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Cyclic mono- and diphosphazenes

R I Tarasova, V V Moskva
S M Kirov Kazan Chemico-Technological Institute

ABSTRACT. Methods of synthesis of 5- and 6-membered heterocyclanes with one or two endocyclic P=N bonds (cyclomono- and cyclodi-phosphazenes) have been considered. Types of reaction common to acyclic analogues and specific types of reaction have been separated. The change of electronic structure and geometry of the P=N bond on changing from linear to cyclic phosphazenes are clearly displayed in the special features of their chemical behaviour.

The bibliography has 247 references.

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I. Introduction

The beginning of the seventies was a period of explosive development in investigations on phosphocyclanes in the chemistry of organophosphorus compounds.[1] This phenomenon also applies to heterocyclic compounds with an endocyclic P=N bond (cyclomono- and cyclodiphosphazenes). Acyclic phosphazenes were described for the first time by Staudinger in 1919,[2] however their systematic study began in 1950 with the work of Kirsanov and collaborators.[3–5] The first syntheses of six-membered cyclomono- and cyclodiphosphazenes appeared in the next decade,[5,6] as did those of five-membered analogues with dicoordinated[7] and tetracoordinated phosphorus atoms.[8,9]

The intensive investigations on organic cyclophosphazenes undertaken since the beginning of the seventies are reflected in a series of reviews published mainly in the foreign press.[10–14] Certain problems of the chemistry of these compounds have been touched upon in part.[15,16]

Interest in this area was caused by the special features of the structure and numerous chemical conversions of phosphacyclanes with a P=N bond, revealing broad vistas for the synthesis of various classes of *P,N*-containing compounds available for practical use.

A significant contribution has been made by Soviet investigators in the development of organic cyclophosphazene chemistry as is evident from an analysis of the literature.[6,10,11,14–16] There has been no correlation of these achievements in the domestic literature to date. Studies on heterocyclanes with one or two endocyclic P=N bonds are included in the present review. The cyclotriphosphazenes, having their own fairly complete literature converage,[17] have not been considered by us.

In contrast to acyclic compounds with a P=N bond, the nomenclature of which has an arbitrary character to a significant extent,[5,6,10,14] the naming of the corresponding cyclic organophosphorus compounds (OPC) is more uniform and corresponds to contemporary IUPAC rules.

This system will mainly be used in the present review. However it is convenient to use 'phosphazene' nomenclature, which has been widely adopted for some time, for linear and cyclic analogues as a general class of compounds with a P=N bond.[17] This nomenclature will be used for the general naming of the extensive series of compounds with a P=N bond.

The chemistry of heterocyclanes with a P=N bond is constructed on the basis of the experimental and theoretical developments of the acyclic phosphazenes. Consequently the synthetic methods for acycylic analogues are the basis for many means of obtaining cyclophosphazenes. Five of the basic reactions used for obtaining acyclic phosphazenes may be noted.[5]

The Staudinger reaction[2] comprises the reaction of organic azides with derivatives of tricoordinated phosphorus.

$$R_3P+R'N_3\rightarrow R_3P{=}NR'. \quad (1)$$

The reaction of dihalophosphoranes with compounds containing a primary amino group (the phosphazo reaction)[3–5]

$$R_3PX_2+R'NH_2\rightarrow R_3P{=}NR'. \quad (2)$$

The reaction of derivatives of tricoordinated phosphorus with compounds containing an amino group with two labile bonds (oxidation imination)[5,18]

$$R_3P + R'N\begin{matrix}X\\Y\end{matrix}\rightarrow R_3P{=}NR'. \quad (3)$$

An elimination reaction for compounds with a P–N bond[19–21]

$$\begin{matrix}R_3P{-}N\begin{matrix}R'\\Y\end{matrix}\\|\\X\end{matrix}\rightarrow R_3P{=}NR'. \quad (4)$$

A substitution reaction with compounds with a P=N bond

$$R_3P{=}N{-}Y+R'X\rightarrow R_3P{=}NR'. \quad (5)$$

The last type of reaction has been developed most fruitfully for *N*-hetero-substituted phosphazenes.[22–25]

Various modifications of the indicated reactions[26–29] have been proposed for acyclic phosphazenes up to the present time, much experimental and theoretical material has been obtained the complete elaboration of which is outside the scope of the present review.

All the indicated types of reaction are used for the synthesis of cyclophosphazenes. As will be shown below the development of cycloaddition reactions, a specific method of obtaining heterocycles, has great importance.

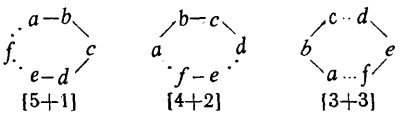
II. Preparative methods

1. Cyclocondensation reactions

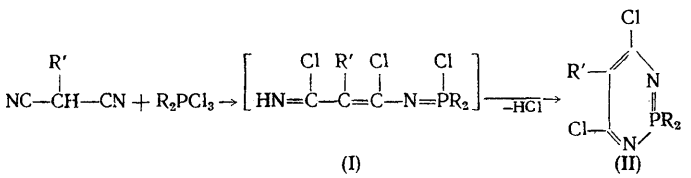
(a) Synthesis of hetero-1,2σ^4-azaphosphorines

The investigations of the Kiev school in conjunction with those of Kirsanov[6] and of Schmidpeter and colleagues[30] have made an important contribution to the development of the synthesis of six-membered cyclophosazenes. The reaction of nitrogen- and phosphorus-containing reactants by the phosphazo reaction with a subsequent cyclocondensation stage was a characteristic of all the proposed methods.

The synthesis of six-membered cyclophosphazenes may be formally represented as a number of elements participating in ring formation by [5 + 1]-,. [4 + 2]- and [3 + 3]-cyclocondensation reaction schemes.



One of the first representatives of the organic cyclophosphazenes, viz. 1,3,2-diazaphosphorine (II), was obtained by the interaction of malonic acid dinitrile with phosphorus pentachloride.[6]

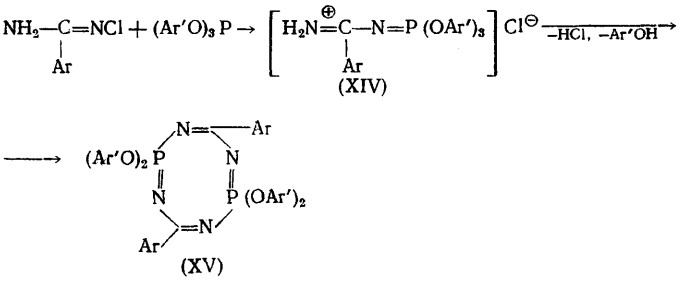


The authors suggested that the formation of a linear phosphazene (I) precedes the concluding stage. Study of the structure and routes of formation of diazaphosphorine (II) by the application of quantum chemical calculation methods has been carried out.[31]

Variants of the [5 + 1] scheme are the reaction of phosphorus pentachloride and certain trichlorophosphoranes with 1-amino-2-cyanoethylenes, *N*-cyanoamidines[6] and acetylurea[32] (Table 1, examples 1a, 1b, 2, 3a). Depending on the structure of the amino-containing reactant 1,3,2- (II) and 1,3,4-diazaphosphorines (III) or 1,3,5,4-triazaphosphorines (IV) were obtained. For [3 + 3] type cyclocondensations *P*-trichloro-*N*-dichloroalkylphosphazenes (VII)[6] and certain *N*-phosphorylated phosphazenes (IX), (X)[33–40] were reacted with nitriles, amidines and their salts. The structure of the resulting phosphorines (II), (IV), and (V) containing one or two P=N bonds was determined by the choice of phosphorus-containing reactant (Table 1, examples 1c, 3b, 4a, b). Triazamono- (IV) and triazadiphosphorines (V) were also obtained by a [4 + 2]-cyclocondensation of linear phosphazenes (VIII) and (XI) (Table 1, examples, 3c, 4c).[42]

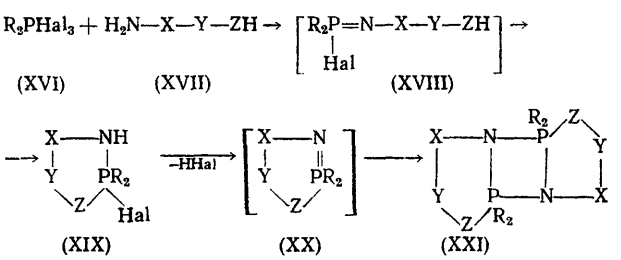
The multistage process of interacting *P*-trichloro-*N*-dichloroalkylphosphazene (VII) with ammonium chloride was carried out through the intermediate formation of alkylidenediphosphazene salts (XII) with isolation of triazadiphosphorine (V) [33,43,44] or a mixture of it with triazaphosphorine (IV) [6] (Table 1, example 4d). The synthesis of thioanalogues (VI) of triazadiphosphorines by a [5 + 1] scheme has been described.[45–50]

It is interesting to note the [4 + 4]-cyclocondensation reaction of hydrochloride salts of *P*-triaryloxy-*N*-iminoarylphosphazenes (XIV) as a rare example of the formation of 1,3,5,7,2,6-tetra-azadiphosphorine (XV).[51]



b) Synthesis of hetero-1,2σ^4-azaphospholes

Many methods of obtaining five-membered cyclophosphazenes are based on the interaction of halophosphoranes (XVI) with amino-containing compounds (XVII).



It is possible to represent the process by a single scheme, the initial stage of which is the formation of a linear phosphazene (XVIII). The latter undergoes intramolecular cyclisation into azaphospholine (XIX) with a pentacoordinated phosphorus atom. Further conversion of phosphacyclanes (XIX) occurs with elimination of hydrogen halide and the formation of 1,2σ^4-azaphospholes (XX) or their dimers (XXI).

The type of azaphosphole ring is determined mainly by the amino-component of the reaction for which oxalic acid diamides,[52] 2-aminoalkyl nitriles,[53] 4,5-diaminopyrimidines,[54] amidrazone hydrochlorides,[55,56] 1,2-aminophenols[57–60] and hydrazides of carboxylic[61–63] and thiocarboxylic acids[64] have been studied. The reaction of numerous reactants with phosphorus pentachloride or trichlorophosphoranes leads to the formation of 1,3,2σ^4-diaza- (XXII), (XXIII), 1,2,3,4σ^4-triaza- (XXIV), (XXV), and also isomer (XXVI), 4,5-benzo-1,3,2σ^4-oxaza- (XXVII), and 1,3,4,2σ^4-oxadiaza- (XXVIII) phospholes (Table 2).

In the majority of cases hetero-1,2σ^4-azaphospholes are unstable in the monomeric forms, they rapidly dimerise at the moment of formation. Exceptions are certain representatives of triazaphospholes (XXIV) and spirobis(triazaphosphole) (XXV). The latter is formed from triazaphosphole (XXIV) with an excess of amidrazone hydrochloride (XXIX).[65] 4,5-Pyrimidino-1,3,2-diazaphosphole (XXIII), characterised as the monomer,[54] seemingly exists in the dimeric form.

The problem of the stability of the monomeric and dimeric forms of hetero-1,2,-azaphospholes and the reason which causes a mixture of them in equilibrium has been discussed in several papers by Schmidpeter[53–57,64] and in detail in a review.[14] These problems will be considered in the present review only within the limits necessary for the characterisation of the chemical behaviour of the azaphospholes.

Table 1. Hetero-1,2σ^4-azaphosphorines by cyclocondensation reactions.

