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Reactions of α-Aminoalkylphosphonates with Iso(thio)cyanatophosphates(phosphonates, phosphinates). Synthesis of 1,3,4-Diazaphospholidines and 1,3,4-Oxaza(thiaza)phospholines

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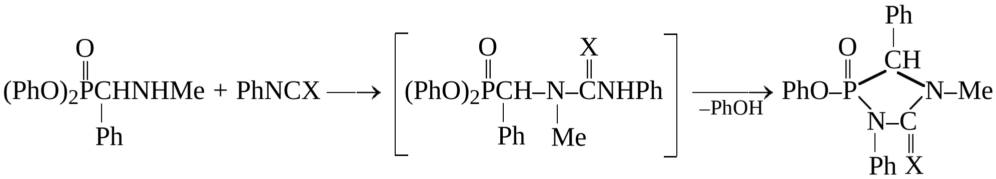
Abstract — Phenyl α-aminoalkylphosphonates add to phenyl iso(thio)cyanates to give saturated heterocycles, 1,3,4-diazaphospholidin-2-(thi)ones. The reaction of diphenyl (α-methylamino)benzylphosphonate with diethyl isothiocyanatophosphate involves initial formation of 1,3,4-tiazaphospholidine-2-thiones containing exo- and endocyclic phosphorus atoms. These products are readily hydrolyzed in air, yielding diethyl isothiocyanatophosphate and phenyl hydrogen (α-methylamino)benzylphosphonate. The final products of the reaction of chloromethyl isocyanatophosphonates with aminoalkylphosphonates are 1,3,4-oxazaphospholines. Phenyl aminoalkylphosphonates react with chloromethyl isocyanatophosphonates to give saturated heterocycles, 1,3,4-diazaphospholidines, whereas with chloromethyl isothiocyanatophosphonates 1,3,4-thiazaphospholines are formed.

The chemistry of α-aminoalkylphosphonates have been vigorously progresses over the past decade. Synthetic approaches to these compounds have been devised and improved [1], and their biological activity has been studied. Much emphasis has been paid to chemical modification of α-aminophosphonates [2]. It is known that in the presence of a catalyst, triethylamine, they add to alkyl iso(thio)cyanates, affording *N*,*N*'-disubstituted (thio)ureas. The latter are stable compounds, and only under rigid conditions in the presence of a catalyst, 1,4-diazabicyclo[2.2.2]octane, they undergo cyclization into 1,4,2-diazaphospholidinones [3]. Proceeding with searching for methods of synthesis of new heterophosphacyclanes with endocyclic P–C bonds, derived from alkylphosphonates bearing functional substituents in the α position [4, 5], we turned to reaction of α-aminoalkylphosphonates with aromatic and phosphorylated iso(thio)cyanates. To induce cyclization of the addition products, we used as protic nucleophiles aminoalkylphosphonates having the relatively readily leaving phenoxy groups.

It was found that diphenyl (α-methylamino)benzylphosphonate (**I**) readily adds to phenyl isocyanate (**IIa**) or phenyl isothiocyanate (**IIb**) in the presence of catalytic amounts of triethylamine, yielding 1,3,4-diazaphospholidines **IIIa**, **IIIb**. The reaction involves intermediate formation of *N*,*N*'-disubstituted (thio)ureas **IV** which we failed to detect spectrally because of their fast cyclization.

The structure of compounds **IIIa**, **IIIb** was proved by their ^{1}H, ^{13}C, and ^{31}P NMR and IR spectra. The phosphorus signals were found in a region characteristic of this type of compounds [16.30 (**IIIa**) and 18.65 ppm (**IIIb**)]. The IR spectrum of 1,3,4-diazaphospholidine **IIIa** contains absorptions bands at 1200–1210 (P–O–Ph), 1270–1280 (P=O), 1590 (Ph), and 1710 cm^{-1} (C=O). The carbonyl carbon signal in the ^{13}C NMR spectrum of compound **IIIa** (Table 1) appears at 154.82 ppm, which is typical of compounds of this type. The $^2J_{\mathrm{PNC}}$ geminal constant of the P–N–C fragment is 29.3 Hz, and the $^1J_{\mathrm{PC}}$ constant of the P–C fragment is 116.1 Hz. The molecules of 1,3,4-diazaphospholidines **IIIa**, **IIIb** include two asymmetric centers, predetermining formation in the course of cyclization of a mixture of two diastereomers. Ho-



I **IIa, IIb** **IV** **IIIa, IIIb**

ΔH_f –310.30 ΔH_f**(IIa)** 49.47
ΔH_f**(IIb)** 278.31

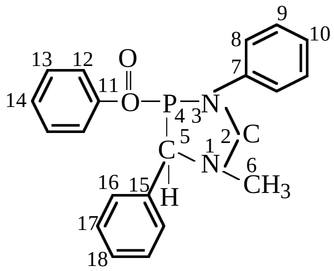
ΔH_f –90.37 ΔH_f**(IIIa)** –250.92
ΔH_f**(IIIb)** 54.66
$\Delta\Delta H_f$**(a)** –80.46
$\Delta\Delta H_f$**(b)** –3.72

II, III, X = O (**a**), X = S (**b**).

wever, the above spectral data for individual compounds, as well as the ^{1}N and ^{31}P NMR spectra of the reaction mixtures of aminoalkylphosphonate **I** with phenyl iso(thio)cyanates **IIa**, **IIb** reveal formation of a single diastereomer, which suggests a high stereooselectivity of the reaction in study. This, in its turn, gives an opportunity to prepare optically pure organophosphorus compounds.

The molecular and crystal structure of 1,3,4-diazaphospholidines **IIIa**, **IIIb** was determined by means of X-ray diffraction. Since **IIIa** and **IIIb** has isostructural crystals and, therefore, similar molecular conformations, we show in Fig. 1 the geometry of only one of the molecules. The heteroring in **IIIa**, **IIIb** has a *twist* conformation: The deviations of N^1 and N^4 from the P^{2}C^{3}C^5 plane are –0.227(2) and 0.212(2) Å in **IIIa** and –0.211(2) and 0.203(2) Å in **IIIb**, respectively. The phenoxy group at phosphorus is pseudoaxial, and the other substituents at the ring are pseudoequatorial. The planes of the phenyl substituents at N^1 and C^3 form with the heteroring mean plane dihedral angles of 65.6(1) and 61.2(1)° in **IIIa** and 66.1(1) and 61.8(1)° in **IIIb**. The conformation of the phenoxy groups at phosphorus is practically orthogonal: The dihedral angle between the P^{2}O^{3}C^{12} and C^{12}–C^{17} 63.2(2)° planes is 63.2(2)° in both molecules. It should be noted that this is a usual conformation of phenoxyl at the phosphorus atom in medium-size heterocycles [6]. The equatorial P=O bond length in both molecules is the same within experimental error [1.461(2) Å (mean)] and coincides with that found in oxazaphospholanes [7]. The axial P^2–O^3 bond length in **IIIa** and **IIIb** is the same [1.578(2) Å (mean)], which, too, coincides within experimental error with the axial P–O bond length in a methoxy-substituted oxazaphospholane [8]. The axial position of the phenoxy group at phosphorus in molecules **III** is stabilized by the anomeric effect [9]. In whole the

Table 1. ^{13}C NMR spectra (δ_C, ppm; *J*, Hz) of diazaphospholidine **IIIa**



Atom	δ_C	*J*
C^2	154.82	29.3 ($^2J_{PNC^2}$)
C^5	61.22	116.1 ($^1J_{PC^5}$), 140.1 ($^1J_{C^5H^5}$)
C^6	30.27	11.2 ($^3J_{C^5NC^6}$), 139.6 ($^1J_{C^6H^6}$)
C^7	132.67	9.6 ($^3J_{C^7C^8C^9H^9}$)
C^8	119.81	163.6 ($^1J_{C^8H^8}$), 4.3 ($^3J_{C^8C^9C^{10}H^{10}}$), 3.6 ($^3J_{C^8C^7C^{8'}H^{8'}}$)
C^9	129.04	161.7 ($^1J_{C^9H^9}$), 8.1 ($^3J_{C^9C^{10}C^{9'}H^{9'}}$)
C^{10}	124.90	161.9 ($^1J_{C^{10}H^{10}}$), 7.5 ($^3J_{C^{10}C^9C^8H^8}$)
C^{11}	149.79	11.2 ($^2J_{POC^{11}}$), 4.5 ($^3J_{C^{11}C^{12}C^{13}H^{13}}$)
C^{12}	119.85	163.3 ($^1J_{C^{12}H^{12}}$), 4.3 ($^3J_{C^{12}C^{13}C^{14}H^{14}}$), 3.6 ($^3J_{C^{12}C^{11}C^{12'}H^{12'}}$)
C^{13}	129.21	162.2 ($^1J_{C^{13}H^{13}}$), 7.8 ($^3J_{C^{13}C^{14}C^{13'}H^{13'}}$)
C^{14}	127.63	161.6 ($^1J_{C^{14}H^{14}}$), 7.4 ($^3J_{C^{14}C^{13}C^{12}H^{12}}$)
C^{15}	131.06	8.5 ($^2J_{PC^5C^{15}}$)
C^{16}	127.60	5.0 ($^3J_{PC^5C^{15}C^{16}}$)
C^{17}	127.39	1.9 ($^4J_{PC^5C^{15}C^{16}C^{17}}$)
C^{18}	129.21	162.2 ($^1J_{C^{18}H^{18}}$)

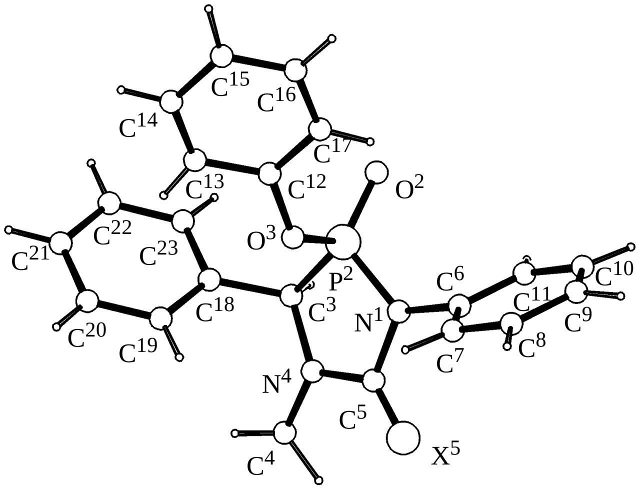
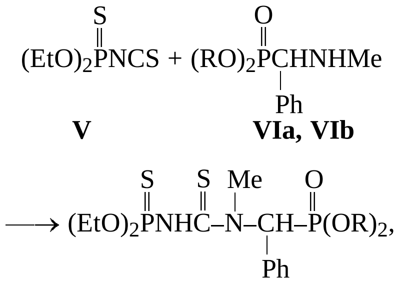


Fig. 1. Steric structure of 1-methyl-4-phenoxy-3,5-diphenyl-1,3,4λ^5-diazaphospholidine-2-one 4-oxide (**IIIa**) and 1-methyl-4-phenoxy-3,5-diphenyl-1,3,4λ^5-diazaphospholidine-2-thione 4-oxide (**IIIb**).

geometric parameters of molecules **III**, listed in Tables 2–4, are normal.

