Studies of phosphorylation reaction of tertiary amines by NMR spectroscopy

L. I. Larina,[a] V. G. Rozinov,[b] and T. N. Komarova[a]*

[a]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. E-mail: larina@irioch.irk.ru
[b]Irkutsk State University, 1 ul. Karla Marksa, 664003 Irkutsk, Russian Federation

Phosphorylation of tertiary amines containing at least two ethyl groups at the nitrogen atom with phosphorus pentachloride was studied. New *C*-chlorophosphorylated enamines were characterized by NMR spectroscopy. A scheme was suggested for the phosphorylation reaction. It was found that the presence of two aryl substituents in the molecule of tertiary ethylamine deactivated the ethyl group to block phosphorylation. Phosphorylation of *N*,*N*-diethylaniline, besides phenyl-substituted phosphorus-containing enamines, also gave phosphorylated enamines chloro-substituted in the ring. Using *N*-ethyl-*N*-methylaniline as an example, a possibility of substitution for two chlorine atoms in the PCl_5 molecule with alkenyl groups was demonstrated.

Key words: tertiary amines, *C*-chlorophosphorylated enamines, phosphorylation, phosphorus pentachloride, NMR spectroscopy.

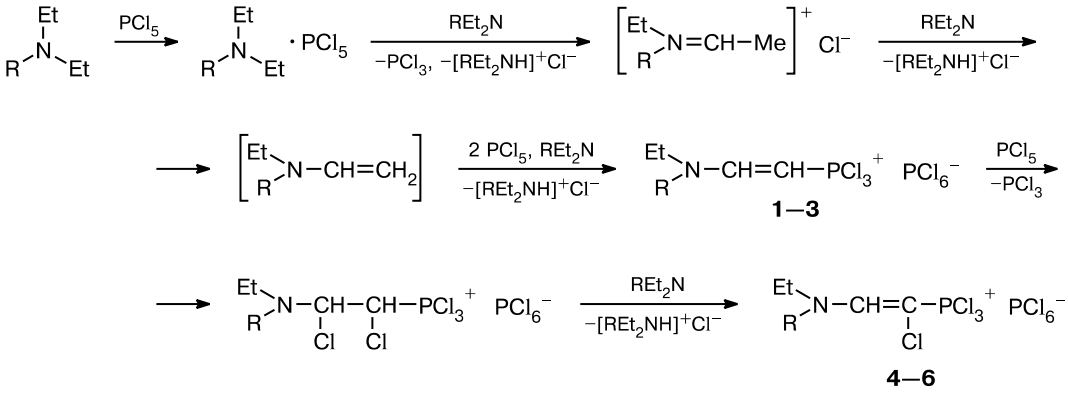
Tertiary amines are known to violently react with phosphorus chlorides. This frequently leads to resinification of the reaction mixture and does not allow one to isolate products as individual compounds. The reactions of tertiary amines with phosphorus chlorides are characterized by the formation of the donor-acceptor complex compounds with subsequent chlorination of the alkyl groups, which in a number of cases leads to iminium salts with the N—C bond cleavage.[1—17] In the presence of excess of tertiary amine, iminium salts are transformed into enamines, which can undergo *C*-phosphorylation with phosphorus pentachloride. For example, *N*-vinylpyrroles substituted in the ring were shown to be easily phosphorylated with phosphorus pentachloride.[18] Enimides and enamides also react with phosphorus pentachloride with the formation of organophosphorus compounds in high yields.[19,20] In addition, many *N*-vinylazoles react with phosphorus pentachloride to give unsaturated organophosphorus compounds.[21,22] An intermediate formation of enamines was detected in the reactions of primary amines with phosphorus pentachloride.[23] A suggestion has been made[23] that the formation of *N*-alkenyl derivatives is characteristic of the chlorination process of aliphatic amines with phosphorus pentachloride. During synthesis of unsaturated organophosphorus compounds from acetonitrile and phosphorus pentachloride,[24] an unsaturated phosphazo compound was formed as the intermediate reaction product very much resembling the *N*-alkenyl derivatives, which, as the authors of the work[23] suggested, were formed in the reaction of primary amines with phosphorus pentachloride. We expected that tertiary amines under certain condition will be phosphorylated with phosphorus pentachloride similarly to dialkyl ethers and dialkyl sulfides.[25]

Earlier, we have shown[26] that phosphorylation of some tertiary amines with phosphorus pentachloride led to *C*-chlorophosphorylated enamines. In the present work, we studied phosphorylation of tertiary *N*-ethylamines with phosphorus pentachloride in greater details using 2D and multinuclear ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. It was found that tertiary amines, in the molecules of which at least two ethyl groups are present (triethylamine, diethylaniline, diethylbenzylamine), reacted with phosphorus pentachloride under mild condition (15—20 °C) to give 2-aminoethenyltrichlorophosphonium hexachlorophosphorates (**1**—**3**) and 2-amino-1-chloroethenyltrichlorophosphonium hexachlorophosphorates (**4**—**6**). The following sequence of transformations was suggested to explain the formation of compounds **1**—**6** (Scheme 1).

Apparently, the reaction starts with the appearance of donor-acceptor complexes of tertiary amines with phosphorus pentachloride, similar to the complex compounds described in the literature.[2—14] Then, the complex compounds undergo chlorination at the methylene group at α-position to the nitrogen atom. Because of instability of tertiary α-chloroamines, they lose the chlorine as an anion, that leads to the formation of iminium salts. In the pres-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0040—0047, January, 2013.

