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Cyclodiphosphazanes

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The chemistry of four-membered cyclic compounds containing both nitrogen and phosphorus, which may find application in the preparation of thermostable plastics and the synthesis of biologically active compounds, has been widely investigated in recent years. This review deals with problems concerning the determination of the structure, the investigation of the physical and chemical properties of cyclodiphosphazanes containing trivalent tetraco-ordinate and pentaco-ordinate phosphorus atoms, and the methods of their synthesis and chemical reactions.

20 The bibliography includes 103 references.

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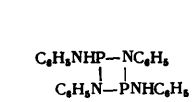
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I. INTRODUCTION

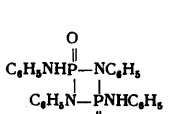
Towards the end of the 19th and the beginning of the 20th century, Michaelis[1,2] described for the first time compounds containing a four-membered ring with alternating phosphorus and nitrogen atoms. The work of Michaelis and his school led to the development of the simplest methods for the synthesis of such compounds. Then for a long time this class of organic phosphorus derivatives remained sidetracked from the mainstream of the development of organic chemistry. It was not until a few years ago that four-membered ring compounds containing both phosphorus and nitrogen atoms again attracted the attention of investigators. The year 1959 must be regarded as the start of the new period in the study of these compounds, when Kirsanov and Zhmurova published their investigation of dimeric trichlorophosphazoarenes[3]. In recent years new synthetic methods have been developed for these compounds, their reactivity has been investigated, and physicochemical studies have been made to determine their structure and to elucidate the mutual effects of the atoms.

Four-membered ring compounds containing both trivalent and tetraco-ordinate and pentaco-ordinate phosphorus atoms have now been obtained.

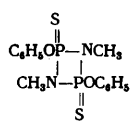
There is no agreement as regards the nomenclature of such cyclic systems. In Sasse's monograph[4] they are referred to as derivatives of imidophosphorous, imidophosphoric, imidophosphonic, imidothiophosphoric, and imidothiophosphonic acids. In chemical literature in English they are sometimes called 1,3,2,4-diazadiphosphetidines[5]. The term "dimeric phosphazo-compounds" is fairly frequently encountered. The name cyclodiphosphazanes proposed by Shaw et al[6] and also by Davydova and Voronkov[7] is the most apt. For example:



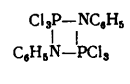
2,4-dianilino-1,3-diphenylcyclodiphospha(III)azane



2,4-dianilino-2,4-dioxo-1,3-diphenylcyclodiphosphazane



1,3-dimethyl-2,4-diphenoxy-2,4-dithionocyclodiphosphazane



2,2,2,4,4,4-hexachloro-1,3-diphenylcyclodiphosphazane

This nomenclature will in fact be adhered to in the present review.

II. THE STRUCTURE OF THE CYCLODIPHOSPHAZANE RING

To establish the structure of cyclodiphosphazanes, various physicochemical methods have been used: X-ray diffraction measurements of dipole moments, infrared and ultraviolet spectroscopy, Raman spectroscopy, and nuclear magnetic resonance (NMR). The data obtained made it possible not only to establish the relative positions of the atoms in the molecule but also to arrive at certain conclusions concerning the nature of the nitrogen–phosphorus bond.

Unfortunately almost all studies of this kind deal with compounds with tetra- and penta-co-ordinate phosphorus atoms. There are no physicochemical data in the literature for cyclodiphosphazanes with a trivalent phosphorus atom.

1. Vibration and Electronic Spectra

Most investigators attribute the intense absorption in the region 850–865 cm^{-1} in the infrared spectra of dialkyl- or diaryl-hexachlorocyclodiphosphazanes to P–N vibrations of the four-membered ring[8–10]. The intense band at 1160–1165 cm^{-1} may be assigned to N–alkyl vibrations[11] but not to P–N–P bridge vibrations or P–N stretching vibrations[8–12].

The vibration frequencies in the infrared and Raman spectra of hexafluorodimethylcyclodiphosphazane have been assigned (Table 1)[13] by analogy with the spectra of alkylfluorophosphoranes[14,15].

The spectra of dithionocyclodiphosphazanes have been investigated in greatest detail[11]. The intense absorption bands in the region 850–900 cm^{-1} in the infrared spectra 1,3-dialkyldithionocyclodiphosphazanes are due to antisymmetric vibrations of the four-membered ring. The replacement of the *N*-alkyl group by an *N*-aryl group leads to an increase of the vibration frequency by about 100 cm^{-1}. The symmetrical vibrations of the ring are revealed only in the Raman spectrum in the region 430–570 cm^{-1}. The infrared spectroscopic data for bis(diphenylthiophosphono)-*N*-alkylamines are satisfactorily consistent with these results. The P–N–P antisymmetric vibration band in their spectra lies in the region 912–928 cm^{-1}, while the band due to the P–N–P symmetrical vibrations is in the region[16] 528–583 cm^{-1}.

The absorption bands at 1150–1180 cm^{-1} in the infrared spectra of 1,3-dialkyl-2,4-dithionocyclodiphosphazanes have been assigned to N–C (alkyl) vibrations. In the spectra of the *N*-aryl analogues these bands occur at 1250–1270 cm^{-1}. 2,4-Dialkyl-2,4-dithionocyclodiphosphazanes absorb in the region 615–630 cm^{-1}, which may be attributed to P=S vibrations. In the spectrum of 2,4-diphenyl-2,4-dithionocyclodiphosphazane the absorption shifts to the region 650–670 cm^{-1}. Such as increase in the P=S vibration frequency as a function of the immediate environment of the phosphorus atom is consistent with the available data[17,18].

Table 1. Infrared and Raman spectra of hexafluorodimethylcyclodiphosphazane

Frequencies of band maxima, cm^{-1}		Assignment
i.r. (vapour)	Raman (liquid)	
1264	1202	C–N antisymmetric
~964	960	C–N symmetrical
934	904	P–F_{eq} antisymmetric
858	839,5	P–F_{eq} symmetrical
807	741,5	P–F_{ax}
614	626	P–N_{eq}
535	563	P–N_{ax}

The ultraviolet spectra 2,4-dialkyl-1,3-diaryl-2,4-dithionocyclodiphosphazanes are virtually identical with those of the dianilides of methylthiophosphonic [methylphosphonothioic? (Ed. of Translation)] acid[11] (Table 2).

Compared with the spectra of *NN'*-dialkyldiaminophenylphosphonothioates, those of 1,3-dialkyl-2,4-diphenyl-2,4-dithionocyclodiphosphazanes show a bathochromic shift of the nearest absorption band [band at the lowest frequency? (Ed. of Translation)] together with an increase in its intensity, and an additional maximum appears at 245 nm.

