Russian Journal of General Chemistry, Vol. 72, No. 7, 2002, pp. 1071–1081. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 7, 2002, pp. 1145–1156.

Synthesis and Structure of 1,3,4-Oxaza(thiaza)phospholines

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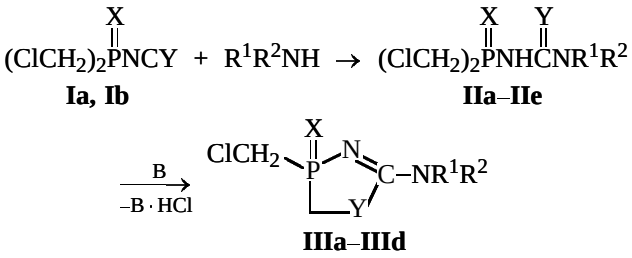
Received October 19, 2000

Abstract—Bis(chloromethyl)phosphinic (-phosphinothioic) iso(thio)cyanates add secondary amines to form *N*-phosphorylated (thio)ureas, which cyclize in the presence of a base to 1,3,4λ^5-oxaza(thiaza)phospholines. Phosphorylated ureas obtained by addition of ammonia and primary amines to chloromethylphosphonic (-phosphinic) isocyanates cyclize to give 1,4,2-diazaphospholidines or 1,3,4-oxazaphospholines. Prototropic transformations in the series of 1,3,4λ^5-oxazaphospholines were revealed; the electronic and steric structures of the tautomers were studied. Chloromethylphosphonothioic (-phosphinothioic) isothiocyanates add primary amines to give 1,3,4λ^5-thiazaphospholines.

Our present efforts are aimed at developing synthetic routes to heterocyclic phosphorus compounds containing endocyclic P–C bonds. These routes are based on intramolecular transformations of polyfunctional derivatives of four-coordinate phosphorus, including chloromethyl groups in combination with other structural fragments. By such procedures, we were able to prepare various saturated and unsaturated, mono- and bicyclic polyheterophosphacyclanes [1–5]. One of the simplest and most convenient routes to functionally substituted chloromethylphosphonates (-phosphonothioates, -phosphinates, phosphinothioates) is addition of protic nucleophiles to the corresponding phosphorylated iso(thio)cyanates. The reaction of ethyl 1-alkoxy-1-chloroalkylhosphonoisocyanatidates with primary amines was reported in [6]. Previously we showed that phosphorylated (thio)ureas cyclize under the action of bases to give 1,3,4-azaphospholines [1, 7]. To extend the synthetic potential of this approach, examine the conditions of cyclization of phosphorylated ureas (or thioureas), and prepare new types of 1,3,4λ^5-oxaza(thiaza)phospholines, we studied the reactions of some primary and secondary amines with phosphorylated iso(thio)cyanates.

We found that bis(chloromethyl)phosphinic (-phosphinothioic) iso(thio)cyanates **Ia**, **Ib** readily add secondary amines to give *N*-phosphorylated (thio)ureas **IIa**–**IIe**. In the presence of a base, the oxygen atom of the carbonyl group or the sulfur atom of the thiocarbonyl group undergoes intramolecular alkylation with the chloromethyl group, with elimination of HCl and cyclization into 1,3,4λ^5-oxaza(thiaza)phospholines **IIIa**–**IIId**.

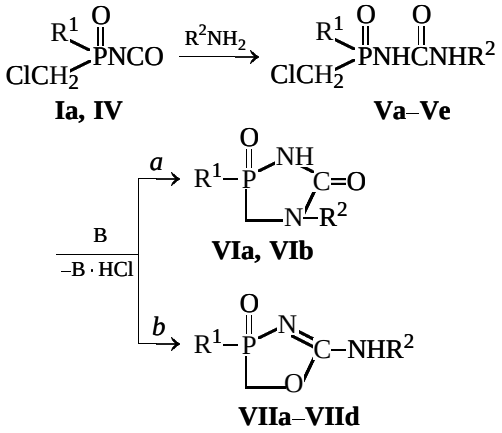


I, X = Y = O (**a**), X = Y = S (**b**); **II**, X = Y = O, R^1 = R^2 = Et (**a**); X = Y = O, R^1 = R^2 = Pr (**b**); X = Y = O, R^1 = R^2 = Bu (**c**); X = Y = O, R^1, R^2 = $N(CH_2CH_2)_2O$ (**d**); X = Y = O, R^1, R^2 = $N(CH_2)_5$ (**e**); **III**, X = Y = O, R^1 = R^2 = Et (**a**); X = Y = O, R^1, R^2 = $N(CH_2CH_2)_2O$ (**b**); X = Y = O; R^1, R^2 = $N(CH_2)_5$ (**c**); X = Y = S, R^1, R^2 = $N(CH_2CH_2)_2O$ (**d**).

Compounds **IIa**–**IIe** and **IIIa**–**IIId** were prepared in good yields; their structure was determined by NMR and IR spectroscopy. The characteristic absorption bands of the carbonyl (1670–1690 cm^{-1}) and NH (3100 cm^{-1}) groups present in the IR spectra of phosphorylated ureas are absent in the spectra of **IIIa**–**IIId**, but a band appears at 1610–1625 cm^{-1}, belonging to the endocyclic C=N bond. Formation of phospholines **IIIa**–**IIId** is also confirmed by a downfield shift of the ^{31}P NMR signals. It should be noted that the reac-

tion of isothiocyanate **Ib** with morpholine is very fast and strongly exothermic; it directly yields **IIId**. This is due to easier alkylation of the thiocarbonyl sulfur, compared to carbonyl oxygen.

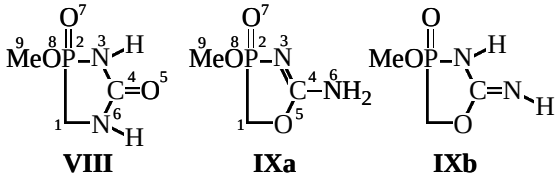
Reactions of phenyl chloromethylphosphonoisocyanatidate **IV** with primary amines yield *N*-phosphorylated ureas **Va**–**Ve** containing two labile protons: at the bridging and terminal nitrogen atoms. In this case, two pathways of intramolecular alkylation are possible: that of the terminal nitrogen atom, yielding the saturated 1,4,2λ^5-diazaphospholidine system (compounds **VIa** and **VIb**, pathway *a*), and that of the carbonyl oxygen atom, yielding 1,3,4λ^5-oxazaphospholines **VIIa**–**VIId** (pathway *b*). We found that both pathways are actually realized, depending on the presence and structure of the substituent R^2 at the terminal nitrogen atom.



IV, R^1 = PhO; **V**, R^1 = PhO, R^2 = H (**a**); R^1 = PhO, R^2 = *t*-Bu (**b**); R^1 = $ClCH_2$, R^2 = H (**c**); R^1 = $ClCH_2$, R^2 = *t*-Bu (**d**); R^1 = $ClCH_2$, R^2 = Ph (**e**); **VI**, R^1 = PhO, R^2 = H (**a**); R^1 = $ClCH_2$, R^2 = H (**b**); **VII**, R^1 = PhO, R^2 = H (**a**); R^1 = PhO, R^2 = *t*-Bu (**b**); R^1 = $ClCH_2$, R^2 = *t*-Bu (**c**); R^1 = $ClCH_2$, R^2 = Ph (**d**).

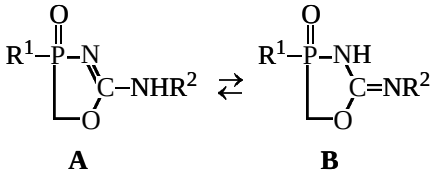
Pathway *a* is realized with *N*-(bischloromethylphosphinyl)urea **Vc** containing a primary amino group. After its treatment with triethylamine, we isolated 2-chloromethyl-2,5-dioxo-1,4,2λ^5-diazaphospholidine **VIb**. Introduction of alkyl or aryl substituents at the terminal nitrogen atom of phosphorylated urea **V** yields 1,3,4λ^5-oxazaphospholines **VIIa**–**VIId** as the only products. *N*-(*O*-Phenylchloromethylphosphonyl)-urea **Va** cyclizes by two pathways to give a mixture of 1,3,4λ^5-diazaphospholine **VIIa** and 1,4,2λ^5-diazaphospholidine **VIa**. Compound **VIa** was isolated analytically pure.

