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**Dedicated to the 90th Anniversary of Corresponding Member
of the Russian Academy of Sciences A.N. Pudovik**

Reaction of (Chloromethyl)phosphonic(-phosphinic) Iso(thio)cyanates with Alcohols and (α-Hydroxyalkyl)phosphonates

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Abstract—Alcohols and α-hydroxyphosphonates undergo the addition to (chloromethyl)phosphonic(-phosphinic) iso(thio)cyanates, yielding phosphorylated (thio)urethanes. The latter undergo cyclization to form, depending on their structure, saturated or unsaturated five-membered P,N,O,S-containing heterocycles.

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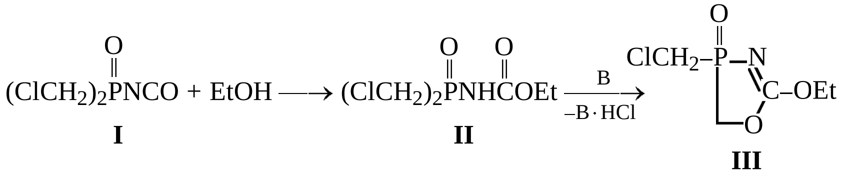
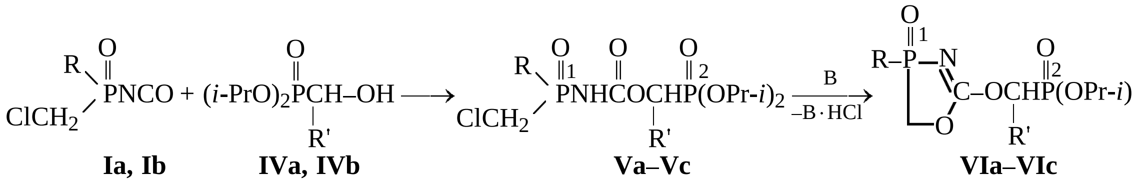
We previously showed that (chloromethyl)phosphinothioylthioureas of the general formula $R(ClCH_2)\cdot P(S)NHC(S)NR^1R^2$ in the presence of bases easily cyclize to form unsaturated phosphacyclanes, viz. 1,3,4-thiazaphospholes [1, 2]. The cyclization process includes intramolecular attack of the thione sulfur atom on the chloromethyl carbon atom with expulsion of chloride ion, formation of a cyclic molecular skeleton, and separation of base hydrochloride. According to nonempirical and semiempirical calculations, the need in equimolar amount of base in the reaction mixture for the intramolecular cyclization of (chloromethyl)phosphinothioylthiourea to occur is caused by the following circumstances. In the system under study, a complex between the base (triethylamine) and thiourea initially forms. As a result, the N–H bond weakens or even cleaves, and an ion pair forms. The attack of chloride ion on the proton of the secondary amino group results in dehydrochlorination of the molecule and formation of an unsaturated phosphacyclane with an endocyclic P–C bond [3]. In this connection (chloromethyl)phosphinoyl derivatives of carbamates and carbamothioates can be considered as promising candidates for cyclization. In the course of intramolecular cyclization of these compounds, additional possibility for chloride ion to attack the alkoxyl carbon atom with evolution of alkyl halide and formation of an unsaturated cyclic structure appears on the stage of carbocation formation.

(Chloromethyl)phosphinoylcarbamate **II** was prepared by the addition of ethanol to bis(chloromethyl)phosphinic isocyanate (**Ia**). In the presence of base it undergoes heterocyclization due to intramolecular reaction of the chloromethyl and carbonyl groups to give an unsaturated heterocycle, 1,3,4-oxazaphosphole **III** (δ_P 60.23 ppm). The reaction is accompanied by separation of base hydrochloride due to the involvement of the mobile proton of the secondary amino group that intervenes the phosphoryl and carbonyl fragments.



[†] Deceased.

