Russian Chemical Reviews **67** (9) 749 – 759 (1998) © 1998 Russian Academy of Sciences and Turpion Ltd

UDC 547.1′118:564.268

Reactions of phosphorus acid halides with *N*-silylated organic compounds †

A B Ouryupin, I A Rakhov, T A Mastryukova

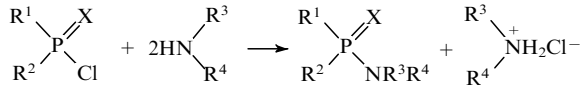
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Abstract. Data on reactions of *N*-silylated amines, carboxamides, amino acids, and their derivatives with trivalent and pentavalent phosphorus acid halides are summarised. The effect of structural factors on the direction of phosphorylation is discussed. The bibliography includes 133 references.

I. Introduction

The necessity of development of new methods for the synthesis of phosphorus acid amides is associated with the fact that some of these compounds are widely used as bioregulators and key reagents in the synthesis of new medicinal preparations.[1] The phosphoramidite method for the formation of internucleotide bonds remains so far the most efficient in the automated synthesis of oligonucleotides.[2] However, analysis of literature data on the methods for the preparation of compounds with the P – N bond allows one to reveal certain drawbacks in the popular methods for the synthesis of amides of phosphorus acids.[3,4] The vast majority of the methods is based on low-selective reactions of phosphorylating reagents with amines or their salts. The use of a large excess of bases (sometimes toxic) hinders purification of the target amides, which creates additional experimental difficulties.



The use of *N*-silylated nitrogen-containing compounds may appear to be the solution of the problem. At present, serious attention has been drawn to the studies on the reactivity of these compounds.[5,6] The reaction of these silylated compounds with phosphorus acid halides is very attractive for the synthesis of phosphoramidites and phosphoramidates, as it produces volatile halogenosilanes, which can be easily removed from the reaction mixture and repeatedly used in the reaction cycle. Other advantages of the use of silylamines instead of amines have been reviewed.[5] The ultimate result of this type of reactions definitely depends both on the structural features of the electrophilic phosphorylating agent and on the nature of the silicon – nitrogen bond that affects the nucleophilicity and configuration of the nitrogen atom.[7,8]

Since there is no universal scale of nucleo- and electrophilicity,[9] this review compares the reactivity of *N*-silylated nitrogen-containing compounds, which are combined into different groups according to formal structural features, with respect to phosphorus acid halides. In each case, the reaction features that can be attributed to the contribution of the phosphorus component are discussed additionally.

II. Reactions with *N*-silylamines

A characteristic feature of *N*-silylamines is their rather high reactivity with respect to phosphorus acid halides, particularly those of trivalent phosphorus. This may result from changes in hybridisation of the nitrogen atom and, as a consequence, from changes in its nucleophilicity due to the introduction of the silyl group.[5,7]

The steric factor also exerts a significant effect on the reactivity of silylamines. Generally speaking, the N – Si bond in silylamines is so labile that the latter may act as silylating agents, for example, diethyl(trimethylsilyl)amine (**1**). However, the ability of the Si – N bond to undergo cleavage decreases dramatically with an increase in the volume of the alkyl groups at the silicon atom (*e.g.*, in the case of triisopropyl and *tert*-butyldimethylsilyl groups).[10] A similar effect was also noted in acid hydrolysis of *N*-*tert*-butyldimethylsilyl- and *N*-triisopropylsilyl-β-lactams.[11] Methods for the synthesis of *N*-triisopropylsilylated compounds and their stability have been reviewed.[12] *tert*-Butyldipropylsilylated primary amines appeared to be inert to acylation.[13] Therefore, this review deals exclusively with the replacement of the trimethylsilyl group at the nitrogen atom by a phosphorus-containing fragment.

1. Reactions with trivalent phosphorus acid halides

It has been shown[14–21] that reactions of silylamines, mainly amine **1**, with a series of trivalent phosphorus acid chlorides occur under mild conditions.

$$\underset{\mathbf{1,\,2}}{MeOPCl_2} + 2\,Me_3SiNR_2 \xrightarrow{20\ ^\circ C} \underset{(68\%-82\%)}{MeOP(NR_2)_2} + 2\,Me_3SiCl$$

R_2N = Et_2N (**1**), Me_2N (**2**), .

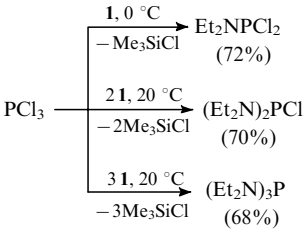
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Received 2 December 1997
Uspekhi Khimii **67** (9) 827 – 838 (1998); translated by S S Veselyi

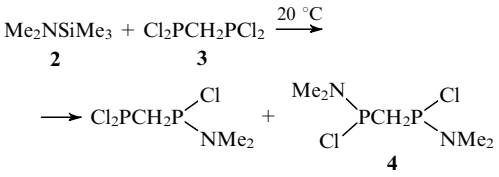
† The review is devoted to the memory of academician M I Kabachnik (1908 – 1997).

For example, arylphosphonous dichlorides,[16] alkylphosphorodichloridites,[17,18] and heterocyclic phosphorochloridites[19–21] react with amine **1** at room temperature or even at lower temperatures to give the corresponding phosphoramidites in high yields.

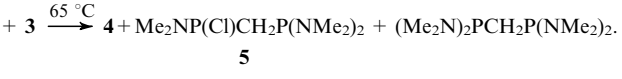
An appropriate ratio of the reagents makes it possible to obtain products of the stepwise replacement of the halogen atoms at the phosphorus atom by amino groups.[14]



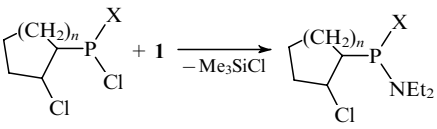
A decrease in reactivity of trivalent phosphorus acid chlorides with respect to *N*-silylamines upon replacement of the chlorine atoms with amino groups has also been found in the studies of the reaction of dimethyl(trimethylsilyl)amine (**2**) with methylenebis(phosphonous dichloride) (**3**).[22]



Sequential substitution of the chlorine atoms at different phosphorus atoms in methylenebis(phosphonous dichloride) takes place at room temperature with an excess of amine **2**. The chlorine atom in the diamide **4** is replaced by the dimethylamino group only on heating of the reaction mixture. The chlorine atom in the triamide **5** is even more difficult to replace.



Mild reaction conditions and completeness of the reaction of aminosilanes with trivalent phosphorus acid chlorides were demonstrated for compounds the preparation of which by other methods had been a problem. For example, dehydrochlorination could be avoided in the synthesis of *N*,*N*-diethyl-*P*-(2-chlorocyclopentyl)- and -(2-chlorocyclohexyl)phosphonamidites.[15]

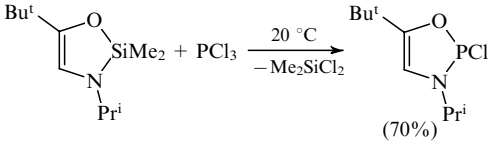


(51%–69%)

n = 1, 2; X = Cl, MeO.