To examine the possibillity of predicting the cyclization pathway of phosphorylated ureas, we have performed quantum-chemical calculations of the relative energies of isomeric 1,3,4λ^5-oxazaphospholine **VIIb** and 1,4,2λ^5-diazaphospholidine **VIb**, and also of phospholidine **VIII** and oxazaphospholine **IX** (*ab initio*, HF/3-21G*, GAMESS program [8], and MNDO and PM3 [9, 10]).



All the three methods show that the phospholidine structure **VIII** is preferable relative to the oxazaphospholine structure **IX** (by 87, 55, and 78 kJ mol^{-1}, respectively). The MNDO and PM3 calculations also indicate that the saturated diazaphospholidine heterocycle **VIb** is more stable than the unsaturated oxazaphospholine derivative **VIIb** (by 31 and 70 kJ mol^{-1}, respectively). Thus, the diazaphospholidine form is more stable for both derivatives. Thus, the cyclizations under consideration are not thermodynamically controlled. Preferable formation of 1,3,4-oxazaphospholine structure **VIIb** rather than more stable diazaphospholidine structure **VIb** may be due to kinetic control of this reaction or to steric hindrance produced by the bulky *tert*-butyl group at the terminal nitrogen atom.

It should be noted that compounds **VIIa**–**VIId** prepared from *N*-phosphorylated *N*'-substituted ureas contain an amidine group, which suggests the possibility of a tautomeric equilibrium between the 1,3,4λ^5-oxazaphospholine form **A** and 1,3,4λ^5-oxazaphospholidine form **B**. Indeed, both forms were detected by ^{31}P NMR spectroscopy. Each of 1,3,4λ^5-oxazaphospholines **VIIa**–**VIId** gives two downfield singlets (see Experimental). For **VIIb**, the chemical shifts δ_P (ppm) are 53.41 (**A**, 88.7%) and 48.36 (**B**, 11.3%). The tautomeric equilibrium is also manifested in the ^{13}C and ^1H NMR spectra (Table 1, Experimental).



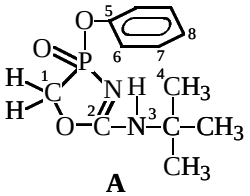
The electronic structures and geometries of the tautomers were studies by semiempirical and *ab initio* (HF/3-21G*, GAMESS program) calculations. As examples, we also took oxazaphospholines **VIIb** and **IX** with endocyclic and exocyclic C=N bonds. The total energy of isomers **IXa** and **IXb** is –778.858767 and –778.848057 au, respectively, i.e., the structure with

the endocyclic C=N bond appeared to be more stable by 28.1 kJ mol^{-1}. Similar difference (~25 kJ mol^{-1}) was obtained by MNDO and PM3 calculations [9, 10]. For **VIIb**, according to MNDO calculations, form **B** is more stable (by 10 kJ mol^{-1}), whereas PM3 calculations give an opposite result: form **A** is more stable by 18 kJ mol^{-1}. Apparently, the total energies of these tautomers are close, but form **A** is somewhat more stable, as also indicated by NMR data. Figure 1 shows the steric structures of tautomers **A** and **B** of **VIIb**.

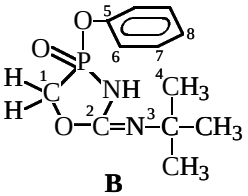
The atomic charges, atomic populations of HOMO, and bond lengths and orders in **VIII** and tautomers **A** and **B** of **IX**, calculated *ab initio* (HF/3-21G*), are compared in Tables 2 and 3. All the structures are characterized by the presence of very polar bonds with the largest negative charges on the nitrogen atoms; in both heterocycles, the negative charge on the three-coordinate N atom is larger than that on the imine N atom. Passing from tautomer **A** to **B** should also be accompanied by a shift of the electron density from the phosphorus atom. The highest occupied molecular orbitals in these structures appreciably differ both in energy and in composition. The HOMO (π_{CO}) energy in **VIII** is –10.88 eV. The HOMO energy in **IXa** (–8.73 eV) is considerably lower (in absolute value) compared to **IXb** (–10.33 eV), but the LUMO energies in these tautomers are close (5.41 and 5.96 eV, respectively). The HOMO of **IX** is mainly localized on the endo- and exocyclic nitrogen atoms. It is a combination of antibonding orbitals π_{CN}, π^*_{CN}, and n_N. The interference of the orbital interactions [11] of n_N with π_{CN} and π^*_{CN} results in that the contribution of the central atom of the N=C–N triad to HOMO of both tautomeric forms is insignificant.

The electronic structure of this triad was discussed previously [11, 12]. Note that tautomer **B** with the exocyclic multiple bond also has two isomeric structures, of which the structure with the cisoid arrangement of the OCNH atoms is more stable. The structure with the transoid arrangement of the OCNH atoms (*E* –787.838219 au) is less stable (by 25.8 kJ mol^{-1}) and will not be considered further. The bond lengths and orders in the molecules in question are compared in Table 3. First, it should be noted that the orders of all the bonds in structure **B** are low and do not exceed 0.85. Proton migration to the N^3 atom is accompanied not only by apparent elongation of the N^3–C^4 bond, but also by slight elongation of the P^3–N^3 and C^4–O^5 bonds. These changes are manifested more clearly in the bond orders. According to calculations, the arrangement of all the five atoms in both tautomers is approximately coplanar. The exocyclic C–O bond is in the *gauche* position relative to the P=O bond; the

Table 1. ^{31}P and ^{13}C NMR spectra of tautomers **A** and **B** of **VIIb**



A



B

Atom	**A**, δ, ppm (*J*, Hz)	**B**, δ, ppm (*J*, Hz)
^{31}P	53.41	48.36
C^1	59.37 (J_{PC^1} 98.5, J_{C^1H} 153.5, 155.6)	59.37 (J_{PC^1} 98.5, J_{C^1H} 153.5, 155.6)
C^2	161.95 ($^2J_{PC^2}$ 8.5)	162.16 ($^2J_{PC^2}$ 8.5)
C^3	52.21	53.35
C^4	28.34 (J_{C^4H} 127.1)	29.09 (J_{C^4H} 126.6)
C^5	150.65 ($^2J_{POC^5}$ 8.5)	150.65 ($^2J_{POC^5}$ 8.5)
C^6	120.72 ($J_{C^6H^6}$ 164.3)	120.49 ($J_{C^6H^6}$ 164.3)
C^7	129.53 ($J_{C^7H^7}$ 162.4, $^3J_{C^7H^7}$ 8.5)	128.16 ($J_{C^7H^7}$ 162.4, $^3J_{C^7H^7}$ 8.5)
C^8	127.76 ($J_{C^8H^8}$ 163.0, $^3J_{C^8H^8}$ 7.4)	123.63 ($J_{C^8H^8}$ 163.0, $^3J_{C^8H^8}$ 7.4)

Table 2. Effective atomic charges and atomic populations of HOMO of **VIII** and tautomers **IXa** and **IXb** (HF/3-21G* calculations)

Atom	Charge[a]			HOMO population		
	VIII	**IXa**	**IXb**	**VIII**	**IXa**	**IXb**
C^1	–0.549	–0.499	–0.482	0.063	0.001	0.009
P^2	1.630	1.521	1.604	0.001	0.029	0.018
N^3	–1.035	–0.825	–1.022	0.005	0.896	0.477
C^4	1.142	1.091	1.052	0.697	0.075	0.178
O^5	–0.642	–0.675	–0.682	1.058	0.070	0.172
N^6	–0.907	–0.961	–0.775	0.007	0.447	0.997
O^7	–0.613	–0.613	–0.611	0.011	0.399	0.064
O^8	–0.724	–0.723	–0.723	0.001	0.121	0.041

[a] In electron charge units.