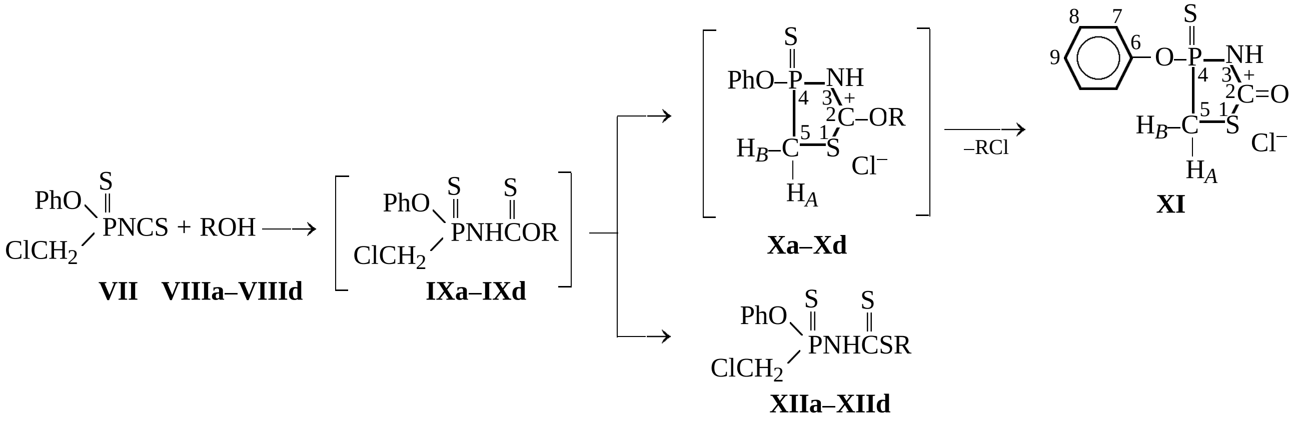
In the absence of base, phosphorylated carbamate **II** fails to cyclize because of the weak tendency of the carbonyl group for cyclization. The reactions of (α-hydroxyalkyl)phosphonates **IVa, IVb** with isocyanates **Ia, Ib** were carried out analogously. The reactions proceed easily at room temperature for several days and give rise to diphosphorylated carbamates **Va**–**Vc** as stable crystals. Their structure was established by IR and ^{1}H and ^{31}P NMR spectroscopy, and their composition was confirmed by elemental analysis. The ^{31}P NMR spectra contain two singlets at 16.70–18.50 (P^1) and 20.30–30.30 ppm (P^2).



I, R = $ClCH_2$ (**a**), PhO (**b**); **IV**, R' = H (**a**), CH_3 (**b**); **V, VI**, R = $ClCH_2$, R' = H (**a**); R = $ClCH_2$, R' = Me (**b**); R = PhO, R' = CH_3 (**c**).

Carbamates **Va**–**Vc** under the action of base undergo intramolecular cyclization with liberation of equimolar amount of base hydrochloride and formation of oxazaphospholes **VIa**–**VIc**. Cyclization is accompanied by a downfield shift of signals of P^1. The resulting chemical shifts, 56.1, 56.3, and 59.2 ppm for **VIa**–**VIc**, respectively, are close to that of oxazaphosphole **III** (60.23 ppm). At the same time, the chemical shifts of P^2 remain almost unchanged in going from carbamates **Va**–**Vc** to oxazaphospholes **VIa**–**VIc**. Note that the reactions are not unidirectional and give *a* number of minor phosphorus-containing products in each case. Oxazaphospholes **VI** proved to be hydrolytically unstable, which complicated their isolation from the reaction mixtures.

Intramolecular cyclization in the absence of base seemed more probable on replacement of the carbonyl group by thiocarbonyl, that is in going from phosphorylated carbamates to phosphorylated carbamothioates. The latter were prepared by addition of alcohols to isothiocyanate **VII**. The process was carried out at room temperature for several hours and gave finally 4-phenoxy-4-thioxo-1,3,4λ^5-thiazaphospholidin-2-one (**XI**).