2. Nuclear Magnetic Resonance Spectra

The ^{1}H-NMR spectra of hexachlorodimethylcyclodiphosphazane show a 1 : 2 : 1 triplet at 3.00 p.p.m. † with a spin–spin interaction constant $J_{P-N-C-H}$ = 20 Hz.[8,19]

† In the ^{1}H-NMR spectra the chemical shifts are given in terms of the δ scale relative to tetramethylsilane as an internal standard.

The signal due to H–C–N–P protons in the homologues of this compound occurs in the region 3.29–3.58 p.p.m. with an interaction constant of 28–29 Hz. In the NMR spectra of the fluoro-analogues $[CH_3NPF_2X]_2$, where X = F, alkyl, or aryl, the chemical shift of the protons is 2.32–2.48 p.p.m. with an interaction constant J = 12.5–12.9 Hz {for $[CH_3NPF_3]_2$, $J_{P-N-C-H}$ = 14.5 Hz [19,20]}.

The ^{31}P chemical shifts in the spectra of $[RNPCl_3]_2$ and $[CH_3NPF_2C_6H_5]_2$ are +78.2–79.8 and +56.1 p.p.m. respectively (relative to 30% of phosphoric acid)[8,21], i.e. the phosphorus nucleus in chlorocyclodiphosphazanes is more screened than in the fluoro-derivatives. The marked shift indicates that the phosphorus atom in these compounds has a co-ordination number of 5 (for PCl_5, I = +80 p.p.m.).[22]

Table 2. Positions and intensities of the ultraviolet absorption bands of solutions in heptane

Compound		λ_{max}, nm	ϵ_{max}
$[CH_3P(S)NCH_3]_2$	(I)	220	10500
$[CH_3P(S)NC_2H_5]_2$	(II)	222	11000
$[CH_3P(S)NC_6H_5]_2$	(III)	236,280	29000,1500
$[CH_3P(S)NC_6H_4CH_3{-}4]_2$	(IV)	239,280	42000,1800
$[CH_3P(S)NC_6H_4Cl{-}4]_2$	(V)	243,285	42800,1900
$[CH_3P(S)NC_6H_4OCH_3{-}4]_2$	(VI)	238,282	40000,2700
$[CH_3P(S)NC_6H_4OC_2H_5{-}4]_2$	(VII)	238,282	47000,2500
$[C_6H_5P(S)NCH_3]_2$	(VIII)	220,242,283	20000,11500 s, 8500
$[C_6H_5P(S)NC_3H_7\text{-}изо]_2$	(IX)	220,245,292	25000,12800,9000
$[C_6H_5P(S)NC_6H_5]_2$	(X)	236,265,300	41700,9500, 3000 s
$[C_6H_5P(S)NC_6H_4OC_2H_5{-}4]_2$	(XI)	236,270,295	41200,9000,4000 s
$C_6H_5P(S)[NHC_3H_7\text{-}изо]_2$	(XII)	255	2500
$CH_3P(S)(NHC_6H_5)(NHC_2H_5)$	(XIII)	238,278	177000,1300
$CH_3P(S)(NHC_6N_5)_2^*$	(XIV)	238,278	28000,2300

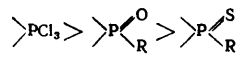
*In alcohol. The letter s denotes a shoulder.

In the spectra of 1,3-dialkyl-2,4-dioxocyclodiphosphazanes the constant for the spin–spin interaction of the proton with the phosphorus nucleus via three H–C–N–P bonds is 13.0–16.3 Hz, the chemical shift of the proton signal amounting to 2.6–3.37 p.p.m.[19]

In the ^{31}P–NMR spectra there is a signal in the region between −7.0 and +5.7 p.p.m.,[10,19] which is characteristic of the P=O group[23].

In the ^{1}H–NMR spectrum of 1,3-dimethyl-2,4-diphenyl-2,4-dithionocyclodiphosphazane Trippett[24] observed a 1 : 2 : 1 triplet (δ = 2.32 p.p.m., J = 14 Hz) and a second triplet, 10 times less intense, at 2.56 p.p.m. (J = 15.5 Hz). According to Mel'nikov et al.[11], the NMR spectrum of a preparation obtained by a different method contains 1 triplet at 2.52 p.p.m. (J = 15 Hz). The ^{1}H-NMR spectrum of the 1,3-dibenzyl analogue of this compound was found to have two triplets of approximately equal intensity at 4.14 and 3.99 p.p.m. (J = 15.0 and 18.0 Hz). The two triplets are probably due to the presence in the specimens investigated of *cis*- and *trans*-isomers of 1,3-dimethyl- and 1,3-dibenzyl-2,4-diphenyl-2,4-dithionocyclodiphosphazanes. These data agree satisfactorily with the results of the measurements of the dipole moment of 1,3-dimethyl-2,4-diphenyl-2,4-dithionocyclodiphosphazane[25].

The chemical shifts in the ^{31}P-NMR spectra of dithionocyclodiphosphazanes are in the range between −51.5 and −60 p.p.m.,[10] i.e. the screening of the phosphorus atom decreases in the sequence



3. Bond Lengths and Valence Angles

Hess and Forst[26] and also Hoard and Jacobson[27] determined by X-ray diffraction the angles and bond lengths in 2,2,2,4,4,4-hexachloro-1,3-dimethylcyclodiphosphazane. Cox and Corey[28] and Weiss and Hartmann[29] made similar measurements (Table 3) for 2,2,4,4-tetrafluoro-1,3-dimethyl-2,4-diphenylcyclodiphosphazane $[MeNPF_2Ph]_2$ and a compound which was isolated by Becke-Goehring et al.[10] (see p. 27).

Table 3. Bond lengths (in ångstroms) and angles (in degrees).

Bonds and angles	Ref.26	Ref.27	Ref.28	Ref.29
Bonds				
P—Cl axial	2.152	2.133	—	2,16
P—N axial	1.776	1.769	1.78	1.71
P—F axial			1.62	
P—Cl radial	2.022; 2.018	2.026		2.05
P—N radial	1.629	1.635	1.64	1.66
P—F radial			1.57	
P—C			1.79	
N—C	1.476	1.475	1.44	
Angles				
P—N—P	98.3	99.5	99.4	99.1
N—P—N	81.7	80.5	80.6	80.7

A centrosymmetric structure with a planar four-membered ring is characteristic of the molecules of cyclodiphosphazanes with a pentacovalent phosphorus atom (see Figure). Each phosphorus atom exhibits dsp^3 hybridisation and consists of a trigonal bipyramid. In such hybrid structures the axial orbitals are longer than the radial orbitals by a factor of 1.1–1.2. This ratio is 1.05–1.07 for P–Cl bonds, 1.085–1.09 for P–N bonds, and 1.08 for P–F bonds. The P–N–P and N–P–N angles are 98.3–99.5°C and 80.5–81.7°C respectively.

