. Fosfora, Akad. Nauk SSSR, Otd. Obshch. Tekh. Khim.* p. 191 (1967); *Chem. Abstr.* **69**, 2442 (1968).

543. Zhmurova, I. N., and Martynyuk, A. P., *Zh. Obshch. Khim.* **37**, 896 (1967); *Chem. Abstr.* **68**, 29350 (1968).

544. Zhmurova, I. N., and Martynyuk, A. P., *Zh. Obshch. Khim.* **38**, 876 (1968); *Chem. Abstr.* **69**, 59346 (1968).
545. Zhmurova, I. N., Martynyuk, A. P., and Derkach, G. I., *Zh. Obshch. Khim.* **38**, 163 (1968); *Chem. Abstr.* **69**, 52209 (1968).
546. Zhmurova, I. N., Voitsekhovskaya, I. Yu., and Kirsanov, A. V., *Zh. Obshch. Khim.* **31**, 3741 (1961); *Chem. Abstr.* **57**, 9702 (1962).
547. Zhmurova, I. N., and Yurchenko, R. I., *Zh. Obshch. Khim.* **38**, 613 (1968); *Chem. Abstr.* **69**, 107589 (1968); Zhmurova, I. N., Yurchenko, R. I., and Kirsanov, A. V., *Zh. Obshch. Khim.* **38**, 2078 (1968); *Chem. Abstr.* **70**, 28999 (1969); Zhmurova, I. N., and Kirsanov, A. V., *Zh. Obshch. Khim.* **36**, 1248 (1966); *Chem. Abstr.* **65**, 16826 (1966); Zhmurova, I. N., Tukhar, A. A., and Yurchenko, R. I., *Zh. Obshch. Khim.* **39**, 2201 (1969); *Chem. Abstr.* **72**, 31921 (1970); Zhmurova, I. N., Slominskii, Yu. L., Tolmachev, A. I., and Yurchenko, R. I., *Zh. Obshch. Khim.* **39**, 1732 (1969); *Chem. Abstr.* **72**, 31667 (1970); Zhmurova, I. N., Tukhar, A. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **40**, 2154 (1970); *Chem. Abstr.* **74**, 88103 (1971); Zhmurova, I. N., Tolmachev, A. I., Yurchenko, R. I., and Slominskii, Yu. L., *Zh. Obshch. Khim.* **40**, 2553 (1970); *Chem. Abstr.* **75**, 22455 (1971); see also Zhmurova, I. N., *Usp. Khim., Fosfororg. Seraorg. Soedin., Izd. Nauk. Dumka, Kiev* No. 1, p. 5 (1969); *Chem. Abstr.* **72**, 111534 (1970).
548. Zhuravleva, L. P., Grinyuk, M. A., and Kirsanov, A. V., *Zh. Obshch. Khim.* **35**, 998 (1965); *Chem. Abstr.* **63**, 9799 (1965).
549. Zhuravleva, L. P., and Kirsanov, A. V., *Zh. Obshch. Khim.* **32**, 3752 (1962); *Chem. Abstr.* **58**, 11253 (1963).
550. Ziegler, M., *Angew. Chem.* **79**, 322 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 369 (1967).
551. Ziegler, M. L., *Z. Anorg. Allg. Chem.* **362**, 257 (1968).
552. Ziegler, M. L., and Weiss, J., *Angew. Chem.* **81**, 430 (1969); *Angew. Chem. Int. Ed. Engl.* **8**, 455 (1969).
553. Ziegler, M. L., and Weiss, J., *Z. Anorg. Allg. Chem.* **361**, 136 (1968).
554. Zioudrou, C., *Tetrahedron* **18**, 197 (1962).