The stabilities of the participants of the reaction, calculated by the PM3 method [10] and reflected in the enthalpies of formation (in the scheme we give ΔH_f, kJ/mol, for the most stable conformers), provide evidence showing that the processes in question are favored by energy. Therewith, the reaction with phenyl isocyanate (**IIa**) is more exothermic [$\Delta\Delta H_f$(**a**) –80.46 kJ/mol] than the reaction with phenyl isothiocyanate (**IIb**) [$\Delta\Delta H_f$(**b**) –3.72 kJ/mol]. Generally, formation of diazaphospholidine structures with a C=O group (type **IIIa**) is favored over formation of their C=S analogs (type **IIIb**). We have found abundant evidence for the latter conclusion and will discuss this problem in a separate publication. The point to be noted here is that the X-ray structures of **IIIa** and **IIIb** are the most stable in the gas phase, too. The molecular conformations of the compounds are similar: The phenoxy group at phosphorus is pseudo-axial in both cases, and the phenyl substituents at N^1 and C^3 are strongly rotated with respect to the heteroring plane (the $P^2N^1C^6C^{11}$ and $P^2C^3C^{18}C^{23}$ torsion angles are 74.5 and 74.0° in **IIIa** and 84.3 and 71.9° in **IIIb**, respectively).

The reactions of diethyl isothiocyanatothiophosphate (**V**) with dialkyl (α-methylamino)benzylphosphonates **VIa**, **VIb** occur exothermically without catalysts to give *N*-(diethoxythiophosphoryl)-*N*'-methyl-*N*'-(α-dialkoxyphosphoryl)benzylthioureas **VIIa**, **VIIb**. The structure and composition of the products were proved by their elemental analyses and ^{1}H and ^{31}P NMR and IR spectra.



$$(EtO)_2\overset{\overset{S}{\|}}{P}NCS + (RO)_2\overset{\overset{O}{\|}}{P}\underset{\underset{Ph}{|}}{C}HNHMe$$

V **VIa, VIb**

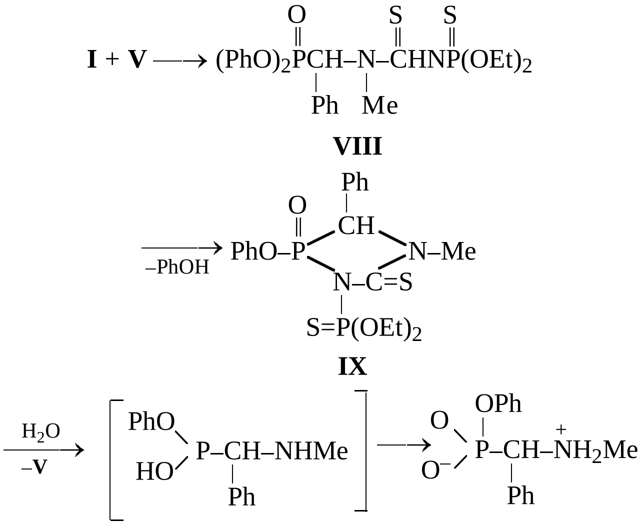
$$\longrightarrow (EtO)_2\overset{\overset{S}{\|}}{P}NH\overset{\overset{S}{\|}}{C}\text{–}\overset{\overset{Me}{|}}{N}\text{–}\underset{\underset{Ph}{|}}{C}H\text{–}\overset{\overset{O}{\|}}{P}(OR)_2,$$

VIIa, VIIb

VI, VII, R = Et (**a**), *i*-Pr (**b**).

Phosphorylated ureas of the same structure have been described in [11]. Compounds **VIIa**, **VIIb** are thermally stable and undergo no cyclization.

Aminobenzylphosphonate **I** adds to isothiocyanatothiophosphate **V** much harder than aminoalkylphosphonates **VI** (within some days at 20°C). In the presence of catalytic amounts of triethylamine, the reaction time decreases to several hours. According to ^{31}P NMR data, the primary reaction product is thiourea **VIII** (δ_P 62.03 and 12.71 ppm) which fast cyclizes into compound **IX** (δ_P 61.12 and 21.83 ppm). *N*-Phosphorylated diazaphospholidine **IX** is hydrolytically unstable and easily converts in air into isothiocyanatothiophosphate **V** (δ_P 46.29 ppm) and phenyl (α-methylamino)benzylphosphonate **X** (exists as internal salt **XI**). Special experiments showed that phenol fails to react with isothiocyanatothiophosphate **V** in our experimental conditions.



$$\mathbf{I} + \mathbf{V} \longrightarrow (PhO)_2\overset{\overset{O}{\|}}{P}\underset{\underset{Ph}{|}}{C}H\text{–}\underset{\underset{Me}{|}}{N}\text{–}\overset{\overset{S}{\|}}{C}HN\overset{\overset{S}{\|}}{P}(OEt)_2$$

VIII

$$\xrightarrow[-PhOH]{}$$

IX

$$\xrightarrow[-V]{H_2O} \left[\begin{matrix}PhO \\ HO\end{matrix}\!\!>\!P\text{–}\underset{\underset{Ph}{|}}{C}H\text{–}NHMe\right] \longrightarrow \begin{matrix}O \\ O^-\end{matrix}\!\!>\!\overset{\overset{OPh}{|}}{P}\text{–}\underset{\underset{Ph}{|}}{C}H\text{–}\overset{+}{N}H_2Me$$

X **XI**

The reactions of chloromethyl isocyanatophosphonates(phosphinates) **XIIa**, **XIIb** with α-aminoalkylphosphonates **XIIIa**, **XIIIb** might be expected to form *N*-phosphorylated ureas **XIVa**–**XIVc** capable

Table 2. Bond lengths *d* (Å), bond angles ω (deg), and torsion angles τ (deg) in molecules **IIIa** and **IIIb**

Parameter	**IIIa**	**IIIb**	Parameter	**IIIa**	**IIIb**
Bond	*d*		Angle	τ	
P^2–O^2	1.462(2)	1.460(2)	O^{2}P^{2}O^{3}C^{12}	9.3(2)	15.9(2)
P^2–O^3	1.579(2)	1.577(2)	N^{1}P^{2}O^{3}C^{12}	138.3(2)	145.5(2)
P^2–N^1	1.655(2)	1.673(2)	C^{3}P^{2}O^{3}C^{12}	–124.8(2)	–117.9(2)
P^2–C^3	1.823(3)	1.807(3)	O^{2}P^{2}N^{1}C^5	–139.9(2)	–137.5(2)
O^3–C^{12}	1.398(3)	1.405(2)	O^{2}P^{2}N^{1}C^6	51.9(2)	53.0(2)
Œ^5–C^5	1.206(3)	1.654(2)	O^{3}P^{2}N^{1}C^5	93.1(2)	95.1(1)
N^1–C^5	1.417(3)	1.390(3)	O^{3}P^{2}N^{1}C^6	–75.2(2)	–74.4(2)
N^1–C^6	1.437(4)	1.445(3)	C^{3}P^{2}N^{1}C^5	–14.2(2)	–13.3(2)
N^4–C^3	1.464(3)	1.474(3)	C^{3}P^{2}N^{1}C^6	177.6(2)	177.3(2)
N^4–C^{24}	1.462(4)	1.353(3)	O^{2}P^{2}C^{3}N^4	140.9(2)	139.7(1)
N^4–C^5	1.356(4)	1.464(3)	O^{2}P^{2}C^{3}C^{18}	–93.9(2)	–94.5(2)
C^3–C^{18}	1.510(4)	1.514(3)	O^{3}P^{2}C^{3}N^4	–87.4(2)	–88.4(2)
			O^{3}P^{2}C^{3}C^{18}	37.7(2)	37.5(2)
Angle	ω		N^{1}P^{2}C^{3}N^4	16.4(2)	15.4(4)
O^{2}P^{2}O^3	114.85(9)	114.94(9)	N^{1}P^{2}C^{3}C^{18}	141.6(2)	141.2(2)
O^{2}P^{2}N^1	117.9(1)	118.3(1)	P^{2}O^{3}C^{12}C^{13}	119.3(2)	112.8(2)
O^{2}P^{2}C^3	119.4(1)	118.3(1)	P^{2}O^{3}C^{12}C^{17}	–66.2(3)	–72.8(3)
O^{3}P^{2}N^1	102.4(1)	102.29(9)	P^{2}N^{1}C^{5}O^5	–173.5(2)	–174.5(1)
O^{3}P^{2}C^3	106.1(1)	107.3(1)	P^{2}N^{1}C^{5}N^4	6.6(3)	6.1(3)
N^{1}P^{2}C^3	93.0(1)	92.6(1)	C^{6}N^{1}C^{5}O^5	–5.0(4)	–5.6(3)
P^{2}O^{3}C^{12}	127.3(2)	125.7(1)	C^{6}N^{1}C^{5}N^4	175.1(2)	175.0(2)
P^{2}N^{1}C^5	113.8(2)	114.1(2)	P^{2}N^{1}C^{6}C^7	99.4(3)	99.0(3)
P^{2}N^{1}C^6	123.4(2)	120.3(1)	P^{2}N^{1}C^{6}C^{11}	–79.2(3)	–77.2(3)
C^{5}N^{1}C^6	121.8(2)	124.6(2)	C^{5}N^{1}C^{6}C^7	–68.0(3)	–69.3(3)
C^{3}N^{4}C^5	117.4(2)	116.8(2)	C^{5}N^{1}C^{6}C^{11}	113.5(3)	114.5(3)
C^{3}N^{4}C^{24}	120.0(2)	119.0(2)	C^{4}N^{4}C^{3}P^2	–177.7(2)	–178.6(2)
C^{24}N^{4}C^5	119.8(2)	121.9(2)	C^{4}N^{4}C^{3}C^{18}	59.2(3)	57.6(3)
P^{2}C^{3}N^4	102.2(2)	102.8(2)	C^{5}N^{4}C^{3}P^2	–16.5(3)	–15.7(2)
P^{2}C^{3}C^{18}	112.8(1)	113.0(1)	C^{5}N^{4}C^{3}C^{18}	–139.6(2)	–139.5(2)
P^{2}C^{3}H^3	107.(1)	103.(1)	C^{3}N^{4}C^{5}O^5	–172.2(3)	–172.1(2)
N^{4}C^{3}C^{18}	115.9(2)	116.0(2)	C^{3}N^{4}C^{5}N^1	7.7(3)	7.3(3)
O^{5}C^{5}N^1	123.3(3)	124.1(2)	C^{4}N^{4}C^{5}O^5	–10.9(4)	–9.7(4)
O^{5}C^{5}N^4	126.5(2)	125.1(2)	C^{4}N^{4}C^{5}N^1	169.0(2)	169.7(2)
N^{1}C^{5}N^4	110.2(2)	110.8(2)	P^{2}C^{3}C^{18}C^{19}	–91.2(3)	–91.8(3)
			P^{2}C^{3}C^{18}C^{23}	86.1(3)	84.3(3)
			N^{4}C^{3}C^{18}C^{19}	26.1(4)	26.6(3)
			N^{4}C^{3}C^{18}C^{23}	–156.5(2)	–157.3(2)

for heterocyclization involving the chloromethyl and urea C=O groups. Compounds **XIVa**–**XIVc** were isolated analytically pure in high yields. Their IR spectra display absorption bands characteristic of phosphorylated ureas, ν, cm^{-1}: 1645 (C=O), 3100 (NH).