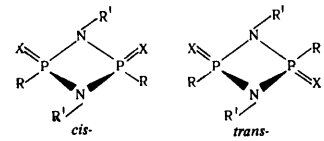
In 2,4-dichloro-1,3-dimethyl-2,4-dithionocyclodiphosphazane containing an sp^3-hybridised phosphorus atom, P–N bonds are of the same length (1.67 Å), i.e. they assume the average value for the radial and axial bond lengths[30]. The lengths of other bonds and the angles between them are given below.

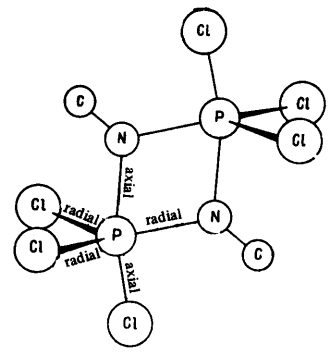
Bond length	P—S (Cl)*	1.93 Å
	N—C	1.46 Å
Angle	N—P—N	84.0°
	P—N—P	96.0°
	N—P—S (Cl)	114.7°
	S—P—Cl	111.5°

*Weiss and Hartmann do not distinguish S and Cl; usually the P–Cl bond length is 0.01 Å.[23]

4. Dipole Moments

Cyclodiphosphazanes with a tetraco-ordinate phosphorus atom can exist as *cis*- or *trans*-isomers[25]:





The occurrence of *cis*- and *trans*-isomerism in the series of 2,4-dithionocyclodiphosphazanes has been fairly convincingly confirmed by the measurements and calculations of their dipole moments (Table 4), although the calculations were based on a simplified scheme and the extrapolated results of a relatively small number of measurements by different investigators. The considerable deviation of experimental dipole moments of the *trans*-isomers from zero may be explained by their partial inversion in solution.

Table 4. Dipole moments of certain dithionocyclodiphosphazanes.

R	R'	μ_{exp}	$\mu_{cis.\ calc}$
CH_3	CH_3	6.11	7.18
C_6H_5	C_6H_5	5.84	6.70
CH_3	C_6H_5	1.82	7.18
C_6H_5	CH_3	0.7	6.70
Cl	C_6H_5	1.32	3.57

5. Bond Energies

Only one study has been made on the thermochemistry of cyclodiphosphazanes, namely that of Fowell and Mortimer[31], who found that the average P–N bond energy in 2,2,2,4,4,4-hexachloro-1,3-dimethylcyclodiphosphazanes is 74.3 kcal mole^{-1} according to measurements of the heat of hydrolysis. This is close to the P–N bond energy in cyclotriphosphazenes (72.3 kcal mole^{-1}) and cyclotetraphosphazenes (72.5 kcal mole^{-1})[32] and greatly

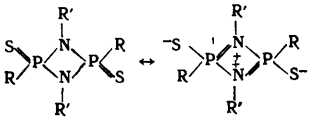
exceeds the energy of the same bond in tri(diethylamino)-phosphine (66.8 kcal mole^{-1}).[33] The fact that the formation of the cyclodiphosphazane ring is favoured by thermodynamic factors is indicated also by chemical data. The reaction of tri(diethylamino)phosphine with aniline yields the corresponding cyclodiphospha(III) azane[34].

The P–Cl bond energy is 63.1 kcal mole^{-1},[31] i.e. is smaller by 13.1 kcal mole^{-1} than in PCl_5.[35]

6. The Nature of the Phosphorus–Nitrogen Bond

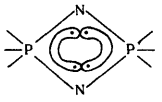
The available physicochemical data on the structure of cyclodiphosphazanes permit certain conclusions concerning the nature of the P–N bond. The shortening of the P–N bond, the planarity of the dimer, the location of the N atoms in the same plane (according to X-ray diffraction analysis), the thermochemical data, and the relatively high stability of the ring in cyclodiphosphazanes with tetra- and penta-co-ordinate phosphorus atoms (see sections IV and V) are evidence of an additional interaction between nitrogen and phosphorus atoms.

The idea that dithionocyclodiphosphazane molecules are stabilised by isomerisation, described by the resonance of the structures[24]



is not confirmed by physicochemical investigations.

It is most probable that the molecules of cyclodiphosphazanes are stabilised by the interaction of the unshared electron pairs of the nitrogen atoms with the *d* orbitals of the adjacent phosphorus atoms[26,36] via three-centre π-molecular orbitals[37,38]:



III. CYCLODIPHOSPHAZANES WITH TRICO-ORDINATE PHOSPHORUS ATOMS

The reaction of phosphorus trichloride with aromatic amines in a non-polar solvent yields 2,4-diaminocyclodiphospha(III) azanes[39,40]:

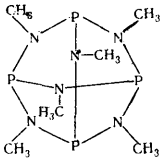
$$10\,C_6H_5NH_2 + 2\,PCl_3 \rightarrow \underset{C_6H_5N-PNHC_6H_5}{\overset{C_6H_5NHP-NC_6H_5}{|\ \ |}} + 6\,C_6H_5NH_2 \cdot HCl.$$

An excess of the amine introduced into the reaction or a tertiary amine may be used as the acceptor of hydrogen chloride[5]. Phenyldichlorophosphine reacts similarly[39].

The reaction of phosphorus trichloride with ammonia and primary aliphatic amines does not take place unambiguously. With ammonia, a number of products are formed, according to the following mechanism[41,42]:

$$PCl_3 + NH_3 \rightarrow P(NH_2)_3 \rightarrow [HNP(NH_2)]_n \rightarrow (PNH)_n \rightarrow PN.$$

The reaction of phosphorus trichloride with methylamine gives a compound with a urotropine-like structure[43,44]:



When straight-chain primary amines containing two and more carbon atoms are introduced into the reaction, the corresponding cyclodiphospha(III) azanes are formed[40].

The reaction of aniline hydrochloride with phosphorus trichloride yields 2,4-dichloro-1,3-diphenylcyclodiphospha(III) azane[45]. Its 1,3-dimethyl analogue has been obtained by the amination of phosphorus tetrachloride with heptamethyldisilazane[46]:

$$2\,C_6H_5NH_2 \cdot HCl + 2\,PCl_3 \rightarrow \underset{C_6H_5N-PCl}{\overset{ClP-NC_6H_5}{|\ \ |}} + 6\,HCl,$$

$$2[(CH_3)_3Si]_2NCH_3 + 2\,PCl_3 \rightarrow \underset{CH_3N-PCl}{\overset{ClP-NCH_3}{|\ \ |}} + 4\,(CH_3)_3SiCl.$$

It is noteworthy that the reaction of *N*-ethylhexamethyldisilazane with phosphorus trichloride yields a mixture containing 2,4,6-trichloro-1,3,5-triethylcyclotriphosphazane and 2,4,6,8-tetrachloro-1,3,5,7-tetraethylcyclotetraphosphazane[47].