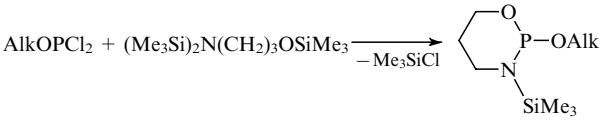
Tris(diphenylamino)phosphine was synthesised in quantitative yield from tetraphenylphosphorodiamidochloridite and *N*-(trimethylsilyl)diphenylamine. In this case, it was possible to escape difficulties associated with the purification of the product from triethylamine hydrochloride.[23]

The synthesis of 5-*tert*-butyl-2-chloro-3-isopropyl-1,3,2-oxazaphospholene from phosphorus trichloride and 5-*tert*-butyl-3-isopropyl-2,2-dimethyl-1,3,2-oxazasilolene was described.[24]



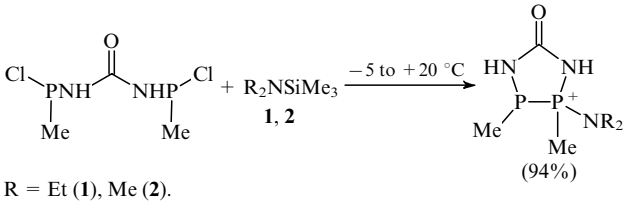
(70%)

Silylamines were also used in syntheses of heterocyclic derivatives of trivalent phosphorus. The reaction of alkylphosphorodichloridites with *N*,*N*,*O*-tris(trimethylsilyl)-3-aminopropanol afforded 2-alkoxy-3-trimethylsilyl-1,3,2-oxazaphosphorinanes.[25]



(32%–45%)

Cyclic products are also formed in the reaction of *N*,*N*′-bis(methylchlorophosphino)urea with amines **1** and **2**.[26,27]

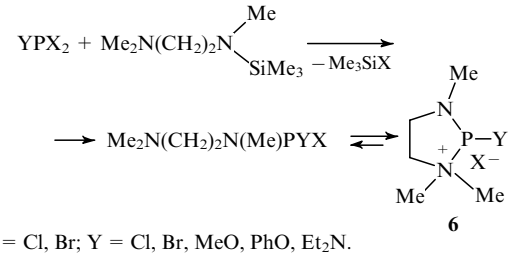


(94%)

R = Et (**1**), Me (**2**).

It is worth noting that in this case the nucleophilicity of the amide nitrogen atom becomes comparable with that of the nitrogen atom in silylamines. This opens possibilities for the intramolecular replacement of the chlorine atom.

The participation of the P—N fragment in the delocalisation of the positive charge enables the formation of cyclic products **6** in reactions of di- and trihalides of trivalent phosphorus with *N*,*N*,*N*′-trimethyl-*N*′-trimethylsilylethylenediamine.[28] The presence of an unshared electron pair on substituent Y at the phosphorus atom is a prerequisite for cyclisation.



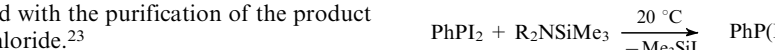
X = Cl, Br; Y = Cl, Br, MeO, PhO, Et_2N.

The result of phosphorylation of silylamines depends also on the nature of the halogen at the phosphorus atom. Unlike acid chlorides, which react completely with amines according to ^{31}P NMR spectroscopy, acid bromides react with amines in a reversible manner.[29,30] An equilibrium mixture containing comparable amounts of the reaction product, *i.e.* phosphoramidite, and acid bromide is formed at room temperature.[29,30]



$R^1 = R^2 = Me_2N$, $R^1 + R^2 = -OCH_2CMe_2CH_2O-$; R^3 = Me, Et.

It was noted previously[31,32] that the reaction of phosphorus triiodide with silylamides does not go to completion. A similar phenomenon was also observed for phenylphosphonous diiodide.[33]



R = Me, Et.

Moreover, the reverse reaction is possible theoretically. This has been shown using the reaction of tris(dimethylamino)-phosphine with iodotrimethylsilane as an example.[32]

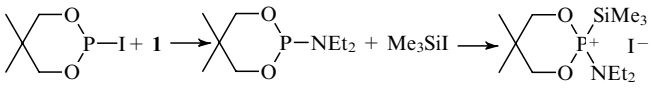


Finally, the reversibility of the reaction of dialkylphosphinous diiodides with the amine **1** in dichloromethane at room temperature has been demonstrated recently.[34]

$$Alk_2PI + Et_2NSiMe_3 \rightleftharpoons Alk_2PNEt_2 + Me_3SiI.$$

1

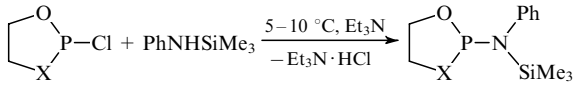
Studies of this kind of reactions are complicated by side reactions of phosphoramidites that are formed with organoiodine compounds.[29, 32, 34] For example, the reaction of the amine **1** with 2-iodo-5,5-dimethyl-1,3,2-dioxaphosphorinane results in the phosphoramidite **7**, which immediately reacts with the product of this reaction, *viz*., iodotrimethylsilane.[29]



7

Unlike acyl fluorides,[35] trivalent phosphorus acid fluorides do not react with silylamines. All attempts to carry out such transformations failed.[29, 36, 37] Thus, the reaction of silylamines with P(III) acid chlorides remains the most suitable for the synthesis of phosphoramidites.

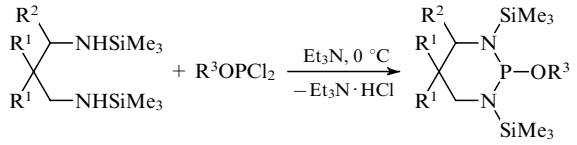
It should be noted that phosphorylation of silylamines in the presence of a base may occur with the preservation of the N–Si bond. For example, the reaction of 2-chloro-1,3,2-diheterophospholanes with *N*-trimethylsilylaniline under mild conditions afforded the corresponding 2-(*N*-trimethylsilyl-*N*-phenylamino)-1,3,2-diheterophospholanes.[38]



(33% – 39%)

X = O, NPh.

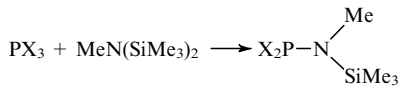
Similarly, Menshutkin's chlorides can react, though partly, at the N–H bond of *N*,*N*′-bis(trimethylsilyl)trimethylenediamines.[39, 40]



(12% – 25%)

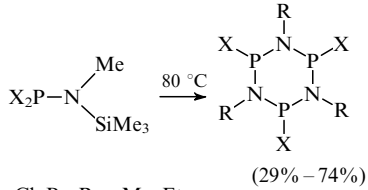
R^1, R^2 = H, Me; R^3 = Me, Et, Ph.

With disilazanes, it becomes possible to obtain products of substitution of one or two trialkylsilyl groups, depending on the reaction conditions. Monosubstitution occurs with equimolar amounts of the reagents and at low temperature.[41, 42]



X = Cl, Br.

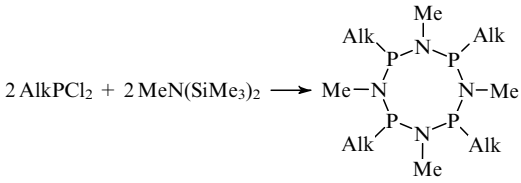
The resulting *N*-silylamidophosphorodihalidites are thermally unstable and can be transformed to cyclotriphosphazanes on heating of the reaction mixture.[42,43]



(29% – 74%)

X = Cl, Br; R = Me, Et.