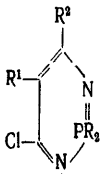
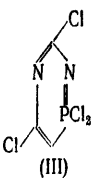
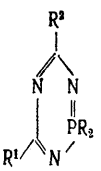
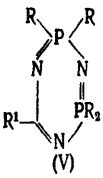
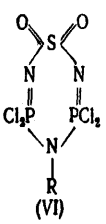
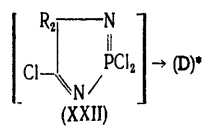
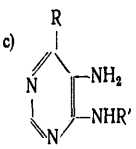
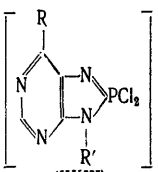
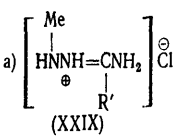
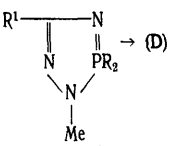
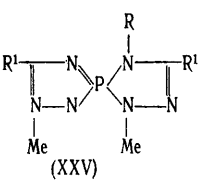
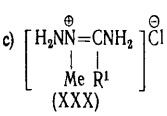
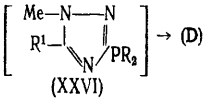
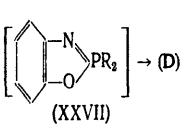
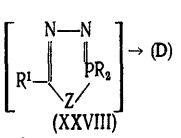
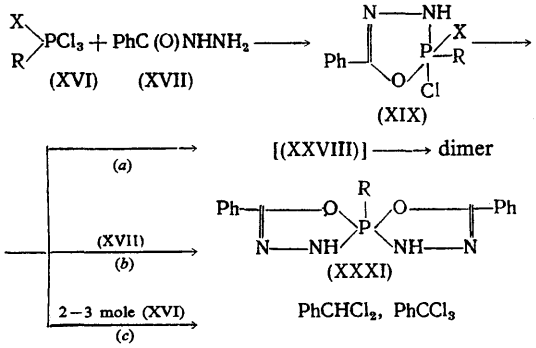
No.	Reactants		Reaction type	Azaphosphorine	^{31}P NMR, δ ppm	Refs.
	amino component	phosphorus component				
1	a) $R^1C(NH_2)=CCN$	R_2PCl_3	[5+1]	 (II)		[6]
	b) $NC-CH(R^1)-CN$	R_2PCl_3	[5+1]			
	c) R^1CH_2CN	$R^2CCl_2N=PCl_3$ (VII)	[3+3]			
2	$MeCNHCNH_2$ (O, O)	PCl_5	[5+1]	 (III)	53.0	[32]
3	a) $R^1C(NH_2)=NCN$	R_2PCl_3	[5+1]			
	b) $R^1C(NH_2)=NH.HCl$	(VII)	[3+3]	 (IV)	57.0 (R=Cl, N=PCl_2, R^1=R^2=Cl); 26.4 (R^1=H, R^2=NMe_2)	[6, 40—42]
	c) PhNHCH=NPh	$Me_2NC(NH_2)=NP(Ph)_2=NH$ (VIII)	[4+2]			
	d) $NH_2OH.HCl$	(VII)	[4+2]			
4	a) $R^1C(NH_2)=NH\cdot HCl$	$[R_2P(Cl)-N=PR_2(Cl)]^{\oplus}Cl^{\ominus}$ (IX)	[3+3]	 (V)	14.4 (R=Ph, R^1=H); 27.1 (R=Me, R^1=H); 36.0 (R=Cl, R^1=NMe_2); 40—43 (R=Ph, R^1=Ph, Cl)	[33—39, 43, 44]
	b) $R_FC(NH_2)=NH$	$Cl_2P(Ph)-N=PCl_2(Ph)$ (X)	[3+3]			
	c) PhNHCH=NPh	$R_2P(Cl)=N-P(NH_2)(Ph)=NH$ (XI)	[4+2]			
	d) NH_4Cl	$[RC(=\overset{\oplus}{N}PCl_3)(N=PCl_3)]\overset{\ominus}{X}$ (XII)	[5+1]	(IV)+(V)		[6]
5	a) $MeNH_2$	$(Cl_2P=N)_2SO_2$ (XIII)	[5+1]	 (VI)		[45—50]
	b) $(Me_3Si)_2NH$	(XIII)	[5+1]			

Table 2. Hetero-1,2σ^4-azaphospholes by cyclocondensation reactions.

No.	Reactants		Azaphospholes and their dimers	^{31}P NMR, δ ppm	Refs.
	amino component	phosphorus component			
1	a) NH_2CCNH_2 (O, O)	PCl_5	 → (D)* (XXII)	−48.0 (D)	[52—54]
	b) $NH_2C(R_2)CN$	PCl_5			
	c) 	PCl_5	 (XXIII)	—	[49]
2	a)  (XXIX)	R_2PCl_3	 (XXIV)	47.5—64.0 (M) **	[55, 56]
	b) (XXIX)	(XXIV)	 (XXV)	50.0 (M) (R^1=Ph, R=Me)	[65]
	c)  (XXX)	R_2PCl_3	 → (D) (XXVI)	−63.0 (D) (R^1=Cl)	[55, 56]
3	a) $C_6H_4(NH_2)(OH)$-1,2	R_2PCl_3	 → (D) (XXVII)	−43.0 — −48.0 (D)	[57—60, 68, 71]
	b) »	$RP(NEt_2)_2$			
	c) $C_6H_4(OH)(N_3)$-1,2	Et_2PCl			
4	a) R^1CNHNH_2 (Z)	R_2PCl_3	 → (D) (XXVIII)	−31.0 — −53.0 (D) (Z=O)	[61—64, 67]
	b) »	R_2PCl (Z)		−24.0 — −42.0 (D) (Z=S)	

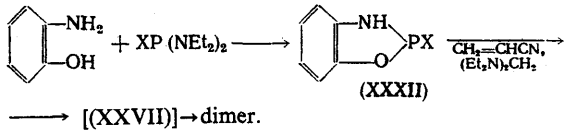
*D — dimer; **M — monomer.

The interaction of carboxylic acid hydrazides with halophosphoranes was historically the first and has been studied in most detail. The final result of the reaction depends mainly on the ratio of the initial reactants. At an equimolar ratio the process proceeds in accordance with the presented overall scheme and leads to dimers of 1,3,4,2σ^4-oxadiazaphospholes (XXVIII) (route a).[61,62] Hydrazides of thiocarboxylic acids reacted similarly at a 1 : 1 ratio.[64] At a two- and three-fold excess of phosphorus pentachloride decomposition of the intermediate oxadiazaphospholine (XIX) occurs (route c),[66] and in the case of a two-fold excess of hydrazide (XVII) spirodi(oxadiazaphospholines) (XXXI) were isolated.[63]



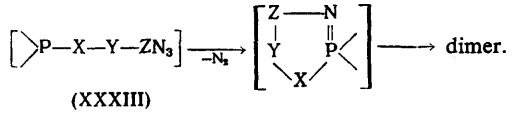
The acid chlorides of P(IV) acids or their thio analogues[61–64,67] were also used in reactions with carboxylic acid hydrazides (XVII). The latter were reacted at a ratio 1 : 1 and the former 1 : 3. In both cases dimers of 1,3,4,2σ^4-oxadiazaphospholes (XXVIII) were isolated as in the reactions with phosphoranes.[67]

The original method of synthesis of hetero-1,2,σ^4-azaphospholes was proposed in studies.[68–71] The authors used the high lability of the proton on the endocyclic nitrogen atom of 4,5-benzo-1,3,2-oxazaphospholanes (XXXII). As a result reaction was effected with acrylonitrile[68,70] and bisdiethylaminomethane[71] with the formation of 4,5-benzo-1,3,2-oxazaphospholes (XXVII), existing in the dimeric form.

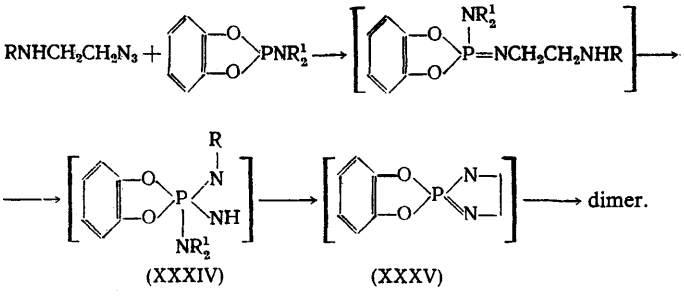


Analogous dimers of 4,5-benzo-1,3,2-oxazaphospholes (R = X = Ph) were formed from 4,5-benzo-2-methoxy-1,3,2σ^5-oxazaphospholanes by removing methanol thermally.[72] The course of the reaction through the unstable form (XXVII) was shown by reaction with aldehydes.

Intramolecular cyclocondensation of the Staudinger reaction type has also been studied with the aim of synthesising hetero-1,2-azaphospholes. In this scheme reaction was carried out between 2-hydroxyphenyl azide and diethylchlorophosphine[57,58] (Table 2, example 3c) and between 2-azidoalcohols and 1,2,4,3σ^2-triazaphospholes.[73] In both cases the 2-azidoaryl or 2-azidoalkyl derivatives of P(III) acids of the (XXXIII) type formed in the first step were subject to intramolecular cyclisation with separation of nitrogen.

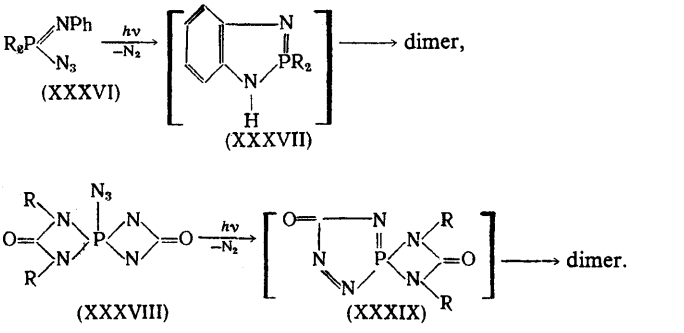


On interacting *N*-(2-azidoethyl)alkylamines with cyclic phosphites the first step was a Staudinger reaction completed by intramolecular cycloaddition and the formation of spirophosphoranes (XXXIV).[74]



The reaction led to the isolation of dimers of 1,3,2σ^4-diazaphospholines (XXXV). One of the alternative routes of forming them, proposed by the authors, may be the elimination of amine from a molecule of spirophosphorane (XXXIV).

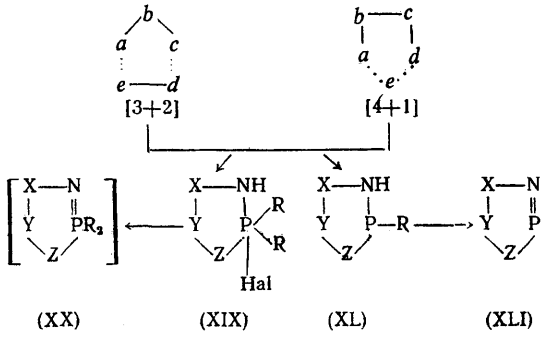
Azides of P(IV) (XXXVI) and P(V) (XXXVIII) derivatives may also be starting materials for obtaining dimers of hetero-1,2σ^4-azaphospholes (XXXVII) and (XXXIX). Photolytic decomposition of the azides was effected with simultaneous intramolecular cyclisation in the first case at the *ortho* position of the phenyl group and in the second at the nitrogen of the diazaphosphetidine ring.[12]



c) Synthesis of hetero-1,2σ^2-azaphospholes

The cyclocondensation reaction involving compounds of tricoordinated phosphorus is a source of many five-membered cyclophosphazenes with the coordinated of phosphorus equal to two. The first information on cyclophosphazenes with a low phosphorus coordination was published in 1963,[7] however the purpose directed synthesis of hetero-1,2σ^2-azaphospholes began to be intensively developed only after the work of Charbonnel and Barrans.[75]

When developing the analogy between the syntheses of hetero-1,2σ^4- and 1,2σ^2-azaphospholes it should be noted that the precursors of the desired products in both processes are unstable intermediates of type (XIX) or (XL). They may be formed by [3 + 2]- or [4 + 1]-cyclocondensation schemes. Conversion of the intermediates into 1,2σ^4- (XX) or 1,2σ^2-azaphospholes (XLI) respectively occurs with loss of one of the exocyclic substituents at phosphorus and by reduction of the phosphorus coordination to 4 or 2.



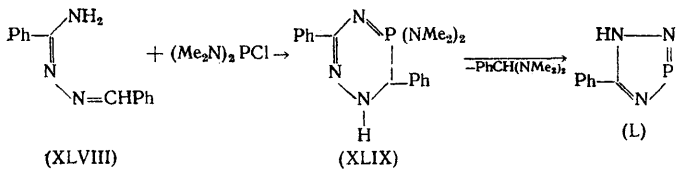
(XX) (XIX) (XL) (XLI)

The types of hetero-1,2σ^2-azaphospholes (XLIII)–(XLVII), (LI) and (LVII) synthesised on the basis of cyclocondensation reactions are shown in Table 3. As is seen from Tables 2 and 3 the synthesis of hetero-1,2σ^4-azaphospholes proceeds mainly by a [4 + 1] scheme but a [3 + 2]-cyclocondensation scheme also occurs for hetero-1,2σ^2-azaphospholes. In addition to these, intramolecular cyclocondensation (Table 3, example 1b)[13] and 'reductive elimination' (example 1c)[34] reactions have been developed for 1,3,2σ^2-diazaphosphole (XLIII).

The first representative of the azaphospholes, viz. 4,5-benzo-1,3,2σ^2-azaphosphole (XLV),[7] as shown by later investigations,[76] exists in crystals in the form of a tetramer.

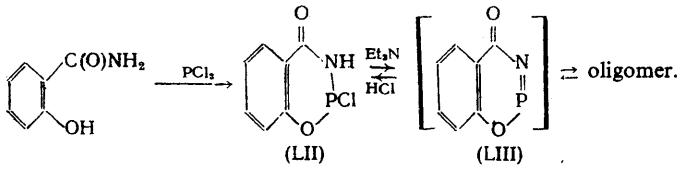
1,2,4,3σ^2-Triazaphospholes (XLVI) and (XLVII) were obtained by reacting methylimidates with chlorophosphines.[75] This reaction takes place through a stage of forming phosphinoimidates[77] (Table 3, example 2a). The latter react with monosubstituted hydrazines with the separation of two regioisomers α-(XLVI) and β-(XLVII) possessing different thermal stabilities. Only one α-isomeric form (XLVI) was isolated from the reaction of amidrazone hydrochlorides with tris(dimethylamino)phosphines[77,78] (example 2b).