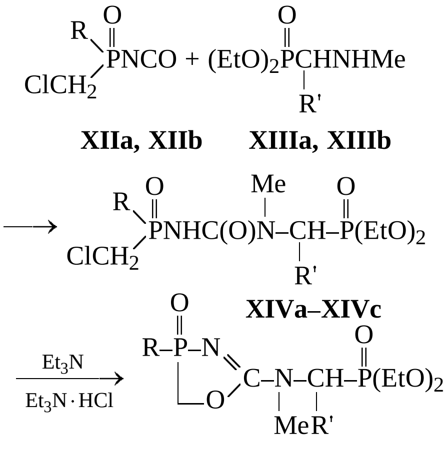
Treatment of phosphorylated ureas **XIVa**–**XIVc** with equimolar amount of triethylamine produces intramolecular alkylation of the carbonyl oxygen with the chloromethyl group, resulting in elimination of hydrogen chloride and formation of 1,3,4-oxazaphosphol-2-ines **XVa**–**XVc**. Compounds **XVa**–**XVc** are transparent light yellow nonfluid liquids which were characterized crude, since they decomposed on attempted isolation by chromatography or high-vacuum distillation. According to ^{1}H and ^{31}P NMR data, 1,3,4-oxazaphospholines **XVa**–**XVc** are formed as mixtures of two diastereomers. Thus, in the ^{31}P NMR spectrum of compound **XVa** we observe a double set of signals assigned to endocyclic (δ_P 50.76 and 50.41 ppm) and exocyclic (17.86 and 18.04 ppm)

Table 3. Atomic coordinates in diazaphospholidine **IIIa**, equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_ia_j)B(i,j)$ (Å^2) and isotropic temperature factors of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B*
P^2	0.60821(7)	0.17348(4)	0.12743(6)	3.02(1)
O^2	0.5442(2)	0.24238(9)	0.0874(2)	3.94(4)
O^3	0.5114(2)	0.10929(9)	0.0596(2)	3.69(4)
O^5	0.8361(2)	0.0917(1)	0.4458(2)	4.81(5)
N^1	0.6582(2)	0.1527(1)	0.2888(2)	3.46(5)
N^4	0.8490(2)	0.1139(1)	0.2365(2)	3.66(5)
C^3	0.7825(3)	0.1551(1)	0.1148(2)	3.19(6)
C^4	0.9954(3)	0.0903(2)	0.2682(3)	5.28(8)
C^5	0.7887(3)	0.1163(1)	0.3346(2)	3.56(6)
C^6	0.5667(3)	0.1583(1)	0.3692(2)	3.41(6)
C^7	0.4988(3)	0.1004(2)	0.3961(3)	4.42(7)
C^8	0.4106(3)	0.1072(2)	0.4726(3)	5.47(8)
C^9	0.3890(3)	0.1718(2)	0.5206(3)	5.50(8)
C^{10}	0.4562(3)	0.2295(2)	0.4930(3)	5.28(8)
C^{11}	0.5453(3)	0.2234(2)	0.4171(3)	4.39(7)
C^{12}	0.3825(3)	0.1114(1)	–0.0453(2)	3.20(6)
C^{13}	0.3723(3)	0.0770(2)	–0.1632(3)	4.29(7)
C^{14}	0.2432(3)	0.0729(2)	–0.2619(3)	5.39(8)
C^{15}	0.1244(3)	0.1043(2)	–0.2446(3)	5.50(8)
C^{16}	0.1372(3)	0.1384(2)	–0.1273(3)	5.19(8)
C^{17}	0.2658(3)	0.1420(2)	–0.0266(3)	4.08(7)
C^{18}	0.7752(2)	0.1204(1)	–0.0162(2)	3.15(6)
C^{19}	0.7737(3)	0.0486(1)	–0.0321(3)	3.91(6)
C^{20}	0.7642(3)	0.0195(2)	–0.1534(3)	4.37(7)
C^{21}	0.7528(3)	0.0608(2)	–0.2629(3)	4.43(7)
C^{22}	0.7522(3)	0.1327(2)	–0.2484(3)	4.77(7)
C^{23}	0.7639(3)	0.1623(1)	–0.1264(3)	3.82(6)
H^3	0.830(2)	0.198(1)	0.123(2)	2.9(5)
H^7	0.505(2)	0.054(1)	0.356(2)	4.4(6)
H^8	0.365(3)	0.062(2)	0.498(2)	7.1(8)
H^9	0.340(3)	0.174(2)	0.589(3)	10(1)
H^{10}	0.447(3)	0.276(2)	0.533(3)	8.8(9)
H^{11}	0.598(3)	0.261(1)	0.399(2)	5.7(7)
H^{13}	0.455(3)	0.054(1)	–0.165(2)	5.1(6)
H^{14}	0.232(2)	0.051(1)	–0.344(2)	4.3(6)
H^{15}	0.031(3)	0.109(1)	–0.317(2)	5.7(7)
H^{16}	0.048(3)	0.158(2)	–0.113(3)	7.6(8)
H^{17}	0.277(3)	0.163(1)	0.056(2)	4.7(6)
H^{19}	0.780(3)	0.021(1)	0.042(2)	4.9(6)
H^{20}	0.763(3)	–0.027(1)	–0.161(2)	6.2(7)
H^{21}	0.745(2)	0.041(1)	–0.350(2)	3.5(5)
H^{22}	0.746(3)	0.162(1)	–0.324(2)	5.7(7)
H^{23}	0.772(2)	0.210(1)	–0.115(2)	4.7(6)
H^{41}	1.044(4)	0.079(2)	0.373(3)	10(1)
H^{42}	0.989(3)	0.057(2)	0.202(3)	10(1)
H^{43}	1.059(4)	0.134(2)	0.257(4)	13(1)

Table 4. Atomic coordinates in diazaphospholidine **IIIb**, equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_ia_j)B(i,j)$ (Å^2) and isotropic temperature factors of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B*
S^5	0.86199(8)	0.07911(4)	0.95596(6)	4.66(2)
P^2	0.59581(6)	0.17173(3)	0.63674(5)	2.74(1)
O^2	0.5296(2)	0.24041(9)	0.6081(1)	3.59(4)
O^3	0.4973(2)	0.10838(8)	0.5758(1)	3.36(4)
N^1	0.6535(2)	0.1475(1)	0.7867(2)	3.14(4)
N^4	0.8451(2)	0.1156(1)	0.7204(2)	3.31(4)
C^3	0.7701(2)	0.1576(1)	0.6110(2)	2.89(5)
C^5	0.7864(3)	0.1144(1)	0.8178(2)	3.21(5)
C^6	0.5582(3)	0.1504(1)	0.8664(2)	3.21(5)
C^7	0.5309(3)	0.2142(1)	0.9118(2)	4.25(6)
C^8	0.4320(4)	0.2188(2)	0.9816(3)	5.52(7)
C^9	0.3652(3)	0.1601(2)	1.0062(3)	5.61(7)
C^{10}	0.3921(3)	0.0964(2)	0.9610(3)	5.29(7)
C^{11}	0.4896(3)	0.0915(2)	0.8903(2)	4.25(6)
C^{12}	0.3710(2)	0.1129(1)	0.4770(2)	2.97(5)
C^{13}	0.2494(3)	0.1403(1)	0.4991(2)	3.60(5)
C^{14}	0.1234(3)	0.1397(2)	0.4038(3)	4.90(7)
C^{15}	0.1206(3)	0.1111(2)	0.2891(3)	5.59(8)
C^{16}	0.2433(3)	0.0833(2)	0.2693(2)	5.28(7)
C^{17}	0.3709(3)	0.0836(2)	0.3627(2)	4.26(6)
C^{18}	0.7614(2)	0.1259(1)	0.4844(2)	2.85(5)
C^{19}	0.7650(3)	0.0547(1)	0.4654(2)	3.59(5)
C^{20}	0.7498(3)	0.0285(1)	0.3462(2)	4.31(6)
C^{21}	0.7285(3)	0.0729(2)	0.2457(2)	4.66(7)
C^{22}	0.7238(3)	0.1434(2)	0.2632(2)	4.81(7)
C^{23}	0.7406(3)	0.1705(1)	0.3827(2)	4.00(6)
C^{24}	0.9942(3)	0.0948(2)	0.7343(3)	4.63(7)
H^3	0.809(2)	0.204(1)	0.616(2)	3.2(5)
H^7	0.572(2)	0.254(1)	0.895(2)	4.4(6)
H^8	0.409(3)	0.262(1)	1.010(2)	5.1(6)
H^9	0.298(3)	0.160(1)	1.053(2)	5.9(7)
H^{10}	0.345(3)	0.055(1)	0.976(2)	6.4(7)
H^{11}	0.502(3)	0.051(1)	0.859(2)	5.5(7)
H^{13}	0.256(2)	0.160(1)	0.582(2)	4.1(6)
H^{14}	0.033(3)	0.163(1)	0.418(2)	6.7(8)
H^{15}	0.021(3)	0.108(1)	0.228(2)	6.4(7)
H^{16}	0.238(3)	0.061(1)	0.190(2)	7.3(8)
H^{17}	0.461(4)	0.060(2)	0.357(3)	10(1)
H^{19}	0.784(3)	0.023(1)	0.532(2)	5.3(7)
H^{20}	0.746(3)	–0.021(1)	0.334(2)	4.6(6)
H^{21}	0.711(3)	0.053(1)	0.163(2)	6.3(7)
H^{22}	0.700(3)	0.176(1)	0.201(2)	5.6(7)
H^{23}	0.742(2)	0.219(1)	0.397(2)	3.7(5)
H^{241}	1.055(5)	0.132(2)	0.773(4)	15(1)
H^{242}	1.014(4)	0.090(2)	0.657(3)	10(1)
H^{243}	1.001(4)	0.050(2)	0.756(3)	11(1)