The reaction of alkylphosphonous dichlorides with methylbis(trimethylsilyl)amine also affords mono- and diphosphorylation products, depending on the ratio of the reagents,[44] and boiling of equimolar amounts of the reagents in acetonitrile leads to cyclotetraphosphazanes.[45, 46]



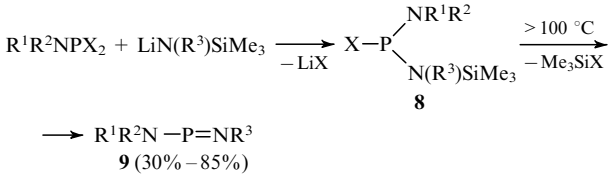
(15% – 50%)

The synthesis of *N*-trimethylsilyldialkylphosphinamidites by boiling dialkylphosphinous chlorides with an excess of hexamethyldisilazane in the presence of a catalyst was also described.[47]

$$Alk_2PCl + (Me_3Si)_2NH \xrightarrow{R_3N \cdot HCl} Alk_2PNHSiMe_3.$$

Trivalent phosphorus acid fluorides are inert with respect to disilazanes.[48] The Si–N bond remains unchanged after heating a mixture of F_2PCl with $(Me_3Si)_2NPF_2$ or $Me_3Si(Bu^t)NPF_2$. This is explained[49] by p_π–d_π overlapping of orbitals of the Si, N, and P atoms resulting in a corresponding decrease in the nucleophilicity of nitrogen.

A method for the synthesis of a series of compounds of two-coordinated phosphorus **9** from *N*,*N*,*N*′-trisubstituted *N*-(trimethylsilyl)phosphorodiamidohalidites **8**, which had been synthesised from $R^1R^2NPX_2$ and $LiN(R^3)SiMe_3$, was developed.[50–56]

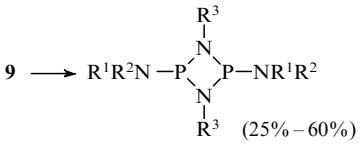


8

9 (30% – 85%)

X = Cl, Br; R^1 or R^2 are bulky substituents, R^3 = Pr^i, Bu^t, R^4_3Si, $C_6H_2Bu^t_3$, adamant-1-yl.

In this case, it was possible to isolate only compounds with bulky substituents at both nitrogen atoms. Otherwise, dimerisation of the imidophosphorous amides **9** to 1,3-diaza-2,4-diphosphetidines takes place.[52–55]

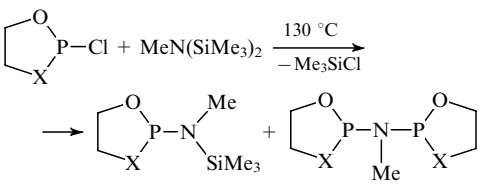


(25% – 60%)

R^1, R^2 = Me, Et, Pr.

The nature of the halogen at the phosphorus atom has no significant influence on the elimination of the halosilane.[50–56] The same method was used for the preparation of the less stable *P*,*N*-dialkyl(aryl)-[57, 58] and *P*-aryloxy-*N*-aryliminophosphines.[59]

Reactions of phosphorochloridites with hexa- and heptamethyldisilazanes were studied.[60, 61] The attractiveness of these reactions is explained by the fact that they allow the syntheses of functionally substituted amides of trivalent phosphorus acids. Unfortunately, phosphorylation of disilazanes occurs under more drastic conditions than phosphorylation of monosilylamines.



(20% – 31%) (13% – 30%)

X = O, NPh;

$$ROPCl_2 + 2\,MeN(SiMe_3)_2 \xrightarrow[-Me_3SiCl]{\Delta} ROP[N(Me)SiMe_3]_2. \quad (10\%-21\%)$$

Phosphorylation of phosphorus-substituted disilazanes can be accompanied by rearrangement to give compounds containing phosphorus in different coordination states.[62]

$$R_2PN(SiMe_3)_2 + R'_2PCl \xrightarrow[-Me_3SiCl]{} R_2P(=NSiMe_3)PR'_2.$$

2. Reactions with pentavalent phosphorus acid halides

Since pentavalent phosphorus has lower electrophilicity than trivalent phosphorus, a general decrease in the rates of phosphorylation of silylamines with the corresponding phosphorus(V) acid halides is observed.

The replacement of the chlorine atoms in pentavalent phosphorus acid chlorides by the amino groups in reactions of acid chlorides with amines **1** and **2** is incomplete even on heating.[14]

$$POCl_3 + 2\,R_2NSiMe_3 \xrightarrow[-2Me_3SiCl]{} (R_2N)_2P(O)Cl \quad (60\%-70\%)$$

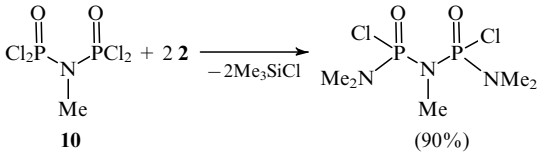
1, **2**

R = Et (**1**), Me (**2**).

Complete replacement of the chlorine atoms in methylenebis(phosphonic dichloride) in its reaction with the amine **2** is possible only on heating.[22]

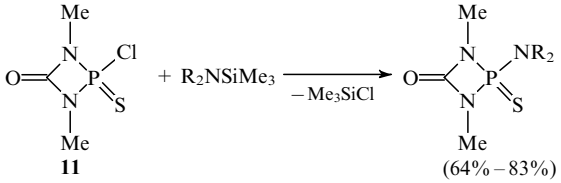
$$Cl_2P(O)CH_2P(O)Cl_2 + 4\,\mathbf{2} \xrightarrow[-4Me_3SiCl]{85\ ^\circ C} (Me_2N)_2P(O)CH_2P(O)(NMe_2)_2 \quad (100\%)$$

The phosphorylating ability of *N*-methyliminodiphosphonic tetrachloride (**10**) is even lower.[63]



10 (90%)

Nucleophilic substitution of the chlorine atom at a less electrophilic thiophosphoryl centre occurs more readily when the latter is incorporated into a strained four-membered ring, as in compound **11**.[64]



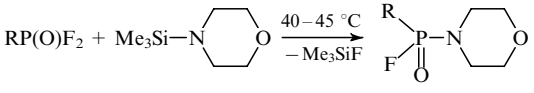
11 (64%–83%)

R = Me, Et.

However, the presence of electron-withdrawing and bulky phenyl groups at the nitrogen atom of the silylamine prevents the cleavage of the Si—N bond in this reaction.

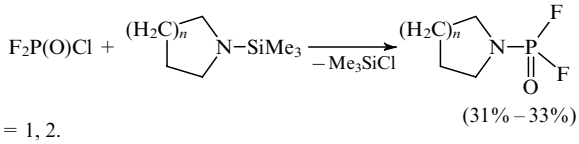
Chlorocyclotriphosphazenes also belong to pentavalent phosphorus acid chlorides, but we considered that there is little sense in repeating in this review the previously published data [65, 66] on their reactions with silylamides.

Unlike trivalent phosphorus acid fluorides, P(V) fluoro-derivatives react with silylamines in some cases. For example, the reaction of *N*-trimethylsilylmorpholine with the mixture of isobutenyl- and 2-chloroisobutylphosphonic difluorides affords products of replacement of one of the fluorine atoms.[67]



R = $Me_2C{=}CH$, Me_2CClCH_2.