An unusual method of obtaining *N*-protonated 1,2,4,3σ^2-triazaphospholes (L) has been described.[79] It is based on the reaction of tetramethyldiaminochlorophosphine with azine (XLVIII), the resulting 1,2,5,4σ^4-triazaphosphorine (XLIX) is converted into triazaphosphole (L) with separation of aminal.



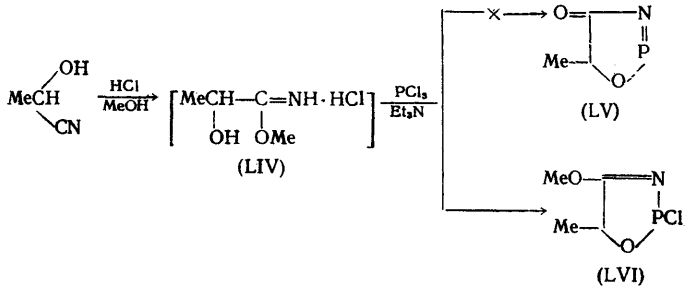
(XLVIII) (XLIX) (L)

In contrast to the stable monomeric diaza- and triazaphospholes described above (Table 3) 1,3,2σ^2-oxazaphosphole (LI) was obtained as the tetramer (Table 3, example 3).[84] Similarly reaction of salicylic acid amide with phosphorus trichloride is terminated by the formation of an oligomer of 4-keto-5,6-benzo-1,3,2σ^2-oxazaphosphorine (LIII).[85] On treatment with hydrogen chloride the oligomer is converted once again into oxazaphosphorine (LII) evidently through the monomeric form (LIII).



(LII) (LIII)

Unsuccessful attempts to obtain 4-keto-1,3,2σ^2-oxazaphosphole (LV) also point to the low thermodynamic stability of the endocyclic O–P=N system.[86] 1,3,2σ^3-Oxazaphospholine (LVI) was isolated in place of the desired product from the reaction of imidate hydrochloride (LIV) and phosphorus trichloride.



(LIV) (LV) (LVI)

The reaction of tetrachloromethylenediphosphine with hydrazine led to the formation of 1,2,3,5σ^2-diazadiphosphole (LVII) which is the first representative of a diphospha-1,3-diene system (Table 3, example 4).[87]

2. Cycloaddition reactions

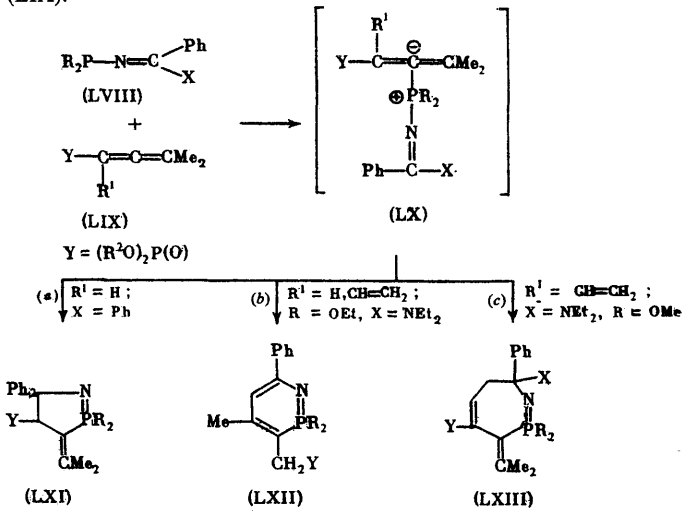
Cycloaddition reactions have a significant role in the chemistry of heterocyclic compounds. Development of these reactions applied to the P=N bond systems has opened new prospects for the synthesis of five- and six-membered cyclophosphazenes. The use of 'non-classical' 1,3-dipoles =P–X=Y (or =P–X≡Y) for the construction of phosphorus-containing rings has been considered.[9,88] Experimentally these ideas were confirmed by the synthesis of [3 + 3]-cyclic adducts with a P=C bond,[16,89] and also of [3 + 2]-cyclic adducts[8,9,90] and [3 + 3]-cyclic adducts[91,92] with P=N bonds.

Cycloaddition reactions involving heteroatomic 1,3-dipoles have been considered in reviews,[15,16] the few examples of obtaining cyclophosphazenes up to that time are included there. Of the approximately 35 types of cyclophosphazenes known today more than half were synthesised by cycloaddition reactions.

a) Synthesis of hetero-1,2σ^4-azaphosphorines

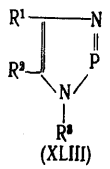
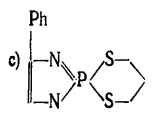
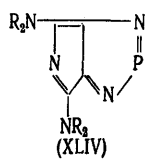
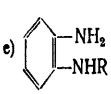
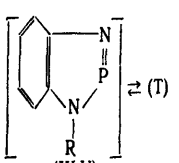
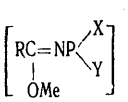
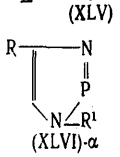
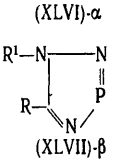
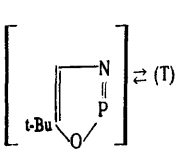
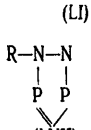
Both [3 + 3]- and [4 + 2]-cycloaddition reactions are used in methods of synthesising the indicated cyclophosphazenes (Table 4).

1,2-Azaphosphorines (LXII) were isolated from the reaction of methyleneaminophosphines (LVIII) and allenylphosphonates (LIX).[93–96]



(LVIII) (LIX) (LX) (LXI) (LXII) (LXIII)

Table 3. Hetero-1,2σ^2-azaphospholes by cyclocondensation reactions.

No.	Reactants: amino component	Reactants: phosphorus component	Reaction type	Azaphosphole monomer→tetramer*	^{31}P NMR, δ ppm	Refs.
1	a) NCC=CCN (NH$_2$, NH$_2$) (XLII)	PCl_3	[4+1]		255 [(R^1=R^2=(N≡C)]	[80—83]
	b) MeNP(NMe$_2$)$_2$ (CH$_2$CN)	—	intramaolecular cycloaddition	 (XLIII)		[13]
	c) 	—	reductive elimination			[34]
	d) R$_2$NH + 2 (XLII)	PCl_3	[4+1]	 (XLIV)	299—301	[78, 81—83]
	e) 	P(NMe$_2$)$_3$, P(OPh)$_3$	[3+2]	 (XLV)	228—236; 81—89 (T)	[7, 76]
2	a) R^{1}NHNH$_2$		[3+2]	 (XLVI)-α	251—256	[75, 77]
				 (XLVII)-β	257	[77, 78]
	b) [RC(=NHNHR^1)NH$_2$]$^{\oplus}$X$^{\ominus}$	(Me$_2$N)$_3$P	[4+1]	(XLVI)	—	
3	t-BuCCH$_2$NH$_2$ (=O)	PCl_3	[4+1]	 (LI)	269.5	[84]
4	RNHNH$_2$	$CH_2(PCl_2)_2$	[3+2]	 (LVII)	—	[87]

*T — tetramer.

Two possible reaction routes have been established for α-unsubstituted ($R^1 = H$) allenylphosphonates, viz. a [3 + 2]-cycloaddition (route a) and a [3 + 3]-cycloaddition (route b).[93,94] The presence of a readily removable group X on the methylene carbon of the methylenaminophosphine (LVIII) is very important for the success of the reaction route.

In the case of α-vinylallenylphosphonate [$R^1 = (CH=CH_2)$] two dipolarophilic centres capable of participating in cycloaddition are competing.[95] The reaction proceeds by routes (b) or (c) depending on the nature of the alkoxy substituents at the phosphorus of methylenaminophosphorine (LVIII). Data from kinetic measurements and quantum chemical calculations were in agreement with the proposed two-stage reaction mechanism through the initial formation of the dipolar ion (LX).[96]

As mentioned above the first [3 + 3]-cycloaddition reaction of phosphorus-nitrogen-containing 1,3-dipoles was carried out for the reaction of diphenylisocyanatophosphine (LXV) with nitrilimines (LXVI) (Table 4, example 2).[91,92] The activity of the phosphorus-containing dipoles in reactions with such classical 1,3-dipoles fell according to the following series.[97,98]

$$ArPNCO > (ArO)_2PNCO > R_2PN{=}C\begin{matrix}R^1\\R^2\end{matrix}$$

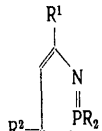
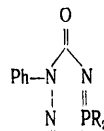
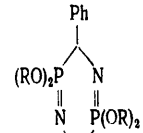
In contrast to methylenaminophosphines (LVIII), which have two alkyl or aryl substituents at the methylene carbon, benzylidene-aminophosphine (LXVIII) possessed increased activity.[99] At the moment of preparation it rapidly dimerised by [3 + 3]-cycloaddition with the formation of 1,4,3,6-diazadiphosphorine (LXIX) (Table 4, example 3).

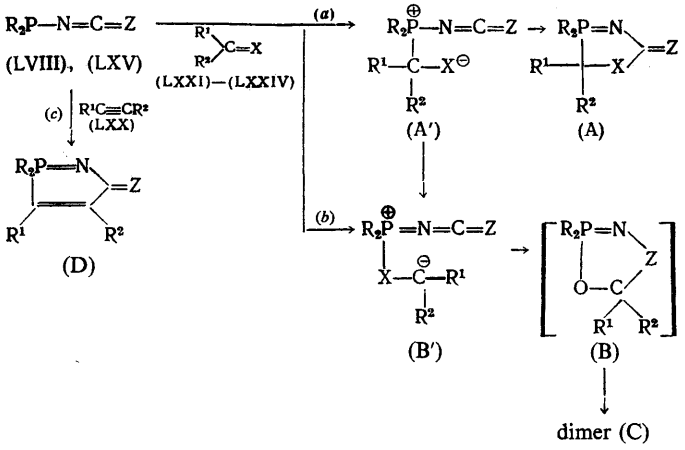
The Diels-Alder reaction has also been investigated with a view to synthesising 1,2-azaphosphorines.[100] The linear phosphazene (LXIV), obtained by reaction of phosphines with alkene azides, was used as diene in this reaction. The [4 + 2]-cycloadduct from the reaction of diene (LXIV) with alkynes was not isolated but was converted into the more stable 1,2-azaphosphorine (LXII) (Table 4, example 1b).

b) Synthesis of hetero-1,2σ^4-azaphospholes and azaphospholines

Like the syntheses of 1,2-azaphosphorines described above, the [3 + 2]-cycloaddition reaction leading to the formation of five-membered cyclophosphazenes has been studied in detail mainly for two phosphorus-nitrogen-containing 1,3-dipoles, viz. methylen-aminophosphines (LVIII) ($Z = R^1, R^2$) and isocyanatophosphines (LXV) ($Z = O, S$) (Tables 5, 6). Reaction of these 1,3-dipoles proceeded with the formation of cyclic adducts of types (A)–(D) depending on the nature of the dipolarophile.

Table 4. Hetero-1,2σ^4-azaphosphorines by cycloaddition reactions.

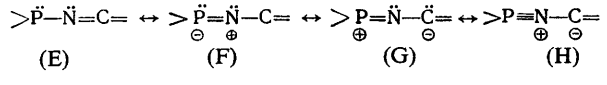
No.	Dipole (diene)	Dipolarophile (dienophile)	Reaction type	Azaphosphorine	^{31}P NMR, δ ppm	Refs.
1	a) $R_2PN{=}C(R^1)X$ (LVIII)	$(R^4O)_2P(O)R^5{-}C{=}CR^2_2$ (LIX)	[3+3]	 (LXII)	39–55	[93–95]
	b) $[R_3P{=}NC{=}CH_2]R^1$ (LXIV)	$R^2C{\equiv}CR^3$	[4+2]			[100]
2	R_2PNCO (LXV)	$R^1C{=}\overset{\oplus}{N}{-}\overset{\ominus}{N}Ph$ (LXVI)	[3+3]	 (LXVII)	—	[91, 92, 97]
3	—	$[PhCH{=}NP(OR)_2]$ (LXVIII)	[3+3]	 (LXIX)	40.7; 38.3 ($R=OCH_2CH_2O$) 42.1; 40.7 ($R=OC_6H_4O$-1,2)	[99]



The [3 + 2]-cycloaddition of phosphorus-containing 1,3-dipoles to dipolarophiles (LXXI)–(LXXIV) was characterised in the majority of studies as a two-stage process, beginning with nucleophilic attack of the phosphorus atom on the electrophilic centre of the dipole (route a).[11,16,97] After formation of the bipolar ion (A') conversion proceeds further to cyclic adduct by direct cyclisation to azaphospholine (A) or through first isomerisation into ion (B') and subsequent cyclisation to the unstable azaphospholine (B) which dimerises.[11] An alternative route (b) was proposed for the reaction of methylenaminophosphines with 4-nitrobenzaldehyde.[101] It is quite probable that the interaction of substituted alkynes (LXX) (route c) may proceed via a concerted cycloaddition mechanism; however, there are no kinetic data to date on this type of reaction. It should be noted that not all the studied combinations of 1,3-dipoles and dipolarophiles lead to the isolation of cyclophosphazenes (A) or (B). In many cases the formation of cyclic adducts is accompanied by their further conversion. They will be considered in more detail when discussing the chemical properties of the five-membered cyclophosphazenes.