Scheme 1



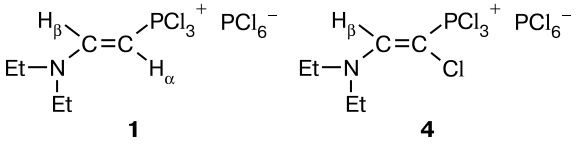
R = Et (**1**, **4**), $PhCH_2$ (**2**, **5**), Ph (**3**, **6**)

ence of excess of tertiary amine, the iminium salts undergo dehydrochlorination, being converted to enamines. The latter are phosphorylated with phosphorus pentachloride similarly to the known enamines.[18—22]

N-Alkyl(aryl)-substituted *N*-vinylamines are the representatives of highly nucleophilic enamines whose reactions with phosphorus pentachloride are usually accompanied by deep resinification caused, probably, by the presence of hydrogen chloride in the reaction medium. For example, such a resinification was observed in the phosphorylation of *N*,*N*-diphenylvinylamine.[19] In contrast to *N*,*N*-diphenylvinylamine, enamines formed from tertiary amines containing at least two ethyl group at the nitrogen atom do not undergo side reactions leading to resinification. Probably, this can be explained by the presence in the reaction medium of tertiary amines combining with hydrogen chloride.

β-Phosphorylated vinyl ethers formed by phosphorylation of dialkyl ethers do not undergo chlorination at the double bond with phosphorus pentachloride.[25] β-Phosphorylated enamines **1**—**3** obtained from tertiary amines possess an increased nucleophilicity of the double bond and are easily chlorinated with phosphorus pentachloride at the double bond in the reaction medium because of the stronger electron-donating properties of the dialkyl- and alkyl(aryl)amino groups as compared to the alkoxy groups of β-phosphorylated vinyl ethers. Less nucleophilic double bonds in phosphorylated derivatives of *N*-vinylheterocycles, for example, *N*-vinylbenzotriazole[22] and *N*-vinylcarbazole[27], do not undergo chlorination.

The chlorination products of the double bonds of β-phosphorylated enamines **1**—**3** are further dehydrochlorinated due to the high C—H acidity of H_α proton placed near the positively charged trichlorophosphonium group (see Scheme 1). This was confirmed by the studies of the reaction mixtures by ^{31}P NMR spectroscopy. For example, two signals are present in the ^{31}P NMR spectrum of the reaction products of phosphorus pentachloride with triethylamine: a doublet of doublets at δ 89.9 ($J(P,H_\alpha)$ = 35.0 Hz, $J(P,H_\beta)$ = 25.9 Hz) and a doublet at δ 80.7 ($J(P,H_\beta)$ = 14.1 Hz) attributable to organyltrichlorophosphonium cations **1** and **4**.

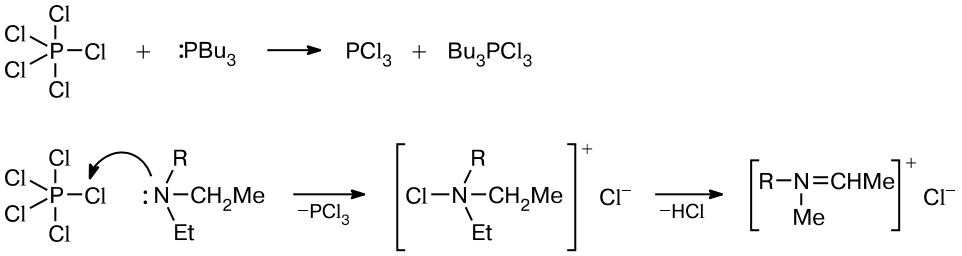


The content of compound **1** in the reaction mixture decreases with time, whereas the content of β-phosphorylated β-chloroenamine (**4**) increases. This indicates that enamine **4** is formed from enaminotrichlorophosphonium hexachlorophosphorate (**1**). After the formation of β-phosphorylated β-chloroenamine (**4**), the phosphorylation process is stopped. The less probable seems the scheme of phosphorylation of tertiary diethylamines, which includes formation of iminium salts $R(Et)N{=}CH{-}Me^+Cl^-$ and starts from the initial attack by the tertiary amine on the electropositive chlorine atom covalently bonded to the phosphorus in the PCl_5 molecule, rather than on the phosphorus atom.

It is known[28] that tertiary phosphines reduce PCl_5, undergoing oxidative chlorination (Scheme 2). If to assume that similar reaction takes place in the initial step of the reaction of tertiary amines with phosphorus pentachloride, then the scheme for the formation of iminium salts $R(Et)N{=}CH{-}Me^+Cl^-$ will look like shown in Scheme 2.

According to this scheme, electrophilic properties in the reaction with tertiary amine are possessed by the chlorine atom in the molecule of phosphorus pentachloride, that leads to the reduction of phosphorus pentachloride to phosphorus trichloride and the formation of quaternary *N*-chloroammonium chloride. The dehydrochlorination of the latter results in the iminium salt.

Scheme 2



Unstable quaternary *N*-chloroammonium chlorides according to the literature data[29,30] can be formed by the reaction of tertiary amines with molecular chlorine in tetrachloromethane. However, it should be taken into account that the existence of such quaternary salts was not strictly confirmed and was challenged by other authors.[13] An argument against this scheme of phosphorylation of tertiary amines is also the fact that halophilic reactions suggest involvement of "soft" nucleophilic agents, whereas tertiary amines are "hard" bases.[28] It is known that in the reaction with "hard" pyridine bases, the acceptor properties in the donor-acceptor bond are exhibited by the phosphorus atom of phosphorus pentachloride. Stable phosphorus-centered donor-acceptor complexes of different pyridines with PCl_5 with the hexacoordinated phosphorus atom in the complex are studied.[9] Therefore, it is most likely that the phosphorus-centered donor-acceptor complexes are formed in the first step of the reaction of tertiary amines with PCl_5 as a result of the attack of the base on the phosphorus atom.