The reaction of tri(triethylamino)phosphine with aniline or *p*-toluidine at 60–70°C leads to the formation of 2,4-dianilino-1,3-diarylcyclodiphospha(III) azanes[34]:

$$3\,ArNH_2 + [(C_2H_5)_3N]_3P \rightarrow \underset{ArN-PNHAr}{\overset{ArNHP-NAr}{|\ \ |}}.$$

The synthesis of 1,3-dibenzyl-2,4-di(benzylamino)-cyclodiphospha(III)azane by the thermal dissociation of the di(benzylamide) of pentafluorophenylphosphonus acid[48] is interesting:

$$2\,C_6F_5P(NHCH_2C_6H_5)_2 \xrightarrow{200°} \underset{C_6H_5CH_2N-PNHCH_2C_6H_5}{\overset{C_6H_5CH_2NHP-NCH_2C_6H_5}{|\ \ |}}$$

Cyclodiphosphazanes can form part of certain polymeric compounds. Thus the thermal decomposition of the amides of pentafluorodimethylphosphinous acid, obtained by the ammonolysis of di(trifluoromethyl)phosphine with liquid ammonia at −78°C, yields linear and cross-linked polymers:

$$(CF_3)_2PH + NH_3 \rightarrow CF_3\overset{NH_2}{\overset{|}{P}}CHF_2 \xrightarrow{\Delta t} (CF_3P-NH)_n.$$

The mechanism of their formation is probably as follows[49]:

$$RP{=}NH \xrightarrow{RP=NH} \underset{HN-PR}{\overset{RP-NH}{|\ \ |}} \xrightarrow{RP=NH} \underset{HN-PR\ R}{\overset{RP-N-PNH_2}{|\ \ |\ \ |}} \rightarrow$$

$$\xrightarrow{\overset{RP-NH}{|\ \ |}{}_{HN-PR}} \underset{HN-PR\ R\ RP-NH}{\overset{RP-N-P-N-PR}{|\ \ |\ \ |\ \ |\ \ |}} \rightarrow \left[\underset{-N-PR\ R}{\overset{RP-N-P-}{|\ \ |\ \ |}}\right]_n.$$

Cyclodiphosphazanes containing a trivalent phosphorus atom are present in solution with a corresponding phospha(III)azo-compounds. On raising the temperature and increasing the polarity of the solvent, the equilibrium shifts to the right[5,40]:

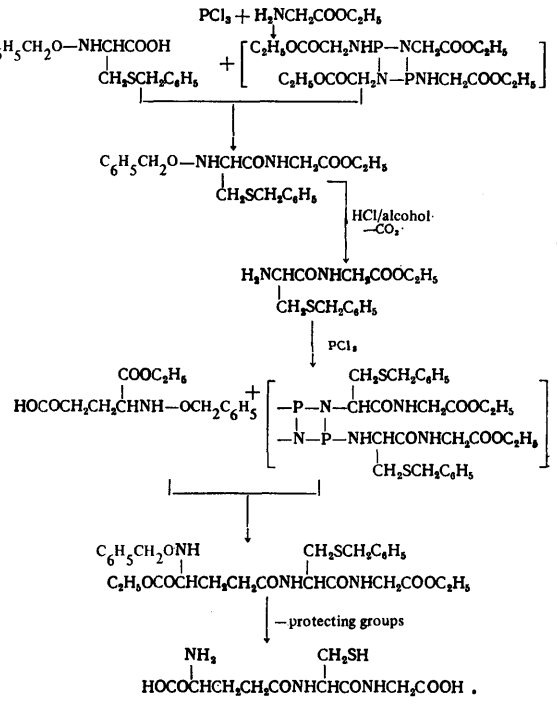
$$\underset{-N-P-}{\overset{-P-N-}{|\ \ |}} \rightleftarrows -P{=}N-.$$

This equilibrium accounts to a large extent for the ease of the dissociation of the cyclodiphosphazane ring under the action of nucleophilic reagents.

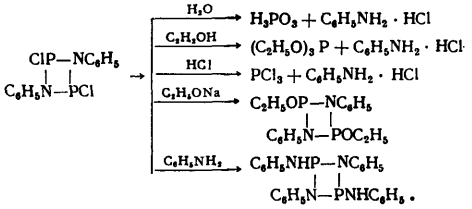
When water reacts with diaminocyclodiphospha(III)-azanes, diamides of phosphorous acid are formed. Inorganic acids decompose cyclodiphosphazanes to phosphorous acids and substituted ammonium salts. Organic acids react with formation of carboxylic acid amides[45,50,51]:

$$\underset{RNHP-NR}{\overset{RN-PNHR}{|\ \ |}} + 2\,R'COOH \rightarrow 2\,R'CONHR + 2\,H_3PO_3.$$

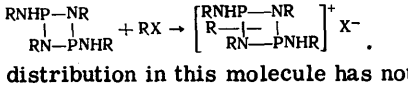
The salts of carboxylic acids do not react with cyclodiphosphazanes. Preparative methods for the synthesis of acid amides, substituted ureas, and di-, tri-, and tetrapeptides have been developed on the basis of these data [50-56]. In the synthesis of peptides, amino-acid derivatives are allowed to react with phosphorus trichloride, the reaction mass being subsequently treated with the amino-acid without isolating the cyclodiphospha(III)azane in a pure form. The following elegant synthesis of glutathione may be quoted as an example [51]:



2,4-Dichloro-1,3-diphenylcyclodiphospha(III)azane also readily reacts with nucleophilic reagents, undergoing ring rupture, under the conditions of acid catalysis. It undergoes substitution reactions with alkaline nucleophilic reagents (sodium alkoxides, piperidine, aniline) [45,56]:



Cyclodiphospha(III) azanes also enter into addition reactions with electrophilic reagents via the unshared electron pairs. Thus in the reaction with alkyl halides, arylalkyl halides, and halogenomethyl ethers, 1,3-dialkyl-2,4-di(alkylamino)cyclodiphosphazanes are converted into the corresponding salts [5]:



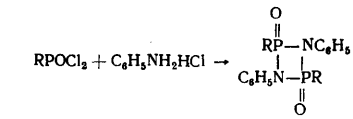
The charge distribution in this molecule has not been investigated.

N-Methylaniline has been isolated after the reaction of 2,4-dianilino-1,3-diphenylcyclodiphosphazane with methylmagnesium iodide and dimethyl sulphate [53].

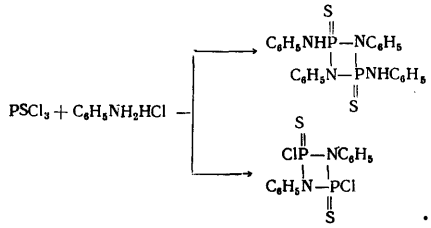
IV. CYCLODIPHOSPHAZANES WITH TETRACOORDINATE PHOSPHORUS ATOMS

Cyclodiphosphazanes with tetraco-ordinate phosphorus atoms are obtained both from linear molecules and from pre-formed cyclic structures.