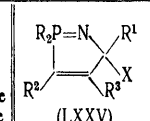
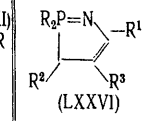
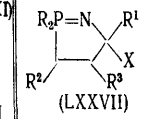
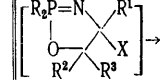
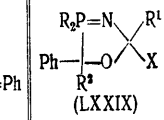
Various structures for the synthesised heterophosphacyclanes (LXXV)–(LXXXIV) were achieved by varying the dipolarophile component of the reaction.

As is seen from Tables 5 and 6 a wide range of dipolarophiles of the classes of unsaturated and carbonyl compounds (LXX)–(LXXIV) was investigated in the reactions with phosphorus- and nitrogen-containing 1,3-dipoles. Analysis of the experimental data showed that a decisive role in determining the course of the processes and also the formation of regioisomers is played by the initial step comprising nucleophilic attack by the phosphorus atom of the 1,3-dipole on the electrophilic centre of the dipolarophile. This was confirmed by the observation that cycloaddition reactions are accelerated with an increase in the nucleophilicity of the phosphorus atom.[96,97,128] and also the order of addition to substituted alkenes,[9,102,104,119] aldehydes[121–128] and other dipolarophiles.[129–131] Consequently structures (E) and (F) of the resonance structures of 1,3-dipoles make the major contribution.

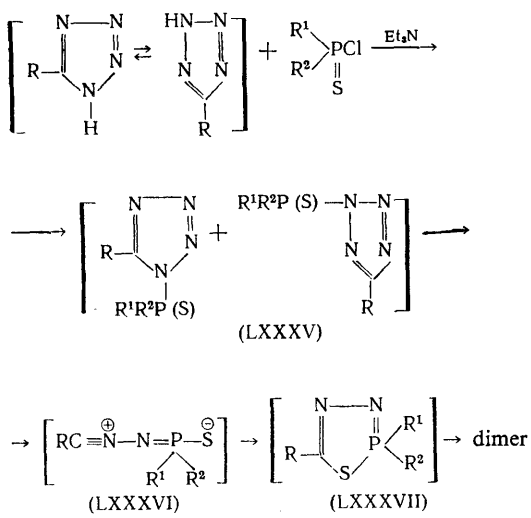


In this case the order of addition of certain carbonyl compounds requires particular consideration. The reaction of these compounds proceeds with the formation of monomers of type (A) or the regioisomeric cyclic adducts (B), which exist in the form of dimers (C). The different order of addition is explained by isomerisation of the bipolar ion (A') into ion (B') (see general scheme.[11] However in certain cases with an insignificant difference in structure of dipolarophile (examples 4, 5 in Table 5, examples 4c, 5a in Table 6, etc.) the process is directed either towards 1,4,3-oxazaphospholines (LXXIX), (LXXXIII), or towards 1,3,2-oxazaphospholines (LXXVIII), (LXXXIV) or their dimers. There is still no complete explanation for this.

Table 5. Hetero-1,2σ^4-azaphospholes and 1,2σ^4-azaphospholines by cycloaddition reactions of methylenaminophosphines (LVIII).

No.	Dipolarophile	Azaphospholes, azaphospholines	^{31}P NMR, δ ppm	Refs.
1	$R^2C{\equiv}CR^3$ (LXX) a) $R^2{=}R^3{=}$COOMe b) $R^2{=}$H, $R^3{=}$COOMe c) $R^2{=}$Me, $R^3{=}$COOMe d) $R^2{=}$Ar, $R^3{=}$COOMe	 (LXXV)	47.4 (R=R^1=X=Ph, $R^2{=}R^3{=}$COOMe)	[9, 102–104]
2	$R^2CH{=}CHR^3$ (LXXI) a) $R^2{=}$Me, $R^3{=}$COOR b) $R^2{=}$Me, $R^3{=}$CN c) $R^2{=}$Ph, $R^3{=}$COOR d) $R^2{=}$Ph, $R^3{=}$C(O)R e) $R^2{=}$H, $R^3{=}$CN	 (LXXVI)	57.9 (R=Ph, $R^1{=}$OEt, $R^2{=}$H, $R^3{=}$CN)	[105]
3	$R^2CH{=}CR^3R^4$ (LXXII) a) $R^2{=}R^4{=}$H, $R^3{=}$COOMe b) $R^2{=}R^4{=}$H, $R^3{=}$C(O)Me c) $R^2{=}R^4{=}$H, $R^3{=}$CN d) $R^2{=}(R^5O)_2P(O)$; $R^3, R^4{=}(=CR^6_2)$	 (LXXVII)	48–75	[9, 94, 102–104]
4	 (LXXVIII)		46.0 (R=OMe, R^1=Ph, X=OEt, R^2=CN, R^3=Ph) −58.0 (D) ($R^1{=}$X=Ph, $R^2{=}$H, $R^3{=}C_6H_4NO_2$-4)	[101, 107–110]
5	 (LXXIX)		—	[106]

Of other cycloaddition reactions it is possible to cite the method of obtaining dimers of 1,3,4,2-thiadiazaphospholes (LXXXVII) from thiophosphorylated tetrazoles (LXXXV).[64] Pyrolysis of the latter leads to ring opening and the formation of a linear phosphazene (LXXXVI) which undergoes rapid intramolecular cycloaddition and dimerisation.

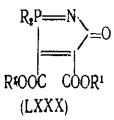
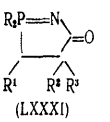
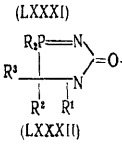
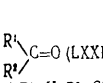
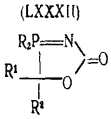
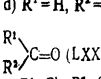
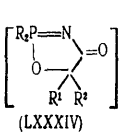


(LXXXV)

(LXXXVI) (LXXXVII)

The $1,2\sigma^2$-azaphospholes, which retain their endocyclic P=N bond during several transformations, may be starting materials for obtaining hetero-$1,2\sigma^4$-azaphospholes. [4 + 1]-Cycloaddition reactions of α-dicarbonyl compounds[133] and esters of azodicarboxylic acids[134] to $1,2\sigma^2$-azaphospholes are known. A series of spirocyclic phosphazenes was obtained in this way both in the dimeric[134] and in the monomeric form.[133]

Table 6. Hetero-$1,2\sigma^4$-azaphospholines by cycloaddition reactions of isocyanatophosphines (LXV).

No.	Dipolarophile	Azaphospholine	^{31}P NMR, δ ppm	Refs.
1	$R^1OOC{\equiv}CCOOR^1$ (LXX)	 (LXXX)	–	[90, 98, 111]
2	$R^1CH{=}CR^2R^3$ (LXXI) a) R^1=H, R^2=Br, R^3=CN b) R^1=H, R^2=Br, R^3=COOMe c) R^1=Me, R^2=CN, R^3=COOEt	 (LXXXI)	24–30	[112, 113]
3	a) $CCl_3CH{=}NR^1$ (LXXIII) b) R^1NCO (LXXIV)	 (LXXXII)	62.0 (R=OMe, R^3=H, R^2=CCl_3; –70– –80 (D) [R^2, R^3=(=O)]	[129–132]
4	 a) R^1=H, R^2=CCl_3 b) R^1=H, R^2=XC_6H_4	 (LXXXIII)	71–76 (R=OAlk); 59–62 (R=Ph)	[8,121–128]
	c) R^1=Ph, R^2=CN d) R^1=H, R^2=CCl_3	[(LXXIII)]→(D)	–40– –60 (D) (R=$OAlk_F$)	[114–116]
5	 a) R^1=Ph, R^2=C(O)Ph b) R^1=R^2=CF_3 c) R^1=CF_3, R^2=(iso-PrO)$_2$P(O)	 (LXXXIV)	–54.0 (D) (R=OMe, R^1=R^2=Ph)	[117–120]

Several other reactions of $1,2\sigma^2$-azaphospholes and also the conversions of $1,2\sigma^4$-azaphosphole dimers, described in part III of the present review, may be considered as sources for obtaining five-membered cyclophosphazenes.

Only one type of four-membered cyclophosphazene is known as yet, viz. diazadiphosphetine (XC), obtained by photolysis of diisopropylphosphine azide (LXXXVIII).[12,135,136] Reaction occurred through a reactive intermediate (LXXXIX) which was dimerised already at –42 °C.

$$[(\text{iso-Pr})_2\text{N}]_2\text{PN}_3 \xrightarrow{h\nu} \{[(\text{iso-Pr})_2\text{N}]_2\text{P}{\equiv}\text{N}\} \rightarrow \{[(\text{iso-Pr})_2\text{N}]_2\text{P}{=}\text{N}\}_n$$

(LXXXVIII) (LXXXIX) n = 2 (XC); 3 (XCI).

The molecular structure of dimer (XC) was demonstrated by X-ray structural analysis.[135] Trimerisation of the intermediate (LXXXIX) was observed in addition to dimerisation. The formation of diazadiphosphetine (XC) (42% yield) was preferred in comparison with triazatriphosphorine (XCI) (3% yield).

III. Special features of structure and reactivity

Much attention has been paid in recent years to the clarification of the special features of the electronic structure of the P=N bond. The data obtained enable an understanding of the peculiarities of the structure and chemical behaviour of phosphazenes when compared with their heteroanalogues. It is known that in their properties phosphazenes occupy an intermediate position in the series of compounds with isoelectronic groups P=X (X = C, N, O, S).[28,29] They have a higher bond order than phosphorus ylids which was confirmed by their higher ionisation potentials[138] and by the P=N bond lengths.[137]

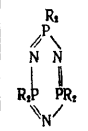
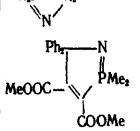
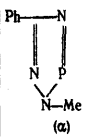
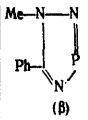
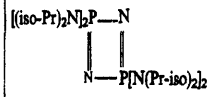
A model molecule $Me_3P{=}NH$ was assigned to the π-type from the results of HOMO quantum chemical calculations and this was confirmed experimentally by photoelectron spectroscopic data.[138] At the same time the P=N bond is significantly more polarised than the phosphoryl or thiophosphoryl bonds.[139–141]

The special features found for the P=N bond, particularly the double bond character with a significant contribution of polar structure and its ready polarisability, mainly predetermine the chemical behavior of acyclic and cyclic phosphazenes. However a change in the electronic properties of the P=N group and the geometry of its components caused by the presence of a ring introduce specific features into their chemical behaviour. A theoretical analysis of the structure of acyclic and five-membered cyclic phosphazenes with a tetracoordinated phosphorus atom has been carried out.[14] In comparison with acyclic analogues[137] transition into a cyclic phosphazene is accompanied by a significant reduction in the endocyclic angles at phosphorus and nitrogen (Table 7). As a result of the angular strain in the five-membered phosphazene ring there is an increase in the *p*-character of the valence orbitals of the phosphorus atom and in the lengths of the endocyclic bonds with neighbouring atoms. The changes in structure and electronic properties are displayed in an increase in the electrophilicity of the phosphorus atom, an increase in the polarity of the P=N bond,[14] and a tendency to transition of the five-membered cyclophosphazenes into phosphacyclanes with pentacoordinated phosphorus. In the latter the gain in energy is explained by the small structural changes required for conversion of σ^4- into σ^5-phosphacyclanes.[57,142]

Conclusions on the specific features of the P=N bond in five-membered rings were confirmed by the accumulated experimental

material both on some of their physical properties and on their chemical behaviour. The value of the screening constant of the phosphorus atom nucleus was an indicator in this respect. A very broad range for the chemical shifts of the ^{31}P nucleus (δ_P + 40 to −98 p.p.m.) was characteristic of acyclic phosphazenes with tetracoordinated phosphorus. Their values were in a complex non-additive dependence on the nature of the substituents at phosphorus and nitrogen.[143–147]

Table 7. Structural parameters of the endocyclic Y−P=N−X fragment of cyclophosphazenes.

