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Diazadiphosphetidines

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The methods of synthesis and certain chemical properties of four-membered rings containing alternating nitrogen and phosphorus atoms with different degrees of coordination are examined. Attention is drawn to studies on the structure of diazadiphosphetidine rings by ^{31}P NMR and X-ray diffraction.
The bibliography includes 108 references.

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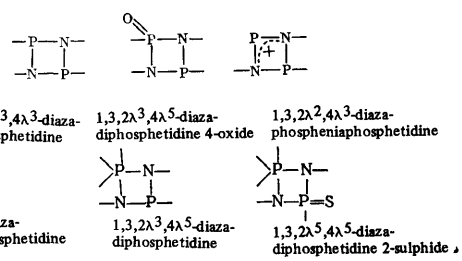
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I. INTRODUCTION

Phosphorus forms extremely readily four-membered cyclic compounds with other atoms. Rings are known in which there are alternating phosphorus and sulphur, phosphorus and silicon, phosphorus and boron, phosphorus and aluminium, and phosphorus and transition metal atoms. The derivatives of four-membered nitrogen- and phosphorus-containing heterocycles are particularly numerous and important[1-6]; compounds of this class were discovered a long time ago by Michaelis[7,8]. Since the publication of Kirsanov and Zhmurova's report in 1959 concerning the synthesis of dimeric trichlorophosphazoaryls[9], a new period has begun in the study of four-membered nitrogen–phosphorus heterocycles, mainly with phosphorus(V) atoms.

Considerable advances have been made in recent years in the development of methods for the synthesis and investigation of the structure (by ^{31}P and ^{19}F NMR and X-ray diffraction) and reactivity of four-membered heterocycles with phosphorus(III) atoms and also with phosphorus atoms having other types of coordination.

There is no unanimity concerning the nomenclature of compounds of this kind, but according to the IUPAC nomenclature[10] they should be referred to as diazadiphosphetidines:



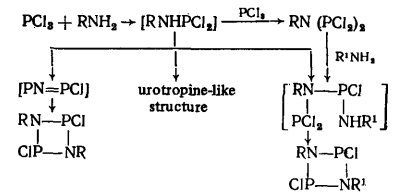
In 1970 we published a review on the chemistry of four-membered rings with alternating nitrogen and phosphorus atoms[11]. The present review includes the literature for the period from 1969 to the first half of 1978 inclusive.

II. SYNTHESIS OF DIAZADIPHOSPHETIDINES

1. Diazadiphosphetidines with Phosphorus(III) Atoms

One of the most universal methods of synthesis of diazadiphosphetidines is the reaction of amines or their hydrochlorides with PCl_3, alkyl- and aryl-dichlorophosphines, phosphoramidodichloridites, and alkyl phosphorodichloridites.

The synthesis of 1,3,2λ³, 4λ³-diazadiphosphetidines from PCl_3 can proceed via two pathways depending on the reaction conditions—in the presence of an excess of PCl_3 or with equimolar proportions of the reactants:

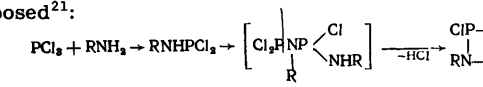


This mechanism has been confirmed by the results of a number of studies. The reaction of anilines or their hydrochlorides with an excess of PCl_3 at temperatures up to 30 °C leads to bisdichlorophosphinoalkyl(aryl)amines[12,13]. When bisdichlorophosphinoarylamines are heated to 100–150 °C, PCl_3 is split off and an unstable iminochlorophosphine, which rapidly dimerises, is apparently formed[14]. It has been recommended[15] that diazadiphosphetidines be synthesised from a mixture of arylamine hydrochloride and PCl_3 by refluxing for several hours in a suitable solvent, for example in *sym*-tetrachloroethylene. The interaction of phosphorus trichloride with methylamine yields a compound with a urotropine-like structure, while the reaction with sterically hindered higher alkylamines produces the corresponding diazadiphosphetidines[16-19].

The reaction of one mole of PCl_3 with three moles of lower alkylamines leads to a mixture of bisdichlorophosphinoalkylamine and 1,3-dialkyl-2,4-dichlorodiazadiphosphetidine, which are difficult to separate, but the cyclic compounds obtained in the reactions with propyl- and t-butylamines can be readily isolated by distillation. When PCl_3 interacts with t-butylamine or its hydrochloride, the reaction mixture contains t-butyl phosphoramidodichloridite in addition to the diazadiphosphetidine[19]. The reaction of PCl_3 with four-moles of t-butylamine gives rise only to a diazadiphosphetidine which is asymmetric with respect to the phosphorus atoms[20]:

$$2PCl_3 + 8t\text{-}C_4H_9NH_2 \rightarrow \begin{matrix} t\text{-}C_4H_9N\text{——}PCl \\ | \quad\quad | \\ t\text{-}C_4H_9NHP\text{—}NC_4H_9\text{-}t \end{matrix} + 5t\text{-}C_4H_9NH_2 \cdot HCl .$$

When this reaction was carried out in the presence of an excess of t-butylamine, the complete aminolysis product was isolated[20]. Since t-butyl phosphoramidodichloridite condenses to the corresponding diazadiphosphetidine in the presence of triethylamine, the following general reaction mechanism can be proposed[21]:



This course of the reaction is promoted by the presence of bulky substituents at the nitrogen atom[20]. Alkyl phosphorodichloridites can be made to undergo a similar reaction with PCl_3:

$$ROPCl_2 + ArNH_2 \rightarrow \begin{matrix} ROP{-}NAr \\ | \quad | \\ ArN{-}POR \end{matrix} .$$

It is noteworthy that Mitsunobu and Mukaijama[22], who obtained these compounds for the first time, attributed to them the structure of alkyl phenyliminophosphites and that their true structure was demonstrated by Kawashima and Inamoto using ^{31}P NMR and mass spectrometry[23].

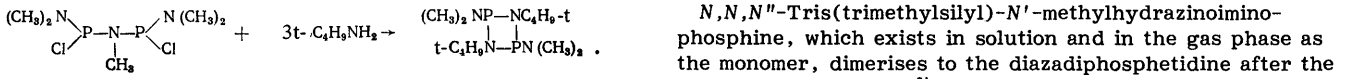
The interaction of *N,N*-dialkylphosphoramidous dichlorides with aniline yielded 2,4-dianilino-1,3-diphenyldiazadiphosphetidine[24,25]:

$$R_2NPCl_2 + C_6H_5NH_2 \rightarrow \begin{matrix} C_6H_5NHP{-}NC_6H_5 \\ | \quad | \\ C_6H_5N{-}PNHC_6H_5 \end{matrix} .$$

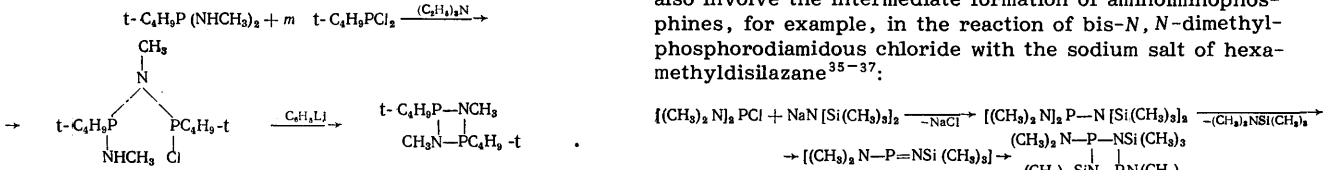
Sulphonamides can be used in this reaction instead of aniline. Thus the reaction with tolunene-4-sulphonamide in pyridine gave a high yield of 2,4-bis(dimethylamino)-1,3-bis(toluene-4-sulphonyl)diazadiphosphetidine[26]:

$$ArSO_2NH_2 + (CH_3)_2NPCl_2 \rightarrow \begin{matrix} ArSO_2N{-}PN(CH_3)_2 \\ | \quad | \\ (CH_3)_2NP{-}NSO_2Ar \end{matrix} .$$