XVI, XVII, XX, R = NMe_2 (**a**), Me (**b**), Ph (**c**).

Thiazaphospholidine **XI** is a white crystalline substance whose structure was established by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and electron impact (EI) mass spectrometry. The IR spectrum of 1,3,4-thiazaphospholidine contains absorption bands of the P–O–Ph (1190), Ph (1590), C=O (1680) and NH (3150) groups. In the ^{1}H NMR spectra, protons of the PCH_2 group give an octet at 4.02–4.22 ppm (*ABX*

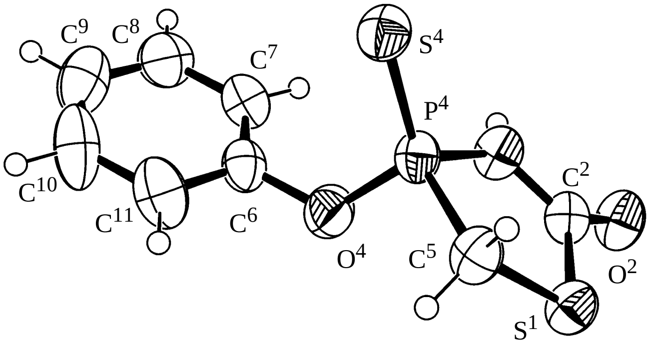


Fig. 1. Spatial arrangement of 4-phenoxy-4-thioxo-1,3,4λ^5-thiazaphospholidin-2-one (**XI**).

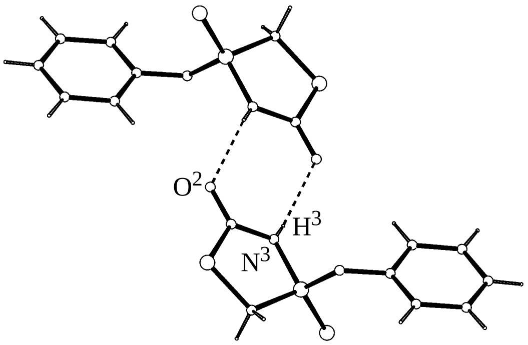


Fig. 2. System of hydrogen bonds in the crystal of **XI**.

system), which points to an endocyclic position of the methylene group. Phenyl protons appear as a multiplet at 7.22–7.44 ppm (A_2B_2C system).

The fragmentation pattern of compound **XI** under electron impact agree well with the proposed structure. The mass spectrum contains an intense M^+ ion peak at *m/z* 245 (see Experimental). The fragmentation of the phospholidine ring proceeds along three pathways: (a) rupture of the P–N and C–S bonds to form *m/z* 202 ions; (b) rupture of the P–C and C–S bonds to form *m/z* 199 ions; and (c) rupture of the P–N and P–C bonds to form of *m/z* 156 ions. All the three fragmentation pathways suggest charge localization on the phosphorus-contaning fragment. The P–O bond rupture leads to an $[M - \mathrm{PhO}]^+$ ion at *m/z* 152. Further decomposition of the above-mentioned ions gives ions with lower *m/z* values. The proposed fragmentation pathways of molecule **XI** under electron impact agree with the exact ion masses obtained by high-resolution mass spectrometry. The experimental masses fit well those calculated from the elemental composition of phospholidine **XI**.

The molecular and crystal structure of 4-phenoxy-4-thioxo-1,3,4λ^5-thiazaphospholidin-2-one (**XI**) was studied by means of X-ray diffraction. It was found that the conformation of the thiazaphospholidine ring in compound **XI** is C-*envelope* (Fig.1). The S^1, C^2, N^3, and P^4 atoms form a plane within 0.01Å. The C^5 atom deviates from it by 0.234(2) Å. The phenoxy group is axial with respect to the five-membered heteroring, and the thiophosphoryl substituent is equatorial. The P–O bond is perpendicular to the phenyl ring plane. The Ph–O bond is almost eclipsing the P=S bond [torsion angle 17.2(3)°]. The geometric parameters of compound **XI** are presented in the table. The crystals of compound form $N^3–H^3\cdots O^2$ [1 – *x*, 1 – *y*, 1 – *z*] hydrogen bonds with the geometric parameters: $N^3–H^3$ 0.62(6)Å, $H^3\cdots O^2$ 2.28(6)Å, $N^3\cdots O^2$ 2.869(5)Å, and ($N^3–H^3\cdots O^2$) angle 161(8)° (Fig. 2).