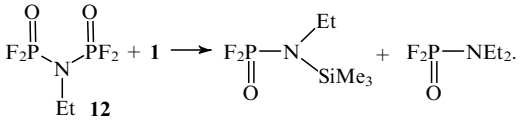
N-Silylated pyrrolidine and piperidine react rather smoothly with phosphorus oxofluoride POF_3. However, in their reaction with phosphorus oxochloridedifluoride, substitution of the chlorine atom is the first to occur.[68]



(31%–33%)

n = 1, 2.

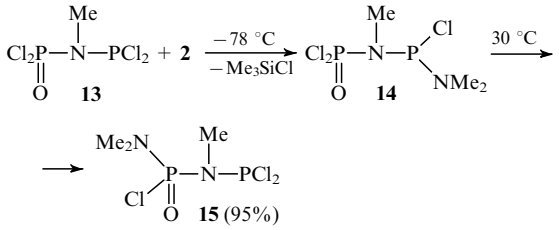
Unlike *N*-methyliminodiphosphonic tetrachloride (**10**), *N*-ethyliminodisphophonic tetrafluoride (**12**) reacts with the amine **1** with the cleavage of the P—N bond.[69]



12

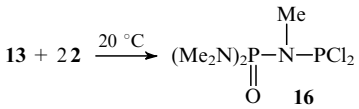
Although reactions of silylamines with phosphorus acid fluorides are rather interesting from the synthetic point of view, they are little studied. Undoubtedly, this can be explained by the high toxicity of the latter compounds. Phosphorylation of silylamines with phosphorous acid bromides and iodides has not been described in literature.

The reaction of the amine **2** with mixed amidotetrachloride **13** can serve as a characteristic of the relative ability of the halogen atoms in trivalent and pentavalent phosphorus acid halides to be replaced by the amino groups of silylamines.[70,71] At −78 °C and with an equimolar ratio of the reagents, the product of the replacement of one chlorine atom at the trivalent phosphorus atom by the dimethylamino group (compound **14**) is formed selectively. The structure of compound **14** is confirmed by ^1H and ^{31}P NMR spectroscopic data. An increase in the reaction temperature to 30 °C and exposure of the reaction mixture at this temperature for 1 h result in migration of the dimethylamino group from the trivalent phosphorus atom to the pentavalent one to give compound **15**.



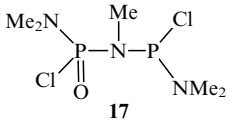
13 **14** **15** (95%)

The reaction of the tetrachloride **13** with 2 equivalents of the amine **2** at room temperature affords the product of replacement of both chlorine atoms at the pentavalent phosphorus atom by the dimethylamino groups (compound **16**).



16

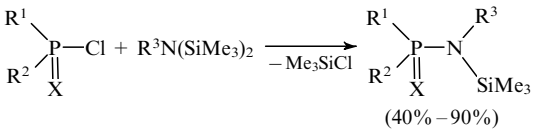
In the authors' opinion, compound **17** is formed as an intermediate in this reaction.



17

This assumption is supported by the fact that compound **17**, synthesised independently, undergoes rearrangement at room temperature to form compound **16**.

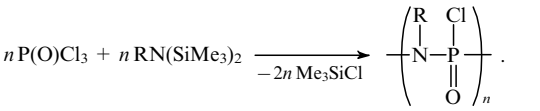
As in the case of P(III) derivatives, the reaction of P(V) acid chlorides with disilazanes can be used for the preparation of *N*-silylated amides.[72,73]



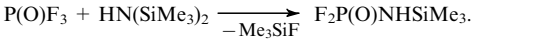
(40%–90%)

R^1, R^2 = Alk, Ar, AlkO, ArO; X = O, S, NR^4.

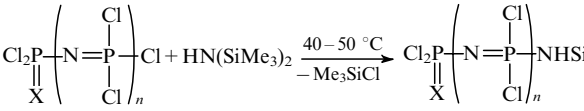
Successful synthesis of these amides requires that appropriate reaction conditions are selected depending on the structure of the phosphorylating agent used. Reactions at room temperature mainly involve more electrophilic $MePOCl_2$ and 1-chloro-1-oxophosphol-3-ene,[72] whereas diphenyl phosphorochloridate reacts at 60 °C,[73] and phosphinothioic chlorides react only at 130–150 °C.[74] *N*,*N*-Bis(trimethylsilyl)-*P*-phenylphosphonothioic diamide is obtained under even more drastic conditions (in the presence of aluminium chloride).[75] As a rule, reactions of this type afford a monophosphorylation product, except for the reaction of disilazanes with $POCl_3$.[76]



The reaction of hexamethyldisilazane with POF_3 afforded the corresponding *N*-silylmonoamide in moderate yield.[76]



Monosubstitution of the chlorine atoms in mixed imidochlorides can be used for the preparation of acyclic oligophosphazenes.[77]



X = O, S.

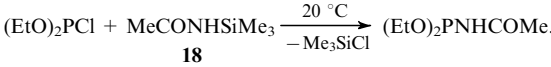
Thus, reactions of both trivalent and pentavalent phosphorus acid chlorides with silylamines are of significant interest for the synthesis of phosphoramidites and phosphoramidates.

III. Reactions with *N*-silylamides

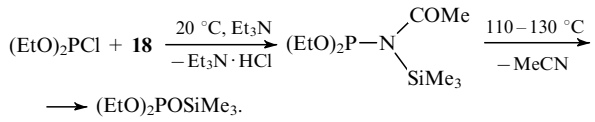
Many *N*-phosphorylated amides and lactams are known to be physiologically active substances with a broad spectrum of action.[1,78] In addition, certain *N*-phosphorylated amides are used as condensation agents in the synthesis of carboxamides and esters.[79] The development of convenient methods for their synthesis is therefore of large practical importance.

The introduction of an acyl group into a silylamine molecule changes substantially both the nucleophilic properties of the nitrogen atom and the geometry of the molecule. Studies of the reactivity of silylamides performed by representatives of the Kazan' school of chemists allowed them to elucidate the regularities of the reaction of silylamides with trivalent and pentavalent phosphorus acid chlorides.[80–87]

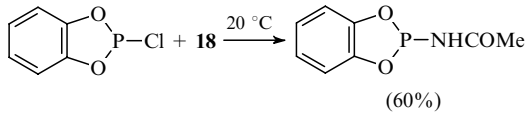
Reaction conditions have a significant effect on the direction of the reaction of diethyl phosphorochloridites with *N*-trimethylsilylacetamide (**18**).[8,80] For example, cleavage of the Si–N bond with the formation of *N*-diethoxyphosphinetriylacetamide takes place at room temperature.



The Si–N bond remains unchanged in the presence of triethylamine; in this case, the reaction product is *N*-trimethylsilyl-*N*-(diethoxyphosphinetriyl), and only heating of the reaction mixture to 110–130 °C brings about the elimination of the acetonitrile molecule and the formation of a Si–O–P bond.