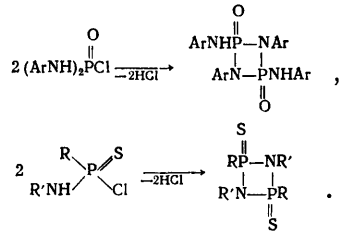
When the hydrochlorides of aromatic amines [2,57,58] or the free amines themselves [59] are heated for many hours with phosphorus oxychloride, phosphoramidic dichlorides, aryl phosphorodichloridates, or phenylphosphonic dichlorides in xylene, 2,4-dioxocyclodiphosphazanes are obtained:



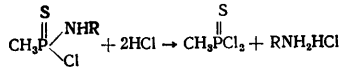
The reaction of this phosphoryl chloride with aniline hydrochloride leads to 2,4-dianilino-1,3-diphenyl or 2,4-dichloro-1,3-diphenyl-2,4-dithionocyclodiphosphazanes depending on the reactant ratio and the process conditions [60]:



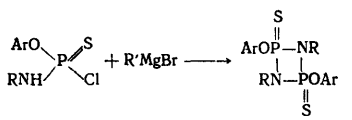
The thermal dehydrochlorination of the chlorides of pentavalent phosphorus acid amides containing a primary or a secondary nitrogen atom results in the formation of the corresponding 2,4-dioxo- or 2,4-dithionocyclodiphosphazanes [1,11,58]:



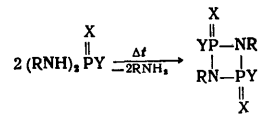
The last reaction is carried out at a reduced pressure of 100–200 mmHg and 120–150°C. Methylphosphonothionic dichloride and the hydrochloride of the corresponding amine were isolated as side products. Their formation may be explained by the following mechanism [11]:



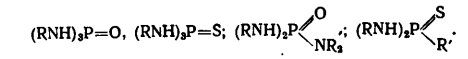
The attempts to employ tertiary amines as acceptors for hydrogen chloride in this process were unsuccessful. However, quite unexpectedly, it was found that organomagnesium compounds may be used as dehydrochlorinating agents. Thus the reaction of butyl- or pentyl-magnesium bromide with aryl *N*-alkylphosphoramidochloridothionates led to the corresponding dithionocyclodiphosphazanes together with aryl (*N*-alkyl)alkylphosphonoamidothionates [61]:



The most general method for the synthesis of dioxo- and dithiono-cyclodiphosphazanes of different structures is thermal deamination of the amides of phosphorus acids containing at least two secondary amide groups[1,24,58,62-66]:

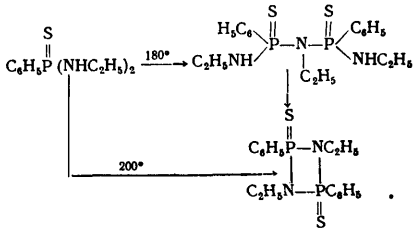


Compounds of the following types have been used as the starting materials:

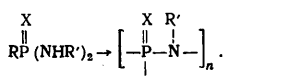


The reaction is carried out in a stream of an inert gas at 200–300°C. The derivatives of thioic acids usually decompose at a lower temperature and give higher yields of the final products than oxygen analogues. When phosphorothionic tri(isobutylamide) was heated in the temperature range 260–280°C, the corresponding dithionocyclodiphosphazane was isolated in a 56% yield. The preparation of the oxygen analogue required a temperature of 280–295°C and the yield fell to 21%.[64]

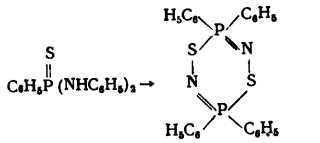
Ibrahim and Shaw[65] obtained data demonstrating indirectly that thermal cyclisation of phosphorus acid amides takes place in steps. Thus on heating to 180°C phenylphosphonothionic di(ethylamide) is converted into di-*N*-ethylphenylphosphonamidothionylethylamine, while the reaction at 200°C leads to the formation of the corresponding dithionocyclodiphosphazane:



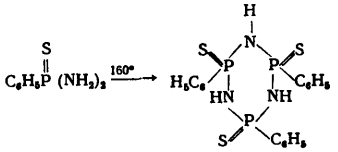
The synthesis of dioxo- and dithiono-cyclodiphosphazanes by the thermal deamination of the amides of phosphorus acid is accompanied by a side process—polycondensation involving the formation of polymers with phosphorus—nitrogen bonds[67-69]:



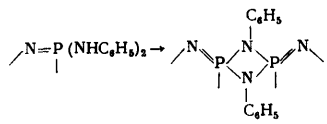
Cleavage of the dianilide of phenylphosphonothionic acid at 265°C leads to the formation of 1,1,4,4-tetraphenyl-2,5-diaza-3,6-dithia-1,4-diphosphacyclohexa-1,4-diene[65] and not tetraphenyldithionocyclodiphosphazane:



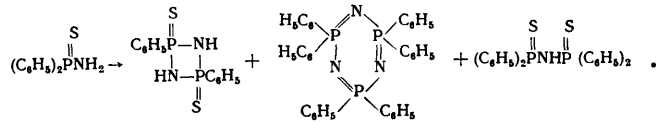
Thermal deamination of phenylphosphonothionic diamide at 160°C results in the formation of 2,4,6-triphenyl-2,4,6-trithionocyclotriphosphazane, while *N*-alkyl homologues yield under these conditions dithionocyclodiphosphazanes[65]:



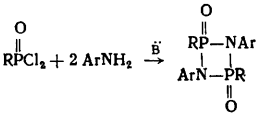
Probably the polymeric products formed in the thermal condensation of hexa-anilinocyclotriphosphazenes include cyclodiphosphazane structures[70]:



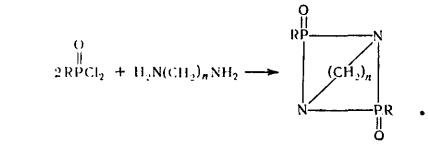
2,4-Diphenyl-2,4-dithionocyclodiphosphazane in a yield of 17% together with bisdiphenylphosphonothionic imide and 2,2,4,4,6,6-hexaphenylcyclotriphosphazene were isolated from a mixture obtained on thermal decomposition of diphenylphosphinothionic amide at 280°C for 30 min[71]:



The reaction of the dichlorides of alkyl(aryl)phosphonic acids with primary aliphatic or aromatic amines in the presence of bases (molar ratios of the reactants 1 : 1 : 2) in inert solvents constitutes a convenient method for the synthesis of 1,3-dialkyl(aryl)-2,4-dialkyl(aryl)-2,4-dioxocyclodiphosphazanes[66,72-76]:

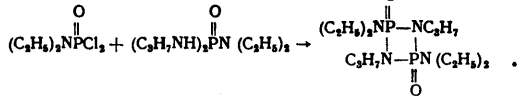


According to Binder and Heinle[72], the reaction of one mole of an alkylenediamine with two moles of a phosphonic acid dichloride can lead to the formation of dioxocyclodiphosphazanes with an alkylene bridge between the nitrogen atoms:



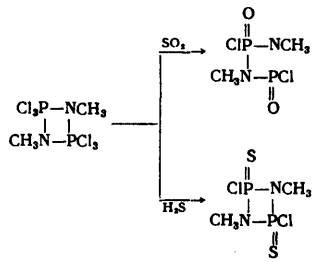
However, the structure of the compound obtained was not proved.