No.	Compound	Bond length P=N, Å	Angle P=N−X, deg	Angle Y−P=N, deg	Refs.
1		1.54—1.60	120—148	115—126	[17]
2		1.579	111.5	98.6	[142]
3	 (α)	1.616	108.9	92.4	[154]
4	 (β)	1.627; 1.637	106.6	97.0; 97.0	[155] [156]
5		1.651	85.0	95.0	[135]

The screening constants for five-membered cyclophosphazenes lie within much closer limits and depend to a lesser degree on the environment of the phosphorus atom. For example, for the most studied 1,2σ^4-azaphospholes and 1,2σ^4-azaphospholines the resonance signals were observed in the region δ_P 76 to 48 p.p.m. (Tables 5, 6) and for 1,3,2σ^4-diaza- and 1,2,4,3σ^4-triazaphospholes were in the region 83 to 61 p.p.m.[30] It is characteristic that this region of appearance in low field is comparable with that for acyclic phosphazenes with a polarised P=N bond.[28,137,141,143–146]

The narrow range of values for the ^{31}P nuclear screening constants in the hetero-1,2σ^4-azaphospholes and -azaphospholines may serve as a diagnostic tool when establishing the structure of these cyclanes. The exceptions were the five-membered spirocyclophosphazenes in which the chemical shift of the ^{31}P nucleus was displaced towards higher field (50 to 15 p.p.m.).[60,73,133]

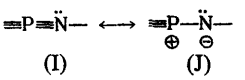
The ^{31}P nuclear resonance signals for hetero-1,2σ^4-azaphosphorines were observed within the limits δ_P 14 to 57 p.p.m. (Tables 1, 4). The breadth of the limits and the displacement towards higher field indicate the less polar character of the P=N bond in six-membered cyclophosphazenes. This conclusion was confirmed by the chemical behaviour of the azaphosphorines, distinguished by high stability. The changes mentioned in the character of the phosphazene bond were the result of a reduction of the angular stress in the six-membered ring and its partial aromaticity due to the delocalisation of π-electrons in the endocyclic P=N−X system.[6,17,34] The degree of delocalisation of π-electron density and the conductance of the electronic influence of the P=N−X fragment of diaza- and triazaphosphorines has been studied[148,150] using the ^{35}Cl NMR method and quantum chemical calculations.

In contrast to hetero-1,2σ^4-azaphospholes the corresponding phosphacyclanes with a dicoordinated phosphorus atom possess a lower inclination to react at the P=N bond.[13,77,151–153] The increased stability of the 1,2σ^2-azaphospholes is explained by the presence of aromatic character in these heterocycles. The molecular structure of 1,2σ^2-azaphospholes demonstrates the closeness of the configuration of the valence *p*-orbitals of the phosphorus atom to an ideal orthogonal configuration (Table 7).[154–158]

The resonance region of the dicoordinated phosphorus atom nucleus was specific (Table 3). It is easily possible to distinguish hetero-1,2σ^2-azaphospholes from the corresponding compounds of tetracoordinated phosphorus by ^{31}P NMR spectral data. Important characteristics were obtained by NMR spectral methods (^{31}P, ^1H, ^{13}C) and were used for the identification of the structures of these cyclanes.[13] A correlation of ^{15}N and ^{31}P nuclear chemical shifts has been carried out.[159]

1. Interaction with nucleophilic and electrophilic reagents

The nucleophilic character of the phosphazene bond is explained by the contribution of both the resonance structure (I) and structure (J). In addition it is known that compounds with a P=N bond also possess electrophilic properties in the display of which a significant role is played by the contribution of structure (J).[137,138,141]

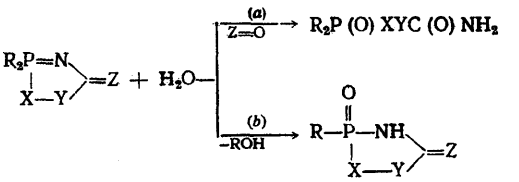


(I) (J)

The stability of acyclic phosphazenes $R_3P{=}NR^1$ towards the action of nucleophilic reagents depends on the substitutents R and R_1 and varies within wide limits.[5,28,29,137]

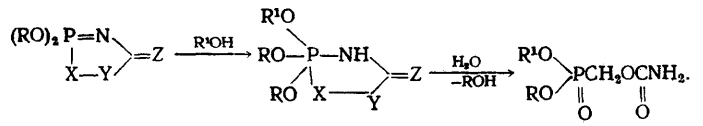
Regarding the polar character of the P=N bond the cyclophosphazenes are more stable to the action of water, alcohols, amines and other reagents with labile protons.

Hetero-1,2σ^4-azaphospholes and -azaphospholines are readily, partially at the time of isolation, subject to hydrolysis. This reaction occurs in the majority of cases with opening of the ring at the P=N bond (route *a*), however there are examples of ring retention (route *b*).



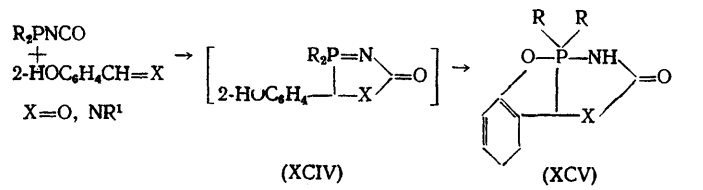
1,2-Azaphospholes,[90,111] azaphospholines,[93–95] and 1,3,4-oxazaphospholines[122–128] react by route (*a*). A wide range of *C*-phosphorylated carbamates has been obtained based on this and investigated.[121,125,160–163] A course of hydrolysis by route (*b*) has been recorded for 1,2,4,3-triazaphospholes,[56] phosphorylated 1,2-azaphospholes[94] and 1,3,4-diazaphospholines.[164]

The interaction of five-membered cyclophosphazenes with alcohols is readily effected. Relatively stable addition products (XCII) were successfully obtained for 1,3,2σ^4- [101] and 1,3,4-σ^4-oxazaphospholines.[165] These were rapidly hydrolysed with the isolation of carbamates (XCIII) with mixed substituents on phosphorus.[166]



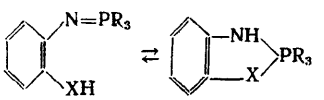
Z=O, (R^2, R^3) (XCII) (XCIII)

The thermodynamically more stable cyclic phosphoranes (XCV) were obtained on interacting isocyanatophosphines with ortho-hydroxysubstituted aromatic aldehydes [167,168] and amines,[169] and also with fluorinated acetylacetone.[170]



(XCIV) (XCV)

The intermediate formation of cyclic adducts (XCIV) was not recorded either during the reaction process or in solutions of phosphabicyclane (XCV).[168] In contrast to this it was possible to observe the tautomeric equilibrium of phosphazene and phosphorane structures in a series of linear *N*-2-hydroxy(amino)phenyl-phosphazenes (XCVI).[171–173]

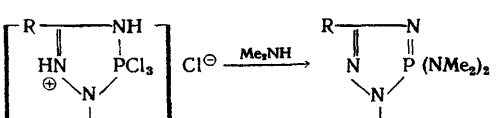


(XCVI)

This fact, and also the examples given above of reactions with water and alcohols demonstrate the low thermodynamic stability of five-membered rings with a P=N bond, being subject to facile conversion into phosphacyclanes with a pentacoordinated phosphorus atom.

The reactions of dimeric five-membered cyclophosphazenes with water and alcohols seemingly occur through the monomer formation stage. The presence of the monomer even in infinitesimally small concentration enables rapid flow of the process because of its high reactivity. The hydrolysis of 1,3,2σ^4-diazaphosphole dimers [52,53] and the reaction of 1,2,4,3σ^4-triazaphospholes with *p*-cresol [56] proceed in this way.

Five-membered cyclophosphazenes are more stable towards the action of amines. Treatment of 1,2,4,3σ^4-triazaphospholine salts (XCVII) or its dimer with a secondary amine leads only to replacement of chlorine atoms at phosphorus and isolation of free triazaphosphole (XXIV).[56] Products of addition at the P=N bond were not observed.

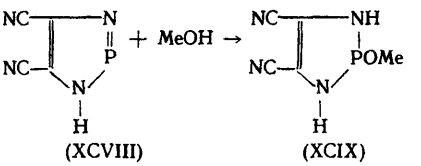


(XCVII) (XXIV)

The low reactivity towards amines made it possible to develop a synthesis of monomeric spirocyclophosphazenes (XXV) based on the reaction of triazaphosphole dimers (XXIV) with *N*-methyl-benzamidrazone hydrochloride (XXIX) [65] (Table 2, example 2b).

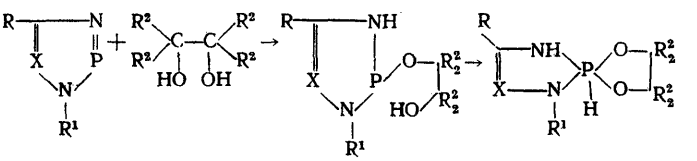
In contrast to the dimers of triazaphospholes (XXIV) the dimers of oxa- and thiadiazaphospholes (XXVIII) react with diethylamine in the dimeric form. Replacement of chlorine at phosphorus was readily effected in this way.[64]

The reactivity of hetero-1,2σ^4-azaphospholes was reduced in comparison with their analogues with a tetracoordinated phosphorus atom and depended on the degree of aromaticity of the azaphosphole ring. 1-Methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVII) (β-isomer), possessing little aromaticity, did not react with alcohols or amines, but 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVI) (α-isomer) adds alcohols, primary and secondary amines at the P=N bond.[77] However such weak nucleophiles as carboxylic acids, aromatic amines or β-naphthol did not react with the α-isomer. Alcohol added more readily to 1,3,2σ^2-diazaphosphole (XCVIII) with the formation of the corresponding 1,3,2-diaza-phospholine (XCIX).[81]



(XCVIII) (XCIX)

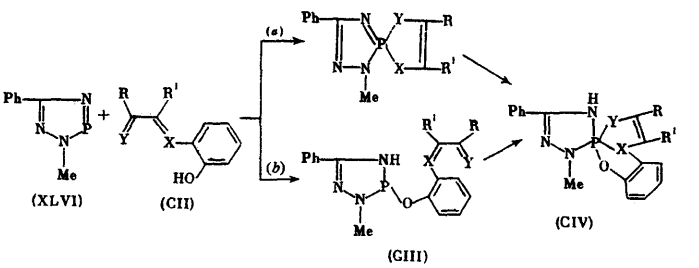
The reaction of 1,2-diols with 1,2,4σ^2-triaza- (XLVI) [77] and 1,3,2σ^2-diazaphosphole (XLIII) [81] was accompanied by subsequent cyclisation at the tricoordinated phosphorus atom of intermediate (C) with the formation of spirophosphoranes (CI).



(XLIII), (XLVI) (C) (CI)

1,2-Aminoalcohols and 1,2-diamines reacted in a similar manner.

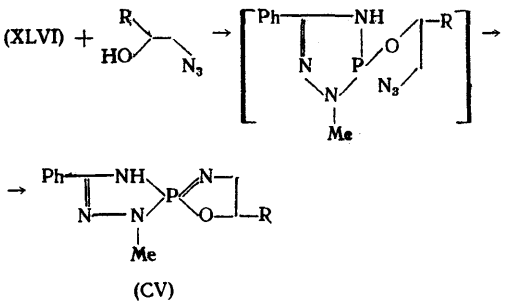
The reaction of 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (XLVI) with phenols (CII) containing a diene grouping in the ortho position has been studied.[153]



(XLVI) (CII) (CIII) (CIV)

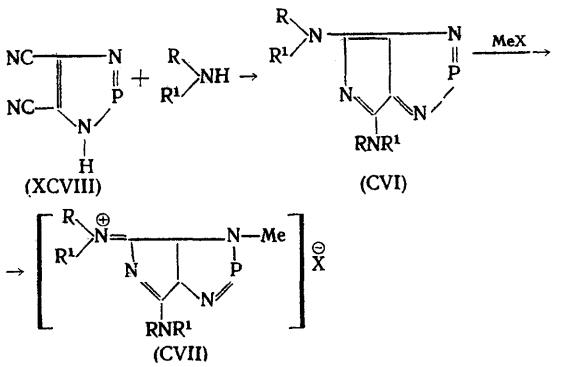
The authors claimed that of the two possible routes the process is effected by route (*b*) with the initial 1,2-addition of the hydroxyl group of reactant (CII) and subsequent intramolecular [4 + 1]-cycloaddition of the intermediate (CIII). The interaction of triazaphosphole (XLVI) with azido alcohols is assigned to the same type.[73] As in the reactions shown above the present process does not stop at the stage of addition of the P=N bond. Cyclisation is

further brought about by a reaction of the Staudinger type with the formation of a new spirocyclophosphazene (CV).