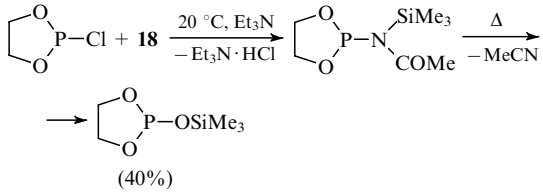


Under similar conditions (room temperature, inert solvent), 2-chlorobenzo-1,3,2-dioxaphospholene reacts with amide **18** to give 2-acetylaminobenzo-1,3,2-dioxaphospholene.[81]



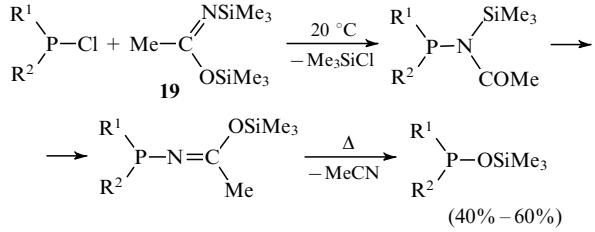
(60%)

Similarly, but in the presence of triethylamine, the reaction of 2-chloro-1,3,2-dioxaphospholane with amide **18** afforded 2-(*N*-acetyl-*N*-trimethylsilylamino)-1,3,2-dioxaphospholane, which is transformed to 2-trimethylsilyloxy-1,3,2-dioxaphospholane on heating.[82]



(40%)

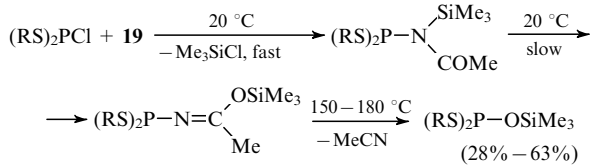
The product of disilylation of acetamide, compound **19**, has the structure of an imidate in which one of the trimethylsilyl groups is linked with the nitrogen atom, and the second group, with the oxygen atom.[8,88] Phosphorylation of this compound with phosphorochloridites at room temperature affords *N*-trimethylsilyl-*N*-dialkoxy- or alkoxy(amino)phosphinetriyl)acetylamides. Their structures were confirmed by IR and ^1H and ^{31}P NMR spectra.[82–86] Their conversion into the corresponding trimethylsilyl phosphites was explained by the possible presence of isomeric *N*-(1-trimethylsilyloxyethylidene)phosphoramidites in the reaction mixture.



(40%–60%)

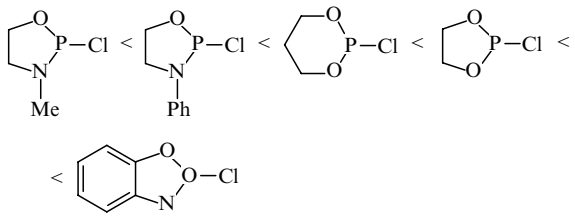
$R^1 = R^2$ = OAlk, R^1 = OAlk, $R^2 = NHR^3$.

The *O*-silylated isomer appeared to be more stable than the *N*-silylated one and was isolated after phosphorylation of compound **19** with dialkyl phosphorochloridedithioite.[85]

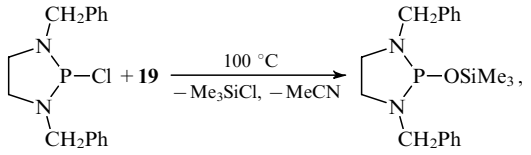


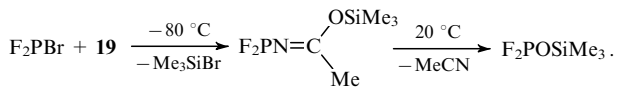
(28%–63%)

The reaction under discussion also proceeds in a similar way with other phosphorochloridites. In this case, the ease of the formation of silyl phosphites increases in the following series:[83]

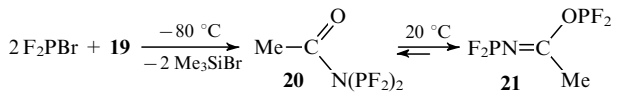


Isomerisation of the phosphorylation intermediate followed by its decomposition is also observed in some cases.[86, 89]





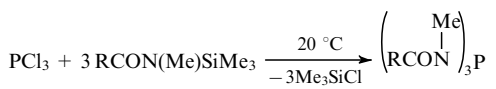
If the latter reaction is carried out with an excess of F_2PBr, bisphosphorylated acetamide is obtained. It is formed as a mixture of *N*,*N*- (**20**) and *N*,*O*-isomers (**21**), the isomer **20** undergoing rearrangement into the isomer **21**.[89]



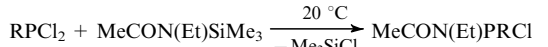
Thus, the reaction of trivalent phosphorus acid chlorides with *N*,*O*-bis(trimethylsilyl)acetamide is a convenient general method for the synthesis of highly reactive trivalent phosphorus acid silyl esters.

The reactivity of disilylamides with respect to phosphorochloridites decreases upon introduction of electron-withdrawing substituents at the carbonyl carbon atom, for example, when methyl group of acetamide is substituted by a phenyl or methoxy group. Methyl *N*,*N*-bis(trimethylsilyl)carbamate does not react with diethyl phosphorochloridite and 2-chlorobenzo-1,3,2-dioxaphospholene,[86, 89] and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide does not react with PF_2Br.[89]

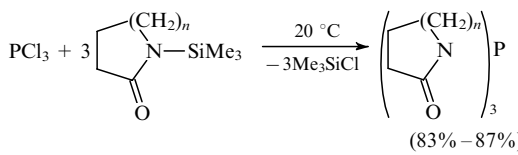
Contrary to silylated primary amides, *N*-silylated secondary amides and lactams can be selectively phosphorylated at the nitrogen atom with phosphorus trichloride and alkylphosphonous dichlorides.[90, 91]



(52%–56%)



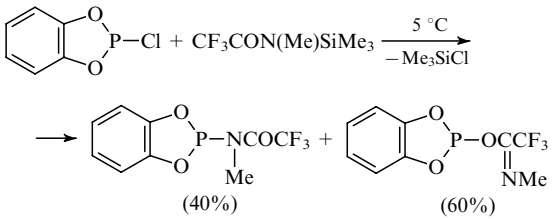
(60%–65%)



(83%–87%)

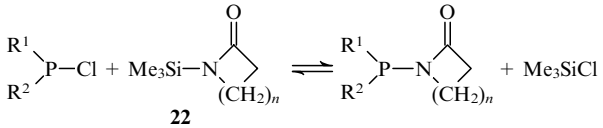
n = 1, 2.

Nevertheless, there is an example of the formation of a mixture of *N*- and *O*-phosphorylation products in the reaction of *N*-methyl-*N*-trimethylsilyltrifluoroacetamide with 2-chlorobenzo-1,3,2-dioxaphospholene.[92]



(40%) (60%)

It was found recently that the reaction of some trivalent phosphorus acid chlorides with silyllactams **22** may be reversible, and the position of equilibrium is determined by the structure of the phosphorylating agent.[93]

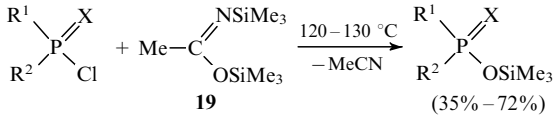


22

n = 1–4.

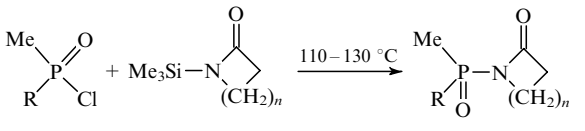
The reversibility of the process was proved by mixing equimolar amounts of *N*-phosphoryllactams and chlorotrimethylsilane. In this case, the compositions of the reaction mixtures were the same as those in the reactions of phosphorochloridites with silyllactams. The reversibility of the reaction of *N*-trimethylsilyl-β-lactams with trivalent phosphorus acid chlorides was postulated on the basis of indirect data.