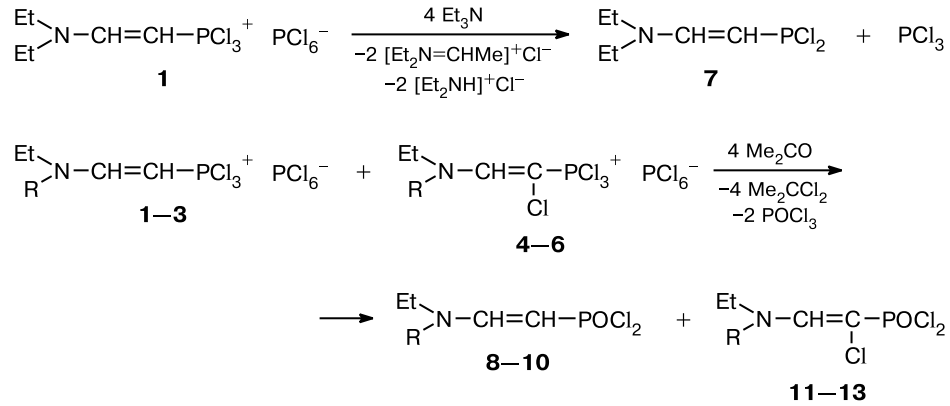
Carrying out the phosphorylation of triethylamine in the presence of excess of amine led to the arising in the reaction medium of 2-(diethylamino)ethenylphosphinic dichloride (**7**), which was indicated by the presence of the signal in the region δ 160 in the ^{31}P NMR spectrum. Apparently, compound **7** was formed through the reduction of 2-aminoethenyl-1-trichlorophosphonium hexachlorophosphorate (**1**) with the excess of amine (Scheme 3).

It was impossible to separate crystalline enaminotrichlorophosphonium hexachlorophosphorates **1**—**6** from triorganylammonium chlorides present in the reaction mixture, since solubility of compounds **1**—**6** in organic solvents is close to that of triorganylammonium salts. This poses a serious preparative problem in the studies of phosphorylation of tertiary amines with phosphorus pentachloride. Phosphorylation products of tertiary amines can be obtained in the pure form if enaminotrichlorophosphonium hexachlorophosphorates can be converted into phosphonic dichlorides **8**—**13**, that can be achieved by treatment of compounds **1**—**6** with sulfur dioxide or anhydrous acetone (see Scheme 3). Since hydrochlorides of tertiary amines are insoluble in diethyl ether, in contrast to phosphonic chlorides, compounds **8**—**13** were successfully isolated in the pure form by extraction with diethyl ether.

The structures of phosphorus-containing enamines **1**—**6** and **8**—**13** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Tables 1 and 2).

The spin-spin coupling constants $^3J(H_\alpha,H_\beta)$ (13—14 Hz) for those phosphorylated enamines which have both vinyl protons in the molecule indicate the *trans*-orientation of

Scheme 3



R = Et (**1**, **4**, **8**, **11**), $PhCH_2$ (**2**, **5**, **9**, **12**), Ph (**3**, **6**, **10**, **13**)

Table 1. Parameters of ^{1}H and ^{31}P NMR spectra of compounds **1—6** and **8—13**

Compound	R	X	$^{1}H^{a}$								$^{31}P^{b}$	
			δ					*J*/Hz			δ	$^{3}J(P,H_\beta)$/Hz
			H_α	H_β	Ph	CH_2	Me	H_α,H_β	P,H_α	P,H_β		
1	Et	H_α	5.65	8.00	—	—	—	13.7	33.7	25.9	89.9	25.9
2	$PhCH_2$	H_α	5.50	7.81	—	—	—	13.9	34.0	23.8	80.1	23.8
3	Ph	H_α	4.55	7.60	—	—	—	13.1	34.3	21.4	79.8	21.4
4	Et	Cl	—	7.50	—	—	—	—	—	14.1	80.7	14.1
5	$PhCH_2$	Cl	—	7.65	—	—	—	—	—	13.9	82.0	13.9
6	Ph	Cl	—	7.50	—	—	—	—	—	13.7	72.0	13.7
8	Et	H_α	5.12	7.06	—	3.51	1.27	13.7	25.8	21.5	35.0	21.5
9	$PhCH_2$	H_α	5.20	7.25	7.1—7.5	3.2—3.5	1.28	14.2	25.5	21.2	36.2	21.9
10	Ph	H_α	4.95	7.20	7.1—7.3	3.93	1.25	14.1	26.4	21.8	37.0	21.8
11	Et	Cl	—	7.15	7.2—7.4	3.35	1.18	—	—	11.6	36.1	11.6
12	$PhCH_2$	Cl	—	7.34	7.1—7.4	3.3—3.5	1.23	—	—	12.1	35.9	12.1
13	Ph	Cl	—	7.51	7.2—7.5	3.55	1.20	—	—	11.1	34.8	11.4

[a] It is impossible to assign chemical shift for both the ethyl and phenyl groups in compounds **1—6**, since them and tertiary amine hydrochlorides present in the crystalline reaction product have similar ethyl and phenyl substituents.
[b] The PCl_6^- anion in organyltrichlorophosphonium hexachlorophosphorates **1** and **3—6** has a singlet signal in the region δ −(297—298). For $Ph_2N—CH=C(Cl)$, the values $\delta(^{31}P) = 34.6$, $^{3}J(P,H_\beta) = 11.6$ Hz.

H_α and H_β protons. The NMR spectra of β-phosphorylated β-chloroenamines are characterized by the decreased spin-spin coupling constant values $^{3}J(P,H)$ by 7—10 Hz as compared to β-phosphorylated enamines containing no chlorine atom at the double bond. This fact can be used for the identification of chlorophosphorylated enamines. For example, *N*,*N*-diphenylvinylamine reacts with PCl_5 in benzene with an instant resinification and darkening of the reaction mixture. Using ^{31}P NMR spectra, 1-chloroethenyl-2-diphenylaminophosphonic dichloride was identified in the reaction mixture after it was treated with sulfur dioxide.[19]

The ^{31}P NMR spectrum was assigned to 1-chloroethenyl-2-diphenylaminophosphonic dichloride based on the comparison with the NMR data for phosphorus-containing enamines of similar structure (see Table 1) obtained by phosphorylation of tertiary diethylamines.