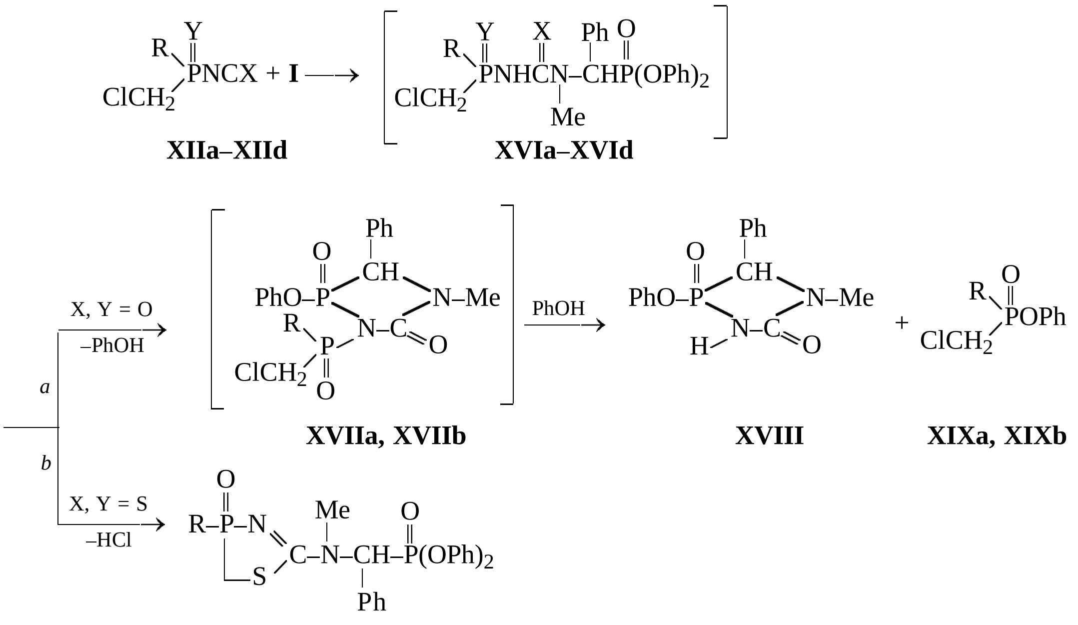
XIIa, XIIb **XIIIa, XIIIb** **XIVa–XIVc**

XVa–XVc

XII, R = PhO (**a**), $ClCH_2$ (**b**); **XIII**, R' = Ph (**a**), *i*-Pr (**b**); **XIV**, **XV**, R = PhO, R' = Ph (**a**); R = PhO, R' = *i*-Pr (**b**); R = $ClCH_2$, R' = Ph (**c**).

phosphorus atoms. The proton of the CH group at the exocyclic phosphorus atom appears in the ^1H NMR spectrum as two doublets at 5.61 ($^2J_{HCP}$ 23.01) and 6.00 ppm ($^2J_{HCP}$ 22.26 Hz); protons of the methylene group at the endocyclic phosphorus atom give a complex multiplet at 3.95–4.28 ppm. The IR spectra of the phosphacyclanes show absorption of the endocyclic C=N bond (1610 cm^{-1}) and lack absorption of the urea C=O group.

Of particular interest was to study the reaction of aminophosphonate **I** with chloromethyliso(thio)cyanatophosphonates(phosphinates) **XIIa**–**XIId**. We suggested that the primarily formed ureas **XVIa**–**XVId** can take two cyclization pathways depending on their structure. The first pathway (*a*) involves elimination of phenol to form saturated heterocycles **XVIIa**, **XVIIb** having exo- and endocyclic phosphorus atoms. The second pathway (*b*) is cyclization involving the chloromethyl and thiocarbonyl groups and yielding unsaturated heterocycles **XXa**, **XXb**.



XIIa–XIId **XVIa–XVId** **XVIIa, XVIIb** **XVIII** **XIXa, XIXb**

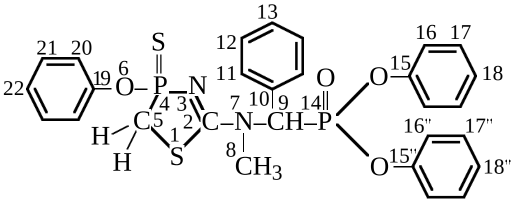
XXa, XXb

XII, R = PhO, X = Y = O (**a**); R = $ClCH_2$, X = Y = O (**b**); R = PhO, X = Y = S (**c**); R = $ClCH_2$, X = Y = S (**d**). **XIX, XX**, R = PhO (**a**), R = $ClCH_2$ (**b**).

It was found that, actually, the nature of the heterocumulene (phosphorylated isocyanate or isothiocyanate) strongly affects the synthetic result of the reaction. Aminoalkylphosphonate **I** preferentially adds to chloromethyl isocyanatophosphonates(phosphinates) **XIIa**, **XIIb** by the first pathway with elimination of phenol and formation of phosphacyclanes **XVIIa**, **XVIIb**. Under the action of the phenol eliminated, the latter undergo exocyclic P–N cleavage to give esters **XIXa**, **XIXb** and 1,3,4-diazaphospholidine **XVIII**. The reaction products were isolated pure, and their composition and structure were proved by elemental analysis and ^{1}H and ^{31}P NMR and IR spectroscopy, and mass spectrometry. The ^{1}H and ^{31}P NMR spectra of diazaphospholidine **XVIII** contain two sets of signals from two diastereomers. One of them (δ_P 20.80 ppm) was isolated in the individual state by fractional crystallization from acetonitrile. Evidence for the structure of product **XVIII** was obtained by high-resolution mass spectrometry. In the electron impact mass spectrum, the peak at *m*/*z* 302 relates to the molecular ion $[M]^+$ of 1-methyl-4-phenoxy-5-phenyl-1,3,4λ^5-diazaphospholidin-2-one 4-oxide (**XVIII**). The exact mass of this ion 302.0834 is nicely consistent with calculation (302.0822) for the elemental composition $C_{15}H_{15}N_2O_3P$. The base peak at *m*/*z* 120 is assignable to the ion $[PhCHNHMe]^+$ which is likely to be formed by P–C and C–N bond cleavage in the five-membered ring of **XVIII** with attendant migration of one hydrogen atom to the charged fragment. The major fragmentation pathways of molecule **XVIII** under electron impact are associated with $OPh^{\cdot}$ expulsion. This fragmentation pathway gives rise to a peak at *m*/*z* 209. The ion with *m*/*z* 166 is probably formed by further fragmentation of the *m*/*z* 209 ion, involving P–N and C–N bond cleavage. The ion with *m*/*z* 225 is formed by elimination of a phenyl group from the molecular ion. Further fragmentation of the *m*/*z* 225 and 120 ions gives rise to the following ions: $[PhOPO]^+$ *m*/*z* 140, $[PO]^+$ *m*/*z* 47, $[PhCHNMe]^+$ *m*/*z* 119, $[PhCNMe]^+$ *m*/*z* 118, $[PhCHN]^+$ *m*/*z* 104, $[PhCH_2]^+$ *m*/*z* 91, and $[Ph]^+$ *m*/*z* 77. For all the fragment ions the experimental *m*/*z* values are nicely consistent with those calculated from the elemental composition.

The cyclization by pathway *b* took place in cases, where isothiocyanates **XIIc**, **XIId** were used as heterocumulenes. The resulting phosphorylated thioureas prefer intramolecular alkylation of the thiocarbonyl sulfur atom with the chloromethyl group, resulting in elimination of hydrogen chloride and formation of 1,3,4-thiazaphosphol-2-ines **XXa**, **XXb**. Accoring to ^{13}C and ^{31}P NMR data, compounds **XXa**, **XXb** are a mixture of diastereomers. The signals of endocyclic phosphorus atoms are located downfield (δ_P 104–117 ppm), which is characteristic of 1,3,4-thiazaphospholines [4]. Moreover, in the ^{13}C NMR spectra of phosphonates **XXa**, **XXb**, because of the presence of an asymmetric carbon atom, respective signals of the two phenyl rings at the second phosphorus atom have different chemical shifts (Tables 5 and 6). It should

Table 5. ^{13}C NMR spectra $[(CD_3)_2CO]$ (δ_C, ppm; *J*, Hz) of compound **XXa**

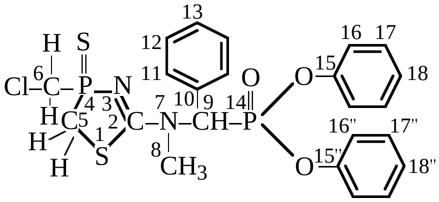


Atom	δ_C	*J*
P^4	114.86 (main)	
	115.29	
P^{14}	9.85 (main)	
	10.44	
C^2	172.45	13.8 ($^{2}J_{P^4C^2}$), 6.5 ($^{3}J_{P^{14}C^9N^7C^2}$), 2.2 ($^{3}J_{C^2N^7C^8H^8}$), 5.0 ($^{3}J_{C^2SC^5H^5}$)
C^5	36.71	57.9 ($^{1}J_{P^4C^5}$), 146.1, 148.0 ($^{1}J_{C^5H^5}$)
C^8	33.94	140.7 ($^{1}J_{C^8H^8}$), 5.3 (^{3}J $IXC8N7C9H9)
C^9	60.20	59.6 ($^{1}J_{P^{14}C^9}$), 136.2 ($^{1}J_{C^9H^9}$)
C^{10}	132.21	4.5 ($^{2}J_{P^{14}C^9C^{10}}$)
C^{11}	125.78	162.9 ($^{1}J_{C^{11}H^{11}}$), 2.9 ($^{3}J_{P^{14}C^9C^{10}C^{11}}$), 7.2 ($^{3}J_{C^{11}C^{12}C^{13}H^{13}}$), 3.3 ($^{3}J_{C^{11}C^{10}C^{11'}H^{11'}}$)
C^{12}	129.56	161.5 ($^{1}J_{C^{12}H^{12}}$), 7.5 ($^{3}J_{C^{12}C^{13}C^{12'}H^{12'}}$)
C^{13}	130.20	Not determined because of signal overlap
C^{15}	150.30	9.6 ($^{2}J_{P^{14}OC^{15}}$), 9.7 ($^{3}J_{C^{15}C^{16}C^{17}H^{17}}$), –2.4 ($^{3}J_{C^{15}C^{16}C^{17}H^{17}}$)

Table 5. (Contd.)