Reactions of silylated amides with pentavalent phosphorus acid chlorides are insufficiently studied. It was shown that, as in the case of phosphorochloridites, the reaction of *N*,*O*-bis(trimethylsilyl)acetamide **19** with phosphorus oxochloride, methylphosphonic dichloride, diethyl phosphorochloridate, diethyl and dimethyl phosphorothiochloridate is accompanied by the formation of silyl phosphates.[87]



19 (35%–72%)

Previously, it was found that *N*-silylated lactams react, although under drastic conditions, with alkyl(aryl) methylphosphonochloridates and *N*,*N*-diethyl-*P*-methylphosphonamidochloridate to form the products of substitution at the nitrogen atom, as in the reaction with phosphorus trichloride.[94]

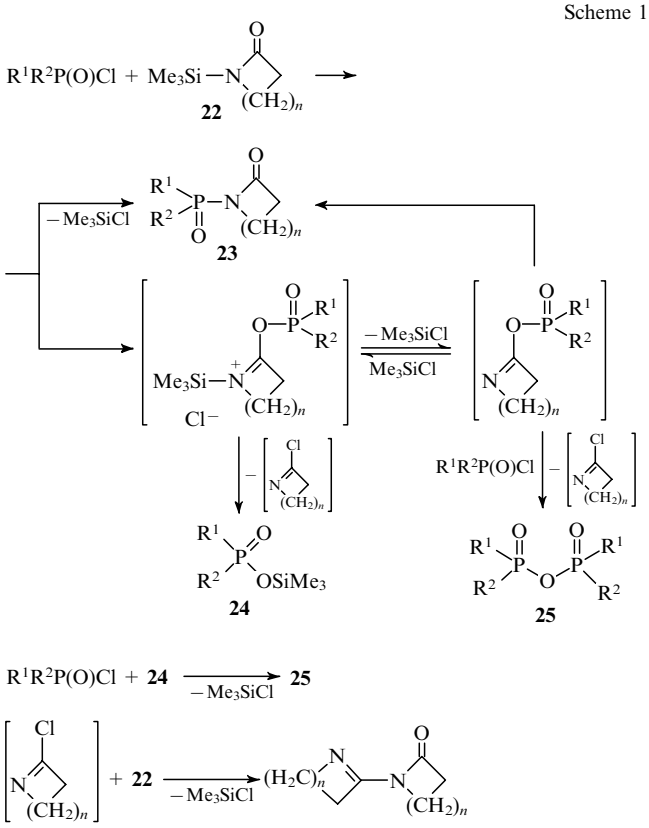


(60%–80%)

R = OEt, OPh, NEt_2; n = 2, 3.

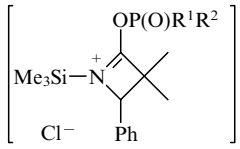
A scheme was proposed recently, according to which pentavalent phosphorus acid chlorides $R^1R^2P(O)Cl$ react with silyllactams **22** both at the nitrogen atom and the oxygen atom of the carbonyl group (Scheme 1).[95] Strictly speaking, the possibility of silylotropy should be taken into account when estimating the reactivity of *N*-silyllactams; however, under the conditions used,[95] the trimethylsilyl group had to be bound to the nitrogen atom. Therefore, the nature of the products obtained was explained by the authors from the viewpoint of dual reactivity of the silyllactam system. The formation of *N*-phosphoryllactams **23** may result from both the direct attack at the nitrogen atom and the O→N isomerisation of the *O*-phosphorylated intermediates which are also the sources of side products, namely, silyl phosphates **24** and pyrophosphates **25**. The predominance of one or another pathway of decomposition of the intermediates depends on different factors including the nature of the organophosphorus fragment. Successive replacement of the alkyl groups in the chloride by

Scheme 1



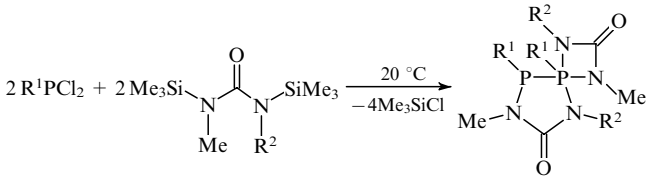
alkoxy groups decreases the yield of *N*-phosphorylated derivatives **23**. The authors explain this fact by a decrease in the rate of nucleophilic attack by the nitrogen atom on the phosphorus atom in the intermediate and by a larger contribution of other directions of its transformation.

It should be noted that attack on the oxygen atom of *N*-trimethylsilyl-β-lactams by pentavalent phosphorus acid chlorides is hindered by severe steric requirements to the assumed transition state.



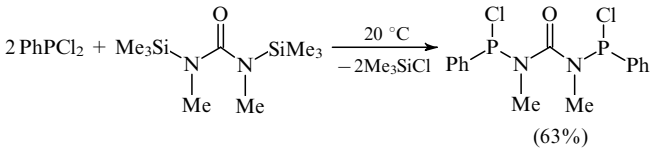
The structure of the products formed in the reaction of *N*,*N*′-bis(trimethylsilyl)ureas with trivalent phosphorus acid chlorides is determined by the nature of substituents at the phosphorus atom.[96–100]

The attack of phenyl- and methylphosphonous dichloride on the nitrogen atom of the Si–N bond in urea is accompanied by subsequent cleavage of one of the P–N bonds, probably due to the high strain of the corresponding diazaphosphetidine ring.[96,97]

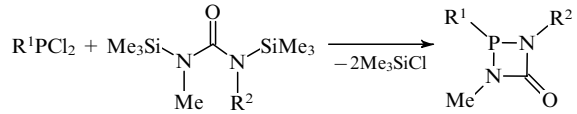


R^1 = Me, Ph; R^2 = Me, Ph, 3-$CF_3C_6H_4$.

In the presence of an excess of phenylphosphonous dichloride, the reaction stops at the usual step of replacement of the trimethylsilyl group.[99]

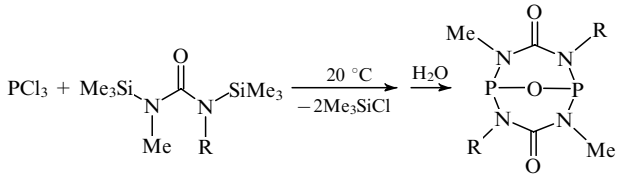


Replacement of the alkyl groups in the starting alkylphosphonous dichlorides by electron-withdrawing groups (CCl_3 or C_2F_5) changes the direction of this reaction resulting in the formation of 1,3,2-diazaphosphetidin-4-ones.[97,98]



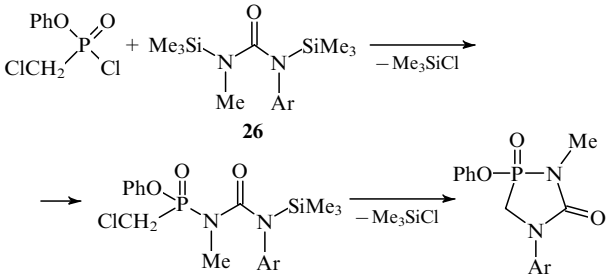
R^1 = CCl_3, C_2F_5; R^2 = Me, 3-$CF_3C_6H_4$.

On the contrary, replacement of the alkyl group in alkylphosphonous dichlorides by a chlorine atom[97] or a dialkylamino group[99] favours the formation of bicyclic compounds.