Table 3. Bond lengths (*d*) and orders (*p*) in molecules of **VIII** and of tautomers **IXa** and **IXb** (HF/3-21G* calculations)

Bond	*d*, Å			*p*		
	VIII	**IXa**	**IXb**	**VIII**	**IXa**	**IXb**
C^1–P^2	1.812	1.835	1.810	0.786	0.740	0.774
P^2–N^3	1.657	1.645	1.643	0.843	1.001	0.863
N^3–C^4	1.401	1.279	1.395	0.868	1.577	0.875
C^4–O^5	1.209	1.371	1.380	1.789	0.927	0.844
C^1–O^5	1.466	1.475	1.460	0.847	0.764	0.793
C^4–N^6	1.364	1.325	1.239	0.909	0.981	1.796
P^2=O^7	1.462	1.462	1.461	1.940	1.940	1.936

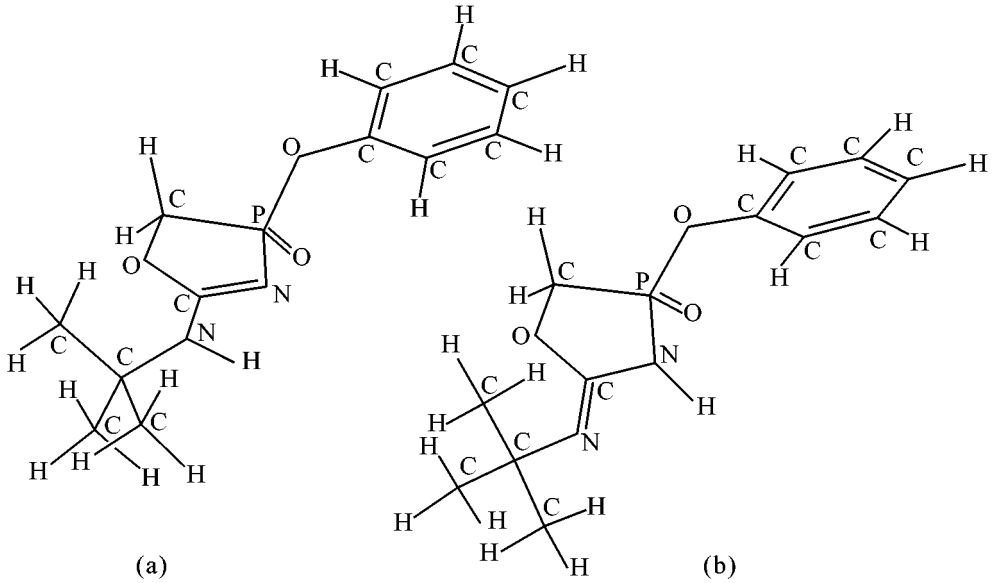


Fig. 1. Steric structure of tautomers **A** and **B** of **VIIb** (PM3 calculations).

torsion angle $C^9O^8P^2O^7$ in forms **A** and **B** is –22.2° and –24.6°, respectively.

Phosphinate **Ia** reacts with primary amines (*tert*-butylamine, aniline) similarly to phosphonate **IV**. However, we failed to isolate cyclic products **VIIc** and **VIId** analytically pure. The ^{31}P NMR spectrum of each of the products contains two signals with δ_P in the ranges 64–66 and 58–60 ppm in a ~3.5 : 1 ratio, which suggests that these compounds also exist in solutions as tautomeric mixtures. According to the ^1H NMR and IR spectra, the cyclic products contain small amounts of the amine hydrochlorides. To confirm the structures of the products, they were subjected to hydrolysis. The hydrolysis products are crystalline compounds sparingly soluble in organic solvents. Based on elemental analysis and spectra, these products were identified as isouroniomethyl-(chloromethyl)phosphinates **Xa** and **Xb**. The ^{31}P NMR spectrum of each of these inner salts contains one singlet, δ_P (ppm) 23 (**Xa**) and 24 (**Xb**); their IR spectra contain absorption bands (cm^{-1}) at 1230–1240 (PO_2^-), 1565–1580, and 2600–2780 (NH_2^+).

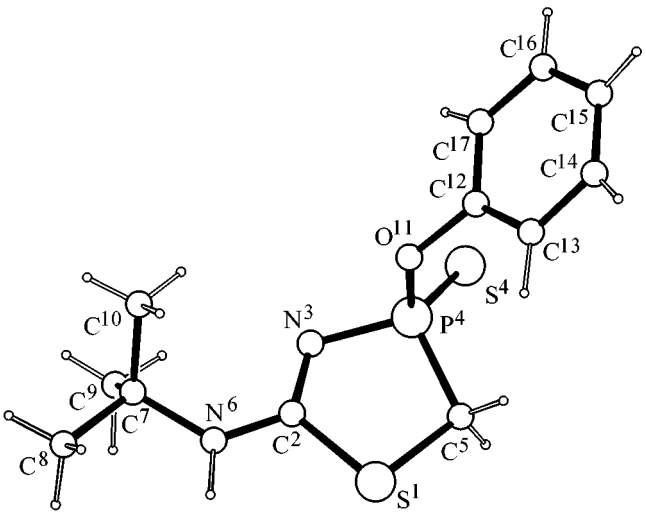
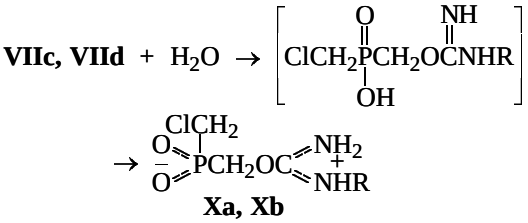


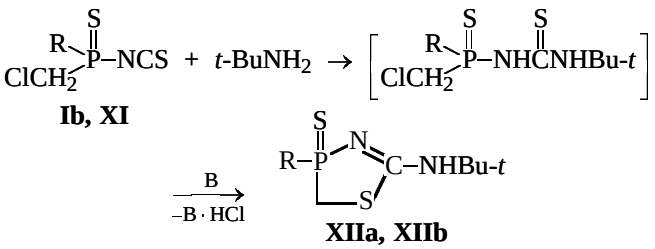
Fig. 2. Geometry of an independent molecule of **XIIb** in the crystal.



Xa, Xb

X, R = *t*-Bu (**a**), Ph (**b**).

Phosphinothioate **Ib** and *O*-phenyl chloromethylphosphonoisothiocyanatidothioate **XI** react with primary amines to form 1,3,4λ^5-thiazaphospholines **XIIa** and **XIIb**. The compositions of **XIIa** and **XIIb** were confirmed by elemental analysis, and their structures were determined by ^1H, ^{31}P, and ^{13}C NMR and IR spectroscopy. The IR spectra of thiazaphospholines **XIIa** and **XIIb** contain absorption bands at 1565–1575 cm^{-1}, characterizing vibrations of the endocyclic C=N bond. According to the spectral data, phospholines **XIIa** and **XIIb** in solutions occur in a single tautomeric form.



XI, R = PhO; **XII**, R = $ClCH_2$ (**a**), R = PhO (**b**).

The crystal and molecular structure of 2-*tert*-butylamino-4-phenoxy-4-thioxo-1,3,4λ^5-thiazaphospholine **XIIb** was studied by single crystal X-ray diffraction. Two independent molecules of **XIIb** in the crystal have approximately the same geometries; one of them is shown in Fig. 2. The ring conformation in this molecule is P-*envelope*, although, taking into account the presence of the C=N bond, the C^5-*envelope* conformation could be expected. The torsion angle about the C^2=N^3 bond is 12.7(2)°, and that about the S^1–C^2 bond is 0.5(2)°. In the other molecule, the ring conformation is *twist*, with the above-mentioned torsion angles being –7.4(3)° and –7.1(2)°, respectively. The phenoxy group at P occupies the axial position, which is typical of phosphacyclanes with endocyclic P–O and P–N bonds. The bond lengths and bond angles in the independent molecules coincide within experimental error. The exocyclic P–O bond is somewhat elongated [average 1.605(2) Å] as compared to the values typical of four-coordinate phosphorus, whereas the endocyclic P–N bond is somewhat shortened [average 1.638(8) Å], which may be due to the anomeric effect.