Atom	δ_C	*J*
$C^{15''}$	150.93	8.8 $({}^{2}J_{P^{14}OC^{15''}})$, –1.7 $({}^{2}J_{C^{15''}C^{16''}H^{16''}})$, 9.6 $({}^{3}J_{C^{15''}C^{16''}C^{17''}H^{17''}})$
C^{16}	120.55	4.3 $({}^{3}J_{P^{14}OC^{15}C^{16}})$, 164.3 $({}^{1}J_{C^{16}H^{16}})$, 7.9 $({}^{3}J_{C^{16}C^{17}C^{18}H^{18}})$, 4.4 $({}^{3}\mathrm{JC}^{16}\mathrm{C}^{15}\mathrm{C}^{16'}\mathrm{H}^{16'})$
$C^{16''}$	120.80	4.3 $({}^{3}J_{P^{14}OC^{15''}C^{16''}})$, 163.0 $({}^{1}J_{C^{16''}H^{16''}})$, 7.9 $({}^{3}J_{C^{16''}C^{17''}C^{18''}H^{18''}})$, 4.4 $({}^{3}J_{C^{16''}C^{15''}C^{16'''}H^{16'''}})$
C^{17}	130.80	163.5 $({}^{1}J_{C^{17}H^{17}})$, 7.9 $({}^{3}J_{C^{17}C^{18'}C^{17'}H^{17'}})$
$C^{17''}$	130.07	100.4 $({}^{1}J_{C^{17''}H^{17''}})$, 8.3 $({}^{3}J_{C^{17''}C^{18''}C^{17'''}H^{17'''}})$
C^{18}	129.41	160.0 $({}^{1}J_{C^{18}H^{18}})$, 8.1 $({}^{3}J_{C^{18}C^{17}C^{16}H^{16}})$
$C^{18''}$	129.41	160.0 $({}^{1}J_{C^{18''}H^{18''}})$, 8.1 $({}^{3}J_{C^{18''}C^{17'''}C^{16'''}H^{16'''}})$
C^{19}	151.47	10.4 $({}^{2}J_{P^{4}OC^{19}})$, 5.8 $({}^{3}J_{C^{19}C^{20}C^{21}H^{21}})$
C^{20}	121.85	4.4 $({}^{3}J_{P^{4}OC^{19}C^{20}})$, 163.9 $({}^{1}J_{C^{20}H^{20}})$, 8.4 $({}^{3}J_{C^{20}C^{21}C^{22}H^{22}})$, 5.0 $({}^{3}J_{C^{20}C^{19}C^{20'}H^{20'}})$
C^{21}	129.78	162.5 $({}^{1}J_{C^{21}H^{21}})$, 8.8 $({}^{3}J_{C^{21}C^{22}C^{21'}H^{21'}})$
C^{22}	125.16	162.8 $({}^{1}J_{C^{22}H^{22}})$, 1.2 $({}^{2}J_{C^{22}C^{21}H^{21}})$, 7.5 $({}^{3}J_{C^{22}C^{21}C^{20}H^{20}})$, 0.8 $({}^{5}J_{P^{4}OC^{19}C^{20}C^{21}C^{22}})$

Table 6. ^{13}C NMR spectra $[(CD_3)_2CO]$ (δ_C, ppm; *J*, Hz) of compound **XXb**



Atom	δ_C	*J*
P^{4}	104.25 (main)	
	104.06	
P^{14}	10.08 (main)	
	10.92	
C^{2}	173.33	
C^{5}	34.13 (main)	32.7 $({}^{1}J_{P^{4}C^{5}})$, 147.6 $({}^{1}J_{C^{5}H^{5}})$, 3.0 $({}^{3}J_{C^{5}P^{4}C^{6}H^{6}})$
	34.00	34.2 $({}^{1}J_{P^{4}C^{5}})$, 146.6 $({}^{1}J_{C^{5}H^{5}})$, 3.0 $({}^{3}J_{C^{5}P^{4}C^{6}H^{6}})$
C^{6}	43.42 (main)	70.2 $({}^{1}J_{P^{4}C^{6}})$, 154.0 $({}^{1}J_{C^{6}H^{6}})$
	43.07	70.2 $({}^{1}J_{P^{4}C^{6}})$, 154.0 $({}^{1}J_{C^{6}H^{6}})$
C^{8}	34.32	139.3 $({}^{1}J_{C^{8}H^{8}})$
C^{9}	60.22	135.3 $({}^{1}J_{C^{9}H^{9}})$, 161.7 $({}^{1}J_{P^{14}C^{9}})$
C^{10}	132.46 (main)	4.0 $({}^{2}J_{P^{14}C^{9}C^{10}})$
	132.45	5.6 $({}^{2}J_{P^{14}C^{9}C^{10}})$
C^{11}	125.80	162.9 $({}^{1}J_{C^{11}H^{11}})$, 7.4 $({}^{3}J_{P^{14}C^{9}C^{10}C^{11}})$, 7.5 $({}^{3}J_{C^{11}C^{12}C^{13}H^{13}})$, 3.3 $({}^{3}J_{C^{11}C^{10}C^{11'}H^{11'}})$
C^{12}	129.55	162.0 $({}^{1}J_{C^{12}H^{12}})$, 8.2 $({}^{3}J_{C^{12}C^{13}C^{12'}H^{12'}})$
C^{13}	130.04	Not determined because of signal overlap
C^{15}	140.0 (main)	9.9 $({}^{2}J_{P^{14}OC^{15}})$, 9.6 $(3^{J}{}_{C^{15}C^{16}C^{17}H^{17}})$, –1.6 $({}^{4}J_{C^{15}C^{16}C^{17}\text{¢}^{18}H^{18}})$
	140.61	9.6 $({}^{2}J_{P^{14}OC^{15}})$, 9.6 $(3^{J}{}_{C^{15}C^{16}C^{17}H^{17}})$, –1.6 $({}^{4}J_{C^{15}C^{16}C^{17}\text{¢}^{18}H^{18}})$

Table 6. (Contd.)

Atom	δ_C	J
C^{16}	110.31 (main)	162.1 ($^1J_{C^{16}H^{16}}$), 4.2 ($^3J_{P^{14}OC^{15}C^{16}}$)
	110.48	162.1 ($^1J_{C^{16}H^{16}}$), 4.1 ($^3J_{P^{14}OC^{15}C^{16}}$)
C^{17}	119.68 (main)	160.7 ($^1J_{C^{17}H^{17}}$), 7.6 ($^3J_{C^{17}C^{18}C^{17'}H^{17'}}$)
	119.60	160.7 ($^1J_{C^{17}H^{17}}$), 7.6 ($^3J_{C^{17}C^{18}C^{17'}H^{17'}}$)
C^{18}	118.96 (main)	160.7 ($^1J_{C^{17}H^{17}}$), 7.6 ($^3J_{C^{17}C^{18}C^{17'}H^{17'}}$), 160.5 ($^1J_{C^{18}H^{18}}$), 6.1 ($^3J_{C^{18}C^{17}C^{16}H^{16}}$)
	119.01	160.5 ($^1J_{C^{18}H^{18}}$), 6.1 ($^3J_{C^{18}C^{17}C^{16}H^{16}}$)

be noted that the signals of endocyclic methylene protons in the ^{1}H NMR spectra of compounds **XXa**, **XXb** have different chemical shifts and coupling constants, which we earlier observed with similar compounds [12].

The molecular structure of 1,3,4-thiazaphosphol-2-ine **XXa** was examined by means of X-ray diffraction. The heteroring in molecule **XXa** has a *twist* conformation: The deviations of S^1 and N^3 from the $P^4C^5C^3$ plane are –0.2613(7) and 0.174(2) Å, which corresponds to a torsion of 5° along the $C^2{=}N^3$ double bond [the $P^4N^3C^2S^1$ torsion angle is –5.2(3)°]. The phenoxy group at P^4 is axial, and the thiophosphoryl group is pseudoequatorial (Fig. 2). The conformation of the phenoxy group is usual, close-to-orthogonal, like in molecules **III** (see torsion angles in Tables 7 and 8). The N^8 atom has a planar trigonal coordination, and its substituents are in the plane of the thiourea fragment: The $S^1C^2N^8C^8$ torsion angle is 4.1(3)°, which is determined by conjugation of the lone electron pair of N^8 with the $C^2{=}N^3$ double bond. This conclusion is supported by the fact that the $C^2{-}N^8$ bond is slightly shortened and the $C^2{=}N^3$ bond is slightly lengthened. In whole the geometric parameters of molecule **XXa** are normal.

Along with the experimental study of the latter reaction, we performed, by the PM3 method, a theoretical analysis of the energy changes associated with the formation of diazaphospholidine **XVIII** at X, Y = O (pathway *a*) and thiazaphospholine **XX** at X, Y = S (pathway *b*). We also calculated the heat effects of theoretically possible alternative processes, such as formation of a thiazaphospholidine structure from isothiocyanate **XIIc** and of an oxazaphospholine structure from isocyanate **XIIa**. As seen from the enthalpies of formation of individual compounds and the heat effects of the reactions (Table 9), the isolated compounds **XVIII** and **XX** are formed by thermodynamically favorable exothermic reactions. The formation of the other structures, thiazaphospholidine and oxazaphospholine is unfavorable (the corresponding reactions are endothermic). Thus, the difference in the major cyclization pathways of ureas and thioureas reveals itself: The former tend to form saturated heterocycles of the diazaphospholidine type and the latter, unsaturated heterocycles (thiazaphospholines).