Asymmetric diazadiphosphetidines substituted at the nitrogen atoms are also synthesised by the reaction of bis-(dimethylaminochlorophosphino)methylamine or bis(dichlorophosphino)methylamine with t-butylamine[15,27]:



The reactions of diamides with dichlorophosphines or with PCl_3, which proceed via a similar mechanism, are similar to the above. When the bis(dimethylamide) of t-butylphosphonus acid was allowed to react with t-butyldichlorophosphine in the presence of triethylamine, the product was a phosphonamidous chloride, which was converted by phenyllithium into a mixture of the *cis*- and *trans*-isomers of 2,4-di-t-butyl-1,3-dimethyldiazadiphosphetidine[28]:



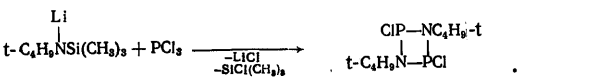
This mixture could be resolved into the individual isomers. The same method was used to obtain 1,3-di-t-butyl-4-chloro-2-methyl- and 1,3-di-t-butyl-2,4-dimethyl-diazadiphosphetidines[29].

It is noteworthy that the reaction of methylphosphonous di(t-butylamide) with PCl_3 takes place stereospecifically and leads to only the *cis*-isomer[29].

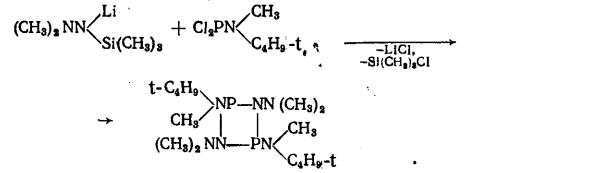
The considerable successes in the synthesis of diazaphosphetidines with phosphorus(III) in recent years have been associated with the application of trimethylsilylated amines. It has been shown[14,20,30] that heptamethyldisilazane and hexamethylphenyldisilazane react with PCl_3 in 1:1 proportions to form methyl- and phenyl-bisdichlorophosphinoamines. In the presence of an excess of the disilazanes, the reaction proceeds to 2,4-dichloro-1,3-dimethyl- or 2,4-dichloro-1,3-diphenyl-diazadiphosphetidines:

$$PCl_3 + RN[Si(CH_3)_3]_2 \rightarrow (Cl_2P)_2NR \xrightarrow{RN[Si(CH_3)_3]_2} \begin{matrix} ClP{-}NR \\ | \quad | \\ RN{-}RCl \end{matrix} .$$

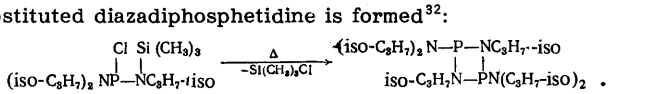
The reaction of lithium t-butyltrimethylsilylamide with PCl_3 yielded 1,3-di-t-butyl-2,4-dichloro-1,3,2λ^3,4λ^3-diazadiphosphetidine[20,21]:



The lithium derivatives of *N,N*-dimethyl- and *N'*-trimethylsilylhydrazine are readily converted into the corresponding diazadiphosphetidines by reaction with *N*-t-butyl-*N*-methylphosphoramidous dichloride[31]:



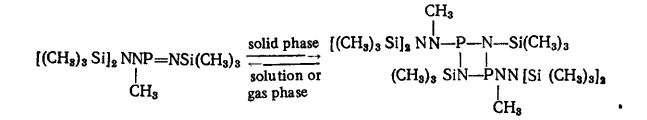
In the thermolysis of *N,N',N'*-tri-isopropyl-*N*-trimethylsilylphosphorodiamidous chloride, chlorotrimethylsilane is split off and a mixture of the *cis*- and *trans*-isomers of a substituted diazadiphosphetidine is formed[32]:



Coordination-unsaturated aminoiminophosphines have been used successfully in the synthesis of diazadiphosphetidines. For example, *N,N',N'*-tris(trimethylsilyl)aminoiminophosphine and *N,N*-di-isopropyl-*N'*-trimethylsilylaminoiminophosphine dimerise to the corresponding diazadiphosphetidines[33,34]:

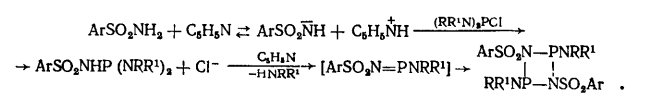
$$RR'NP{=}NSi(CH_3)_3 \rightarrow \begin{matrix} RR'NP{-}NSi(CH_3)_3 \\ | \quad | \\ (CH_3)_3Si{-}PNRR' \end{matrix} .$$

N,N,N"-Tris(trimethylsilyl)-*N'*-methylhydrazinoiminophosphine, which exists in solution and in the gas phase as the monomer, dimerises to the diazadiphosphetidine after the removal of the solvent[34]:



Certain other syntheses of diazadiphosphetidines apparently also involve the intermediate formation of aminoiminophosphines, for example, in the reaction of bis-*N,N*-dimethylphosphorodiamidous chloride with the sodium salt of hexamethyldisilazane[35-37]:

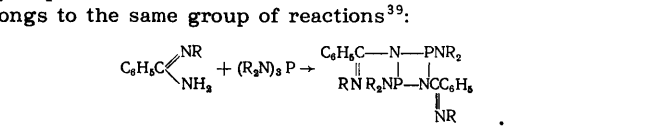
Arenesulphonamides react via a similar mechanism with substituted phosphorodiamidous chlorides in the presence of pyridine[26]:



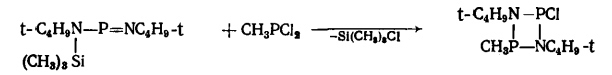
The thermal decomposition of phosphorous trianilide (110 °C, toluene) involves the elimination of one aniline molecule and the formation of the corresponding diazadiphosphetidine[38]:

$$(C_6H_5NH)_3P \rightarrow [C_6H_5N{=}P{-}NHC_6H_5] \rightarrow \begin{matrix} C_6H_5N{-}PNHC_6H_5 \\ | \quad | \\ C_6H_5NHP{-}NC_6H_5 \end{matrix} .$$

The formation of diazadiphosphetidines in the transamination of phosphorous triamides with substituted benzamidines belongs to the same group of reactions[39]:



4-Chloro-2-methyldiazadiphosphetidine has been obtained by the reaction of *N,N'*-di-t-butyl-*N*-trimethylsilylaminoiminophosphine with methyldichlorophosphine[29]:

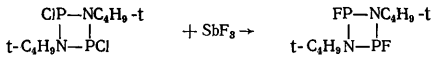


As a rule, 1,3,2λ^3,4λ^3-diazadiphosphetidines are formed as mixtures of the *cis*- and *trans*-isomers, although certain diazaphosphetidines with bulky substituents at the nitrogen atoms are obtained in the *cis*-form[35]. After prolonged heating in 1,2-dichlorobenzene at 100 °C, the isomeric composition of the mixture changes towards an increase of the amount of the *trans*-isomer. Thus pure *cis*-2,4-bisdimethylamino-1,3-bistrimethylsilylaminodiazadiphosphetidine is converted into a mixture containing 30% of the *cis*-isomer and 70% of the *trans*-isomer[35].

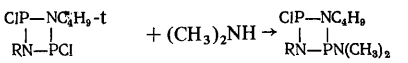
^{31}P NMR is a convenient method for the determination of the *cis*- and *trans*-structures of diazadiphosphetidines. The signal in the region of ~−100 p.p.m.corresponds to the *cis*-isomers while in the case of the *trans*-isomers the signal shifts downfield (to between −180 and −220 p.p.m.)[23,33,35].