Bock and Wiegrabe[64] proposed an interesting method for the synthesis of dioxocyclodiphosphazanes with various substituents at the nitrogen atom. When the dichloride of *NN*-diethylphosphoramidic acid was heated with phosphoric *NN*-diethyldi(*N'*-propyl)triamide in benzene in the presence of triethylamine, the product was 1,3-dipropyl-2,4-di(diethylamino)-2,4-dioxocyclodiphosphazane:

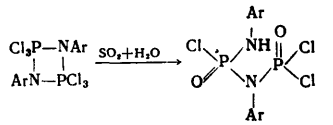


The conversion of 2,2,2,4,4,4-hexachlorocyclodiphosphazanes into 2,4-dichloro-2,4-dioxo- or 2,4-dichloro-2,4-dithiono-cyclodiphosphazanes takes place when the

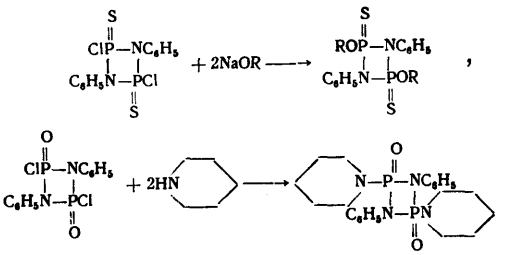
former compounds are treated with sulphur dioxide or hydrogen sulphide in the presence of pyridine[10,19].



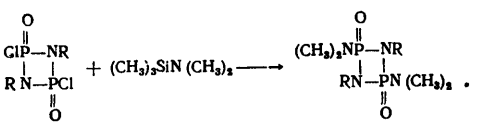
Treatment of hexachlorocyclotriphosphazanes with sulphur dioxide in the presence of moisture in phosphorus oxychloride results in ring rupture and the formation of *NN'*-diaryl-*N*-(dichlorophosphinyl)phosphorodiamidic chloride[77]:



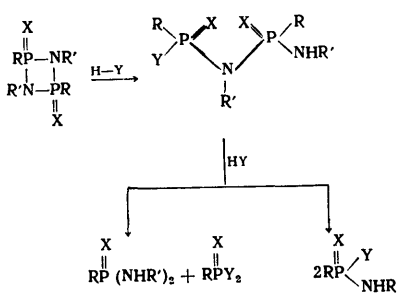
Substitution of a halogen in 2,4-dichloro-2,4-dioxo- or 2,4-dichloro-2,4-dithiono-cyclodiphosphazanes may be used for the introduction of various substituents into the molecule. Thus the reaction with sodium alkoxides or phenoxides under mild conditions leads to the formation of 2,4-dialkoxy-derivatives. The reactions with amines or anilines yield 2,4-diamino-derivatives of 2,4-dioxo- or 2,4-dithiono-cyclodiphosphazanes[2,60]:



Halogen substitution in 2,4-dichloro-2,4-dioxocyclodiphosphazanes by dialkylamino- and alkylthio-groups has also been achieved by reaction with dialkylamino- and alkylthio-trimethylsilanes respectively[19]:

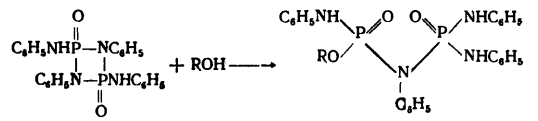


Cyclodiphosphazanes with tetraco-ordinate phosphorus atoms are fairly stable. However, nucleophilic reagents with a labile hydrogen atom, such as water, alcohols, phenols, amines, β-diketones, esters of β-keto-acids, etc. at a high temperature rupture the four-membered ring[1,2,8,62,63,78,79]. The process takes place in steps:

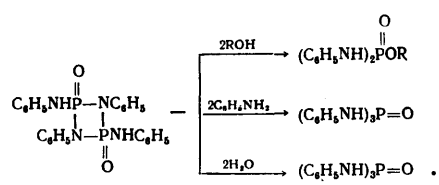


Initially one P–N bond dissociates and an unsymmetrical diphosphoric imide (or a diphosphonic imide or their thio-analogues) is formed and reacts with a molecule of the nucleophilic reagent with dissociation of the second P–N bond. This may result in the formation of both symmetrical and unsymmetrical compounds[63,79].

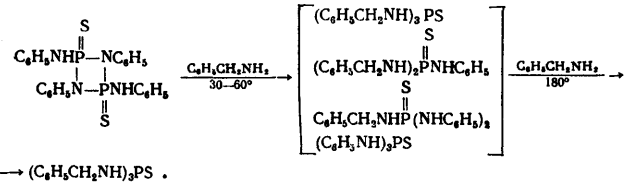
The cleavage reactions of 2,4-dioxocyclodiphosphazanes have been investigated in greater detail. Michaelis[1,2] showed that the process may also be stopped at the first stage. For example, when one mole of phenol, ethyl alcohol, or sodium alkoxide reacts with 2,4-dianilino-1,3-diphenyl-2,4-dioxocyclodiphosphazane, the corresponding diphosphoric imides are formed[2,58]:



Esters of *NN*-diphenylphosphorodiamidic acid have been isolated after reaction with two moles of phenol or alcohol. The reaction with two moles of water gives phosphoric trianilide. The latter was also isolated after the reaction with aniline:

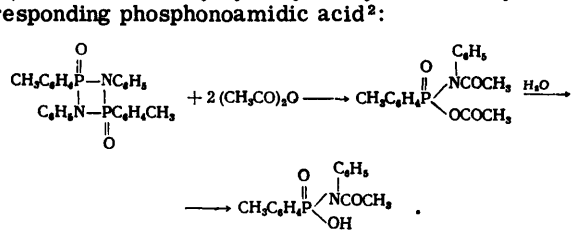


The reaction of 2,4-dianilino-1,3-diphenyl-2,4-dithiono-cyclodiphosphazane with benzylamine at 30–60°C leads to a mixture of phosphorothionic triamides, which could not be separated. If the mixture is heated with an excess of benzylamine at 180°C, transamination takes place and phosphorothionic tri(benzylamide) is formed[63]:



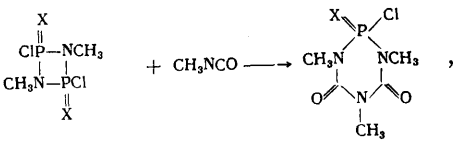
The reaction of 2,4-dimethyl-1,3-diphenyl-2,4-dithionocyclodiphosphazane with butylamine in a sealed tube at 160–170°C for several hours yielded a mixture of products containing the dianilide, *N*-butyl-*N'*-phenyldiamide, and di-(n-butylamide) of methylphosphonothionic acid. The mixture could be separated by thin-layer and column chromatography[79].