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrophotometer at 400–3600 cm^{-1} in mineral oil or in thin film. The ^{31}P NMR spectra were obtained on a Bruker MSL-400 Fourier spectrometer at 161.97 MHz and on a KGU-4 spectrometer at 10.2 MHz, external reference 85% H_3PO_4. The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer at 60 MHz (internal reference TMS) and a Bruker WM-250 spectrometer at 250.132 MHz. The ^{13}C NMR spectra were run on a Bruker MSL-400 Fourier spectrometer at 100.6 MHz. The mass spectrum was obtained on an MX-1310 instrument; ionizing energy 70 eV, collector

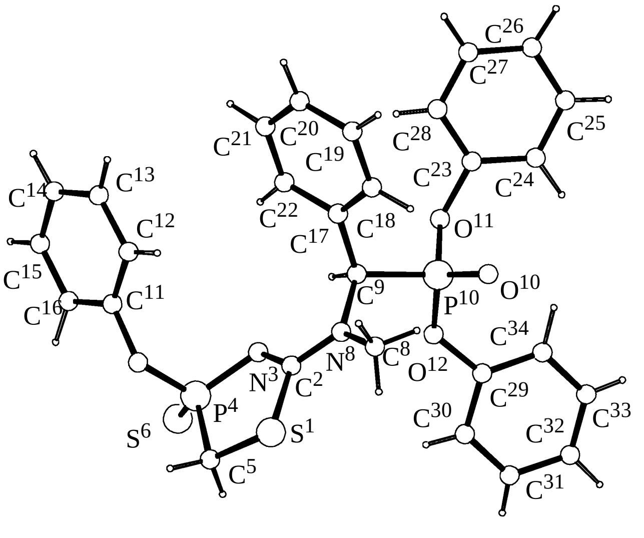


Fig. 2. Steric structure of diphenyl [*N*-(4-phenoxy-4-thioxo-Δ^2-1,3,4λ^5-thiazaphospholidin-2-yl)-*N*-methylamino](phenyl)methylphosphonate (*XXa*).

Table 7. Bond lengths *d* (Å), bond angles ω (deg), and torsion angles τ (deg) in molecule **XXa**

Bond	*d*	Bond	*d*
S^1–C^2	1.787(2)	O^7–C^{11}	1.404(3)
S^1–C^5	1.793(3)	O^{11}–C^{23}	1.411(3)
S^6–P^4	1.923(1)	O^{12}–C^{29}	1.400(2)
P^4–O^7	1.608(2)	N^3–C^2	1.298(3)
P^4–N^3	1.634(2)	N^8–C^2	1.337(3)
P^4–C^5	1.821(3)	N^8–C^8	1.466(3)
P^{10}–O^{10}	1.455(2)	N^8–C^9	1.480(3)
P^{10}–O^{11}	1.577(2)	C^9–C^{17}	1.512(3)
P^{10}–O^{12}	1.580(2)	P^{10}–C^9	1.814(2)
Angle	ω	Angle	ω
$C^2S^1C^5$	94.8(1)	$P^{10}O^{11}C^{23}$	124.7(1)
$S^6P^4O^7$	114.31(8)	$P^{10}O^{12}C^{29}$	128.9(2)
$S^6P^4N^3$	116.07(9)	$P^4N^3C^2$	115.4(2)
$S^6P^4C^5$	117.7(1)	$C^2N^8C^8$	121.4(2)
$O^7P^4N^3$	107.2(1)	$C^2N^8C^9$	118.2(2)
$O^7P^4C^5$	98.1(1)	$C^8N^8C^9$	120.0(2)
$N^3P^4C^5$	101.1(1)	$S^1C^2N^3$	120.0(2)
$O^{10}P^{10}O^{11}$	114.8(1)	$S^1C^2N^8$	116.7(2)
$O^{10}P^{10}O^{12}$	117.52(9)	$N^3C^2N^8$	123.3(2)
$O^{10}P^{10}C^9$	118.5(1)	$S^1C^5P^4$	106.5(2)
$O^{11}P^{10}O^{12}$	102.05(9)	$P^{10}C^9N^8$	111.4(1)
$O^{11}P^{10}C^9$	103.05(9)	$P^{10}C^9C^{17}$	114.0(2)
$O^{12}P^{10}C^9$	98.2(1)	$N^8C^9C^{17}$	114.3(2)
$P^4O^7C^{11}$	124.4(2)		
Angle	τ	Angle	τ
$C^5S^1C^2N^3$	–5.2(2)	$O^{11}P^{10}C^9N^8$	–167.2(1)
$C^5S^1C^2N^8$	174.3(2)	$O^{11}P^{10}C^9C^{17}$	61.7(2)
$C^2S^1C^5P^4$	11.7(2)	$O^{12}P^{10}C^9N^8$	–62.7(2)
$S^6P^4O^7C^{11}$	63.9(2)	$O^{12}P^{10}C^9C^{17}$	166.2(2)
$N^3P^4O^7C^{11}$	–66.2(2)	$P^4O^7C^{11}C^{12}$	102.2(3)
$C^5P^4O^7C^{11}$	–170.6(2)	$P^4O^7C^{11}C^{16}$	–82.4(3)
$S^6P^4N^3C^2$	141.4(2)	$P^{10}O^{11}C^{23}C^{24}$	–81.9(3)
$O^7P^4N^3C^2$	–89.5(2)	$P^{10}O^{11}C^{23}C^{28}$	101.4(2)
$C^5P^4N^3C^2$	12.7(2)	$P^{10}O^{12}C^{29}C^{30}$	–150.9(2)
$S^6P^4C^5S^1$	–142.5(1)	$P^{10}O^{12}C^{29}C^{34}$	30.3(3)
$O^7P^4C^5S^1$	94.5(2)	$P^4N^3C^2S^1$	–5.2(3)
$N^3P^4C^5S^1$	–14.96(0.17)	$P^4N^3C^2N^8$	175.4(2)
$O^{10}P^{10}O^{11}C^{23}$	20.7(2)	$C^8N^8C^2S^1$	4.1(3)
$O^{12}P^{10}O^{11}C^{23}$	149.0(2)	$C^8N^8C^2N^3$	–176.5(2)
$C^9P^{10}O^{11}C^{23}$	–109.5(2)	$C^9N^8C^2S^1$	176.1(2)
$O^{10}P^{10}O^{12}C^{29}$	30.5(2)	$C^9N^8C^2N^3$	–4.5(3)
$O^{11}P^{10}O^{12}C^{29}$	–95.9(2)	$C^2N^8C^9P^{10}$	125.9(2)
$C^9P^{10}O^{12}C^{29}$	158.8(2)	$C^2N^8C^9C^{17}$	–103.2(2)
$O^{10}P^{10}C^9N^8$	64.8(2)	$C^8N^8C^9P^{10}$	–62.0(2)
$O^{10}P^{10}C^9C^{17}$	–66.3(2)	$C^8N^8C^9C^{17}$	69.0(3)

Table 8. Atomic coordinates in structure **XXa**, equivalent isotropic temperature factors of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)$ (Å^2) and isotropic temperature factors of hydrogen atoms B_{iso} (Å^2)

Atom	x	y	z	B	Atom	x	y	z	B
S^1	0.97655(4)	–0.35732(9)	0.58554(3)	4.75(2)	C^{29}	0.8095(1)	0.2724(3)	0.6233(1)	3.20(5)
S^6	1.14439(4)	0.0763(1)	0.54954(3)	5.49(2)	C^{30}	0.8005(2)	0.2569(4)	0.5623(1)	5.05(7)
P^4	1.11204(4)	–0.1210(1)	0.59075(3)	4.11(1)	C^{31}	0.7336(2)	0.3362(5)	0.5219(1)	6.85(9)
P^{10}	0.89388(3)	0.11141(8)	0.72672(2)	3.02(1)	C^{32}	0.6780(2)	0.4279(5)	0.5435(1)	5.98(8)
O^7	1.1859(1)	–0.2485(2)	0.62553(8)	4.73(4)	C^{33}	0.6881(2)	0.4408(4)	0.6044(1)	4.60(6)
O^{10}	0.82382(8)	0.0332(2)	0.74140(7)	3.92(4)	C^{34}	0.7543(1)	0.3618(3)	0.6456(1)	3.73(5)
O^{11}	0.93481(9)	0.2707(2)	0.76899(7)	3.55(3)	H^9	1.018(1)	0.047(2)	0.7144(8)	2.0(4)
O^{12}	0.87978(9)	0.1934(3)	0.66100(7)	4.56(4)	H^{12}	1.209(1)	–0.297(3)	0.740(1)	5.2(6)
N^3	1.0606(1)	–0.0721(3)	0.63908(8)	3.79(4)	H^{13}	1.321(2)	–0.238(4)	0.819(1)	8.0(8)
N^8	0.9573(1)	–0.1677(3)	0.67914(8)	3.41(4)	H^{14}	1.431(1)	–0.094(4)	0.803(1)	6.1(7)
C^2	1.0019(1)	–0.1807(3)	0.6397(1)	3.39(5)	H^{15}	1.427(1)	–0.012(3)	0.706(1)	5.3(6)
C^5	1.0465(2)	–0.2890(4)	0.5443(1)	5.49(7)	H^{16}	1.316(1)	–0.078(3)	0.619(1)	5.7(6)
C^8	0.8945(2)	–0.2993(4)	0.6804(1)	5.04(6)	H^{18}	0.927(1)	–0.203(3)	0.813(1)	4.2(5)
C^9	0.9799(1)	–0.0302(3)	0.7271(1)	2.95(5)	H^{19}	1.001(1)	–0.303(3)	0.909(1)	4.3(5)
C^{11}	1.2513(1)	–0.1958(3)	0.6749(1)	3.64(5)	H^{20}	1.147(1)	–0.261(4)	0.943(1)	6.1(7)
C^{12}	1.2507(2)	–0.2456(3)	0.7327(1)	4.20(6)	H^{21}	1.209(1)	–0.113(3)	0.882(1)	5.4(6)
C^{13}	1.3184(2)	–0.2092(4)	0.7808(1)	4.83(6)	H^{22}	1.134(1)	–0.028(3)	0.7835(9)	3.3(5)
C^{14}	1.3848(2)	–0.1224(4)	0.7709(1)	4.82(7)	H^{24}	0.813(1)	0.428(4)	0.798(1)	6.3(7)
C^{15}	1.3829(1)	–0.0705(4)	0.7131(1)	4.56(6)	H^{25}	0.805(1)	0.473(3)	0.895(1)	5.5(6)
C^{16}	1.3162(1)	–0.1077(4)	0.6640(1)	4.18(6)	H^{26}	0.906(1)	0.411(3)	0.982(1)	5.4(6)
C^{17}	1.0246(1)	–0.1007(3)	0.7895(1)	3.00(5)	H^{27}	1.025(2)	0.264(4)	0.969(1)	7.7(8)
C^{18}	0.9859(1)	–0.1861(3)	0.8273(1)	3.77(5)	H^{28}	1.031(1)	0.198(3)	0.8721(9)	3.7(5)
C^{19}	1.0305(2)	–0.2464(4)	0.8842(1)	4.55(6)	H^{30}	0.838(2)	0.205(4)	0.550(1)	6.7(7)
C^{20}	1.1131(2)	–0.2195(4)	0.9039(1)	4.82(6)	H^{31}	0.724(2)	0.332(5)	0.484(1)	10(1)
C^{21}	1.1527(2)	–0.1335(4)	0.8671(1)	4.46(6)	H^{32}	0.633(2)	0.481(4)	0.514(1)	8.3(8)
C^{22}	1.1087(1)	–0.0747(3)	0.8102(1)	3.54(5)	H^{33}	0.655(1)	0.489(3)	0.620(1)	5.0(6)
C^{23}	0.9262(1)	0.3032(3)	0.8277(1)	3.17(5)	H^{34}	0.761(1)	0.364(4)	0.691(1)	6.1(7)
C^{24}	0.8581(1)	0.3897(3)	0.8338(1)	3.89(5)	H^{51}	1.019(1)	–0.246(3)	0.508(1)	5.9(7)
C^{25}	0.8530(2)	0.4295(4)	0.8913(1)	4.70(6)	H^{52}	1.081(1)	–0.386(4)	0.537(1)	6.1(7)
C^{26}	0.9145(2)	0.3826(4)	0.9421(1)	4.74(6)	H^{81}	0.865(2)	–0.325(4)	0.639(2)	9.6(9)
C^{27}	0.9818(2)	0.2961(4)	0.9350(1)	4.70(6)	H^{82}	0.855(2)	–0.254(4)	0.699(1)	8.9(9)
C^{28}	0.9887(1)	0.2553(3)	0.8779(1)	3.97(6)	H^{83}	0.917(2)	–0.385(6)	0.708(2)	13(1)