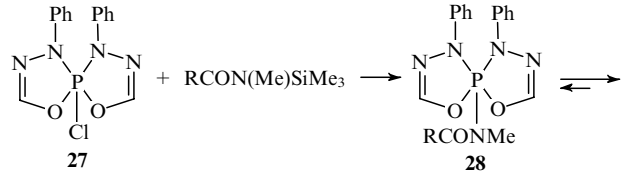
R = 3-$CF_3C_6H_4$.

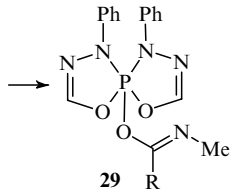
Phosphorylation of unsymmetrical *N*,*N*′-bis(trimethyl-silyl)ureas **26** with phenyl (chloromethyl)phosphonochloridate is complicated by the attack by the second silylamide group of urea on the carbon atom of the chloromethyl group to give 1,4,2-diazaphospholane-2,5-diones.[101]



It is interesting that the nucleophilicity of the nitrogen atom in *N*,*N*-bissilylated sulfamides is so much lower than that in *N*-silylcarboxamides that the former do not react with phosphonous dichlorides.[100]

Reactions of halophosphoranes with silylamides are also ambiguous. The reaction of *N*-methyl-*N*-(trimethylsilyl)trifluoro- and -trichloroacetamides with the chlorophosphorane **27** affords a mixture of *N*- (**28**) and *O*-phosphorylated (**29**) trihaloacetamides. It is noteworthy that, like the product of the reaction of the silylamide **19** with dialkyl phosphorochloridodithioites, the *N*-phosphorylated isomer is less stable and is converted on storage into the *O*-phosphorylated isomer.[102]

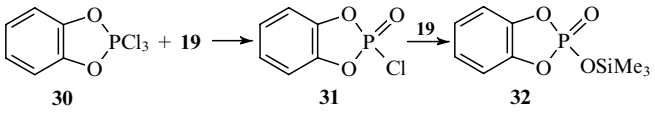




29

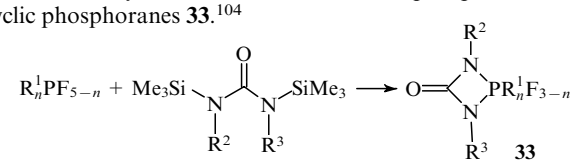
R = CCl_3, CF_3.

It is assumed that the reaction of 2,2,2-trichlorobenzo-1,3,2-dioxaphospholene (**30**) with disilylamide **19** occurs through the step of *O*-phosphorylation of silylamide. With the ratio of the reagents 1 : 1, 2-chloro-2-oxobenzo-1,3,2-dioxaphospholene (**31**) is formed. With an excess of silylamide, the reaction affords the silyl phosphate **32**.[103]



30 **31** **32**

N,*N*′-Disilylated ureas react with fluorophosphoranes to give cyclic phosphoranes **33**.[104]



33

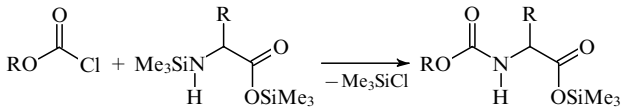
n = 1 – 3.

Thus, practical application of silylamides requires additional studies on the optimisation of conditions for the synthesis of *N*-phosphorylated amides.

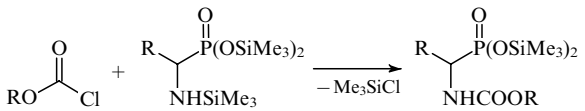
IV. Reactions with *N*-silylated amino acids and other *N*-silylated compounds

N-Silylated amino acids can be regarded as *N*-silylamines that contain a functional group in their alkyl part.

Reactions of *N*,*O*-bis(trimethylsilyl) derivatives of natural α-amino acids with acyl chlorides were used for the protection of the amino group.[105]

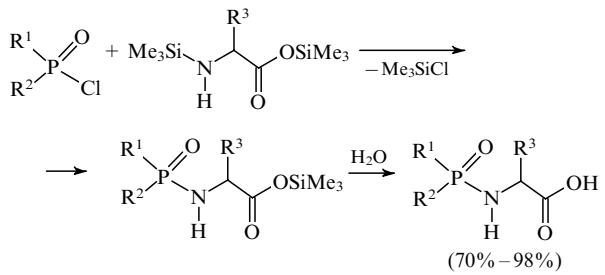


N-Acyl derivatives of α-aminoalkylphosphonic acids were synthesised in a similar way.[106]



No other examples of this type of reaction have been documented.

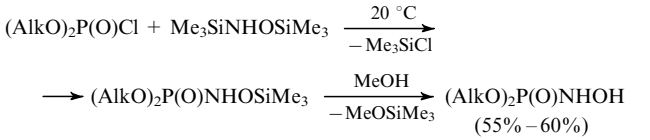
However, it turned out that *N*-phosphorylated amino acids can be obtained by the reaction of *N*,*O*-bis(trimethylsilylated) amino acids with pentavalent phosphorus acid halides.[107 – 109]



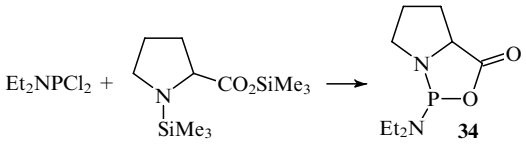
(70% – 98%)

N-Phosphorylated acids are formed in high yields. Intermediate silyl esters of *N*-phosphorylated amino acids were isolated in the case of glycine derivatives.[107]

This type of selective *N*-phosphorylation of *N*,*O*-bissilylated compounds was also used in the synthesis of *N*-(dialkoxyphosphoryl)hydroxylamines.[110]

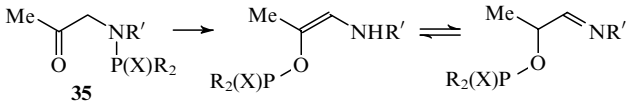


Both silyl groups participate in the reaction of bis(trimethylsilyl)proline with diethylphosphoramidodichloridite, which results in the formation of a bicyclic product (**34**).[111]



34

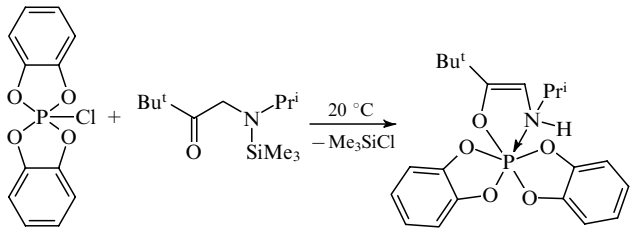
Phosphorylation of silylated α-amino ketones occurs at the nitrogen atom. Phosphoro- and prototropic transformations of primary phosphorylation products **35** are observed in this case.[112]



35

X = O, S or unshared electron pair.