In the series of 1,3- or 2,4-di-t-butyl derivatives the ^{31}P NMR signal also shifts markedly downfield. The ^{31}P NMR signal of *cis*-1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine is at −210.9 p.p.m.[20] The ^{31}P NMR spectra of 2,4-di-t-butyl-1,3-dimethyldiazadiphosphetidine contain signals with chemical shifts of −210.7 p.p.m. (*cis*-isomer) and −281.7 p.p.m. (*trans*-isomer)[40].

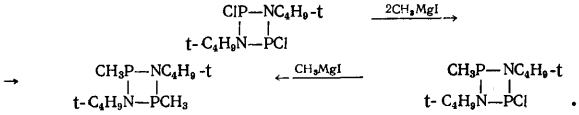
The following group of methods of synthesis of 1,3-2λ^3,4λ^3-diazadiphosphetidines consists of reactions involving the substitution of halogen atoms by nucleophiles or electrophiles. 2,4-Dichlorodiazadiphosphetidines exchange[41] chlorine atoms for fluorine on treatment with SbF_3:



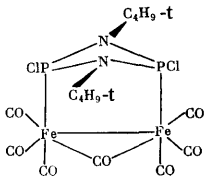
Chlorine atoms are also readily substituted by different nucleophiles. Thus, when 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine is treated with an excess of dimethylamine, a mixture of the corresponding *cis*- and *trans*-isomers is formed[15]. The reaction with diethylamine or t-butylamine yields only the *cis*-isomer. Following the interaction with two moles of dimethylamine, the product of the substitution of only one chlorine atom was obtained[15]:



1,3-Di-t-butyl-2,4-dichloro-1,3,2,4-diazadiphosphetidine and 1,3-di-t-butyl-2-chloro-4-methyl-1,3,2,4-diazadiphosphetidine react with methylmagnesium iodide to form 2,4-dimethyldiazadiphosphetidine[29]:



As phosphorus(III) derviatives, diazadiphosphetidines form complexes with metal carbonyls. The interaction of iron nonacarbonyl with 1,3-di-t-butyl-2,4-dichlorodiazadiphosphetidine in tetrahydrofuran (THF) yielded a derivative of iron heptacarbonyl[42]:

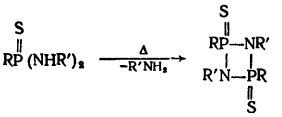


Relative to the initial diazadiphosphetidine, the ^{31}P NMR spectrum of this compound shows an upfield shift of the signal from −207 p.p.m. to +17 p.p.m.[36]

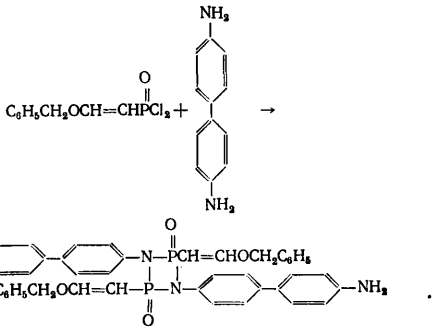
The complexes obtained from a single molecule of 2,4-bisdimethylamino-1,3-bistrimethylsilyldiazadiphosphetidine and two molecules of chromium or molybdenum pentacarbonyl have the *trans*-arrangement of the substituents[36]. Relative to 1,3,2λ^3,4λ^3-diazadiphosphetidine, the ^{31}P NMR spectra of these compounds show a shift of the signal from −107.6 p.p.m. to −155 and −131 p.p.m. respectively[42].

2. Diazadiphosphetidines with Tetracoordinate Phosphorus Atoms

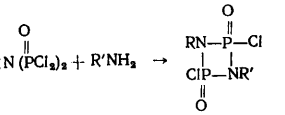
The traditional method of synthesis of diazadiphosphetidines with phosphorus(V) atoms is the pyrolysis of the di- and triamides of phosphorus acids[11]. This method has been used to obtain isomeric 1,3-diethyl-2,4-diphenyl- [43,44] and 1,2,3,4-tetraphenyl-1,3,2λ^5,4λ^5-diazadiphosphetidine 2,4-disulphides[45]:



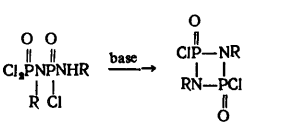
The second traditional method involves the reaction of phosphorus acid dichlorides with primary amines or anilines[11]. It has been used[46] to synthesise 1,3-bis[4-(4-aminophenyl)-phenyl]-2,4-bis(benzyloxyvinyl)-1,3,2λ^5,4λ^5-diaza -diphosphetidine 2,4-dioxide:



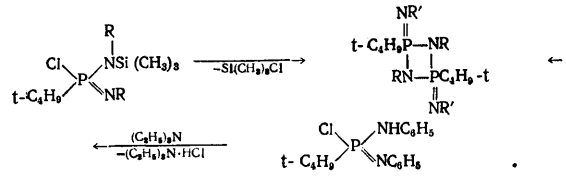
By developing this reaction, a method has been devised for the synthesis of asymmetrically 1,3-disubstituted diazadiphosphetidine 2,4-dioxides by the cyclisation of *N*-alkyl-(aryl)-*N,N*-bis(dichlorophosphono)amines under the influence of primary amines[19,27]:



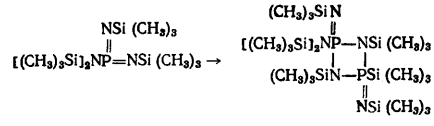
The reaction with thiophosphono-derivatives proceeds with much more difficulty. In all cases mixtures of *cis*- and *trans*-isomers are formed. Acyclic diphosphazans can be converted into diazadiphosphetidines under the influence of bases[20]:



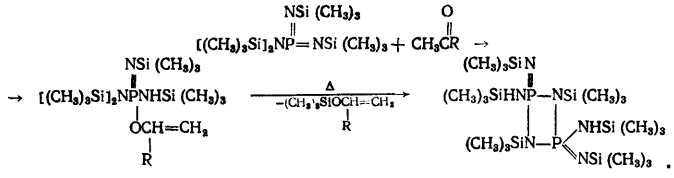
Derivatives of diazadiphosphetidine 2,4-di-imide have been obtained from substituted phosphonamidimidic chlorides[47]:



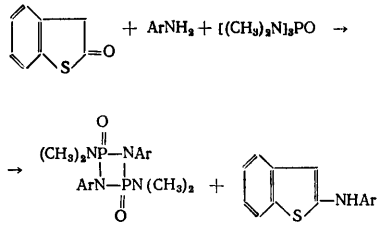
2,4-Diaminodiazadiphosphetidine 2,4-di-imide, fully silylated at the nitrogen atoms, is formed on dimerisation of the corresponding aminodi-iminophosphorane[48]:



In order to obtain hexakis(trimethylsilyl)diazadiphosphetidine, tetrakis(trimethylsilyl)aminodi-iminophosphorane is treated with acetone or acetophenone with subsequent elimination of trimethylsilyl vinyl ether and dimerisation *in vacuo* on heating[49]:

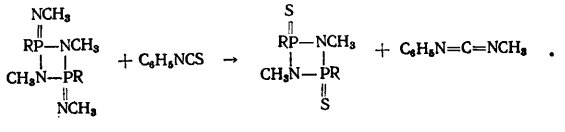


An interesting method for the synthesis of 1,3-diaryldiazaphosphetidine 2,4-dioxides involves the interaction of 2-oxodihydrobenzo[*b*]thiophen and anilines in hexamethylphosphoramide[50]; the yield of the final products is 70–80%:

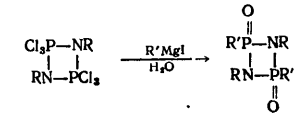


Other methods for the synthesis of diazadiphosphetidine 2,4-dichalcogenides, 2,4-di-imides, and 2,4-imidoximes involve addition or substitution reactions with the phosphorus atoms of the diazadiphosphetidine ring. Reactions involving the addition of sulphur, selenium, tellurium[29,35,40] and trimethylsilyl azide as well as the oxidation of 1,3,2λ^3,4λ^3-diazadiphosphetidines by nitrogen oxides or dimethyl sulphoxide lead to the corresponding diazadiphosphetidine 2,4-disulphides, 2,4-diselenides, 2,4-ditellurides, 2,4-di-imides, and 2,4-dioxides in high yields.