current 30 μA, ion source temperature 120°C. An SVP-5 direct inlet probe was used, *R* 10000. The exact masses were determined automatically against prefluorokerosene to an accuracy of no higher than 10^{-5} amu.

Single-crystal X-ray diffraction analysis of compounds IIIa, IIIb and XXa was performed at the Department of X-ray studies, Center for Collective Use, North-Caucasian Analytical Center (Russian Foundation for Basic Research, project no. 00-03-40133) on an Enraf–Nonius CAD-4 automatic diffractometer at 20°C. Crystal data for compound **IIIa**, $C_{21}H_{19}N_2O_2P$, mp 273°C, monoclinic: at 20°C, *a* 9.994(2), *b* 19.070(3), *c* 10.528(2) Å; β 108.99(2)°, *V* 1897.1(8) Å^3, *Z* 4, d_{calc} 1.33 g/cm^3, space group $P2_1/a$. The unit cell parameters and the intensities of 4202 reflections, 2263 of which had $I \geq 3\sigma$, were measured under MoK_α radiation (λMoK_α 0.71073 Å, graphite monochromator, ω/2θ scanning, θ ≤ 26.3°).

Crystal data for compound **IIIb**, $C_{21}H_{19}N_2OPS$, mp 205–207°C, isostructural to crystals of **IIIa**: *a* 9.681(9), *b* 19.149(9), *c* 11.118(4) Å; β 105.88(6)°, *V* 1982(2) Å^3, *Z* 4, d_{calc} 1.32 g/cm^3, space group $P2_1/a$. The unit cell parameters and the intensities of 4411 reflections, 2984 of which had $I \geq 3\sigma$, were measured under CuK_α radiation (λCuK_α 1.54184 Å,

Table 9. Enthalpies of formation of reagents and products (ΔH_f, kJ/mol) and heat effects ($\Delta\Delta H_f$, kJ/mol) of the reaction of aminophosphonate **I** with chloromethyliso(thio)cyanatophosphonates **XII**

Comp. no.	ΔH_f	Reaction	$\Delta\Delta H_f$
I	–310.30	**I** + **XIIa** ⟶	
XIIa	–516.73	**XVIII** + **XIXa**	–51.19
XIIc	23.46	**I** + **XIIc** ⟶	
XVIII	–406.41	**XVIII** + **XIX**	+147.46
XVIII(S)[a]	21.33	**I** + **XIIa** ⟶	
XIXa	–471.81	**XXa** + HCl	+33.71
XIX(S)[a]	–160.71	**I** + **XIIc** ⟶	
XXa	–264.39	**XXa** + HCl	–62.98
XXa(O)[b]	–707.76		
HCl	–85.56		

[a] **XVIII**(S) is the thio analog of compound **XVIII**, containing two sulfur atoms instead of oxygen atoms and **XIX**(S) is the thio analog of compound **XIX** contains a thiophosphoryl group instead of phosphoryl. [b] **XXa**(O) is the oxygen analog of compound **XXa** containing oxygen atoms in the ring and at the phosphorus atom in the heterocyclic fragment.

graphite monochromator, $\omega/2\theta$ scanning, $\theta \le 76.3°$).

Crystal data for phosphonate **XXa**, $C_{28}H_{26}N_2O_4 \cdot P_2S_2$, mp 126–127°C, monoclinic: at 20°C, *a* 17.074(5), *b* 7.538(4), *c* 22.867(5) Å; β 106.27(2)°, *V* 2825(2) Å^3, *Z* 4, d_{calc} 1.37 g/cm^3, space group $P2_1/n$. The unit cell parameters and the intensities of 4938 reflections, 3856 of which had $I \ge 3\sigma$, were measured under CuK_α radiation (λCuK_α 1.54184 Å, graphite monochromator, $\omega/2\theta$ scanning, $\theta \le 76.3°$).

No intensity decay of control reflections was observed during measurements. For **IIIa**, no absorption corrections (μMo 1.62 cm^{-1}) and for **IIIb** and **XXa**, empirical absorption corrections were applied (μCu 23.41 and 30.69 cm^{-1}, respectively). The structures were solved by direct methods using the SIR program [13] and refined first isotropically and then anisotropically. All hydrogen atoms were revealed by difference synthesis and refined isotropically in final cycles. The final divergence factors were as follows: **IIIa**: *R* 0.042 and R_W 0.048, on 2266 unique reflections; **IIIb**: *R* 0.039 and R_W 0.048, on 2802 unique reflections; and **XXa**: *R* 0.037 and R_W 0.051, on 3664 unique reflections with $F^2 \ge 3\sigma$. All calculations were performed on an Alpha Station 200 computer using the MolEN program package [14]. Molecular drawings were performed and intramolecular contacts were analyzed using the PLATON 98 pogram [15].

The quantum-chemical calculations were performed with full geometry optimization with no symmetry constraints using the MOPAC 6 program package [16]. The matrix of second derivatives of total energy in coordinates was calculated in all cases for characterization of stationary points as energy minima. Consideration was only given to the points for which all second derivatives were positive.

1-Methyl-4-phenoxy-3,5-diphenyl-1,3,4λ^5-diazaphospholidin-2-one 4-oxide (IIIa). Phenyl isocyanate (**IIa**), 0.34 g, was added to a solution of 1 g of phosphonate **I** in 5 ml of dry chloroform. After 12 h, the solvent was removed in a vacuum (0.02 mm), and the crystalline residue was recrystallized from acetonitrile to obtain 0.72 g (67%) of compound **IIIa**, mp 273°C. IR spectrum (KBr), ν, cm^{-1}: 1210 (Ph–O–P), 1275 (P=O), 1590 (Ph), 1710 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.93 s (3H, MeN), 4.93 d (1H, PCH, $^2J_{PH}$ 20.0), 7.3 m (15H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 16.30. Found, %: C 65.95; H 4.96; N 7.23; P 8.45. $C_{21}H_{19}N_2O_3P$. Calculated, %: C 66.65; H 5.07; N 7.41; P 8.18.

1-Methyl-4-phenoxy-3,5-diphenyl-1,3,4λ^5-diazaphospholidine-2-thione 4-oxide (IIIb) was prepared in a similar way from 1 g of phosphonate **I** and 0.38 g of phenyl isothiocyanate (**IIb**). Yield 1.05 g (94%), mp 205–207°C. IR spectrum (KBr), ν, cm^{-1}: 1200 (Ph–O–P), 1270 (P=O), 1590 (Ph). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.0 s (3H, MeN), 4.7 d (1H, PCH, $^2J_{PH}$ 16), 7.1 m (15H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 18.65. Found, %: C 63.56; H 4.87; N 7.07; P 7.49; S 7.58. $C_{21}H_{19}N_2O_2PS$. Calculated, %: C 63.94; H 4.87; N 7.10; P 7.85; S 8.13.

***N*-(Diethoxythiophosphoryl)-*N*'-[(α-diethoxyphosphoryl)benzyl]-*N*'-methylthiourea (VIIa).** Diethyl isothiocyanatothiophosphate (**V**),4.1 g, was added dropwise with stirring to a solution of 4.99 g aminobenzylphosphonate **VIa** in 30 ml of dry diethyl ether, and the reaction mixture was left to stand for 1 day at 20°C. The crystals that formed were separated and recrystallized from chloroform to obtain 7.42 g (82%) of compound **VIIa**, mp 103–104°C. ^{1}H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 1.28 m (12H, MeC), 3.13 s (3H, MeN), 4.10 m (9H, PCH, CH_2OP), 7.27 m (5H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 17.64, 60.22. Found, %: C 43.56; H 7.11; N 5.96; P 12.84; S 14.06. $C_{17}H_{30}N_2O_5P_2S_2$. Calculated, %: C 43.57; H 6.47; N 5.98; P 13.22; S 13.68.

***N*-[Diethoxy(thio)phosphoryl]-*N*'[(α-diisopropoxyphosphoryl)benzyl]-*N*'-methylthiourea (VIIb)** was obtained in a similar way from 1.05 g of phosphonate **VIb** and 0.78 g of isothiocyanate **V**. Yield 1.8 g (98%), mp 96–97°C. ^{1}H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 1.24 m (18H, MeC), 3.13 s (3H, MeN), 4.44 m (7H, PCH, CH_2OP), 7.37 m (5H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 16.29, 59.94. Found, %: C 46.04; H 7.13; N 5.42; P 13.03; S 13.02. $C_{19}H_{34}N_2O_5P_2S_2$. Calculated, %: C 45.95; H 6.91; N 5.64; P 12.47; S 12.91.