The presence in compounds **4—6** and **11—13** of the chlorine atom at the carbon atom the closest to the phosphorus-containing substituent was unambiguously confirmed by ^{13}C NMR spectroscopy (see Table 2). The bonding of the vinyl proton to the carbon atom of the multiple bond the closest to the nitrogen atom of the amino group follows from the ^{13}C NMR spectra, in which a large spin-spin coupling constant $^{1}J(C,H)$ = 164—168 Hz is observed. The spin-spin coupling constants $^{2}J(C,P)$ = = 35—40 Hz indicate the *trans*-(PN)-configuration (*E*-isomers) of compounds **4—6** and **11—13**. A similar pattern was observed[21] in the studies of phosphorylation products of *N*-vinylpyrazoles and a number of other enamines. The conclusions obtained based on the ^{13}C NMR spectroscopic data are in good agreement with the results obtained by ^{31}P NMR spectroscopy. A low value of $^{3}J(P,H)$ (11.5—26 Hz, see Table 1) indicates the *cis*-orientation of the phosphorus relative to β-vinyl proton. For the *trans*-orientation, the $^{3}J(P,H)$ values reach 54—68 Hz, that was demonstrated in the work.[21]

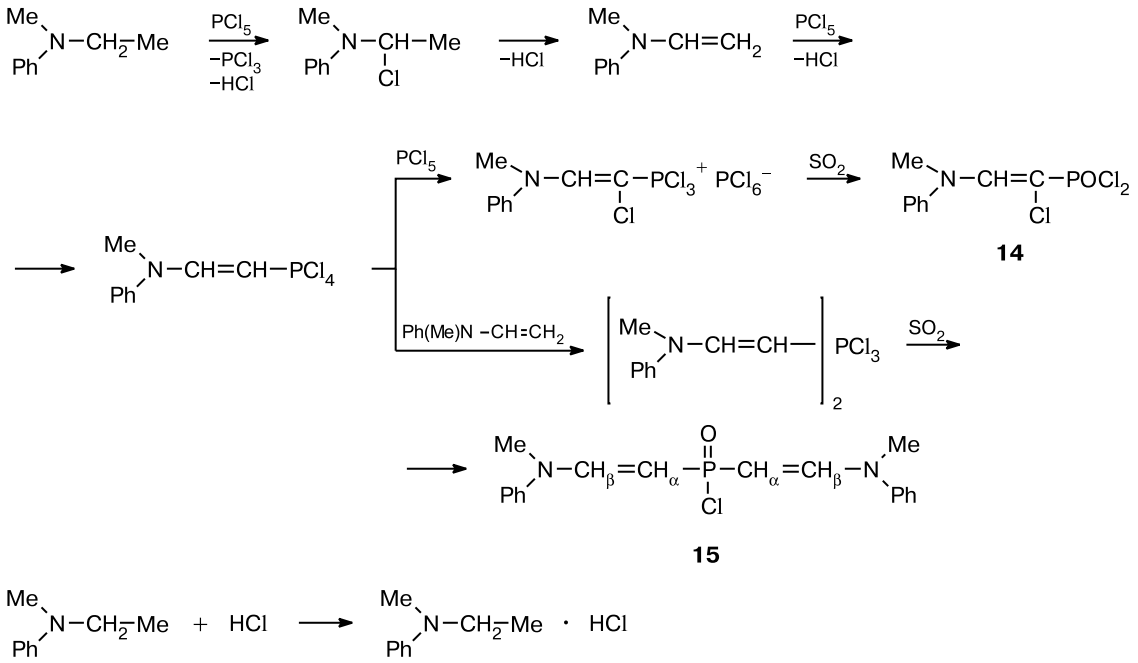
A different pattern is observed in the reaction of phosphorus pentachloride with tertiary amines containing a single ethyl group. The bonding of the amine nitrogen atom with two aryl substituents completely deactivated the ethyl group. Thus, when the reaction between phos-

Table 2. Parameters of ^{13}C NMR spectra of compounds **1—6** and **8—13**

Compound	δ,		*J*/Hz	
	C_α	C_β	$^{1}J(P,C_\alpha)$	$^{2}J(P,C_\alpha)$
1	81.47	153.25	195.4	47.3
2	80.92	155.12	200.2	48.1
3	80.29	150.40	200.8	52.7
4	77.26	158.11	187.1	37.5
5	77.82	157.20	179.5	35.4
6	75.64	159.21	159.6	30.9
8	85.11	150.88	208.9	38.9
9	86.23	149.27	203.8	37.1
10	85.32	150.10	201.4	32.8
11*	86.64	145.19	212.5	39.4
12	86.02	148.95	210.3	39.8
13	84.57	151.44	200.4	33.5

* ^{13}C NMR spectrum of compound **11** (δ: 14.84 (Me); 46.91 (CH_2); 86.64 (CCl, $^{1}J(P,C)$ = 212.5 Hz); 145.16 (CH, $^{2}J(P,C)$ = 39.4 Hz), $^{1}J(C,H)$ = 165.7 Hz).

Scheme 4

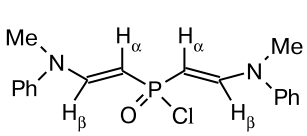


phorus pentachloride and *N*-ethylcarbazole was carried out in benzene, only change of the solution color to cherry was observed. In this case, no crystalline precipitate was formed even after keeping the reaction mixture for 3 days (a crystalline precipitate should be formed in the case of phosphorylation involving the ethyl group and formation of ethenylcarbazolyltrichlorophosphonium hexachlorophosphorate).

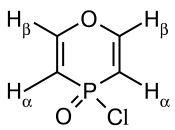
In the ^{31}P NMR spectrum of the reaction solution, besides the signal at δ –81 attributable to the phosphorus in phosphorus pentachloride, a small signal is present in the region δ 219 corresponding to phosphorus trichloride. The presence of the latter signal indicates the chlorination processes taking place, but it is impossible to find out which group (the aromatic ring or the ethyl group) is chlorinated. Most likely, ethylcarbazole is chlorinated in the ring, which, due to the increase of the electron-accepting properties of the chlorinated heterocycle, additionally deactivated the *N*-ethyl group and hinders its phosphorylation.