(CV)

Interesting results have been obtained on reacting 1,3,2σ^2-diazaphosphole (XCVIII) with secondary amines.[80–83] The presence of a diazaphosphole ring activated the nitrile group. The latter proved to be capable of adding amine with the formation of 4,5-pyrrolo-1,3,2σ^2-diazaphosphole (CVI). In this the (σ^2) P=N bond was retained.

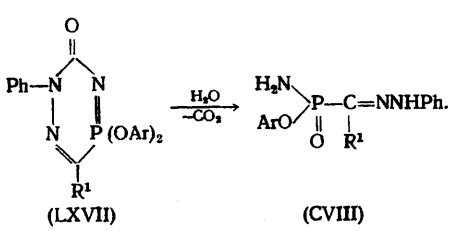


(XCVIII) (CVI) (CVII)

Alkylation of the product (CVI) with the formation of salt (CVII) was carried out on the diazaphosphole ring with retention of the phosphorus coordination.

The six-membered cyclophosphazenes occupy an intermediate position between the five-membered analogues and cyclotriphosphazenes in regard to the action of nucleophiles. Their reactivity is determined to a significant degree by the nature of the substituent at phosphorus. Thus 1,3,5,2,4-triazadiphosphorine (V) (Table 1, example 4) with methyl substituents at phosphorus dissolves readily in cold water without decomposition.[36,42] The corresponding chloro derivatives (V) are hydrolysed under these conditions, the authors claim, at one of the phosphazene bonds without ring scission,[34] but heating 2,2,4,4-tetraphenyl-1,3,5,2,4-triazadiphosphorine with water led to rupture of the ring.

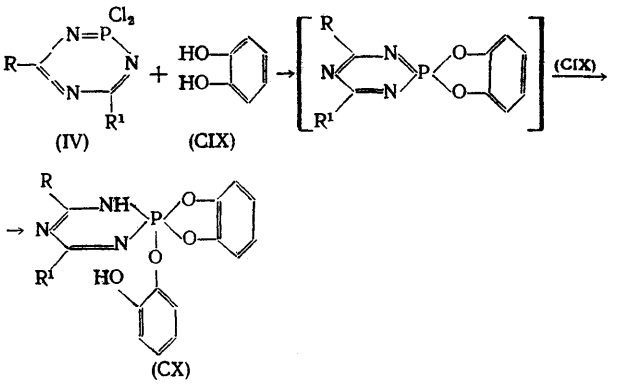
An unusual course for the reaction with water was found for 1,3-aryl-6-oxo-1,2,5,4-triazaphosphorine (LXVII) hydrolysis of which was accompanied by decarboxylation and led to the *C*-phosphorylated hydrazone (CVIII).[97]



(LXVII) (CVIII)

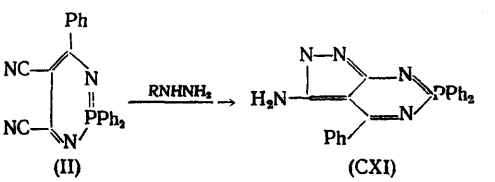
1,2-Azaphosphorines (LXII) (Table 4)[6,93] and eight-membered cyclophosphazenes (XV) [51] are hydrolysed at the P=N bond with retention of the ring.

The reaction of 2,2-dichloro-1,3,5,2-triazaphosphorines (IV) with diols in the presence of base occurs with substitution of chlorine and retention of the phosphazene bond in the ring.[174] However on using ortho-hydroquinones 1,2-addition at the P=N bond was observed in addition to substitution and spirophosphoranes (CX) were obtained.



(IV) (CIX) (CX)

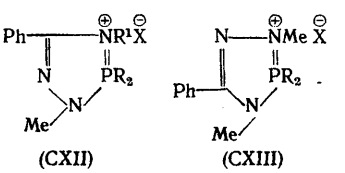
Chloro-substituted 1,3,2-diaza- (II) and 1,3,5,2-triazaphosphorines (IV) enter into exhaustive substitution reactions with aliphatic amines, phenoxides and alkoxides. The P=N bond is not affected by this. 4-Chloro-5-cyano derivatives of (II) react with *N*-substituted hydrazines with the formation of condensed heterocycles (CXI) without participation of the P=N bond.[6]



(II) (CXI)

In contrast to the acyclic phosphazenes[28,29,137,175–178] there are no systematic investigations on the basicity of the cyclophosphazenes which is seemingly connected with their low stability. Nonetheless examples have been described of the formation of cyclophosphazene salts in reaction with hydrogen chloride and with alkyl halides.

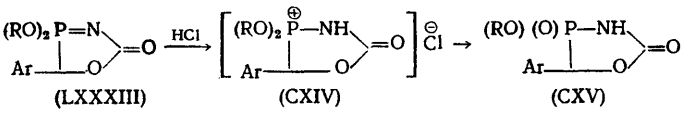
Salts of 1,2,4,3-triazaphospholes (CXII) and (CXIII) have been established by ^{31}P NMR. By removing hydrogen chloride, salt (CXII) (R^1 = H) is readily converted into the corresponding azaphosphole or its dimer.[56]



(CXII) (CXIII)

Alkylation of 1,2,4,3-triazaphospholes (XLVI) and (XLVII) has been carried out with the formation of salts of analogous structure. It was noted that azaphospholines (LXXVII) were more basic than 1,2-azaphospholes (LXXV) (Table 5) in reaction with hydrogen chloride.[179] 1,4,3-Oxazaphospholines (LXXXIII), with alkoxyl substitutents at phosphorus, were readily converted by hydrogen

chloride into oxazaphospholidines (CXV). The reaction evidently proceeds through the formation of phosphonium salt (CXIV).[180]



(LXXXIII) (CXIV) (CXV)

Similarly the monomeric product of addition of the P=N bond appeared on reaction of dimeric 1,3,2-oxazaphospholes (LXXVIII) (Table 5) with hydrogen chloride and was decomposed further with rupture of endocyclic bonds at phosphorus.[67]

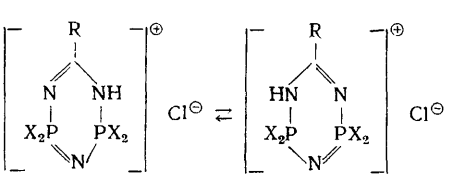
The basic properties of hetero-1,2σ^2-azaphospholes are weakly expressed because of the less polar character of the P=N bond. Thus 1,2,4,5σ^2-triazaphospholes possess such a low basicity that they are not protonated by acetic or trichloroacetic acids and do not give salts with methyl iodide.[77] 1,3,2σ^2-Diazaphospholes display acidic properties with strong bases. Their ammonium and potassium salts react with methyl iodide at the nitrogen atom neighbouring the P=N bond.[81–83] In all these conversions the coordination of phosphorus is retained equal to two.

Hydrogen chloride adds at the P=N bond of hetero-1,2σ^2-azaphospholes. This reaction is the reverse of the dehydrochlorination of 1,2σ^3-azaphospholidines which leads to the formation of azaphospholes with dicoordinated phosphorus.[56,77,81,83,85]

Bromination and chlorination of 1,2,4,3σ^2-triazaphospholes takes place with retention of the P=N bond and leads to the dimer of 1,2,4,3σ^4-triazaphospholes (XXVI) (Table 2).[55,56,77] The authors claim that the target products were the result of a more complex process than a 1,2-addition reaction at the (σ^2) P atom.[13]

Organomagnesium compounds react with 1,2,4,3σ^2-triazaphospholes (XLVI) at the P=N bond, electrophilic attack at the (σ^2) P atom is effected in this.[181]

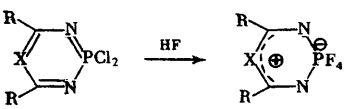
The basicity of hetero-1,2-azaphosphorines is determined by the nature of the substituent at phosphorus as in the reactions with nucleophiles described above. So 2,2,4,4-tetrachloro-1,3,5,2,4-triazaphosphorines (V) are not alkylated by alkyl halides.[33] Replacement of the chlorine atoms at phosphorus by aryl groups leads to a strengthening of the basic properties of the triazaphosphorines (V). In the case of the 2,2,4,4-tetraphenyl derivatives fairly stable hydrochloride salts (CXVI) were obtained, the structure of which has been investigated by NMR spectroscopy (^{31}P, ^{1}H).[34] It was shown that protonation of the nitrogen takes place at position 1 or 5 but the phosphorus atoms in cations (CXVI) are magnetically equivalent. This corresponds to the presence of degenerate tautomerism of both protonated forms.



(CXVI)

Salts (CXVI) were hydrolytically less stable than the free bases, they were readily hydrolysed or alcoholised with ring rupture between nitrogen and phosphorus at positions 1 and 2.[35]

1,3,2-Diaza- (II) and 1,3,5,2-triazaphosphorines (IV) add two molecules of hydrogen fluoride with simultaneous exchange of halogen at phosphorus. The final product was cyclic salt (CXVII) in the molecule of which the negative charge was localised at the (σ^6) P.[182]



(II), (IV) (CXVII)

X = CCl, CH, N

2. Cycloaddition reactions

Cycloaddition reactions have been best studied for five-membered cyclophosphazenes with a tetracoordinated phosphorus atom. This clearly marked trait of their chemical behaviour is caused by the polar character of the P=N bond and an inclination towards transition to the energetically more favourable cyclanes with a pentacoordinated phosphorus atom.

Dimerisation reactions are a characteristic of many types of hetero-1,2σ^4-azaphospholes and azaphospholines. The reasons influencing the position of the equilibrium between monomeric and dimeric forms have been fairly well studied to date.[14,55–58,64] Among azaphospholines and azaphospholes structures have been found for which the position of the equilibrium is shifted either towards the monomeric or the dimeric forms. If attention is paid only to the nature of the endocyclic atoms in the N=P–X fragment then the inclination towards dimerisation of five-membered cyclophosphazenes grows along the series X = C < N < O.[56,57] There are only a very few cyclophosphazenes with an endocyclic P–C bond existing in the dimeric form. 1,3,4σ^4-Oxazaphospholines (LXXXIII) with electron-accepting exocyclic substituents at phosphorus[114–116] and 2-oxo-1,3,4-diazaphospholines (LXXXII) (Table 6, examples 3b 4c, d)[129–131] belong to these.

The preferential existence of cyclanes with an N=P–C fragment in the monomeric form is explained by the transition to the dimer being disadvantaged by the high activation energy of the process. The increase in energy is linked with the need for such a configuration of the dimer when the five-membered ring is forced to occupy a diequatorial position due to the weak apicophilicity of carbon. The indicated transition is unfavoured especially in the presence of apicophilic exocyclic substitutents at phosphorus.[14]

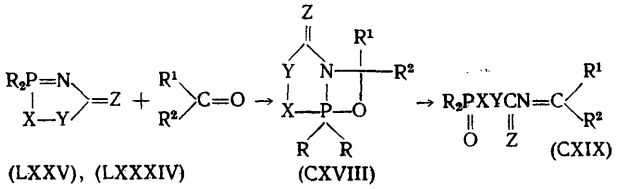
When the neighbouring atom X in the endocyclic N=P–X fragment is nitrogen the position of the monomer⟷dimer equilibrium depends on the fine balance of electronic and steric influences of the exocyclic substituents.[14] Representatives existing only in the form of monomers[56,65,133] or dimers[52,53,56,67,134] are found among this type of 1,3,2σ^4-diazaphospholes.

When an endocyclic N=P–O fragment is present the five-membered cyclophosphazenes exist in the crystal almost exclusively in the dimeric form.[57–60,68–70,73,107,108,110] There is only one example of the monomeric form for 1,3,2σ^4-oxazaphospholine (LXXXIV) in the solid state (Table 6, example 5c).[118]

The possibility of conversion into the monomeric form in solution has been proposed to clarify several chemical properties of the cyclophosphazene dimers. Such a conversion has been observed for dimers of 1,3,2-oxazaphospholines (LXXXIV) in solution.[68,73] The presence of the monomeric form in solution was confirmed experimentally in competing [2 + 2]-cycloaddition reactions.[56,67,72]

In addition to dimerisation five-membered cyclophosphazenes with a tetracoordinated phosphorus atom readily participate in [2 + 2]-cycloaddition reactions with several compounds with

multiple bonds. In contrast to acyclic phosphazenes[5] primary products of cycloaddition (CXVIII) with pentacoordinated phosphorus were isolated or established in the majority of reactions of cyclophosphazenes with carbonyl compounds.