The conversion of diazadiphosphetidine 2,4-di-imide into the corresponding diazadiphosphetidine disulphide on treatment with phenyl isothiocyanate is unusual; even if the individual *cis*- and *trans*-isomers of the di-imide are introduced into the reaction, the final product is a mixture of isomers[47]:



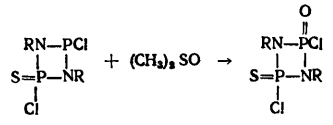
The reaction of 1,3-diphenyl- or 1,3-di-*m*-tolyl-hexachlorocyclodiphosphazanes with ethyl- or phenyl-magnesium iodide and subsequent decomposition with water yielded the corresponding diazadiphosphetidine 2,4-dioxides (yield 48–69%)[51].



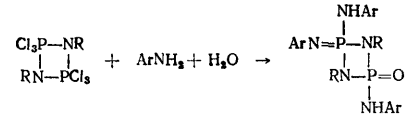
Ethylmagnesium iodide reacts similarly with 1,3-di-*o*-chlorophenyl- and di-*o*-tolyl-hexachlorodiazadiphosphetidines, but, apart from the corresponding dioxides, small amounts of 1,3-di-*o*-chlorophenyl-2,2,4,4-tetraethyl-2,4-dihydroxydiazadiphosphetidine and 2,4,4-triethyl-4-hydroxy-1,3-di-*o*-tolyldiazadiphosphetidine 2-oxide are formed in small amounts[51].

The synthesis of diazadiphosphetidines 2,4-dichalcogenides asymmetric with respect to the phosphorus atoms has been described[20,51].

1,3,2λ^3,4λ^5-diazadiphosphetidine sulphides are readily oxidised by dimethyl sulphoxide to a mixture of the *cis*- and *trans*-isomers of diazadiphosphetidine 2-oxide 4-sulphides asymmetric with respect to phosphorus[20]:

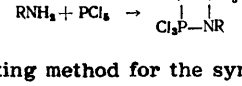


Diazadiphosphetidine 2-imide 4-oxides have been obtained by the aminolysis of hexachlorodiazadiphosphetidines by anilines in the presence of moisture[52]:

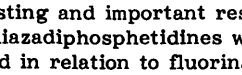


3. Diaxadiphosphetidines Containing Pentacoordinate Phosphorus Atoms

The Kirsanov reaction continues to play a notable role in the synthesis of 1,3,2λ^5,4λ^5-diazadiphosphetidines. Hexafluorodiazadiphosphetidines have been obtained by this method[53,54]:



Another interesting method for the synthesis of compounds of this kind is oxidative imination of phosphorus trichloride by *N*,*N*-dichloroperfluoroarylamines[55]:



The most interesting and important results in the study of the chemistry of diazadiphosphetidines with phosphorus(V) have been obtained in relation to fluorinated derivatives and polycyclic compounds containing the diazadiphosphetidine fragment.

Schmutzler and coworkers developed a number of novel methods for the synthesis of fluorodiazadiphosphetidines. The reaction of alkyl(aryl)tetrafluorophosphoranes or

dialkyl(diaryl)trifluorophosphoranes with heptamethyldisilazane constitutes a convenient method of synthesising fluorinated diazadiphosphetidines[56,57]:

$$RPF_4 + 2CH_3N[Si(CH_3)_3]_2 \rightarrow \begin{matrix} RF_2P{-}NCH_3 \\ | \quad | \\ CH_3N{-}PF_2R \end{matrix} + 4Si(CH_3)_3F .$$

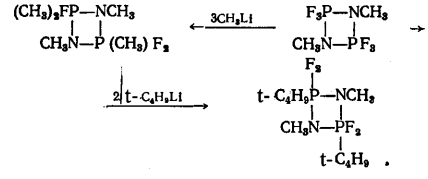
An asymmetric diazadiphosphetidine has also been obtained by this method[58]:

$$CH_3PF_2 + CH_3N[Si(CH_3)_3]_2 + C_6H_5N[Si(CH_3)_3]_2 \rightarrow \begin{matrix} CH_3F_2P{-}NCH_3 \\ | \quad | \\ C_6H_5N{-}PF_2CH_3 \end{matrix} .$$

Instead of disilazanes, one can use the lithio-derivatives of alkylamines[59]:

$$2RNLi_2 + 2R_2PF_3 \rightarrow \begin{matrix} R_2FP{-}NR \\ | \quad | \\ RN{-}PFR_2 \end{matrix} + 4LiF .$$

On reaction with organometallic compounds, hexafluoro-1,3-dimethyldiazadiphosphetidines exchange fluorine atoms for alkyl groups[57-59]:



It is of interest that, when a mixture of 1,2,3,4-tetramethyl- and 1,3-dimethyl-2,4-diphenyl-2,2,4,4-tetrafluorodiazadiphosphetidines is heated, a disproportionation reaction takes place and a compound asymmetric with respect to phosphorus is formed[58]:

$$\begin{matrix} F_2(CH_3)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(CH_3)F_2 \end{matrix} + \begin{matrix} F_2(C_6H_5)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(C_6H_5)F_2 \end{matrix} \rightarrow \begin{matrix} F_2(C_6H_5)P{-}NCH_3 \\ | \quad | \\ CH_3N{-}P(CH_3)F_2 \end{matrix} .$$

Appel et al. quite unexpectedly obtained a diazadiphosphetidine by the hydrofluorination of silylated bisiminophosphorane in trichlorofluoromethane[60]:

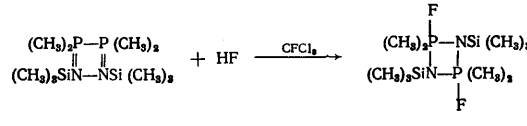


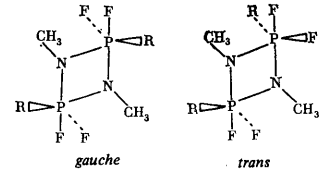
Table 1. The chemical shifts (δ, p.p.m.) of the *gauche*- and *trans*-isomers of 2,4-dialkyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2,4-diazadiphosphetidines between −60° and −70 °C.[56]

Alkyl	CH_3	CH_2Cl	$CHCl_2$	CCl_3
gauche	−51.2	−56.9	−64.8	−59.0
trans	−47.4	−53.1	−62.1	−60.7

The signals in the ^{31}P NMR spectra of diazadiphosphetidines with phosphorus(V) are located in the region of 82.5–38.3 p.p.m., depending on the environment around the phosphorus atom[54]. It is noteworthy that, in a series of compounds of the type $(RF_2PNCH_3)_2$, the spin–spin coupling constant is directly related to the electronegativity of the ligand R:[61]

R	$(C_2H_5)_2N$	C_6H_5	C_6F_5	CCl_3
J_{P-P}, Az	140	111	80	125

Tetrafluorodiazadiphosphetidines can exist as *gauche*- and *trans*-isomers:



In the solid state they exist as the *trans*-isomers, while in solution there is equilibrium between the *gauche*- and *trans*-forms as a result of the pseudo-rotation at the phosphorus atom[56,57]. The *gauche–trans* equilibration process is rapid on the NMR time scale and the presence of the signals of the two isomers in the ^{31}P NMR spectra can be detected only at low temperatures (between −40° and −60 °C) (Table 1). It is noteworthy that in the series of 2,4-dialkyltetrafluorodiazadiphosphetidines the percentage content of the *trans*-isomer increases with increase of the degree of branching of the alkyl group (Table 2)[56,57].