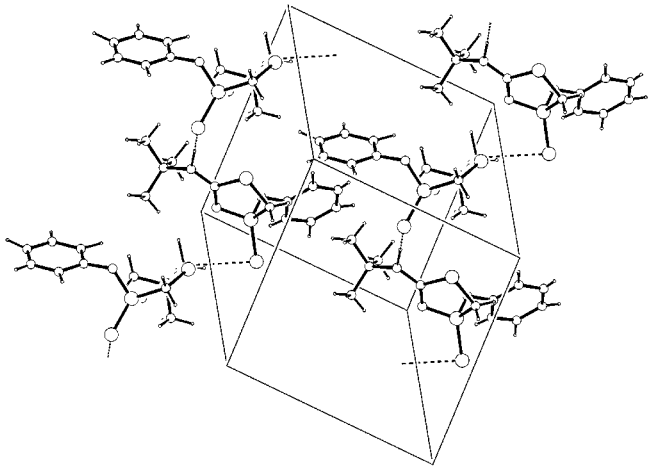


Fig. 3. System of hydrogen bonds in the crystal of **XIIb**.

The other geometric parameters have usual values. The crystal packing of the molecules is determined by intermolecular hydrogen bonds N–H···S with the sulfur atom of the thiophosphoryl group (Fig. 3). The parameters of the N^{6A}–H···$S^{4B'}$ (x, y – 1, z) bond are as follows: N^{6A}–H 1.08(2), N^{6A}···$S^{4B'}$ 3.382(2), H···$S^{4B'}$ 2.37(2) Å; angle N^{6A}–H···$S^{4B'}$ 155(2)°. The parameters of the N^{6B}–H···$S^{4A''}$ (x – 1, y + 1, z) bond are as follows: N^{6B}–H 0.89(2), N^{6B}···$S^{4A''}$ 3.538(2), H···$S^{4A''}$ 2.75(2) Å; angle N^{6B}–H···$S^{4A''}$ 149(2)°. The molecules form infinite zigzag chains running along the *x*-axis. The atomic coordinates, bond lengths, bond angles, and torsion angles for **XIIb** are listed in Tables 4–6.

Table 4. Atomic coordinates in the structure of **XIIb** and the equivalent isotropic temperature factors of nonhydrogen atoms $B = 4/3\Sigma\Sigma(a_{ij})B(i,j)$ (Å^2) and isotropic temperature factors of hydrogen atoms B_{iso}

Atom	First molecule				Second molecule			
	x	*y*	*z*	*B*, B_{iso}	*x*	*y*	*z*	*B*, B_{iso}
S^1	1.42930(7)	0.00858(6)	0.63455(4)	4.58(2)	0.97194(7)	0.10110(7)	0.59906(4)	4.91(2)
S^4	1.02812(7)	–0.22932(7)	0.78426(5)	5.76(2)	0.60690(7)	0.33112(7)	0.51690(4)	4.58(2)
P^4	1.19420(6)	–0.13009(6)	0.77049(4)	3.85(1)	0.76291(6)	0.29298(6)	0.56572(4)	3.41(1)
O^{11}	1.2573(2)	–0.1664(2)	0.8544(1)	4.76(4)	0.8530(2)	0.4242(2)	0.5556(1)	4.39(4)
N^3	1.1839(2)	0.0339(2)	0.7576(1)	3.98(5)	0.7256(2)	0.2125(2)	0.6708(1)	3.52(4)
N^6	1.3259(2)	0.2255(2)	0.6942(1)	3.64(4)	0.8277(2)	0.0683(2)	0.7692(1)	4.65(5)
C^2	1.2968(2)	0.0966(2)	0.7036(1)	3.38(5)	0.8239(2)	0.1320(2)	0.6878(1)	3.64(5)
C^5	1.3361(3)	–0.1497(2)	0.6741(2)	4.63(6)	0.9021(3)	0.1916(3)	0.5121(2)	4.39(6)
C^7	1.2465(3)	0.3188(2)	0.7509(1)	3.81(5)	0.7194(3)	0.0698(3)	0.8556(2)	4.71(6)
C^8	1.3358(3)	0.4460(2)	0.7227(2)	5.85(8)	0.7877(4)	0.0018(4)	0.9279(2)	7.9(1)
C^9	1.1065(3)	0.3491(3)	0.7330(2)	6.28(7)	0.5935(4)	–0.0056(4)	0.8580(2)	7.7(1)
C^{10}	1.2304(3)	0.2576(3)	0.8491(2)	5.36(7)	0.6837(4)	0.2122(3)	0.8667(2)	6.52(8)
C^{12}	1.2619(3)	–0.2965(2)	0.9049(1)	4.16(5)	0.7973(2)	0.5367(2)	0.5905(1)	3.70(5)
C^{13}	1.3838(3)	–0.3674(3)	0.8861(2)	5.43(7)	0.8034(3)	0.5427(3)	0.6748(2)	4.90(6)
C^{14}	1.3838(3)	–0.4947(3)	0.9420(2)	7.75(8)	0.7592(3)	0.6601(3)	0.7056(2)	5.82(7)
C^{15}	1.2720(4)	–0.5431(3)	1.0112(2)	8.19(9)	0.7093(3)	0.7669(3)	0.6550(2)	5.47(7)

Table 4. (Contd.)

Atom	First molecule				Second molecule			
	x	*y*	*z*	*B*, B_{iso}	*x*	*y*	*z*	*B*, B_{iso}
C^{16}	1.1548(4)	–0.4707(3)	1.0288(2)	7.67(9)	0.7030(3)	0.7562(3)	0.5718(2)	5.30(7)
C^{17}	1.1483(3)	–0.3454(3)	0.9754(2)	5.65(7)	0.7459(3)	0.6421(3)	0.5392(2)	4.50(6)
H^{6}	1.430(2)	0.257(2)	0.653(1)	5.7(6)	0.905(2)	0.020(2)	0.767(1)	6.1(6)
H^{13}	1.465(2)	–0.325(2)	0.834(1)	5.6(6)	0.844(2)	0.457(2)	0.711(1)	5.0(5)
H^{14}	1.447(2)	–0.518(2)	0.921(1)	4.5(5)	0.761(3)	0.658(2)	0.764(1)	6.5(7)
H^{15}	1.288(4)	–0.624(3)	1.056(2)	13(1)	0.693(3)	0.853(2)	0.681(1)	6.5(7)
H^{16}	1.068(3)	–0.506(3)	1.074(2)	10.3(9)	0.671(2)	0.819(2)	0.540(1)	4.9(5)
H^{17}	1.088(2)	–0.297(2)	0.982(1)	5.6(6)	0.744(2)	0.632(2)	0.483(1)	4.9(5)
H^{51}	1.313(3)	–0.168(2)	0.631(1)	6.7(7)	0.962(2)	0.237(2)	0.471(1)	4.3(5)
H^{52}	1.378(2)	–0.224(2)	0.693(1)	5.9(6)	0.871(2)	0.136(2)	0.481(1)	4.7(5)
H^{81}	1.349(3)	0.493(3)	0.656(2)	8.3(8)	0.826(3)	–0.077(2)	0.918(2)	7.4(7)
H^{82}	1.422(3)	0.418(3)	0.731(2)	7.5(7)	0.730(3)	0.005(3)	0.983(2)	7.0(7)
H^{83}	1.285(3)	0.511(2)	0.757(1)	6.4(6)	0.889(4)	0.074(3)	0.917(2)	13(1)
H^{91}	1.135(3)	0.390(3)	0.663(2)	9.4(9)	0.537(3)	–0.001(3)	0.918(2)	8.9(8)
H^{92}	1.061(3)	0.266(3)	0.748(2)	8.9(8)	0.619(3)	–0.098(3)	0.848(2)	12(1)
H^{93}	1.060(3)	0.405(2)	0.768(1)	6.4(7)	0.565(3)	0.040(3)	0.815(2)	8.9(8)
H^{101}	1.196(3)	0.319(2)	0.884(1)	6.5(7)	0.637(3)	0.249(3)	0.820(2)	7.9(8)
H^{102}	1.332(3)	0.227(3)	0.856(2)	9.4(9)	0.618(3)	0.207(2)	0.924(2)	7.1(7)
H^{103}	1.170(3)	0.181(3)	0.866(2)	7.6(7)	0.762(3)	0.269(3)	0.857(2)	8.7(8)