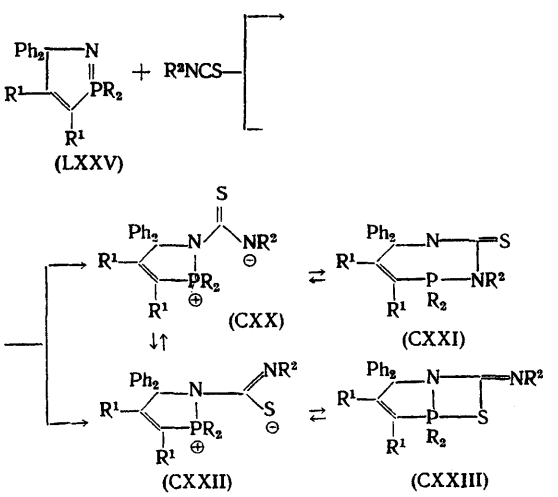
(LXXV), (LXXXIV) (CXVIII) (CXIX)

The interaction of 1,3,2σ^4-oxazaphospholine (LXXXIV) (Table 6, example 5b) with hexafluoroacetone has been described.[120] Stable bicyclic adducts (CXVIII) were successfully isolated and studied by X-ray analysis in reactions of 1,2-azaphospholes (LXXV) (Table 5, example 1c) with ketones.[142,183] On heating, bicyclanes (CXVIII) were converted into linear imines (CXIX).

The same, but less stable, bicyclic adducts of type (CXVIII) were obtained by reaction of 1,2-azaphospholes (LXXV) with chloroacetone.[184] The formation of intermediates (CXVIII) was not observed in analogous reactions with aldehydes, linear imines (CXIX) were isolated directly as final products.[101,183] However, on using chloral, bicyclanes (CXVIII) stable at low temperature were established spectrally.[180]

Dimers of 1,3,2σ^4-oxazaphospholes (LXXXIV) have been successfully introduced into competing [2 + 2]-cycloaddition reactions due to their partial dissociation in solution. A bicyclic adduct of type (CXVIII) was isolated on reaction with methyl isocyanate,[67] but an imine of type (CXIX) on reaction with ketones.[72] Similarly dimers of triazaphospholes (XXVI) (Table 2, example 2) reacted with phenyl isocyanate through the monomeric form with the formation of bicyclic adduct (CXVIII).[56]

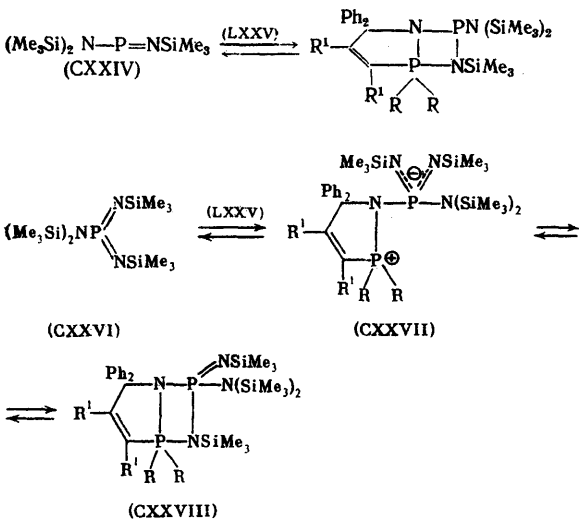
The [2 + 2]-cycloaddition of isothiocyanates to 1,2-azaphosphole (LXXV) occurred by two routes with the participation of both heteroatom double bonds.[185]



(LXXV) (CXX) (CXXI) (CXXII) (CXXIII)

The course of the process along one or the other route was determined by the substituent on the isothiocyanate group. Methyl isocyanate reacted with the C=N bond with the formation of a stable bicyclic adduct (CXXI). Isothiocyanates with more electron-accepting substituents [R^2 = $Ph_2P(S)$; PhC(O)] led to the product of cycloaddition at the C=S bond (CXXIII). When the dipolarophilic activity of the isothiocyanate double bonds [R^2 = $Me_2P(S)$; Me] was the same, reaction occurred simultaneously by the two routes. The composition of the resulting mixture of cyclic adducts depended on the nature of the solvent and on concentration. The latter fact, in the authors' opinion, indicates the presence of a labile equilibrium between the final cyclic adducts (CXXI) and (CXXIII), and their ionic forms (CXX) and (CXII). The presence of such an equilibrium was confirmed spectroscopically.

In addition to carbonyl compounds, linear $\sigma^2\lambda^3$-diazaphosphazene (CXXIV) and $\sigma^3\lambda^5$-triazaphosphazene (CXXVI) have also been used in cycloaddition reactions of 1,2σ^4-azaphospholes (LXXV).[186] Cyclic adducts (CXXV) and (CXXVIII) were found in solution in equilibrium with the starting materials, and in the case of triazaphosphazene (CXXVI) the bipolar ion (CXXVII) also participated in the equilibrium.

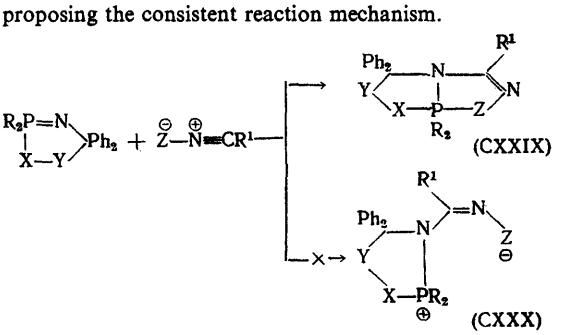


(CXXIV) (CXXVI) (CXXVII) (CXXVIII)

The spectrally observed formation of bipolar ion (CXXVII),[186] and also the possibility of transition of cyclic adducts through bipolar ions (CXXI)⇄(CXX)⇄(CXXII)⇄(CXXIII) [185] point in favour of a stepwise mechanism for the [2 + 2]-cycloaddition reaction of 1,2σ^4-azaphospholes.

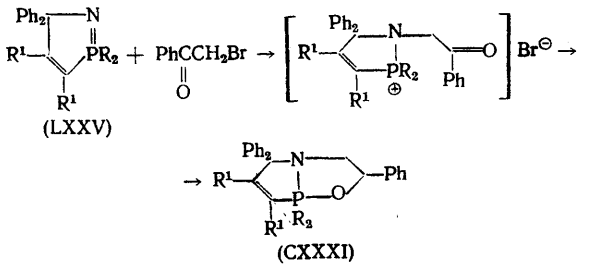
It should be mentioned that the reverse reaction, viz. dissociation into starting materials, is observed for many five-membered cyclophosphazenes and the products of their [2 + 2]-cycloaddition in solution.[123,126,179,183–186] In the majority of cases the process is reversible.

Hetero-1,2σ^4-azaphospholes and azaphospholines take part in [3 + 2]-cycloaddition reactions with such classical 1,3-dipoles as nitriloxide, nitrilimines and nitrones.[179] In all cases, except for 3,4-dihydroquinoline *N*-oxide, the formation of stable crystalline cycloaddition products (CXXIX) was recorded. Checking the reaction by ^{31}P NMR spectroscopy failed to detect the presence of bipolar ion (CXXX) as a possible intermediate which was a basis for proposing the consistent reaction mechanism.



(CXXIX) (CXXX)

In contrast to that given above the reaction of 1,2σ⁴-azaphosphole (LXXV) with bromoacetophenone occurred through the stage of a phosphonium intermediate.[184]



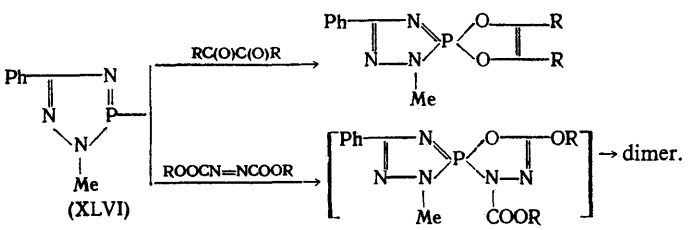
(LXXV) (CXXXI)

The formation of bicyclic adducts analogous to (CXXXI) was also observed in the reaction with styrene oxide. It is impossible to attribute reaction with the latter two reactants to the classical [3 + 2]-cycloaddition reaction.

1,2σ²-Azaphospholes proved to be less inclined towards dimerisation and cycloaddition reactions due to the aromatic character of the azaphosphole ring and the lower polarity of the phosphazene bond.

Of the known types of hetero-1,2σ²-azaphospholes (Table 3) 4,5-benzo-1,3,2σ²-diazaphospholes (XLV) and 1,3,3,σ²-oxazaphospholes (LI) exist in the form of tetramers, however they readily pass into the monomeric form in solution or on heating.[7,76,84]

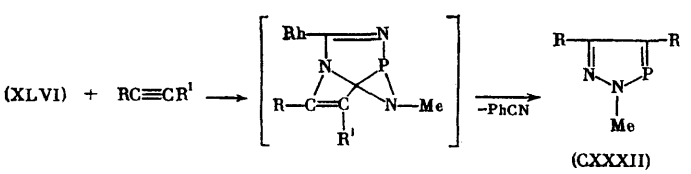
The reduced activity of 1,2,4,3σ²-triazaphospholes (XLVI) was displayed in reactions with 1,2-diketones[133] and esters of azodicarboxylic acid[134] which reacted according to a [4 + 1] type of cycloaddition at the phosphorus atom without participation of the phosphazene bond.



(XLVI)

The reactions shown demonstrate the possibility of using 1,2,4,3σ²-triazaphospholes for the synthesis of the corresponding spirocyclophosphazenes with a tetracoordinated phosphorus atom. However, 1-phenyl-1,2,3,5σ²-diazadiphosphole (LVII) did not react with diacetyl by the reaction indicated.[87]

There are data on the participation of triazaphosphole (XLVI) as dienophile in a [4 + 2]-cycloaddition reaction with a substituted acetylene.[187] The authors claimed the intermediate formation of cyclic adducts the observation of which was unsuccessful. Diazaphospholes (CXXXII) with a (σ²) P=C bond were isolated by elimination of nitrile.

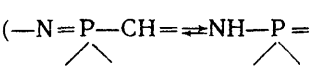


(CXXXII)

A similar reaction has also been described for 1,3,2σ²-diazaphospholes (XLIII).[82]

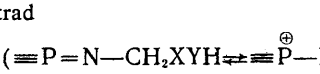
3. Rearrangements in the cyclophosphazene series

Several types of rearrangement and heterotropic conversion have been found for acyclic phosphazenes. Reversible and irreversible silylotropic rearrangements are known[188–193] as are prototropic tautomeric conversions in triad



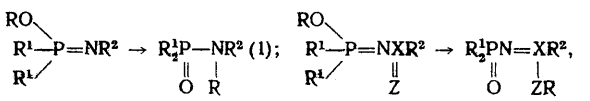
[194–197]

and tetrad



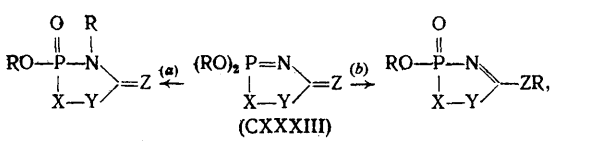
[198–200]

systems. The ring-chain tautomeric equilibrium in compounds with a P=N bond may also be assigned to the latter system.[171,172,200] The imide–amide (1) and imide–imide (2) rearrangements of acyclic phosphazenes have been considered in a review.[27]



X=C, P; Z=O, S.

Two reactions of the latter type in the cyclophosphazene series have been studied widely and systematically by Pudovik and Konovalova and their co-workers.[11,15] The subjects of the investigation, viz. hetero-1,2σ⁴-azaphospholines (CXXXIII), were rearranged thermally without isolation by routes (*a*) or (*b*) in the majority of cases.[115,201–209]

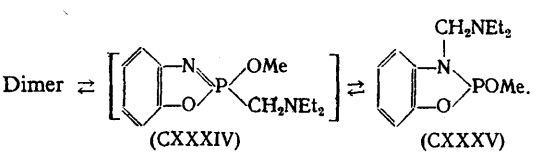


(CXXXIII)

Z=O, S, (R¹, R²).

Frequently both processes occurred simultaneously,[210–212] although rearrangement by route (*b*) was more characteristic for thione derivatives of (CXXXIII).[213–215]

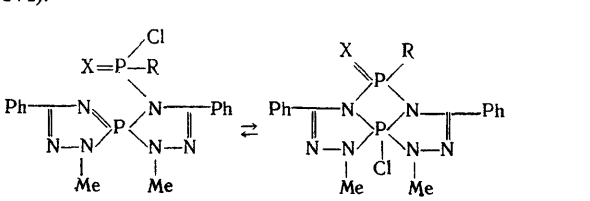
In contrast to compounds (CXXXIII) 4,5-benzo-1,3,2-oxazaphospholine (CXXXIV) underwent an imidophosphonate–amidophosphite rearrangement under distillation conditions.[70,71]



(CXXXIV) (CXXXV)

Oxazaphospholine (CXXXV) formed on distillation is slowly (60 days) transformed at room temperature once again into the dimer evidently through the monomeric form (CXXXIV).