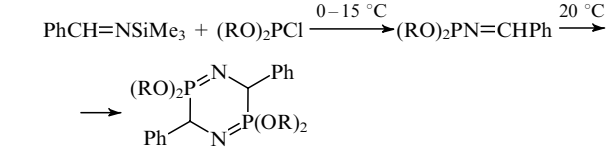
The reaction of 1-(*N*-isopropyl-*N*-trimethylsilylamino)-3,3-dimethylbutan-2-one with spirophosphorane **36** was complicated by the formation of an N→P donor-acceptor bond. As a result, the tricyclic compound **37** with the hexacoordinated phosphorus atom was formed.[113]



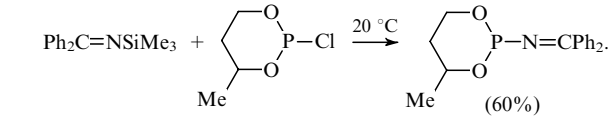
36 **37** (93%)

The peculiarities of the reactions of phosphorus acid chlorides with such amino acid derivatives as *N*-silyllactams, which may be also attributed to *N*-silylamides, have been discussed in Section III.

In the studies of the reactivity of compounds containing a silyl group at the imine nitrogen atom,[114, 115] it was found that phosphorochloridites react with aldimines[114] and ketimines[115] under mild conditions and the *N*-(dialkoxyphosphinetriyl)aldimines that formed undergo rapid dimerisation.



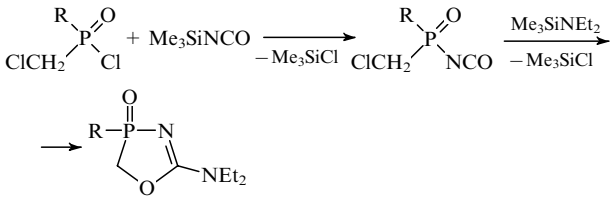
RO = EtO; $(RO)_2$ = $O(CH_2)_2O$, 1,2-OC_6H_4O.



(60%)

Among other *N*-silylated compounds containing a C=N bond, isocyanates and isothiocyanates are worth noting.

Phosphorylation of isocyanatosilanes has been studied very little. Only the syntheses of diethylphosphoramidobisisocyanatidite[116] and phosphorisocyanatidic difluoride[117] have been reported. Recently, the reaction of isocyanatotrimethylsilane with phosphinic chlorides was used in the synthesis of 1,3,4-oxazaphosphol-2-enes.[101]

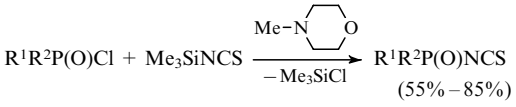


Trimethylsilyl isothiocyanate reacts with trivalent and pentavalent phosphorus acid chlorides only on strong heating.[118, 119]

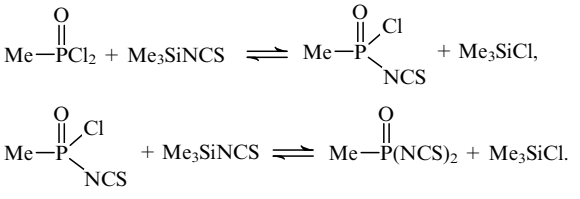
$$R_nP(X)Cl_{3-n} + (3-n)\,Me_3SiNCS \xrightarrow[-Me_3SiCl]{100-150\ ^\circ C} R_nP(X)(NCS)_{3-n} \quad (20\%-82\%)$$

R = Ph, Me, EtO; X = O, S or unshared electron pair; $n = 0-2$.

Because of the large practical importance of phosphoryl isothiocyanates, which are the products of this reaction and which are widely used as intermediates in the synthesis of pesticides and complexones, attempts were made to decrease the reaction temperature by adding catalysts. The use of tin and titanium tetrachlorides for this purpose was unsuccessful.[118, 120] On the contrary, when the reaction was carried out in the presence of *N*-methylmorpholine, it became possible to obtain thermally unstable phosphoryl isothiocyanates at 20 °C in high yields.[121]

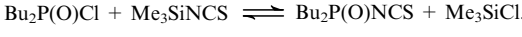


In some cases, the reaction of isothiocyanatotrimethylsilane with pentavalent phosphorus acid chlorides is reversible.[122] Using the ^{31}P NMR method, it was found that the compositions of the reaction mixtures prepared from methylphosphonic dichloride and 2 equivalents of isothiocyanatotrimethylsilane and from methylphosphonic diisothiocyanate and 2 equivalents of chlorotrimethylsilane were identical.



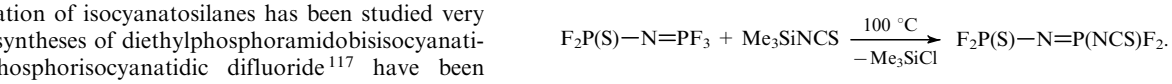
The yield of phosphonic diisothiocyanate may be increased by distilling off the chlorotrimethylsilane that formed in the reaction.

The low yield of dibutylphosphinic isothiocyanate in comparison with those of the corresponding phosphoric and phosphonic isothiocyanates is also explained by the reversibility of the reaction under study.

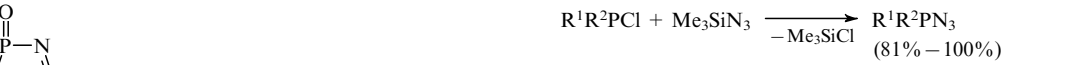


The use of isothiocyanatoalkoxydimethylsilane instead of isothiocyanatotrimethylsilane increases the reactivity of the Si–N bond in reactions with trivalent and pentavalent phosphorus acid chlorides;[123] however, the Si–O bond is cleaved even at low temperatures (20–60 °C) to afford a mixture of products.

Phosphoric acid fluorides are rather low-reactive with respect to Me_3SiNCS even on heating, and the fluorine atom of the phosphorimide moiety is more reactive than that of the thiophosphoramide moiety.[124]

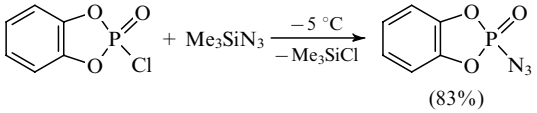


The increased reactivity of the Si–N bond in azidotrimethylsilane and the commercial availability of this compound allow one to consider it as a convenient reagent for the synthesis of thermally labile phosphorus acid azides. For example, phosphorochloridites react with Me_3SiN_3 to give high yields of the product even at 0 °C.[125–130]



R^1, R^2 = Cl, Cl_3CCMe_2O, Et_2N, Pr^i_2N; $R^1 + R^2 = O(CH_2)_2O$, 1,2-OC_6H_4O.

Pentavalent phosphorus acid chlorides[127] and chlorophosphoranes[131] behave similarly.



V. Conclusions

Reactions of phosphorus acid halides, particularly chlorides, with *N*-silylated organic compounds are undoubtedly of interest for synthetic chemists, since they can serve as the basis for the development of methods for the synthesis of both new types of compounds and reactive intermediates. However, no strict quantitative analysis of the regularities of this reaction has been carried out so far, which inhibits practical recommendations regarding optimum conditions of this reaction in particular cases in order to reach the required selectivity.

In the recently published special issues of the 'Chemical Reviews' devoted to current problems of the chemistry of silicon[132] and phosphorus,[133] the problems concerning the application of compounds with a nitrogen–silicon bond in the organophosphorus synthesis were not properly taken into account. We hope that the present review fills this gap.

Based on the literature data and their own experience, the authors have the courage to state that the potential of the reactions under discussion has not been totally exploited. In particular, this refers to phosphorylation of biopolymer fragments under mild conditions, for which methods of silylation have been largely developed. In this case, the result of the reaction may be controlled by varying substituents at the silicon and phosphorus reaction centres. Such studies may be carried out in the near future.

This review was written with the financial support of the Russian Foundation for Basic Research (Project No. 96-15-97298).

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