Table 2. The ratio of the *gauche*- and *trans*-isomers of 2,4-dialkyl-2,2,4,4-tetrafluoro-1,3-dimethyl-1,3,2λ^5,4λ^5-diazadiphosphetidines[56,57].

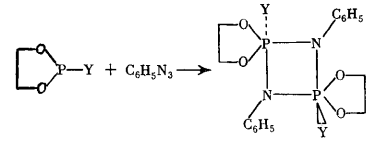
Alkyl	CH_3	C_2H_5	iso-C_3H_7	t-C_4H_9	CH_2Cl	$CHCl_2$	CCl_3
Content of *trans*-isomer, %	47	56	61	92	57	71	76

The thermal decomposition of hexahalogenodiazadiphosphetidines does not take place unambiguously. On heating, hexachloro-1,3-diethyldiazadiphosphetidine splits off methyl chloride and is convered into a polymer[62,63]:

$$x \begin{matrix} CH_3N{-}PCl_3 \\ | \quad | \\ Cl_3P{-}NCH_3 \end{matrix} \xrightarrow[48\ h]{200°} 2x\,CH_3Cl + (NPCl_2)_{2x} .$$

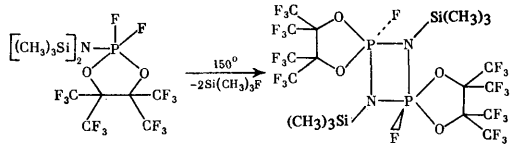
Its hexafluoro-analogue gives rise to a tetramer on heating in a sealed tube at 130 °C; in addition, a salt with the composition $(CH_3N)_4P_3F_6^+PF_6^-$ has been isolated from the residue[62-64].

Kabachnik, Gilyarov, and Tikhonina[65-68] carried out a detailed study of the conditions governing the formation of the diazadiphosphetidine ring from cyclic phosphites—derivatives of ethylene glycol, 1,2-propylene glycol, and catechol—under the conditions of the Staudinger reaction. It was shown that the amides of glycol phosphites react with phenyl azide to form phosphoramidimidates, while esters, thioesters, and fluoride are converted into tricyclic dispirodiazadiphosphetidines:

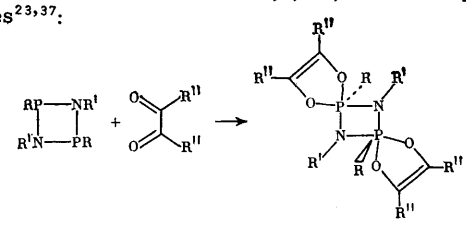


The presence of two signals in the ^{31}P NMR spectra, whose chemical shifts differ by 0.47–0.63 p.p.m., has been explained by the presence of two isomers, whose formation is caused by the pseudorotation at the phosphorus atom in solution.

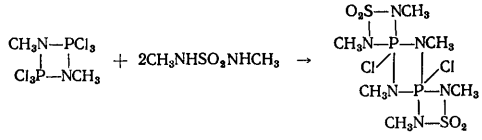
The same tricyclic system has been obtained[69] on heating bis(trimethylsilyl)aminoperfluoropinacolyldifluorophosphorane at 150 °C:



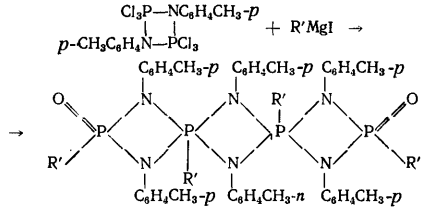
Tricyclic dispiro-1,3,2λ⁵,4λ⁵-diazadiphosphetidines are also formed when α-diketones add to 1,3,2λ³,4λ³-diazadiphosphetidines[23,37]:



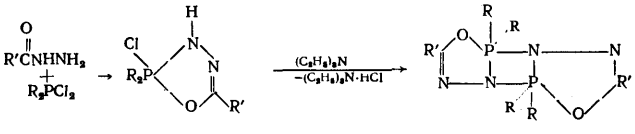
or on interaction of hexachloro-1,3-dimethyldiazadiphosphetidine with 1,3-dimethylsulphamide[70]:



or in the reaction of hexachloro-1,3-di-*p*-tolyldiazadiphosphetidine with ethyl- or phenyl-magnesium iodide[51]:

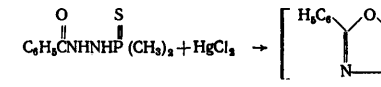


Interesting studies on the synthesis of condensed heterocyclic systems containing the diazadiphosphetidine ring have been carried out by Kabachnik and coworkers[65,66,69] and by Schmidpeter and coworkers[71–73]. As a result of the reaction of the chlorophosphoranes $(CH_3)_nPCl_{5-n}$ ($n = 0–2$), trichlorodiphenylphosphorane, and the chlorides of dimethyl- and diphenyl-phosphinic acids with acylhydrazines and subsequent treatement of the resulting 2-chloro-1,3,4,2-oxadiazaphospholines with triethylamine yielded the dimeric 1,3,4,2-oxa-azaphospholes. The latter constitute a tricyclic system with a diazadiphosphetidine fragment[71–73]:

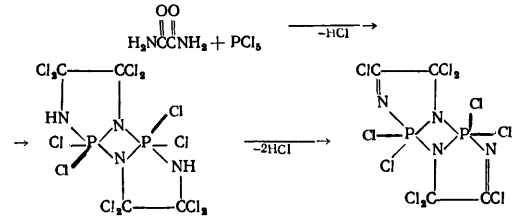


The halogen atoms at the phosphorus atom can be substituted by alkoxy- or phenoxy-groups.

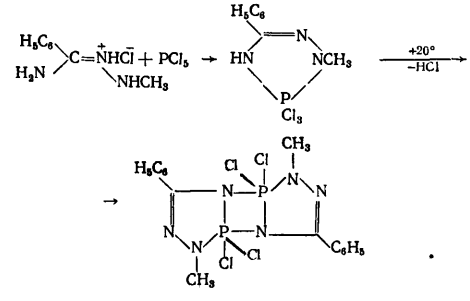
The same tricyclic system has been obtained on treating *N*-benzoyl-*N'*-dimethylphosphinothionylhydrazine with mercury(II) chloride and triethylamine. The reaction proceeds via the intermediate formation of 1,3,4,2-diazaphosphole with subsequent cyclodimerisation[74]:



Tricyclic systems with a similar structure, containing the diazaphosphetidine fragment, have been obtained by the interaction of oxamide with an excess of PCl_5 in dichloroethane at 50–55 °C:[75]

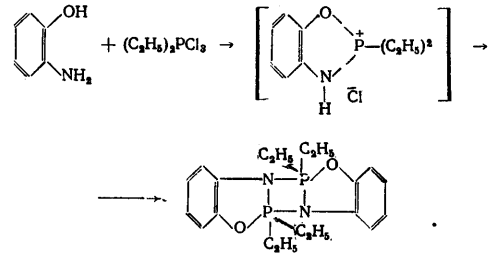


or by treating the hydrochloride of *N*-methylbenzamidrazone with PCl_5. When the reaction is carried out at 0°C, 3,3,3-trichloro-1,2,4-3λ⁵-triazaphosphole is formed. The latter splits off hydrogen chloride at 20 °C and is converted into a cyclic dimer[76]:

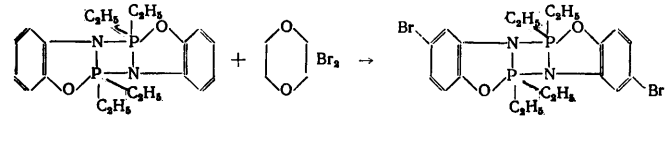


When *o*-aminophenol is treated with PCl_5 or R_2PCl_3, dimeric 1,3,2-oxazaphospholes are formed[65,77,78].