A new type of chlorotropic ring–chain tautomerism has been described for *N*-substituted 3,3-spiro-di(1,2,4,3σ⁴-triazaphospholes) (CXXXVI).[65]

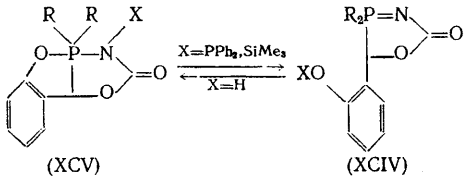


(CXXXVI) (CXXXVII)

X=O, unshared electron pair.

The position of the (CXXXVI)⇄(CXXXVII) equilibrium depends on the electron-accepting properties of the substituent at phosphorus. The equilibrium is completely displaced either to the left or to the right for the extreme members of the series R = Ph, Me_2N, PhO, Cl (X = unshared electron pair), Cl (X = O), an equal mixture of tautomers was observed for an average member.

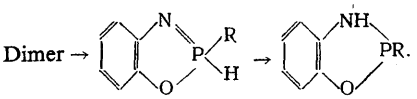
An irreversible phosphoro- and silylotropic transition (σ^5)→(σ^4) P was found in the triad system of oxazaphosphabicyclooctane (XCV).[169]



(XCV) (XCIV)

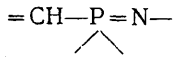
Structure (XCV) with a pentacoordinated phosphorus atom was more stable as the protonated derivative.[167,168]

On the other hand 4,5-benzo-1,3,2-oxazaphospholine (CXXXVIII) was subject in solution to irreversible transition into a form with a lower phosphorus coordination.[68]

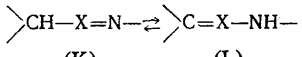


(CXXXVIII) (CXXXIX)

No prototropic conversions have been found in the triad



in the five-membered cyclophosphazene series. 1,2σ^4-Azaphospholines[102–105] and 1,3,4σ^4-oxazaphospholines[121–128] exist only in the imide form (K). In addition the carbocyclic pyrrole[102] and oxazol-2-one[216] analogues of these compounds have the enamine structure (L).



(K) (L)

4. Complex-forming reactions

The electron-donating character of the phosphazene bond is determined by the extent of hybridisation and other electronic parameters of the orbitals occupied by the unshared electron pair of nitrogen.[137] As has been shown in a series of investigations complex formation of linear phosphazenes with salts of mercury and cadmium,[217] Lewis acids,[218–221] iodine[222] and metal carbonyls[138] leads to coordination at nitrogen.

Complexes of 3,3-diphenyl-1,4,3-oxazaphospholines with stannic chloride of composition 1:1 are known in the cyclophosphazene series with tetracoordinated phosphorus.[128] Complex formation in the ligand is effected at the nitrogen atom according to IR spectral data.

Complex formation of hetero-1,2-azaphospholes with a dicoordinated phosphorus atom has been studied most. Competition of both donor centres is possible in the presence of unshared electron pairs on the phosphorus and nitrogen atoms in the 1,2,3σ^2-azaphosphole molecule. Diaza- and 1,2,4,3σ^2-triazaphospholes gave complexes with metal carbonyls where the dicoordinated phosphorus atom was the donor.[223,224] It has been recorded that 1,2,3σ^2-diazaphospholes display weaker donor properties than triazaphospholes. This is linked with the change in degree of orbital hybridisation of the unshared electron pair at phosphorus which is reflected in the size of the endocyclic angles being reduced on going from a triaza- to a diazaphosphole.

Coordination at phosphorus was observed when forming a complex of 2-methyl-5-phenyl-1,2,4,3σ^2-triazaphosphole (α-isomer) with compounds of trivalent gold.[225] However the phosphazene bond does not participate in complexes of the β-isomer and the role of donor is played by the neighbouring nitrogen atom. Seemingly, complex formation of 1,2,4,3σ^2-triazaphosphole with boron trifluoride also occurs without participation of σ^2-phosphorus.[75,77,226,227]

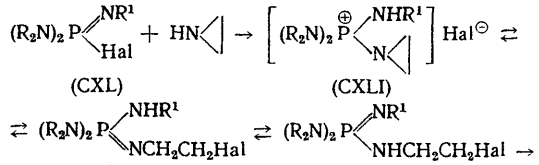
Salts of copper, mercury and cadmium gave solid complexes with 1,2,4,3σ^2-triazaphospholes which have not been studied in detail.[77]

Significant success in developing the chemistry of cyclophosphazenes has been achieved in a comparatively short period. To date the main synthetic routes and chemical transformations of five- and six-membered representatives of these cyclanes have been determined. Rules for the display of their reactivity as a function of structure have been elucidated. There is no doubt that investigations will be extended to larger and smaller rings. There is interest both for the development of theoretical organic chemistry and for purpose-directed hetero-organic synthesis.

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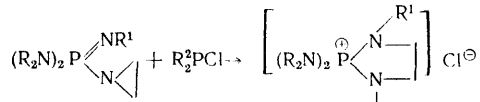
Since preparing the manuscript for printing additional information has appeared on the problem under consideration.

Synthesis of 5-membered cyclophosphazenes. A set of studies has been published recently by Pinchuk, Marchenko and co-workers on the synthesis of 1,3,2-diazaphospholines (CXLV).[228–232] The proposed method is based on the reaction of halodiaminophosphazenes (CXL) with ethylenimine.



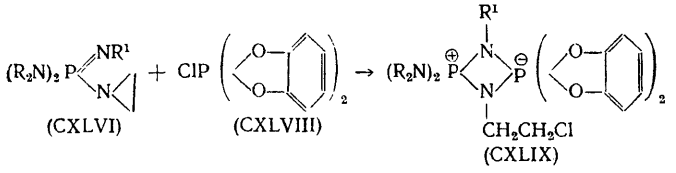
(CXL) (CXLI) (CXLII) (CXLIII) (CXLIV) (CXLV)

Bromodiamidophosphazenes (CXL) are significantly more reactive than the corresponding chloro derivatives. It was shown using the latter that the formation of diazaphospholidinium salts (CXLIV) was a complex process of reversible conversions of the intermediates (CXLI)–(CXLIII).[228] A modification of the indicated reaction was the interaction of aziridinodiaminophosphazene (CXLVI) with a P(III) monoacid chloride.[232]



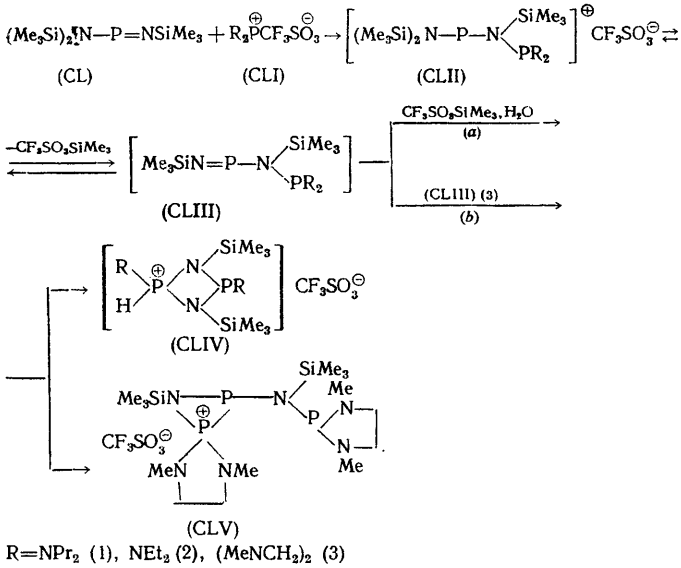
(CXLVI) (CXLVII)

However chlorophosphorane (CXLVIII) unexpectedly adds to phosphazene (CXLVI) with the formation of bonds directly onto the two nitrogen atoms, viz. the imidine and the aziridine.[233]



(CXLVI) (CXLVIII) (CXLIX)

Compounds (CXLIX) represent a new type of diazaphosphetidine containing differently charged tetra- and hexacoordinated phosphorus atoms. The reaction between phosphazenes (CXLVI) and P(III) diacid chlorides proceeds by the same route with the formation of diazaphosphetidines containing tetra- and tricoordinated phosphorus atoms.[234] The reaction of acyclic phosphazene (CL) with phosphenium trifluoromethylsulphonate (CLI) leads to the analogous heterophosphocyclane (CLIV).[235]



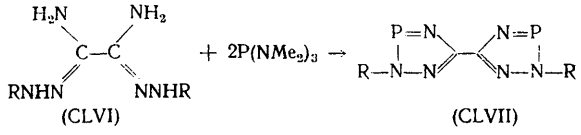
(CL) (CLI) (CLII) (CLIII) (CLIV) (CLV)

R=NPr$_2$ (1), NEt$_2$ (2), (MeNCH$_2$)$_2$ (3)

Compounds (CXLIV), (CXLVII), (CXLIX), (CLIV) and (CLV) are salts of the corresponding five- and four-membered cyclophosphazenes with a significantly polarised P=N bond. The fairly high stability of the indicated salts supports this.

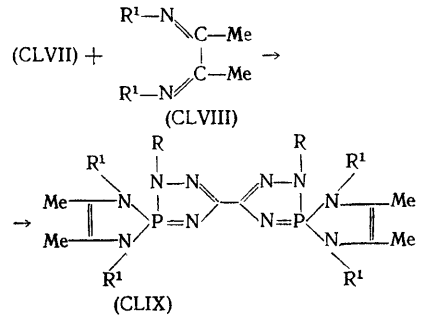
Investigations on the synthesis of hetero-1,2σ^4-azaphospholines by the [3 + 2]-cycloaddition of isocyanates of P(III) acids to dipolarophiles have continued. Examples of the latter which have been studied are chloro-substituted acetaldehydes,[236] hexafluoroacetone, esters of trifluoropyruvic acid,[237] diphenylcarbodiimide[238] and a series of other reactants containing a C=N bond.[239]

New bicyclic 1,2,4,3σ^2-triazaphospholes (CLVII) have been obtained in [4 + 1]-cycloaddition reactions.[240] The skeleton of bicycle (CLVII) is constructed on the basis of the diamidrazone molecule (CLVI), both ends of which are subject to cyclisation under the action of a triaminophosphine.



(CLVI) (CLVII)

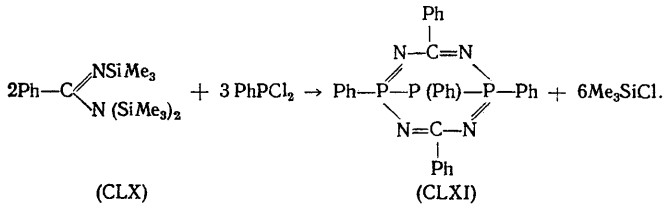
Triazaphospholes (CLVII) react further with di-imines (CLVIII) with retention of the P=N bond and the formation of new bis-spirobicyclophosphazenes (CLIX).



(CLVIII) (CLIX)

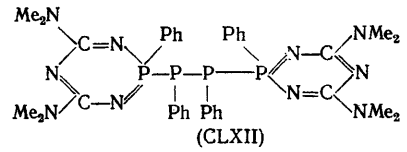
Synthesis of 6-membered cyclophosphazenes. The interaction of *C,N*-diarylnitrilamines with isocyanatophosphites has been studied in continuation of investigations on the [3 + 3]-cyclocondensation reaction.[241,242] New representatives of 1,2,4,5σ^4-triazaphosphorines (LXVII) (Table 4, example 2) have been obtained.

An interesting type of bicyclic diazatriphosphorine (CLXI) is formed by the reaction of phenyldichlorophosphine with silylated amidines (CLX).[243]



(CLX) (CLXI)

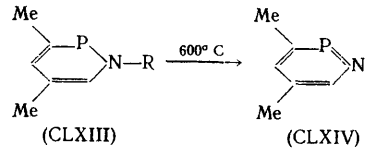
The reaction of phenyldichlorophosphine with dimethylguanidine hydrochloride in the presence of triethylamine leads to an analogous compound.[243] Bicyclic triazaphosphorine (CLXII), in which the rings are separated by a chain of four phosphorus atoms, was described in the same paper.



(CLXII)

The molecular structure of the triazaphosphorine ring in 2,2-bis(aziridinyl)-4,6-bis(trifluoromethyl)-1,3,5,2-triazaphosphorine has been studied.[244]

Synthesis of six-membered cyclophosphazenes (CLXIV) with dicoordinated phosphorus has been effected by vacuum thermolysis of azaphosphorine (CLXIII).[245]



(CLXIII) (CLXIV)

R = t-Bu, t-BuCH$_2$CH$_2$CMe$_2$.

In addition to the synthesis of cyclothiophosphazenes (VI) (Table 1, example 5) new types have been isolated by the reaction of lithium enolates of acetaldehyde with triazathiodiphosphazenes.[246]

Some problems of the chemistry of cyclophosphazenes, viz. isomerisation and tautomerism, have been considered in a review.[247]

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