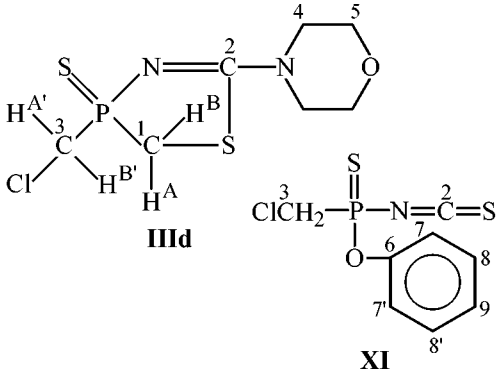
Table 5. Bond lengths (*d*) and angles (ω) in independent molecules of **XIIb**

Bond	*d*, Å		Bond	*d*, Å	
	first molecule	second molecule		first molecule	second molecule
S^{1}–C^{2}	1.793(2)	1.793(2)	N^{6}–H^{6}	1.07(2)	0.89(2)
S^{1}–C^{5}	1.798(2)	1.790(3)	C^{7}–C^{8}	1.520(4)	1.530(4)
S^{4}–P^{4}	1.924(1)	1.927(1)	C^{7}–C^{9}	1.513(4)	1.496(5)
P^{4}–O^{11}	1.607(2)	1.602(2)	C^{7}–C^{10}	1.520(3)	1.506(4)
P^{4}–N^{3}	1.634(2)	1.642(2)	C^{12}–C^{13}	1.372(4)	1.378(4)
P^{4}–C^{5}	1.803(2)	1.806(2)	C^{12}–C^{17}	1.371(3)	1.374(3)
O^{11}–C^{12}	1.396(3)	1.397(3)	C^{13}–C^{14}	1.403(4)	1.387(4)
N^{3}–C^{2}	1.303(3)	1.297(3)	C^{14}–C^{15}	1.348(4)	1.369(4)
N^{6}–C^{2}	1.322(3)	1.331(3)	C^{15}–C^{16}	1.340(5)	1.375(4)
N^{6}–C^{7}	1.488(3)	1.486(3)	C^{16}–C^{17}	1.380(4)	1.368(4)
Angle	ω, deg		Angle	ω, deg	
$C^{2}S^{1}C^{5}$	94.2(1)	94.1(1)	$S^{1}C^{5}P^{4}$	106.2(1)	105.7(1)
$S^{4}P^{4}O^{11}$	114.94(7)	113.51(7)	$N^{6}C^{7}C^{8}$	105.3(2)	105.0(2)
$S^{4}P^{4}N^{3}$	118.05(8)	115.88(7)	$N^{6}C^{7}C^{9}$	109.7(2)	108.5(2)
$S^{4}P^{4}C^{5}$	113.8(1)	117.7(1)	$N^{6}C^{7}C^{10}$	109.9(2)	110.9(2)
$O^{11}P^{4}N^{3}$	100.5(1)	107.5(1)	$C^{8}C^{7}C^{9}$	110.7(2)	112.7(2)
$O^{11}P^{4}C^{5}$	105.8(1)	98.5(1)	$C^{8}C^{7}C^{10}$	109.3(2)	108.2(3)
$N^{3}P^{4}C^{5}$	102.0(1)	101.7(1)	$C^{9}C^{7}C^{10}$	111.8(2)	111.4(3)
$P^{4}O^{11}C^{12}$	124.4(2)	123.6(1)	$O^{11}C^{12}C^{13}$	118.7(2)	118.4(2)
$P^{4}N^{3}C^{2}$	113.2(2)	113.1(1)	$O^{11}C^{12}C^{17}$	119.1(2)	120.2(2)
$C^{2}N^{6}C^{7}$	126.3(2)	127.1(2)	$C^{13}C^{12}C^{17}$	122.1(2)	121.3(2)
$C^{2}N^{6}H^{6}$	115(1)	111.1(1)	$C^{12}C^{13}C^{14}$	115.9(2)	117.9(2)
$C^{7}N^{6}H^{6}$	117(1)	121.1(1)	$C^{13}C^{14}C^{15}$	122.1(3)	121.7(3)
$S^{1}C^{2}N^{3}$	120.6(2)	120.8(2)	$C^{14}C^{15}C^{16}$	120.8(3)	118.6(3)
$S^{1}C^{2}N^{6}$	114.2(1)	114.2(2)	$C^{15}C^{16}C^{17}$	119.7(3)	121.3(2)
$N^{3}C^{2}N^{6}$	125.3(2)	125.0(2)	$C^{12}C^{17}C^{16}$	119.5(3)	119.1(2)

Table 6. Torsion angles (φ) in independent molecules of **XIIb**

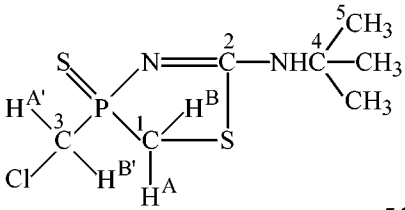
Angle	φ, deg		Angle	φ, deg	
	first molecule	second molecule		first molecule	second molecule
$C^5S^1C^2N^3$	0.5(2)	–7.1(2)	$S^4P^4O^{11}C^{12}$	39.0(2)	57.9(2)
$S^1C^2N^3P^4$	12.7(2)	–7.4(3)	$N^3P^4O^{11}C^{12}$	166.8(2)	–71.6(2)
$C^2N^3P^4C^5$	–19.1(2)	18.1(2)	$C^5P^4O^{11}C^{12}$	–87.4(2)	–176.8(2)
$N^3P^4C^5S^1$	18.3(2)	–21.4(2)	$S^4P^4C^5S^1$	146.54(9)	–149.16(9)
$C^2S^1C^5P^4$	–11.6(1)	16.5(1)	$O^{11}P^4C^5S^1$	–86.4(1)	88.6(1)
$S^4P^4N^3C^2$	–144.6(2)	147.9(2)	$P^4O^{11}C^{12}C^{13}$	98.2(3)	92.8(2)
$O^{11}P^4N^3C^2$	89.6(2)	–84.8(2)			

Table 7. ^{1}H (δ, ppm), ^{31}P [δ_P, ppm (J, Hz)], and ^{13}C [δ_C, ppm (J, Hz)] NMR spectra of **IIId**, **XIIa**, and **XIIb**[a]