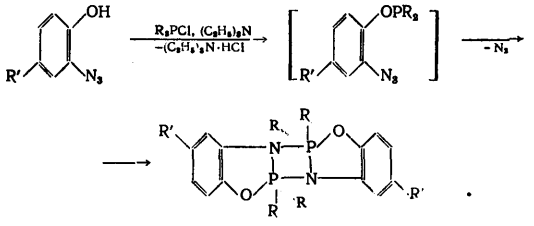
The hydrochloride of benzo-1,3,2-oxazaphosphole has been isolated as an intermediate in the reaction with chlorodiethylphosphorane. On treatment with triethylamine it is converted into the corresponding cyclic product[65]:



The *P,P,P',P'*-tetrachloro derivatives readily undergo reactions involving the substitution of chlorine atoms by alkoxy- and phenoxy-groups. The *P,P,P',P'*-tetraethyl derivatives is brominated by dioxan dibromide in the benzene ring[65]:

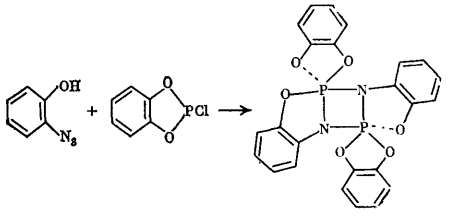


The same pentacyclic system has been obtained by the reaction of *o*-azidophenols with dialkylphosphorochloridites, dialkylchlorophosphines, and tetra-alkylphosphorodiamidous chlorides[65,66,79]:



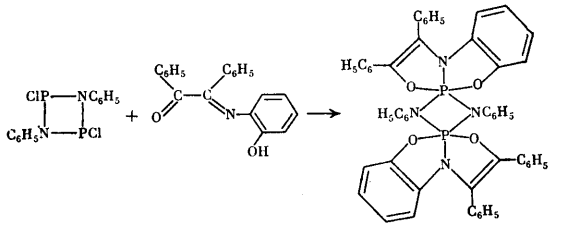
The first stage is carried out at 0 °C and the second (after separating triethylamine hydrochloride) at 20 °C.

When the phosphorochloridite of catechol is introduced into the reaction, a nonacyclic system is formed[66]:



The same system has been obtained also by interaction of *o*-aminophenol with *o*-phenylenedioxytrichlorophosphorane[66].

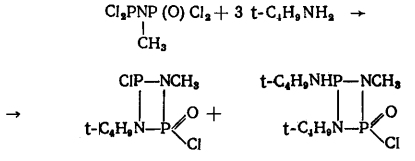
The reaction of 2,4-dichloro-1,3-diphenyl-1,3,2λ^3,4λ^3-diazadiphosphetidine with *o*-hydroxyphenyliminodibenzoyl leads to a pentacyclic phosphorane[80]:

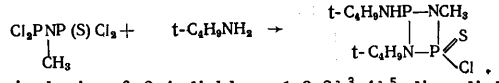


Its ^{31}P NMR spectrum has only one signal at −50.5 p.p.m., which agrees with the fact that the initial diazadiphosphetidine is in the *cis*-form and that substitution at both phosphorus atoms takes place stereospecifically[80].

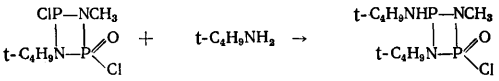
4. Diazadiphosphetidines Containing Tervalent and Tetracoordinate or Pentacoordinate Phosphorus Atoms

When *N*-(dichlorophosphino)-*N*-(dichlorophosphinoyl)-methylamine reacts with three moles of t-butylamine, a mixture of diazadiphosphetidine 4-oxides, differing in the degree of substitution of chlorine atoms at phosphorus(III), is formed. When *N*-(dichlorophosphino)-*N*-(dichlorothiophosphinoyl)methylamine is treated with t-butylamine, a 10 : 1 mixture of isomers of diazadiphosphetidine 2-sulphide is produced[27]:



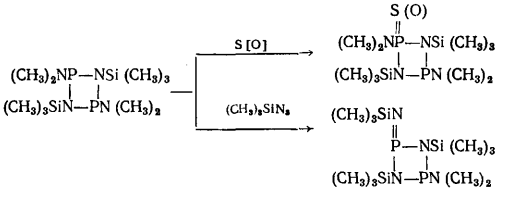


The aminolysis of 2,4-dichloro-1,3,2λ^3,4λ^5-diazadiphosphetidine 2-oxide and 2-sulphide (as mixtures of isomers) by t-butylamine results in the substitution of a chlorine atom at phosphorus(III) and the isomeric composition of the products is altered: the cause of the latter phenomenon is hitherto unknown[27]:

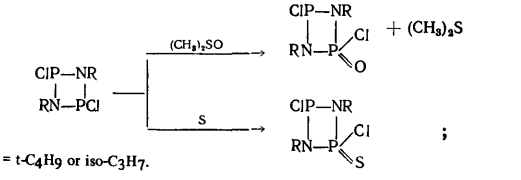


The coordination-unsaturated *N*,*N*,*N'*-tris(trimethylsilyl)-aminoiminophosphine undergoes the (2 + 2)-cycloaddition reaction with tetrakis(trimethylsilyl)aminodi-iminophosphorane and gives rise to a substituted 1,3,2λ^3,4λ^5-diazadiphosphetidine[81]. Structural data suggest that the unshared electron pair at the phosphorus atoms in diazadiphosphetidines has an appreciable amount of *s* character[82,83]. Diazadiphosphetidines containing two phosphorus(III) atoms combine under mild conditions with one mole of sulphur, selenium, or tellurium, giving rise to the corresponding asymmetric diazadiphosphetidine 4-sulphides, 4-selenides, or 4-tellurides[29,34,83,84].

2,4-Bisdimethylamino-1,3-bis(trimethylsilyl)-1,3,2λ^3,4λ^4-diazadiphosphetidine can be oxidised selectively by sulphur, oxygen, or trimethylsilyl azide[29]:



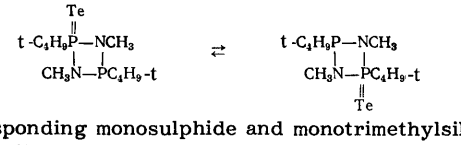
The isopropyl and *s*-butyl derivatives of 1,3,2λ^3,4λ^3-diazadiphosphetidines undergo controlled oxidation by dimethyl sulphoxide and sulphur with formation of diazadiphosphetidine 2-oxides and 2-sulphides[20]:



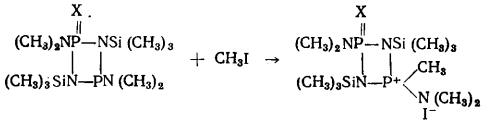
R = t-C$_4$H$_9$ or iso-C$_3$H$_7$.

These compounds are thermally stable and can be purified by vacuum distillation.

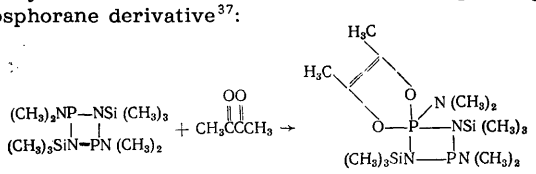
A study of the temperature variation of the ^{1}H and ^{31}P NMR spectra of *cis*-2,4-di-t-butyl-1,3-dimethyl-1,3,2λ^3,4λ^5-diazadiphosphetidine 4-telluride demonstrated the existence of the dynamic equilibrium[84]



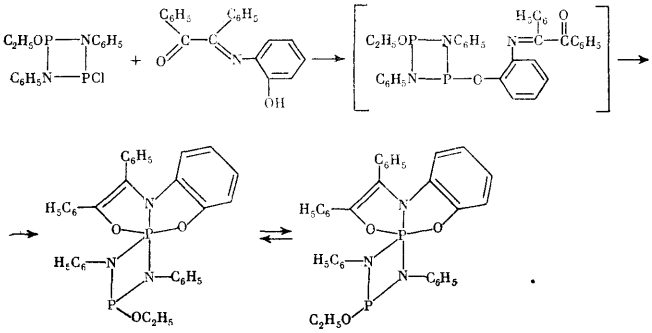
The corresponding monosulphide and monotrimethylsilylimide are readily alkylated by methyl iodide and give rise to derivatives of 1,3-diaza-2-phosphonia-4-phosphetidine[35]:



The reaction of 2,4-bis(dimethylamino)-1,3-bis(trimethylsilyl)-1,3,2λ³,4λ³-diazadiphosphetidine with 1 mole of diacetyl results in the formation of the corresponding monophosphorane derivative[37]:

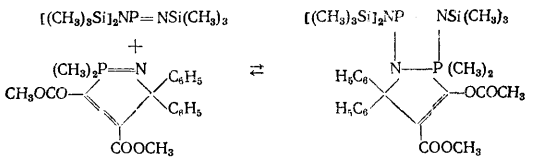


A similar reaction was observed also in the case of *o*-hydroxyphenyliminodibenzoyl[80]:

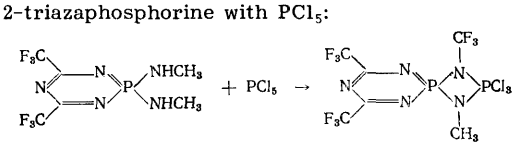


The tricyclic product exists as a mixture of *cis*- and *trans*-isomers. The chlorine atom is probably initially substituted and this is followed by intramolecular cycloaddition[80].

The addition of an azaphosphole (a cyclic product) to aminoiminophosphine yielded a bicyclic adduct, which exists in chloroform solution in equilibrium with the initial compounds. At 70 °C the equilibrium is 60% displaced to the left[91]:

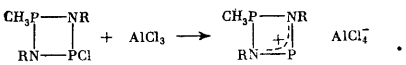


A spiro-compound containing six- and four-membered rings has been obtained[85] by the reaction of 2,2-bis(methylamino)-1,3,5,2-triazaphosphorine with PCl_5:



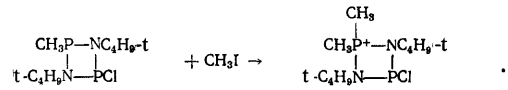
5. Diazaphosphenia- and Diazaphosphonia-phosphetidines

2-Choro-4-methyl-1,3,2,4-diazadiphosphetidine reacts with aluminium chloride to form a zwitter-ionic phosphenium salt—a new representative of the class of substances containing dicoordinate phosphorus ions:



The phosphenium salt is insoluble in ether, pentane, and benzene, but is readily soluble in CH_2Cl_2 and CH_3CN. In its ^{31}P NMR spectrum the doublet with a chemical shift of −252.0 p.p.m. ($^2J_{P-P} = 36$ Hz) is due to the dicoordinate phosphorus atom[29,86], while the doublet with a chemical shift of −201 p.p.m. refers to the phosphorus(III) atom.

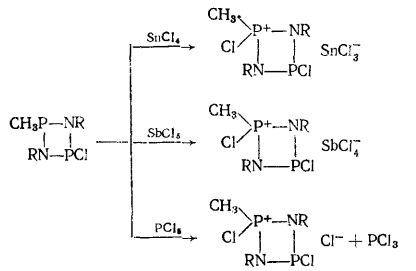
The reaction of 2,4-dimethyl- or 2-chloro-4-methyl-1,3,2,4-diazadiphosphetidine with electrophilic alkyl halides (methyl iodide or bromide, ethyl bromide) leads to cyclic phosphonium salts containing phosphonium and phosphine phosphorus atoms[29]:



Cyclic diazaphosphoniaphosphetidine salts have also been obtained by the alkylation of 2,4-bis(dialkylamino)-1,3-bis(trimethylsilyl)-1,3,2λ³,4λ⁵-diazadiphosphetidines with an excess of methyl iodide at −70 °C. Their isomeric composition was investigated by ^{31}P and ^1H NMR; the reaction products are in most cases pure *cis*-isomers; after they have been heated at 100–130 °C for three days, the *trans*-isomer predominates in the mixture[35].

The ^{31}P NMR spectra of diazaphosphoniaphosphetidines show two signals: in a low field due to the phosphorus(III) atom and in a high field due to the phosphorus(V) atom[29]. The ^{31}P NMR spectra of methylphosphoniaphosphetidine iodides, which are mixtures of *cis*- and *trans*-isomers, contain four signals: −26.2 – −33.8 p.p.m. (P^{IV}), −86.5 – −97.6 p.p.m. (P^{III}), and $J_{P-P} = 33–38$ Hz for the *cis*-isomer and −50.6 – −54.3 p.p.m. (P^{IV}), −120.7 – −137.6 p.p.m. (P^{III}), and $J_{P-P} = 20–33$ Hz for the *trans*-isomer[35].

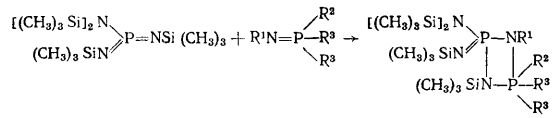
Diazoniaphosphetidine salts are also formed in the reaction of 1,3-di-t-butyl-2-chloro-4-methyl- or 2,4-dimethyl-1,3,2,4-diazadiphosphetidines with Lewis acids ($SbCl_5$, $SnCl_4$, and PCl_5). In all cases 1 : 1 adducts are formed initially and these then rearrange to the salts; the PCl_4^- anion decomposes under these conditions to PCl_3 and Cl^-: [86]



The ^{31}P NMR spectra of these compounds contain doublet P^{IV} signals in the range between −70 and −80.0 p.p.m.

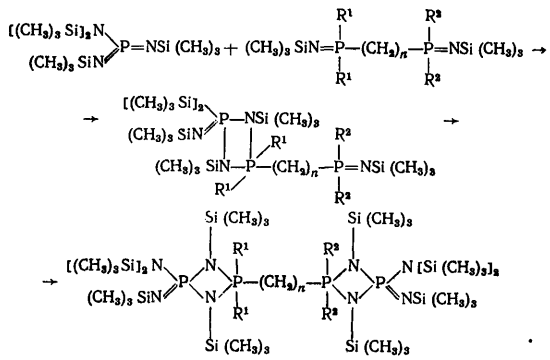
6. Diazadiphosphetidines with Tetracoordinate and Pentacoordinate Phosphorus Atoms

Diazadiphosphetidines with phosphorus(IV) and phosphorus(V) atoms are obtained mainly by the (2 + 2)-cycloaddition of phosphine imides to *N,N,N',N'*-tetrakis(trimethylsilyl)aminodi-iminophosphorane[33,87,88]:



A number of other phosphine imines[89] as well as labelled [^{15}N]*N*-methyltris(dimethylamino)phosphine imide[90] have been introduced into this reaction. The above cyclisation

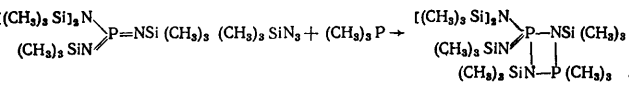
principle has been transferred also to alkylenebisphosphine imides[88]:



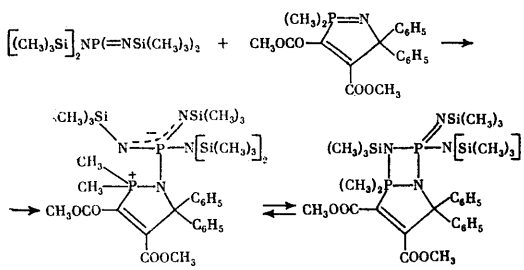
N-t-Butyltriphenylphosphine imide and tris(dimethylamino)-*N*-trimethylsilylphosphine imide do not undergo this reaction even after heating for many hours.

For the silylated methylenebis(methylphenylphosphine imide), it is possible to achieve a controlled addition, to isolate the asymmetric product, and then to convert it into a symmetrical alkylenebis(diazadiphosphetidine). 1,4-Butylene derivatives give rise to symmetrical products only[90].