The reaction of acetic anhydride with 1,3-diphenyl-2,4-ditolyl-2,4-dioxocyclodiphosphazane gave the *N*-acetylated mixed anhydride of phosphonic and acetic acids, which is readily hydrolysed by water and yields the corresponding phosphonoamidic acid[2]:



The reaction of 2,4-dichloro-1,3-dimethyl-2,4-dioxo-cyclodiphosphazane or its sulphur analogue with methyl

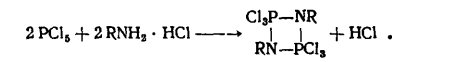
isocyanate results in the formation of 1-chloro-2,4,6-trimethyl-1,2,4,6-phosphatriazane-1,3,5-trione. The process is carried out in a sealed tube in dry benzene at 100°C for several days [80]:



where X = O or S.

V. CYCLODIPHOSPHAZANES WITH PENTACO-ORDINATE PHOSPHORUS ATOMS

The simplest and most general method for the synthesis of 1,3-dialkyl- or 1,3-diaryl-2,2,2,4,4,4-hexachlorocyclodiphosphazanes consists in the reaction between phosphorus pentachloride and primary aliphatic amines and also the hydrochlorides of aliphatic and aromatic amines [3,8,81-87]:



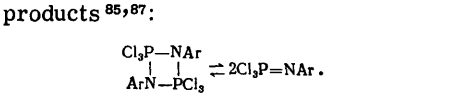
This reaction was discovered by Kirsanov and Zhmurova[3] in 1959. The reaction of phosphorus pentachloride with aniline hydrochloride was first investigated by Gilpin [88], but the latter was unable to establish the structure of the compound produced.

Whether or not the reaction occurs depends on the basicity of the initial amines. An empirical rule has been deduced from experimental data for substituted anilines, according to which hexachlorocyclodiphosphazanes are formed only if the basicity constant of the initial aniline is higher than 1×10^{-13}.

With less basic anilines, the reaction leads to the formation of trichlorophosphazoarenes [85,87]:

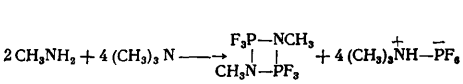


On heating in benzene solution or without solvent up to 150°C and above, hexachlorodiarylcyclodiphosphazanes are frequently converted into phosphazo-compounds, which on evaporation of the solution dimerise and are reconverted into cyclic products [85,87]:



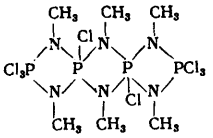
In the case of aliphatic amines, the structure of the aliphatic chain plays an important role rather than the basicity of the compound [8,82-84]. While amines with an unbranched chain and their hydrochlorides form hexachlorodialkylcyclodiphosphazanes in the reaction with phosphorus pentachloride, amines with substituents in α- and β-positions yield as a rule trichlorophosphazoalkanes. Substituents in the γ-position do not have a significant effect on the reaction.

$C_6H_5PCl_4$ can react with aliphatic and aromatic amines [89,90] to form 1,3-dialkyl(diaryl)-2,2,4,4-tetrachloro-2,4-diphenylcyclodiphosphazanes. Amines react with phosphorus pentafluoride in the presence of tertiary amines:



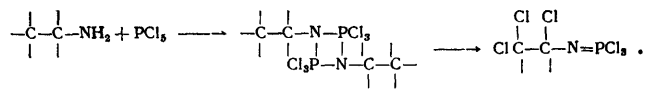
In many cases it is convenient to employ adducts of amines and phosphorus pentafluoride. Thus the 1 : 3 adduct of aniline with phosphorus pentafluoride yields hexafluoro-2,4-diphenylcyclodiphosphazane [91,92].

As regards side reactions, mention should be made of the formation of a tricyclic spirane when phosphorus pentachloride reacts with methylamine hydrochloride [10]:

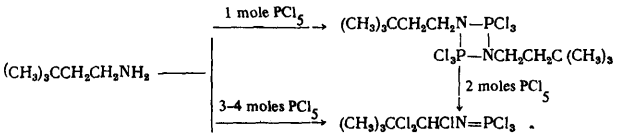


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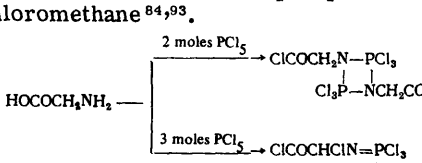
Another side process is the chlorination of the carbon chain of the amine by the excess phosphorus pentachloride. For example, aliphatic amines can be chlorinated simultaneously in the α- and β-positions, This process consists of many stages. A cyclodiphosphazane evidently forms initially and is then chlorinated in stages and converted into a trichlorophosphazochloroalkane [93]:



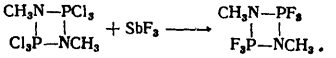
This mechanism is confirmed indirectly by experimental data. Thus the reaction of $\gamma\gamma$-dimethylbutylamine with one mole of phosphorus pentachloride leads to the formation of the corresponding cyclodiphosphazane and the reaction with 3–4 moles of phosphorus pentachloride yields $\alpha\beta\beta$-trichloro-trichlorophosphazo-$\gamma\gamma$-dimethylbutane. The latter has also been isolated as the product of the reaction between two moles of phosphorus pentachloride and 2,2,2,4,4,4-hexachloro-1,3-di-($\gamma\gamma$-dimethylbutyl) cyclodiphosphazane:



Similarly the reaction of glycine with two moles of phosphorus pentachloride leads to the formation of hexachloro-1,3-di(chlorocarbonylmethyl)cyclodiphosphazane. When the amount of phosphorus pentachloride is increased, the product is trichlorophosphazochlorocarbonylchloromethane [84,93].