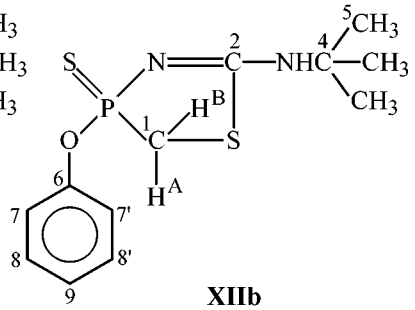


IIId

XI



XIIa



XIIb

Atom	**IIId**	**XIIa**	**XIIb**
^{31}P	106.0	107.00	119.38
C^1	33.09 (J_{PC^1} 31.1, J_{C^1H} 145.2, 148.8)	31.94 (J_{PC^1} 30.5, J_{C^1H} 145.5, 149.3, $^3J_{C^1PC^3H}$ 3.2)	34.64 (J_{PC^1} 55.5, J_{C^1H} 145.2, 148.8)
C^2	169.83 ($^2J_{PC^2}$ 5.5, $^3J_{C^2SC^1H^e}$ 3.6, $^3J_{C^2SC^1H^a}$ 2.0)	165.55 ($^2J_{PC^2}$ 1.2, $^3J_{C^2SC^1H^e}$ 4.2, $^3J_{C^2SC^1H^a}$ 2.3)	164.90
C^3	43.98 (J_{PC^3} 68.5, J_{C^3H} 152.7, $^3J_{C^3PC^1H}$ 1.7)	43.34 (J_{PC^3} 68.2, J_{C^3H} 152.5, $^3J_{C^3PC^1H}$ 1.5)	
C^4	48.78 (J_{C^4H} 139.5)	55.04 ($^2J_{C^4NH}$ 3.5, $^2J_{C^4C^5H}$ 3.6)	55.43
C^5	66.27 ($^5J_{PNC^2NC^4C^5}$ 7.8, J_{C^5H} 144.1)	29.27 (J_{C^5H} 127.9, $^3J_{C^5C^4NH}$ 4.4, $^3J_{C^5C^4C^{5'}H}$ 3.7)	28.53 (J_{C^5H} 127.0, $^3J_{C^5C^4NH}$ 2.8, $^3J_{C^5C^4C^{5'}H}$ 4.6)
H^A	3.77 ($^2J_{PH^A}$ 0.5, $^2J_{H^AH^B}$ –14.4)	3.62 ($^2J_{PH^A}$ 1.1, $^2J_{H^AH^B}$ –13.8)	3.50 ($^2J_{PH^A}$ –3.9, $^2J_{H^AH^B}$ –13.0)
H^B	3.84 ($^2J_{PH^B}$ –8.5)	3.96 ($^2J_{PH^B}$ –14.9)	3.70 ($^2J_{PH^B}$ –13.0)
$H^{A'}$	3.63 ($^2J_{PH^{A'}}$ –6.3, $^2J_{PH^{A'}H^{B'}}$ –13.1)	3.44 ($^2J_{PH^{A'}}$ –1.6, $^2J_{PH^{A'}H^{B'}}$ –12.5)	
$H^{B'}$	3.26 ($^2J_{PH^{B'}}$ –2.1)	3.23 ($^2J_{PH^{B'}}$ –5.1)	

[a] For **XI**, δ, ppm (J, Hz): δ_P 56.76, δ_{C^2} 149.30 (J_{PC^2} 1.9), δ_{C^3} 42.24 (J_{PC^3} 119.5, J_{C^3H} 152.4), δ_{C^6} 148.74 (J_{P^6C} 10.7, $J_{C^6C^7C^8H}$ 8.7, $J_{C^6C^7H}$ –2.4, $J_{C^6C^7C^8C^9H}$ –1.5), δ_{C^7} 120.99 ($J_{POC^6C^7}$ 4.8, J_{C^7H} 163.9, $J_{C^7C^8C^9H}$ 8.0, $J_{C^7C^6C^{7'}H}$ 4.9), δ_{C^8} 129.55 ($J_{POC^6C^7C^8}$ 1.6, J_{C^8H} 162.9, $J_{C^8C^9C^{8'}H}$ 8.9), δ_{C^9} 125.94 (J_{PC^9} 2.2, J_{C^9H} 162.8, $J_{C^9C^8C^7H}$ 7.7). For **XII** C_i^6 150.76 (J_{POC^6} 10.3, $J_{C^6C^7C^8H}$ 9.1, $J_{C^6C^7H}$ –2.4, $J_{C^6C^7C^8C^9H}$ –1.6), C_o^7 121.33 ($J_{POC^6C^7}$ 4.5, J_{C^7H} 163.5, $J_{C^7C^6C^{7'}H}$ 4.6, $J_{C^7C^8C^9H}$ 9.2), C_m^8 129.24 ($J_{POC^6C^7C^8}$ 1.4, J_{C^8H} 161.9, $J_{C^8C^9C^{8'}H}$ 8.7), C_p^9 124.74 ($J_{POC^6C^7C^9}$ 3.6, J_{C^9H} 162.6, $J_{C^9C^8C^7H}$ 8.1), H_o^7 7.19 (J_{PH^7} 1.4, $J_{H^7H^8}$ 7.4, $J_{H^{7'}H^8}$ 0.8, $J_{H^7H^9}$ 2.5), H_m^8 7.32 (J_{PH^8} 2.2, $J_{H^8H^9}$ 7.4); H_p^9 7.16 (J_{PH^9} 1.2).

The structures of **IIId**, **XIIa**, **XIIb**, and also **XI** (taken for comparison) in solution were studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy [13]. The parameters of the spectra are listed in Table 7. It is seen that the molecules of **XIIa** and **XIIb** in solution exist as single isomers. It should be noted that the direct coupling constants in the compounds under consideration take two values (Tables 1, 7). This may be associated with the axial and equatorial positions of the C–H bonds in the ring, by analogy with cyclohexane [14, 15] and 2,2-dimethyl-1,3,2,6-dioxasilaphosphocins [16, 17]. According to the X-ray structural data, the C–H bond lengths with the axial and equatorial hydrogen atoms in **XIIb** are also different: 0.84 and 0.88 Å, respectively. The chemical shifts of these methylene protons are different, and their assignment was based on analysis of the *ABX* pattern in the ^{1}H NMR spectra (*A*, axial proton; *B*, equatorial proton; *X*, phosphorus) assuming that the more negative coupling constants, $^{2}J_{PH^{B}}$ –8.5 to –14.9 Hz, correspond to the equatorial protons of the ring with the dihedral angles $H^{B}C^{1}PS$ ~85°–90°. This is consistent with data for the geminal coupling constants P^{IV}–H [15, 17]. According to X-ray diffraction data, this angle in **XIIb** is about 85°.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer (mulls in mineral oil or thin films) in the range 400–3600 cm^{-1}. The ^{31}P NMR spectra were recorded on Bruker MSL-400 (161.97 MHz) and KGU-4 (10.2 MHz) spectrometers; external reference 85% H_3PO_4. The ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer (100.6 MHz). The ^{1}H NMR spectra were measured on Bruker MSL-400 (400.132 MHz), WM-250 (250.132 MHz), and Varian T-60 (60 MHz) spectrometers; internal reference TMS.

Single crystal X-ray diffraction study of XIIb. Triclinic system; at 20°C: *a* 10.012(1), *b* 10.151(3), *c* 15.960(3) Å; α 77.53(2)°, β 77.03(1)°, γ 86.88(1)°; *V* 1514.7(5) $Å^3$, *Z* 4, d_{calc} 1.32 g cm^{-3}, space group $P\bar{1}$ (two independent molecules). The unit cell parameters and the intensities of 5238 reflections, including 3923 reflections with $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer at 20°C (λMoK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 26.7°$). No decay of the intensities of three check reflections was observed during the experiment; the absorption was small (μMo 4.32 cm^{-1}) and was therefore neglected.

The structure was solved by the direct method using SIR program [18] and refined first in the isotropic and then in the anisotropic approximation. All the hydrogen atoms were revealed from the differential electron density series and were refined isotropically in the final stage. The structure was refined to *R* 0.33, R_W 0.047 for 4005 unique reflections with $F^2 \geq 3\sigma$. All the calculations were performed with a DEC Alpha Station 200 computer using MolEN program package [19]. The intermolecular contacts in the crystal were analyzed, and the molecular and crystal structures plotted, using the PLATON program [20].

***N,N*-Diethyl-*N*'-[bis(chloromethyl)phosphinyl]-urea IIa.** Diethylamine (0.73 g) was added dropwise with stirring to a solution of 1.88 g of **Ia** in 10 ml of dry diethyl ether, cooled to 0°C. After 1 day, the solvent was vacuum-evaporated, and the residue was recrystallized from diethyl ether. Compound **IIa** was obtained; yield 1.8 g (69%), mp 110–111°C. IR spectrum (KBr), ν, cm^{-1}: 1255 (P=O), 1660 (C=O), 3140 (NH). ^{31}P NMR spectrum (acetone): δ_P 32 ppm. Found, %: N 10.25; P 11.65. $C_7H_{15}Cl_2N_2O_2P$. Calculated, %: N 10.73; P 11.86.