We have found that the phosphorylation of *N*-ethyl-*N*-methylaniline whose molecule also has the only ethyl group can lead to the substitution of two chlorine atoms in the PCl_5 molecule with the alkenyl moieties and the formation of enaminophosphinic acid derivatives. Besides reaction pathways described above and leading to the formation of β-phosphorylated β-chloroenamine **14**, a second direction, giving rise to bis[2-(*N*-methyl-*N*-phenylamino)ethenyl]phosphinic chloride, is effected (**15**) (Scheme 4).

In the ^{31}P NMR spectrum, besides the doublet signal at δ 34.2 with the value $^3J(P,H_\beta)$ = 11.8 Hz characteristic of 2-diorganylamino-1-chloroethenylphosphonic chlorides, which belongs to compound **14**, a signal at δ 35.6 (tt, $^3J(P,H_\beta)$ = 16.4 Hz, $^2J(P,H_\alpha)$ = 5.1 Hz) is also present. The indicative splitting of this signal (the triplet of triplets) unambiguously indicates the bonding of the phosphorus atom to two vinyl groups in compound **15**.



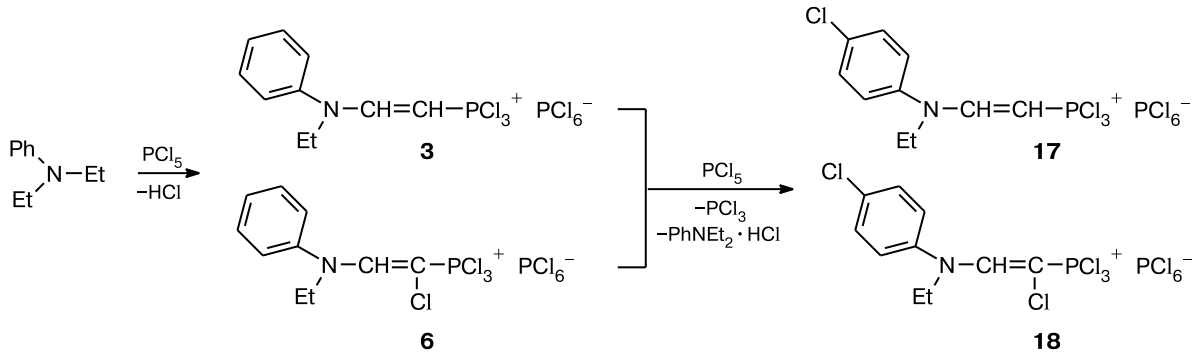
15



16

As a comparison, we can show the NMR spectral characteristics of oxaphosphine (**16**) (δ(^{31}P) = 10.7 (tt, $^3J(P,H_\beta)$ = 31.4 Hz, $^2J(P,H_\alpha)$ = 1.5 Hz)), in which the chlorophosphoryl group (POCl) is also bonded to two vinyl groups, but because of the imposed steric configuration of the heterocycle of compound **16**, the vinyl protons are *cis*-oriented with respect to each other.[31] In compound **16**, the spin-spin coupling constant $J(P,H_\beta)$ is twice as large than in compound **15**, that is in good agreement with the different geometry of the structural fragments of these molecules including the chlorophosphoryl group and the vinyl proton H_β. Similar conclusions follow from the comparison of the spin-spin coupling constants: $J(H_\alpha,H_\beta)$ = 12 and 6.4 Hz for compounds **15** and **16**, respectively.

Scheme 5



The studies of the reaction of *N*,*N*-diethylaniline with phosphorus pentachloride in tetrachloromethane showed that, besides the phosphorylation reaction of the intermediately formed enamine and subsequent chlorination of the double bond of β-phosphorylated enamine, a new direction of the process was realized: chlorination of the benzene ring.

The chlorination of *N*,*N*-dialkylanilines at *ortho*- or *para*-position of the aromatic ring with phosphorus pentachloride is quite expected, since the phenyl ring is activated with the electron-donating substituent, the dialkylamino group, whereas the noticeable electrophilic properties of the chlorine in phosphorus pentachloride are a known fact.[28]

The conclusion that the chlorination in the benzene ring of the organophosphorus compounds formed also occurred in the course of phosphorylation of *N*,*N*-diethylaniline in tetrachloromethane was drawn by us based on the ^{31}P NMR spectroscopic data. Four signals are observed in the ^{31}P NMR spectrum in the region for the resonance signals of the organyltrichlorophosphonium cations. The signal at δ 79.8 (a doublet of doublets) with the spin-spin coupling constant $^{2}J(P,H_{\alpha})$ = 34.3 Hz and $^{3}J(P,H_{\beta})$ = 21.4 Hz belongs to compound **3**. A more downfield signal of lower intensity at is observed δ 82.7, which is also split in a doublet a doublets with very close spin-spin coupling constants: $^{2}J(P,H_{\alpha})$ = 33.6 Hz and $^{3}J(P,H_{\beta})$ = = 22.9 Hz. We assigned this signal to compound **17**. Chlorination of the ethyl group in hexachlorophosphorate **3** is hardly probable, since an acceptor ethenyltrichlorophosphonium group is bonded to the nitrogen atom. An electrophilic substitution of a hydrogen at *para*-position of the phenyl ring as the least sterically hindered is more probable (Scheme 5).

Two doublets of different intensity are observed in the high field of the spectrum. The most strong doublet at δ 72.0 with $^{3}J(P,H_{\beta})$ = 13.7 Hz is attributable to compound **6** and completely agrees with the characteristics of hexachlorophosphorate **6** obtained when the synthesis was carried out in benzene (see Table 1). The less strong doublet we assign to compound **18**. Its chemical shift is at δ 74.0, whereas the spin-spin coupling constant $^{3}J(P,H_{\beta})$ = = 14.5 Hz. These parameters of the ^{31}P NMR spectrum indicate a close likeness of compounds **6** and **18**.