Phenyl hydrogen (α-methylamino)benzylphosphonate (XI). Isothiocyanate **V**, 1.1 g, was added dropwise to a solution of 1.8 g of phosphonate **I** in 10 ml of dry benzene. After 2 days, the precipitate that formed was separated to obtain 0.6 g (43%) of compound **XI**, mp 220–221°C. IR spectrum (KBr), ν, cm^{-1}: 1090 (P–O–Ph), 1230–1250 (PO_2^-), 1590 (Ph), 1620, 2500, 3400 (NH_2^+). ^1H NMR spectrum (D_2O), δ, ppm (*J*, Hz): 2.7 s (3H, MeN), 4.5 d (1H, PCH, $^2J_{PCH}$ 21.4), 7.21 m (10H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 5.0. Found, %: C 60.15; H 6.14; N 5.26; P 10.86. $C_{14}H_{16}NO_3P$. Calculated, %: C 60.64; H 5.83; N 5.05; P 11.17.

***N*-[(Chloromethyl)phenoxyphosphoryl]-*N*'-[(α-diethoxyphosphoryl)benzyl]-*N*'-methylurea (XIVa).** Isocyanate **XIIa**, 1.53 g, was added dropwise with stirring to a solution of 1.7 g of aminobenzylphosphonate **XIIIa** in 10 ml of dry diethyl ether, and the reaction mixture was left to stand for 1 day at 20°C. The crystals that formed were separated and recrystallized from chloroform to obtain 1.48 g (45%) of compound **XIVa**, mp 134–135°C. IR spectrum (KBr), ν, cm^{-1}: 1030 (P–O–Alk), 1170 (Ph–O–P), 1260 (P=O), 1590 (Ph), 1670 (C=O), 3185 (NH). ^1H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 1.2 m (6H, MeC), 2.8 s (3H, MeN), 3.93 m (6H, PCH_2, CH_2OP), 5.77 d (1H, PCH, $^2J_{PH}$ 22), 7.1 m (10H, Ph), 7.9 br.s (1H, PNH). ^{31}P NMR spectrum, δ_P, ppm: 19.00, 17.87. Found, %: C 49.20; H 6.13; Cl 7.29; N 5.45; P 12.12. $C_{20}H_{27}ClN_2O_6P_2$. Calculated, %: C 49.13; H 5.58; Cl 7.25; N 5.73; P 12.67.

***N*-[(Chloromethyl)phenoxyphosphoryl]-*N*'-[(α-diethoxyphosphoryl)isobutyl]-*N*'-methylurea (XIVb)** was synthesized in a similar way from 2.23 g phosphonate **XIIIb** and 2.15 g of isocyanate **XIIa**. Yield 2.2 g (50%), mp 129–130°C. IR spectrum (KBr), ν, cm^{-1}: 1020 (P–O–Alk), 1210 (Ph–O–P), 1250 (P=O), 1590 (Ph), 1665 (C=O), 3200 (NH). ^1H NMR spectrum $[(CD_3)_2CO]$, δ, ppm (*J*, Hz): 0.68 d (6H, MeCN, $^3J_{HH}$ 5.4), 1.31 m (6H, $MeCH_2$), 2.9 s (3H, MeN), 4.21 m (8H, PCH_2, $POCH_2$, PCH), 7.13 m (5H, Ph), 8.61 br.s (1H, PNH). ^{31}P NMR spectrum, δ_P, ppm: 23.22, 18.00. Found, %: C 44.80; H 6.72; Cl 7.76; N 5.69; P 13.34. $C_{17}H_{29}ClN_2O_6P_2$. Calculated, %: C 44.89; H 6.44; Cl 7.79; N 6.16; P 13.62.

***N*-[Bis(chloromethyl)phosphoryl]-*N*'-[(α-diethoxyphosphoryl)benzyl]-*N*'-methylurea (XIVc)** was synthesized in a similar way from 1.82 g of phosphonate **XIIIa** and 1.33 g of isocyanate **XIIb**. Yield 2.68 g (85%), mp 115–116°C. IR spectrum (KBr), ν, cm^{-1}: 1025 (P–O–Alk), 1250 (P=O), 1585 (Ph), 1655 (C=O), 3100 (NH). ^1H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 1.21 m (6H, $MeCH_2$), 3.0 s (3H, MeN), 3.98 m (6H, PCH_2, $POCH_2$), 5.73 d (1H, PCH, $^2J_{PH}$ 22.0), 7.2 m (10H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 32.56, 19.11. Found, %: C 40.52; H 5.56; N 6.47; P 13.92. $C_{15}H_{24}Cl_2N_2O_5P_2$. Calculated, %: C 40.46; H 5.44; N 6.29; P 13.91.

1-Methyl-4-phenoxy-5-phenyl-1,3,4λ^5-diazaphospholidin-2-one 4-oxide (XVIII). *a*. Isocyanate **XIIa**, 2 g, was added to a solution of 3 g of phosphonate **I** in 10 ml of dry acetonitrile. After 1 day, 1.2 g (46%) of compound **XVIII** was separated, mp 194–196°C. IR spectrum (KBr), ν, cm^{-1}: 1245, 1255 (P=O), 1585 (Ph), 1705, 1740 (C=O), 3100– 3230 (NH). ^1H NMR spectrum $[(CD_3)_2CO]$, δ, ppm (*J*, Hz): 2.88 s (3H, MeN), 2.95 s (3H, MeN), 5.20 d (1H, PCH, $^2J_{PH}$ 18.33), 5.24 d (1H, PCH, $^2J_{PH}$ 19.43), 6.67 d (1H, PNH, $^2J_{PH}$ 7.5), 7.40 m (10H, Ph), 8.59 br.s (1H, PNH). ^{31}P NMR spectrum, δ_P, ppm: 20.70, 17.90. Mass spectrum, *m*/*z* (I_{rel}, %): 303 (9.8), 302 (64.0) $[C_{15}H_{15}N_2O_3P]^+$ ($[M]^+$), 225 (2.2) $[M - Ph]^+$, 210 (4.6), 209 (45.4) $[M - PhO]^+$, 182 (3.5), 166 (38.4) $[M - PhO - CONH]^+$, 152 (4.1) $[C_7H_7NOP]^+$, 140 (9.4) $[PhO_2P]^+$, 121 (10.1), 120 (100) $[C_8H_{10}N]^+$, 119 (10.6) $[C_8H_9N]^+$, 118 (70.2) $[C_8H_7N]^+$, 91 (20.6) $[C_7H_7]^+$, 77 (43.0) $[Ph]^+$, 47 (6.8) $[PO]^+$, 42 (28.2). Found, %: C 60.22; H 5.45; N 9.24; P 10.67. $C_{15}H_{15}N_2O_3P$. Calculated, %: C 59.60; H 5.01; N 9.27; P 10.25.

Fractional crystallization of compound **XVIII** from acetonitrile gave an individual diastereomer, mp 205–207°C. IR spectrum (KBr), ν, cm^{-1}: 1255 (P=O), 1585 (Ph), 1710 (C=O), 3100 (NH). ^1H NMR spectrum $[(CD_3)_2CO]$, δ, ppm (*J*, Hz): 2.74 s (3N, MeN), 5.10 d (1N, PCH, $^2J_{PH}$ 19.5), 7.35 m (10H, Ph), 8.52 br.s. (1H, PNH). ^{31}P NMR spectrum, δ_P, ppm: 20.80.

Distillation of the filtrate gave 0.85 g (35%) of phosphonate **XXa**, bp 90°C (0.02 mm). ^{31}P NMR spectrum, δ_P, ppm: 13.0 [17].

b. Isocyanate **XIIb**, 1.4 g, was added to a solution of 2.6 g of phosphonate **I** in 10 ml of dry acetonitrile. After 1 day, 1.84 g (82%) of compound **XVIII** was separated, mp 196°C. IR spectrum (KBr), ν, cm^{-1}: 1245, 1255 (P=O), 1585 (Ph), 1705, 1740 (C=O), 3100–3230 (NH). ^{31}P NMR spectrum, δ_P, ppm: 20.80, 18.0. Distillation of the filtrate gave 0.5 g (28%) of phosphinate **XIXb**, bp 120°C (0.02 mm). ^1H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 3.52 d (2H, PCH_2, $^2J_{PH}$ 9), 3.73 d (2H, PSH_2, $^2J_{PH}$ 9), 7.1 m (5H, Ph).

^{31}P NMR spectrum, δ_P, ppm: 38.0 [17].

Diphenyl [*N*-(4-thioxo-4-phenoxy-Δ^2-1,3,4-thiazaphospholin-2-yl)-*N*-methylamino](phenyl)-methylphosphonate (XXa). Isothiocyanate **XIIc**, 1 g, was added with stirring to a mixture of 1.34 g of phosphonate **I** and 1 ml of triethylamine in 20 ml of dry benzene. After 3 days, triethylamine hydrochloride was separated, the solvent was removed in a vacuum (0.02 mm), and the residue was recrystallized from acetonitrile to obtain 1.9 g (86%) of compound **XXa**, mp 126– 127°C. IR spectrum (KBr), ν, cm^{-1}: 695 (P=S), 1220 (P–O–Ph), 1270 (P=O), 1545 (C=N), 1585 (Ph). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 3.11 s (3N, MeN), 3.64 m (1H, $P^1CH^AN^B$, $^2J_{P^1H^B}$ –4.3, $^2J_{H^AH^B}$ –13.0, $^6J_{P^2H^B}$ 1.2), 4.06 m (1H, PCH^AN^B, $J_{H^AH^B}$ –13.0, $^2J_{P^1H^A}$ 13.7), 6.90 d (1N, P^2CH, $^2J_{P^2H}$ 23.0), 7.47 m (20H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 114.86, 9.85. Found, %: C 57.36; H 4.27; N 4.54; P 11.02. $C_{28}H_{26}N_2O_4P_2S_2$. Calculated, %: C 57.92; H 4.52; N 4.83; P 10.67.

Diphenyl [*N*-(4-chloromethyl-4-thioxo-4-Δ^2-1,3,4-thiazaphospholin-2-yl)-*N*-methylamino](phenyl)methylphosphonate (XXb) was obtained in a similar way from 1.6 g of phosphonate **I**, 1 ml of triethylamine, and 1 g isothiocyanate **XIId**. Yield 2.13 g (87%), mp 136°C. IR spectrum (KBr), ν, cm^{-1}: 680 (P=S), 1210 (P– O–Ph), 1275 (P=O), 1380 ($ClCH_2$), 1550 (C=N), 1585 (Ph). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 3.04 s (3N, MeN), 3.84 m (4N, PCH_2S, PCH_2Cl), 6.88 d (1N, PCH, $^2J_{PH}$ 22.7), 7.46 m (15H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 104.06, 10.08. Found, % : C 51.46; H 4.50; Cl 6.64; N 4.74; P 11.77; S 11.87. $C_{23}H_{23}ClN_2O_3P_2S_2$. Calculated, %: C 51.44; H 4.33; Cl 6.60; N 5.22; P 11.53; S 11.94.

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