Substituted ureas **IIb**–**IIe** were prepared similarly.

***N,N*-Dipropyl-*N*'-[bis(chloromethyl)phosphinyl]-urea IIb.** Yield 73%, mp 80–81°C. IR spectrum (KBr), ν, cm^{-1}: 1215 (P=O), 1640 (C=O), 3100 (NH). ^{31}P NMR spectrum (acetone): δ_P 30 ppm. Found, %: C 37.35; H 6.56; N 9.63; P 10.61. $C_9H_{19}Cl_2N_2O_2P$. Calculated, %: C 37.38; H 6.64; N 9.69; P 10.71.

***N,N*-Dibutyl-*N*'-[bis(chloromethyl)phosphinyl]-urea IIc.** Yield 54%, mp 83–84°C. IR spectrum (KBr), ν, cm^{-1}: 1210 (P=O), 1630 (C=O), 3140 (NH). ^{31}P NMR spectrum (acetone): δ_P 29 ppm. Found, %: C 41.12; H 7.20; N 8.80; P 9.80. $C_{11}H_{23}Cl_2N_2O_2P$. Calculated, %: C 41.64; H 7.32; N 8.83; P 9.76.

***N*-(3-Oxa-1,5-pentylene)-*N*'-[bis(chloromethyl)-phosphinyl]urea IId.** Yield 94%, mp 130–132°C. IR spectrum (KBr), ν, cm^{-1}: 1240 (P=O), 1650 (C=O), 1560, 3150 (NH). ^{31}P NMR spectrum (acetone): δ_P 30 ppm. Found, %: C 29.80; H 4.72; N 9.93; P 11.02. $C_7H_{13}Cl_2N_2O_3P$. Calculated, %: C 30.56; H 4.77; N 10.19; P 11.26.

***N*-(Pentamethylene)-*N*'-[bis(chloromethyl)phosphinyl]urea IIe.** Yield 94%, mp 125–126°C. IR spectrum (KBr), ν, cm^{-1}: 1255 (P=O), 1665 (C=O), 3100 (NH). ^{31}P NMR spectrum (acetone): δ_P 30 ppm. Found, %: C 34.80; H 5.20; N 10.30; P 11.05. $C_8H_{15}Cl_2N_2O_2P$. Calculated, %: C 35.18; H 5.55; N 10.26; P 11.34.

2-Diethylamino-4-oxo-4-chloromethyl-1,3,4λ^5-oxazaphospholine IIIa. Triethylamine (0.4 g) was

added dropwise with stirring to a solution of 1 g of **IIa** in 50 ml of dry diethyl ether. The mixture was allowed to stand for a day, triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was recrystallized from chloroform. Compound **IIIa** was obtained; yield 0.45 g (52%), mp 156–157°C. IR spectrum, ν, cm^{-1}: 1230 (P=O), 1625 (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.20 m (6H, CH_3C), 3.40 m (4H, NCH_2), 3.40 m (2H, $ClCH_2$), 4.60 m (OCH_2). ^{31}P NMR spectrum (acetone): δ_P 59.43 ppm. Found P, %: 13.15. $C_7H_{14}ClN_2O_2P$. Calculated P, %: 13.79.

Oxazaphospholines **IIIb** and **IIIc** were prepared similarly.

2-Morpholino-4-oxo-4-chloromethyl-1,3,4λ^5-oxazaphospholine IIIb. Yield 81%, mp 212–213°C. IR spectrum (KBr), ν, cm^{-1}: 1240 (P=O), 1635 (C=N). ^{31}P NMR spectrum (acetone): δ_P 59.9 ppm. Found, %: C 35.45; H 5.26; N 11.06; P 12.59. $C_7H_{12}ClN_2O_3P$. Calculated, %: C 35.23; H 5.08; N 11.74; P 12.98.

2-Piperidino-4-oxo-4-chloromethyl-1,3,4λ^5-oxazaphospholine IIIc. Yield 63%, mp 179–180°C. IR spectrum (KBr), ν, cm^{-1}: 1230 (P=O), 1625 (C=N). ^{31}P NMR spectrum (acetone): δ_P 59.15 ppm. Found, %: C 39.85; H 6.08; Cl 15.05; N 11.36; P 12.85. $C_8H_{14}ClN_2O_2P$. Calculated, %: C 40.60; H 5.97; Cl 14.98; N 11.84; P 13.09.

2-Morpholino-4-thioxo-4-chloromethyl-1,3,4λ^5-thiazaphospholine IIId. A mixture of 1.3 g of morpholine and 2.5 ml of triethylamine was added dropwise with stirring to a solution of 3.2 g of **Ib** in 50 ml of dry benzene, cooled to 5°C. The mixture was allowed to stand for a day, after which triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was recrystallized from acetonitrile. Compound **IIId** was obtained; yield 3.85 g (98%), mp 108–109°C. IR spectrum (KBr), ν, cm^{-1}: 665 (P=S), 1565 (C=N). ^{31}P NMR spectrum (acetone): δ_P 106 ppm. Found, %: C 30.96; H 4.30; N 9.94; P 11.76. $C_7H_{12}ClN_2OPS_2$. Calculated, %: C 31.05; H 4.48; N 10.35; P 11.44.

***N*-[*O*-Phenyl(chloromethyl)phosphinyl]urea Va.** Ammonia (0.22 g) was passed through a stirred solution of 3.08 g of **IVa** in 50 ml of dry diethyl ether, cooled to –5°C. The resulting precipitate was filtered off and washed with anhydrous acetonitrile and diethyl ether. Compound **Va** was obtained; yield 2.45 g (74%), mp 148–149°C. IR spectrum (KBr), ν, cm^{-1}: 700, 1395 (CH_2Cl), 965 (P–OPh), 690, 760, 1500, 1590 (Ph), 1250 (P=O), 1680 (C=O), 1615, 3390 (NH_2), 3200 (NH). ^1H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 4.1 d (2H, PCH_2, $^2J_{PCH}$ 10), 5.61 br.s (2H, NH_2), 7.37 m (5H, Ph), 8.1 br.s (1H, NH). ^{31}P NMR spectrum (acetone): δ_P 16.36 ppm, %: C 38.01; H 4.19; Cl 14.13; N 11.31; P 12.64. $C_8H_{10}ClN_2O_3P$. Calculated, %: C 38.65; H 4.08; Cl 14.26; N 11.27; P 12.46.

***N*-*tert*-Butyl-*N*′-[*O*-phenyl(chloromethyl)phosphinyl]urea Vb.** *tert*-Butylamine (1.59 g) was added dropwise with stirring to a solution of 5.03 g of **IV** in 10 ml of diethyl ether, cooled to 5°C. The mixture was allowed to stand for 1 day, after which the solvent was removed in a vacuum. Compound **Vb** was obtained; yield 6.32 g (95%), viscous substance. IR spectrum (KBr), ν, cm^{-1}: 1165, 1210 (POPh), 1230 (P=O), 1590 (Ph), 1690 (C=O), 1550, 3200–3400 (NH). ^1H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 1.2 s (9H, CH_3C), 3.87 d (2H, $ClCH_2P$, $^2J_{PH}$ 9), 5.93 br.s (1H, NH), 6.97 m (5H, Ph), 7.93 br.s (1H, NHP). ^{31}P NMR spectrum (acetone): δ_P 18.5 ppm. Found P, %: 9.64. $C_{12}H_{18}ClN_2O_3P$. Calculated P, %: 10.16.