In conclusion, ^{31}P NMR spectroscopy is a reliable and versatile method for establishing stereochemical structure of phosphorylation products of organic compounds with tetra-, penta-, and hexacoordinated phosphorus.[32—40]

Experimental

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DPX-400 and Bruker AV-400 spectrometers (400.13, 100.62, and 161.98 MHz, respectively) in $CDCl_3$, $MeNO_2$, or $PhNO_2$ at ~20 °C. NMR studies of all the hexachlorophosphorates **1**—**4**, **9**, **11**, **13**, and **18** were performed in $MeNO_2$. ^{1}H and ^{13}C NMR chemical shifts were measured relative to Me_4Si with the accuracy of 0.01 and 0.02 ppm, respectively. ^{31}P NMR chemical shift were recorded relative to 85% aqueous H_3PO_4 as an internal standard with the accuracy of 0.1 ppm, constants were measured with the accuracy of 0.1 Hz.

Mixture of enaminotrichlorophosphonium hexachlorophosphorates 1, 4 and triethylammonium chloride. A solution of triethylamine (1.9 g, 0.02 mol) in tetrachloromethane (5 mL) was added dropwise to a colorless solution of phosphorus pentachloride (3.1 g, 0.015 mol) in anhydrous tetrachloromethane (20 mL) at 15—20 °C with stirring and cooling with water. A mixture of phosphorylation products and triethylammonium chloride formed as a finely dispersed white precipitate was filtered off by the reverse filtration of and dried *in vacuo*. A white powder (4.5 g) easily hydrolizable by air moisture was obtained, m.p. 153—158 °C (with decomp.). The crystals were studied by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy in solution in $MeNO_2$ (see Tables 1 and 2).

2-Diethylaminoethenylphosphonic dichloride (8) and 1-chloroethenyl-2-diethylaminophosphonic dichloride (11). Anhydrous acetone (3 mL) was added to a dispersion of crystals of a mixture of triethylammonium chloride and compounds **1**, **4** (4 g) in anhydrous diethyl ether (10 mL). After 24 h, the undissolved triethylammonium chloride was filtered off, diethyl ether was evaporated *in vacuo*, whereas a residual mixture of enaminophosphonic chlorides **8**, **11** obtained as a light yellow oil was studied

by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy in $CDCl_3$ (see Tables 1 and 2). The yield was 0.6 g.

Dichloride 11 (synthesis in benzene). A solution of triethylamine (3.8 g, 0.04 mol) in benzene (10 mL) was added dropwise to a solution of phosphorus pentachloride (6.3 g, 0.03 mol) in anhydrous benzene (40 mL) at 15—20 °C with stirring and cooling. A white precipitate formed over 24 h acquired a light orange color. The reaction mixture was treated with sulfur dioxide until the precipitate was dissolved and a homogeneous solution was formed. The solvent and volatile side products were evaporated *in vacuo*. The residue was extracted with diethyl ether to obtain a brown oil containing according to the ^{31}P NMR data 1-chloroethenyl-2-diethylaminophosphonic dichloride (**11**). Triethylammonium chloride was not extracted with diethyl ether. Recrystallization of the brown oil from anhydrous hexane gave pure compound **11** in 0.5 g (20%) yield. White crystals, m.p. 53 °C. Found (%): C, 28.56; H, 4.59; Cl, 42.60; N, 5.77; P, 12.51.

Dichloride 11 (synthesis in chloroform). A solution of triethylamine (3.8 g, 0.04 mol) in chloroform (5 mL) was added dropwise to a solution of phosphorus pentachloride (6.3 g, 0.03 mol) in anhydrous chloroform (50 mL) with stirring and cooling with water, then the solvent was evaporated *in vacuo*. A brownish gray precipitate was treated with sulfur dioxide, cooling the flask with cold water until a homogeneous solution was formed. Volatile impurities were evaporated *in vacuo*, whereas dichloride **11** was extracted from the residue with diethyl ether and twice recrystallized from anhydrous hexane. The yield was 1.5 g (60%). White crystals, m.p. 53—54 °C. Found (%): C, 28.36; H, 4.69; Cl, 42.30; N, 5.67; P, 12.20. $C_6H_{11}Cl_3NOP$. Calculated (%): C, 28.67; H, 4.42; Cl, 42.46; N, 5.59; P, 12.36.

2-(*N*-Benzyl-*N*-ethylamino)-1-chloroethenylphosphonic dichloride (12). A solution of diethylbenzylamine (13 g, 0.08 mol) in benzene (10 mL) was added dropwise to a solution of phosphorus pentachloride (12.5 g, 0.06 mol) in anhydrous benzene (60 mL) with stirring. To keep the temperature within 15—20 °C, the mixture was cooled with cold water. After 2 days, a jelly-like white precipitate was filtered off and studied by NMR spectroscopy. The mixture contained organyltrichlorophosphonium hexachlorophosphorate (**5**) and diethylbenzylammonium hydrochloride. The reaction mixture was treated with sulfur dioxide until a homogeneous solution was formed. Then (as in the experiments with triethylamine), the solvent and volatile side products were evaporated. The residue, a dense brown liquid, was extracted with diethyl ether to obtain uncrystallizing light yellow oil, which according to the ^{31}P and ^{1}H NMR data was the dichloride **12** (see Tables 1 and 2). The yield was 3.3 g (70%). Found (%): C, 41.75; H, 4.20; Cl, 32.95; N, 4.06; P, 10.40. $C_{11}H_{13}Cl_3NOP$. Calculated (%): C, 42.20; H, 4.16; Cl, 34.08; N, 4.48; P, 9.92.