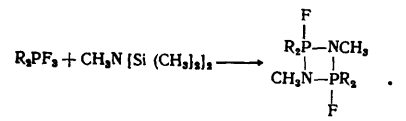


Hexafluorocyclodiphosphazanes can be synthesised in high yields by double decomposition of hexachlorocyclodiphosphazane with antimony trifluoride [94]:

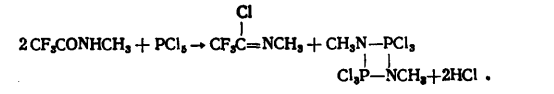


Fluorination can be also achieved with KSO_2F in nitrobenzene but the yields are low [95].

An interesting method for the synthesis of fluorinated cyclodiphosphazanes is the reaction of heptamethyldisilazane with phosphorus pentafluoride, alkyl- and aryltetrafluorophosphoranes, or dialkyl- and diaryl-trifluorophosphoranes [96,97]:

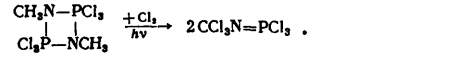


When the methylamide of trifluoroacetic acid was heated with phosphorus pentachloride, dimethylhexachlorocyclodiphosphazane and 1-chloro-2,2,2-trifluoro-*N*-methylethylideneimine were isolated[98]:

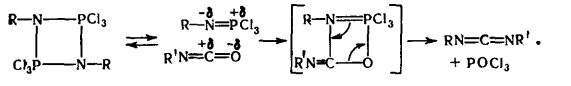


All hexachloro- or tetrachloro-diphenylcyclodiphosphazanes are white crystalline materials readily soluble in organic solvents and readily hydrolysed by atmospheric moisture.

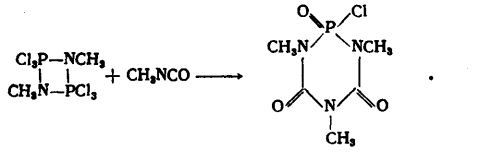
Photochemical chlorination converts hexachlorodimethylcyclodiphosphazane into monomeric trichlorophosphazotrichloromethane[94]:



Hexachlorocyclodiphosphazanes readily react with compounds having a polarised double bond[99]. The reaction takes place above 150°C. Under these conditions, cyclodiphosphazanes probably dissociate to phosphazo-compounds. For example, the reaction of hexachlorodimethylcyclodiphosphazane with phenyl isocyanate in *o*-dichlorobenzene at 175–180°C yields methylphenylcarbodi-imide. Similarly diphenylcarbodi-imide is obtained from hexachlorodiphenylcyclodiphosphazane. The corresponding isothiocyanates and isocyanates are formed analogously in the reaction with carbon disulphide and carbon dioxide. The reaction probably involves the formation of a four-membered cyclic intermediate:

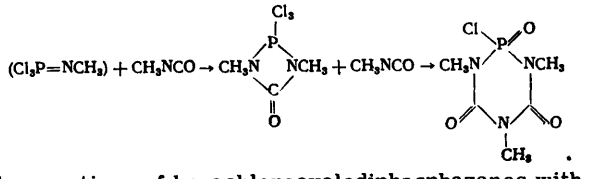


1-Chloro-2,4,6-trimethyl-1,2,4,6-phosphatriazane-1,3,5-trione was obtained on prolonged heating of hexachlorodimethylcyclodiphosphazane with methyl isocyanate in a sealed tube with dry benzene at 100°C:[80]

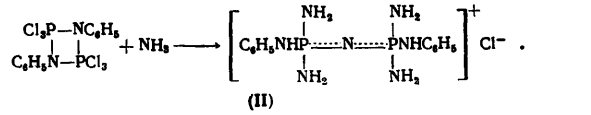


Phosphorus oxychloride and *N*-methyliminophosgene were formed as side products.

To account for the mechanism of this reaction, one may suppose that methyl isocyanate attacks the "intact" four-membered ring with formation of a cyclic system comprising a large number of units as the result of the addition of one or several methyl isocyanate molecules. Transannular double decomposition reaction with other methyl isocyanate molecules yields a six-membered cyclic system which is energetically more favoured. The dissociated bonds are reformed and the process can be repeated. On the other hand, one may suppose that monomeric trichlorophosphazomethane reacts with methyl isocyanate:

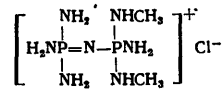


The reactions of hexachlorocyclodiphosphazanes with sulphur dioxide and hydrogen sulphide in the presence of bases were considered in the preceding section. The reaction of hexachlorodiphenylcyclophosphazane with liquid ammonia yields a phosphonium salt (II) in a yield of 41%:[100]



(II)

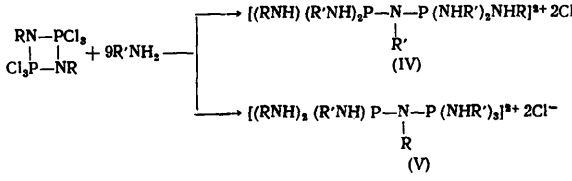
Hexachlorodimethylcyclodiphosphazane reacts similarly with ammonia: both chlorine atoms are substituted with simultaneous cleavage of the ring and the formation of the salt (III), the structure of which has been confirmed by X-ray diffraction analysis[102,103]:



(III)

The reaction of methylamine and hexachlorodiphenylcyclodiphosphazane leads to a polymer with a molecular weight of 1450 and a melting point of 58°C; dimethylamine yields monomeric products[101] with the general formula $C_6H_5N-PCl_n[N(C_2H_5)_2]_{3-n}$.

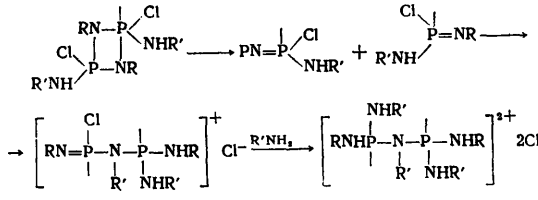
Hexachlorodialkylcyclodiphosphazanes react with an excess of primary amines to form bisphosphonium salts, the structure of which has not, however, been demonstrated[104]:



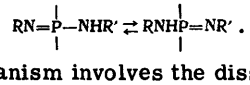
(IV)

(V)

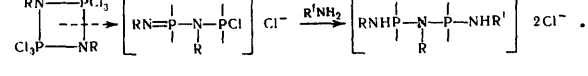
Two mechanisms have been proposed for the aminolysis of hexachlorocyclodiphosphazanes[104]. In the first of these the initial formation of a phosphazo-structure is postulated:



Compounds with the structure (IV) can also be formed by this mechanism if one takes into account the possibility of the tautomerism of the intermediate phosphazo-compound:



The second mechanism involves the dissociation of one phosphorus–nitrogen bond at a definite stage in the substitution of chlorine atoms by alkylamino-groups:



The available experimental data are more consistent with this mechanism; it also agrees with the mechanism proposed for the reaction of cyclodiphosphazanes having tetraco-ordinate phosphorus atoms with nucleophilic reagents[79].

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