***N*-[Bis(chloromethyl)phosphinyl]urea Vc.** Gaseous ammonia (0.5 g) was passed through a stirred solution of 5.51 g of **Ia** in 50 ml of dry diethyl ether, cooled to –5°C. The resulting precipitate was filtered off and washed successively with anhydrous acetonitrile and diethyl ether. Compound **Vc** was obtained; yield 4.2 g (70%), mp 141°C. IR spectrum (KBr), ν, cm^{-1}: 690, 1390 (CH_2Cl), 1240 (P=O), 1620, 3390 (NH_2), 1680 (C=O), 3200 (NH). ^{31}P NMR spectrum (acetone): δ_P 26.8 ppm. Found, %: C 17.42; H 3.29; Cl 35.20; N 13.33; P 15.22. $C_3H_7Cl_2N_2O_3P$. Calculated, %: C 17.58; H 3.45; Cl 34.59; N 13.67; P 15.11.

Substituted ureas **Vd** and **Ve** were prepared similarly.

***N*-*tert*-Butyl-*N*′-[bis(chloromethyl)phosphinyl]urea Vd.** Yield 80%, mp 109–112°C. IR spectrum (KBr), ν, cm^{-1}: 1240 (P=O), 1690 (C=O), 1560, 3180–3355 (NH). ^1H NMR spectrum (Me_2SO), δ, ppm (*J*, Hz): 1.2 s (9H, CH_3C), 3.87 d (4H, $ClCH_2P$, $^2J_{PH}$ 7), 6.33 s (1H, NH), 7.76 br.s (1H, NHP). ^{31}P NMR spectrum (acetone): δ_P 28.5 ppm. Found, %: C 32.67; H 6.47; N 10.82; P 12.04. $C_7H_{15}Cl_2N_2O_2P$. Calculated, %: C 32.20; H 5.80; N 10.73; P 11.86.

***N*-Phenyl-*N*′-[bis(chloromethyl)phosphinyl]urea Vd.** Yield 82%, mp 170–173°C. IR spectrum (KBr),

ν, cm^{-1}: 1240 (P=O), 1590 (Ph), 1670 (C=O), 1540, 3170, 3310 (NH). ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 4.17 d (4H, $ClCH_2P$, $^2J_{PH}$ 8), 7.19 m (5H, Ph), 8.31 br.s (1H, NHP), 8.92 s (1H, NH). ^{31}P NMR spectrum (acetone): δ_P 28 ppm. Found, %: C 39.04; H 4.03; Cl 25.15; N 10.25. $C_9H_{11}Cl_2N_2O_2P$. Calculated, %: C 38.45; H 3.95; Cl 25.22; N 9.97.

2-Phenoxy-2,5-dioxo-1,4,2λ^5-diazaphospholidine VIa. A mixture of 1.5 g of **Va**, 0.8 g of triethylamine, and 50 ml of anhydrous acetonitrile was heated for 8 h at 82°C. The precipitate was filtered, washed with CCl_4, and dried in a vacuum. Compound **VIa** was obtained; yield 0.85 g (66%), mp 210–212°C. IR spectrum (KBr), ν, cm^{-1}: 965 (P–OPh), 1220 (P=O), 1595 (Ph), 1720 (C=O), 3200 (NH). ^{31}P NMR spectrum (acetone): δ_P 20.7 ppm. Found P, %: 14.08. $C_8H_9N_2O_3P$. Calculated P, %: 14.60.

2-Chloromethyl-2,5-dioxo-1,4,2λ^5-diazaphospholidine VIb was prepared similarly. Yield 86%, mp 225°C. ^1H NMR spectrum {$[(CD_3)_2N]_3PO$}, δ, ppm (*J*, Hz): 3.7 d (2H, $ClCH_2P$, $^2J_{PCH}$ 8.5), 4.18 m (2H, CH_2P). ^{31}P NMR spectrum (acetone): δ_P 20.0 ppm. Found P, %: 18.32. $C_3H_6N_2ClO_2P$. Calculated P, %: 18.38.

2-*tert*-Butylamino-4-oxo-4-phenoxy-1,3,4λ^5-oxazaphospholine VIIb was prepared similarly to **IIIa** from 4.1 g of **Vb** and 1.4 g of triethylamine; yield 1.95 g (55%), mp 130–132°C. IR spectrum (KBr), ν, cm^{-1}: 1070, 1210 (POPh), 1240 (P=O); 1590 (Ph), 1660 (C=N), 3195, 3285 (NH). ^1H NMR spectrum (CCl_4), δ, ppm: (**A**) 1.30 s (9H, CH_3C), 3.97 m (2H, CH_2P), 5.05 br.s (1H, NH), 7.16 m (5H, Ph); (**B**) 1.25 s (9H, CH_3C), 3.01 m (2H, CH_2P), 4.49 br.s (1H, NH), 7.16 m (5H, Ph). ^{31}P NMR spectrum (acetone): δ_P 53.41, 48.35 ppm. Found, %: C 54.06; H 6.76; N 10.39; P 12.08. $C_{12}H_{17}N_2O_3P$. Calculated, %: C 53.72; H 6.40; N 10.44; P 11.54.

***N*-*tert*-Butylisouroniomethyl(chloromethyl)phosphinate Xa.** A mixture of 2.63 g of **Vc** and 1.1 g of triethylamine in 30 ml of absolute benzene was heated at 70°C for 3 h. Triethylamine hydrochloride was filtered off, and 0.2 g of water was added to the filtrate. After 4 h, 1.1 g (47%) of **Xa** was separated; mp 207–209°C. ^1H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 1.43 s (9H, CH_3C), 3.45 d (2H, $ClCH_2P$, $^2J_{PH}$ 9), 4.13 d (2H, OCH_2P, $^2J_{PH}$ 7). ^{31}P NMR spectrum (acetone): δ_P 23 ppm. Found, %: C 34.55; H 6.56; N 11.40; P 12.91. $C_7H_{16}ClN_2O_3P$. Calculated, %: C 34.64; H 6.66; N 11.55; P 12.76.

***N*-Phenylisouroniomethyl(chloromethyl)phosphinate Xb** was prepared similarly from 2.9 g of **Vd**, 1.1 g of triethylamine, and 0.2 g of water. Yield 1.2 g (45%), mp 187–189°C. ^{31}P NMR spectrum (acetone): δ_P 24 ppm. Found, %: C 41.41; H 4.69; Cl 13.72; P 12.28. $C_9H_{12}ClN_2O_3P$. Calculated, %: C 41.15; H 4.61; Cl 13.50; P 11.79.

2-*tert*-Butylamino-4-thioxo-4-chloromethyl-1,3,4-λ^5-thiazaphospholine XIIa. *tert*-Butylamine (2.05 g) was added dropwise with stirring to a solution of 3.1 g of **Ib** in 50 ml of absolute benzene. The mixture was allowed to stand for 1 day, after which *tert*-butylamine hydrochloride was filtered off, the filtrate was washed with water (3 × 5 ml) and dried over Na_2SO_4, and the solvent was removed. The residue was recrystallized; 1.3 g (38%) of **XIIa** was obtained, mp 109–110°C. IR spectrum (KBr), ν, cm^{-1}: 680 (P=S), 1570 (C=N), 1515, 3290 (NH). ^{31}P NMR spectrum (acetone): δ_P 107 ppm. Found, % : C 32.98; H 5.41; N 10.57; P 12.00; S 24.81. $C_7H_{14}ClN_2PS_2$. Calculated, %: C 32.74; H 5.51; N 10.91; P 12.06; S 24.97.

2-*tert*-Butylamino-4-thioxo-4-phenoxy-1,3,4λ^5-thiazaphospholine XIIb was prepared similarly from 2 g of **XI** and 1.1 g of triethylamine; yield 2 g (88%), mp 129–130°C. IR spectrum (KBr), ν, cm^{-1}: 660 (P=S), 1205 (P–O–Ph), 1575 (C=N), 1590 (Ph), 1530, 3240, 3285 (NH). ^{31}P NMR spectrum (acetone): δ_P 119.38 ppm. Found, %: C 47.97; H 5.95; N 9.55; P 10.89; S 21.48. $C_{12}H_{17}N_2OPS_2$. Calculated, %: C 47.97; H 5.72; N 9.33; P 10.31; S 21.35.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32 837).

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