A mixture of enaminotrichlorophosphonium hexachlorophosphorates 3, 6 and diethyl(phenyl)ammonium chloride. A solution of *N*,*N*-diethylaniline (6 g, 0.04 mol) in benzene (10 mL) was added dropwise to a solution of phosphorus pentachloride (6.3 g, 0.03 mol) in anhydrous benzene (50 mL) at 15—20 °C with stirring and cooling. A light yellow precipitate, a mixture of phosphorylation products **3**, **6** and diethyl(phenyl)ammonium chloride, was filtered off by reverse filtration and dried *in vacuo*. A yellow powder easily hydrolizable by air moisture. The yield was 10.5 g, m.p. 182—194 °C (with decomp.). The crystals were studied by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy in solutions in $MeNO_2$ (see Tables 1 and 2).

2-(*N*-Ethylanilino)ethenylphosphonic dichloride (10) and 2-(*N*-ethylanilino)-1-chloroethenylphosphonic dichloride (13). Anhydrous acetone (4 mL) was added to a dispersion of crystals of a mixture of diethyl(phenyl)ammonium chloride and compounds **3**, **6** (4.5 g) in anhydrous diethyl ether (15 mL). After 24 h, the undissolved diethyl(phenyl)ammonium chloride was filtered off, diethyl ether was evaporated, whereas a residual oily mixture of enaminophosphonic chlorides **8**, **11** was studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy in $CDCl_3$ (see Tables 1 and 2). The yield was 0.5 g.

Dichloride 13 (synthesis in chloroform). A solution of *N*,*N*-diethylaniline (6 g, 0.04 mol) in chloroform (10 mL) was added in portions to a solution of phosphorus pentachloride (6.3 g, 0.03 mol) in chloroform (60 mL) at 15—20 °C with stirring and intensive cooling of the flask with a stream of cold water. After 2 days, the solvent was evaporated *in vacuo*, a precipitate was treated with sulfur dioxide, volatile products were evaporated *in vacuo*. Dichloride **13** was extracted with diethyl ether. Diethyl ether was evaporated from the extract, whereas the precipitate was recrystallized from anhydrous hexane. The yield was 0.6 g (28%), light yellow crystals, m.p. 82—83 °C. Found (%): C, 40.80; H, 4.13; Cl, 35.00; N, 5.20; P, 9.80. $C_{10}H_{11}Cl_3NOP$. Calculated (%): C, 40.20; H, 3.69; Cl, 35.67; N, 4.70; P, 10.38.

Phosphorylation of *N*,*N*-diethylaniline with phosphorus pentachloride in tetrachloromethane. A solution of *N*,*N*-diethylaniline (3 g, 0.02 mol) in tetrachloromethane (10 mL) was added dropwise to a solution of phosphorus pentachloride (3.2 g, 0.015 mol) in anhydrous tetrachloromethane (40 mL) at ~20 °C with stirring and cooling by water. A light yellow finely crystalline precipitate formed was filtered off after 24 h, washed with tetrachloromethane, and dried *in vacuo*. The yield was 3.8 g, a light yellow powder easily hydrolizable in air, m.p. 193—198 °C (with decomp.). According to the ^{31}P NMR spectroscopic data (see Table 1, a solution in $MeNO_2$), the crystalline reaction product contained 2-(*N*-ethylanilino)ethenylphosphonium hexachlorophosphorate (**3**), 2-(*N*-ethylanilino)-1-chloroethenylphosphonium hexachlorophosphorate (**6**), and chlorination products of hexachlorophosphorates **3**, **6** in the benzene ring, compounds **17**, **18**.

Phosphorylation of *N*-ethyl-*N*-methylaniline with phosphorus pentachloride. Similarly to the syntheses which used *N*,*N*-diethylaniline, the use of PCl_5 (3.8 g, 0.02 mol) and *N*-ethyl-*N*-methylaniline (3.3 g, 0.025 mol) in benzene (50 mL) gave a crystalline product, which after 2 days was filtered off, washed with benzene, and treated with sulfur dioxide until a homogeneous solution was formed. Volatile products were evaporated by careful heating. The residue was extracted with diethyl ether to obtain 1-chloroethenyl-2-(*N*-methyl-*N*-phenylamino)phosphonic chloride (**14**) and bis[2-(*N*-methyl-*N*-phenylamino)ethenyl]phosphinic chloride (**15**). The yield was 0.8 g, light yellow oil. The phosphorylation products were studied by ^{31}P and ^{1}H NMR spectroscopy in $CDCl_3$. No preparative separation of compounds **14** and **15** was attempted.

References

1. H. Wieland, *Chem. Ber.*, 1907, **40**, 4260.
2. M. J. Deveney, M. Webster, *Inorgan. Nucl. Chem. Lett.*, 1967, **3**, 195.
3. W. Wieker, A. Grimmer, *Z. Chem.*, 1967, **7**, 434.