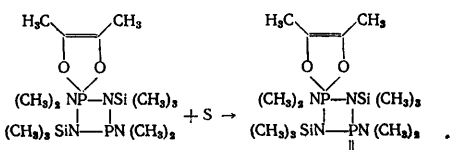
An interesting modification of the reaction involves the heating of the adduct of trimethylsilyl azide and silylated aminodi-iminophosphorane with trimethyl- and triphenylphosphines[88]:



The reaction of azaphosphole with aminodi-iminophosphorane yielded a bicyclic adduct resulting from (2 + 2)-cycloaddition:



On heating in solution, the adduct is reversibly converted into a dipolar ion[91]. A diazadiphosphetidine with a P=S group has been synthesised[37] by the addition of sulphur to the corresponding phosphorus(III) derivative:



III. THE STRUCTURE OF THE DIAZADIPHOSPHETIDINE RING

The structure of the diazadiphosphetidine ring has been investigated by various physicochemical methods, but X-ray diffraction analysis proved to be the most informative.

The structure of 1,3-di-t-butyl-2,4-dichloro-1,3,2λ^3,4λ^3-diazadiphosphetidine has been investigated by X-ray diffraction[92]. The P–N bond length is 1.689 Å, which corresponds to the bond length in dimethylphosphoramidous dichloride (1.69 Å) and indicates partial p_π–d_π bonding[93]. The chlorine atoms are in the *cis*-configuration. The ring in the molecule is not planar, its atoms deviating in succession from the plane of the ring by 0.045 Å. In the molecule of *trans*-1,3-bis(trimethylsilyl)-2,4-di[bis(trimethylsilyl)amino]-1,3,2λ^3,4λ^5-diazadiphosphetidine the P–N bond length (1.727 Å) [33] approaches that of a single P–N bond in $H_3\dot{N}PO_3^{2-}Na^+$ (1.77 Å).[94] The angles are the same in both molecules: ∠N–P–N = 82.5° and ∠P–N–P = 97.5°.

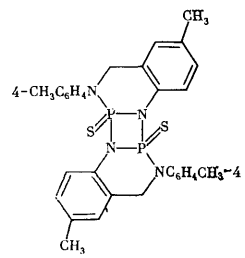
The results of X-ray diffraction studies on several diazadiphosphetidine dioxides and disulphides are presented in Table 3. It is noteworthy that the P...P and N...N distances in diazadiphosphetidine molecules are in the ranges 2.48–2.562 Å and 2.22–2.26 Å, which is less than the sum of the van der Waals radii (3.60 and 3.10 Å). These data indicate the occurrence of the transannular P...P and N...N interaction[95]. The stronger P...P repulsion explains the acute angle at the phosphorus atoms[96].

Table 3. The bond lengths and angles in 1,3,2λ^3,4λ^3-diazadiphosphetidines and 1,3,2λ^5,4λ^5-diazadiphosphetidine 4-oxides and 4-sulphides.

Formula	P–N bond length, Å	Angle, °		Refs.
		N–P–N	P–N–P	
{ClP–NC$_4$H$_9$-t)$_2$* (*cis*)	1.689	82.5	97.3	[92]
([(CH$_3$)$_3$Si]$_2$NP–NSi(CH$_3$)$_3$)$_2$ (*trans*)	1.727	82.5	97.5	[33]
{ClP(O)–NC$_4$H$_9$-*trans*)$_2$**	1.661	85.5	94	[88]
(C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$** (*trans*)	1.688	83.25	96.25	[96]
{C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$* (*cis*)	1.687	84.2	95.2	[99]
(C$_6$H$_5$P(S)–NC$_2$H$_5$)$_2$** (*trans*)	1.686	83.4	96.7	[99]
(C$_6$H$_5$P(S)–NCH$_3$)$_2$**	1.69	84.0	96.0	[45]
(C$_6$H$_5$P(S)–NC$_6$H$_5$)$_2$**	1.695	81.9	98.1	[45]
(ClP(S)–NCH$_3$)$_2$**	1.67	84	96	[100]

*Non-planar ring.
**Planar ring.

In a polycyclic molecule the P–N bond lengths in the diazadiphosphetidine fragment are unusually large and nonidentical, although the ring is planar and the P–N–P (91°) and N–P–N (89°) angles approach the right angle[97]:



In the molecules of diazadiphosphetidine with phosphorus(V) one P–N bond is axial and the other is equatorial[11].

The results of the determination of the bond lengths and angles in 1,3,2λ^5,4λ^5-diazadiphosphetidines obtained by different investigators are listed in Table 4.

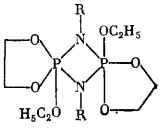
The molecule of *trans*-2,4-diethoxy-2,4-bis(ethylenedioxy)-1,3-di-*p*-tolyl-1,3,2λ^5,4λ^5-diazadiphosphetidine has a centrosymmetric structure and the mutual orientation of

the dioxaphospholan ring and the central four-membered nitrogen-phosphorus ring corresponds to the *trans*-configuration. Two nitrogen–phosphorus bonds occupy axial and equatorial positions in the trigonal bipyramid at the phosphorus atom. The dioxaphospholan ring also has the axial-equatorial configuration, i.e., of the two ring bonds, one P–O bond is axial (1.678 Å) and the other is equatorial (1.635 Å). For the axial-equatorial arrangement of the rings, the existence of the *cis*-isomer becomes impossible.

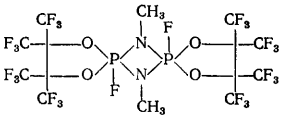
Table 4. The bond lengths and angles in planar $1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidines.

Formula	P-N bond length, Å		Angle, °		Refs.
	axial	equatorial	N–P–N	P–N–P	
$[(CCl_3)F_2P{-}NCH_3]_2$	1.742	1.621	79.9	100.1	[61,94]
$(F_3P{-}NCH_3)_2$	1.735	1.595	77.2	102.9	[105]
$[(C_6H_5)F_2P{-}NCH_3]_2$	1.750	1.631	79.8	100.2	[105]
$[(C_6H_5)F_2P{-}NCH_3]_2$	1.78	1.64	80.6	99.4	[107]
$[(C_6H_5)_2FP{-}NCH_3]_2$	1.779	1.654	78.6	101.8	[108]

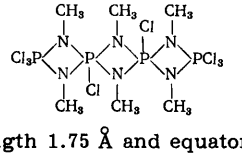
The geometrical characteristics of the diazadiphosphetidine ring are as follows: axial P–N bond length 1.785 Å, equatorial P–N bond length 1.652 Å, ∠N–P–N = 79.7°, and ∠P–N–P = 100.3°; the ring is ideally planar[101]:



Similar data were obtained for tricyclic dispirodiazadiphosphetidines:

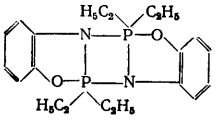


(axial P–N bond length 1.787 Å, equatorial P–N bond length 1.626 Å, ∠N–P–N = 84.1°, and ∠P–N–P = 95.9° [102]) and



(axial P–N bond length 1.75 Å and equatorial P–N bond length 1.64 Å [103]).

The bicyclic phosphabenzoxazole system in the molecule of the dimeric 2,2-diethyl-2-phosphabenzoxazole is planar and forms a dihedral angle of 1.2° with the plane of the four-membered ring. The axial and equatorial P–N bond lengths (1.812 and 1.681 Å) are close to those obtained for other $1,3,2\lambda^5,4\lambda^5$-diazadiphosphetidines, while the N–P–N valence angle is reduced and the P–N–P angle is increased by 4–5°. This finding as well as the appreciable distortion of the trigonal-bipyramidal coordination of the phosphorus atom can be explained by the fact that it is included in two rigid planar rings—the diazadiphosphetidine and oxazaphosphole rings[104]:



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