4. K. Hensen, W. Sarholz, *Theoret. Chim. Acta*, 1968, **12**, 206.
5. M. Webster, M. Deveney, *J. Chem. Soc.*, 1968, **A**, 2166.
6. J. R. Beattie, T. R. Gilson, G. A. Ozin, *J. Chem. Soc.*, 1968, **A**, 2772.
7. R. C. Paul, H. Khurana, S. R. Chadha, *J. Ind. Chem. Soc.*, 1969, **46**, 915.
8. R. C. Paul, S. L. Sehgal, S. R. Chadha, *J. Ind. Chem. Soc.*, 1970, **47**, 1071.
9. K. B. Dillon, R. N. Reeve, T. S. Waddington, *J. Chem. Soc., Dalton Trans.*, 1977, **11**, 1410.
10. K. B. Dillon, R. N. Reeve, T. S. Waddington, *J. Chem. Soc., Dalton Trans.*, 1977, **23**, 2382.
11. W. P. Trost, *Canad. J. Chem.*, 1954, **32**, 356.
12. R. R. Holmes, E. F. Bertaut, *J. Am. Chem. Soc.*, 1958, **80**, 2980.
13. J. R. Beattie, M. Webster, *J. Chem. Soc.*, 1961, **82**, 1730.
14. R. C. Paul, S. R. Chadha, *Ind. J. Chem.*, 1968, **6**, 754.
15. *Iminium Salts in Organic Chemistry*, Ed. H. Bohme, H. L. Viene, New York—London—Sydney—Toronto, 1976, Part I, 619 pp.
16. V. P. Kukharʹ, M. V. Shevchenko, *Zh. Obshch. Khim.*, 1982, **52**, 562 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1982, **52**].
17. M. V. Shevchenko, V. P. Kukharʹ, *Zh. Obshch. Khim.*, 1984, **54**, 1499 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1984, **54**].
18. V. G. Rozinov, G. A. Pensionerova, V. I. Donskikh, L. M. Sergienko, O. V. Petrova, A. V. Kalabina, A. I. Mikhaleva, *Zh. Obshch. Khim.*, 1984, **54**, 2241 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1984, **54**].
19. V. G. Rozinov, L. P. Izhboldina, G. A. Pensionerova, V. I. Donskikh, S. F. Malysheva, N. G. Glukhikh, L. M. Sergienko, G. V. Ratovskii, *Zh. Obshch. Khim.*, 1984, **54**, 1051 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1984, **54**].
20. V. G. Rozinov, L. P. Izhboldina, S. F. Malysheva, V. I. Donskikh, A. V. Kalabina, *Zh. Obshch. Khim.*, 1983, **53**, 934 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1983, **53**].
21. L. I. Larina, V. G. Rozinov, M. Yu. Dmitrichenko, L. A. Esrkova, *Magn. Reson. Chem.*, 2009, **49**, 149.
22. V. G. Rozinov, G. A. Pensionerova, V. I. Donskikh, A. V. Kalabina, E. S. Domnina, G. G. Skvortsova, *Zh. Obshch. Khim.*, 1983, **53**, 697 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1983, **53**].
23. I. N. Zhmurova, B. S. Drach, *Tr. IV konf. "Khimiya i primenenie fosfororganicheskikh soedinenii"* [*Trans. IV Conf. "Chemistry and Application of Organophosphorus Compounds"*] *(Kazan, 1969)*, Nauka, Moscow, 1972, p. 312 (in Russian).
24. V. I. Shevchenko, A. V. Kirsanov, *Uspekhi khimii fosfororganicheskikh i seraorganicheskikh soedinenii* [*Achievements in Chemistry of Organophosphorus and Organosulfur Compounds*], Ed. A. V. Kirsanov, Naukova Dumka, Kiev, 1969, **1**, p. 44 (in Russian).
25. K. A. Petrov, M. A. Raksha, *Zh. Obshch. Khim.*, 1975, **45**, 1503 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1975, **45**].
26. G. A. Pensionerova, V. G. Rozinov, V. I. Glukhikh, *Zh. Obshch. Khim.*, 1978, **48**, 2796 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1978, **48**].
27. V. G. Rozinov, G. A. Pensionerova, V. I. Donskikh, L. M. Sergienko, S. E. Korostova, A. I. Mikhaleva, G. V. Dolgushin, *Zh. Obshch. Khim.*, 1986, **56**, 790 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1986, **56**].
28. B. V. Timokhin, *Russ. Chem. Rev.*, 1985, **54**, 1201.
29. *Comprehencive Organic Chemistry. The Synthesis and Reaction of Organic Compounds*, Eds B. D. Barton, W. D. Ollis, Vol. **2**, Pergamon Press, Oxford, 1979, p. 539.
30. H. Bohme, W. Krause, *Chem. Ber.*, 1951, **84**, 170.
31. V. G. Rozinov, V. E. Kolbina, V. I. Donskikh, *Zh. Obshch. Khim.*, 1987, **57**, 954 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1987, **57**].
32. L. I. Larina, M. Yu. Dmitrichenko, V. G. Rozinov, A. V. Benedyuk, *Zh. Obshch. Khim.*, 2005, **75**, 520 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2005, **75**].
33. A. A. Borisov, L. I. Larina, M. Yu. Dmitrichenko, V. G. Rozinov, A. V. Benedyuk, *Zh. Obshch. Khim.*, 2005, **75**, 1755 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2005, **75**].
34. L. I. Larina, V. G. Rozinov, G. V. Bozhenkov, E. V. Abramova, A. A. Borisov, M. Yu. Dmitrichenko, *14th Intern. Conf. on Chemistry of Phosphorus Compounds* (*Kazan, June 27—July 1, 2005, Abstrs)*, Kazan, 2005, p. 87.
35. L. I. Larina, E. V. Rudyakova, V. A. Savosik, G. G. Levkovskaya, V. G. Rozinov, M. Yu. Dmitrichenko, *Zh. Obshch. Khim.*, 2009, **79**, 1046 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2009, **79**].
36. L. I. Larina, V. G. Rozinov, E. V. Rudyakova, V. A. Savosik, G. G. Levkovskaya, M. Yu. Dmitrichenko, I. A. Bidusenko, *Zh. Obshch. Khim.*, 2010, **80**, 347 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2010, **80**].
37. K. A. Chernyshev, L. I. Larina, E. A. Chirkina, V. G. Rozinov, L. B. Krivdin, *Zh. Org. Khim.*, 2011, **47**, 1823 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2011, **47**].
38. K. A. Chernyshev, L. I. Larina, E. A. Chirkina, V. G. Rozinov, L. B. Krivdin, *Zh. Org. Khim.*, 2011, **47**, 1829 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2011, **47**].
39. K. A. Chernyshev, L. I. Larina, E. A. Chirkina, V. G. Rozinov, L. B. Krivdin, *Zh. Org. Khim.*, 2011, **48**, 679 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2011, **48**].
40. L. I. Larina, V. G. Rozinov, K. A. Chernyshev, *Zh. Obshch. Khim.*, 2012, **82**, 76 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2012, **82**].

Received November 2, 2012;
in revised form December 11, 2012