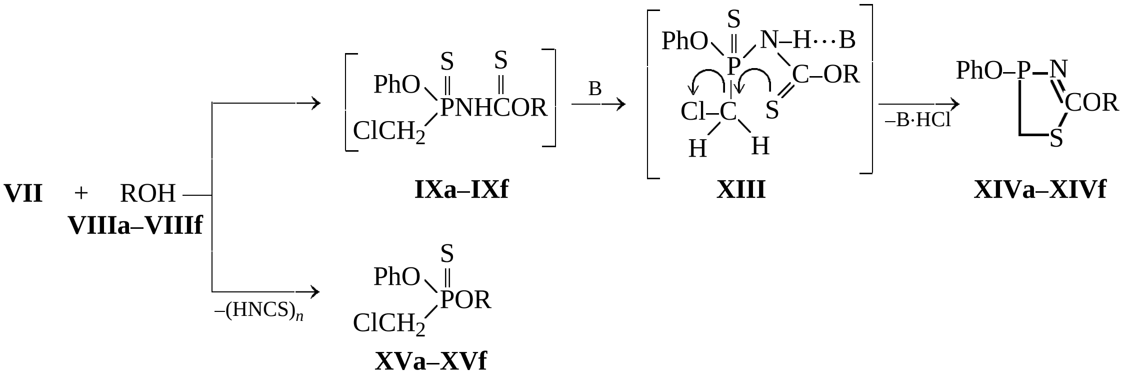
The reaction in question involves formation of phosphorylated carbamothioates**IXa**–**IXd** that were not be isolated pure. Their subsequent transformation

Geometric parameters of **XI**

Bond	*d*, Å	Bond	*d*, Å
$S^1–C^2$	1.756(4)	$P^4–C^5$	1.799(4)
$S^1–C^5$	1.797(4)	$O^2–C^2$	1.215(4)
$S^4–P^4$	1.9091(14)	$O^4–C^6$	1.411(4)
$P^4–O^4$	1.604(3)	$N^3–C^2$	1.358(5)
$P^4–N^3$	1.669(3)	$N^3–H^3$	0.62(6)
Bond angle	ω, deg	Bond angle	ω, deg
$C^2S^1C^5$	97.20(16)	$S^1C^2O^2$	121.0(3)
$S^4P^4O^4$	114.94(11)	$S^1C^2N^3$	114.1(2)
$S^4P^4N^3$	116.84(14)	$O^2C^2N^3$	124.9(3)
$S^4P^4C^5$	118.38(14)	$S^1C^5P^4$	109.39(18)
$O^4P^4N^3$	104.46(17)	$O^4C^6C^7$	120.0(3)
$O^4P^4C^5$	102.62(17)	$O^4C^6C^{11}$	118.0(4)
$N^3P^4C^5$	96.96(16)	$P^4N^3H^3$	125.0(6)
$P^4O^4C^6$	122.3(2)	$C^2N^3H^3$	114.0(6)
$P^4N^3C^2$	120.8(2)		
Torsion angle	τ, deg	Torsion angle	τ, deg
$C^5S^1C^2O^2$	175.2(3)	$N^3P^4C^5S^1$	–12.1(2)
$C^5S^1C^2N^3$	–5.9(3)	$P^4O^4C^6C^7$	69.8(4)
$C^2S^1C^5P^4$	11.1(2)	$P^4O^4C^6C^{11}$	–112.3(4)
$S^4P^4O^4C^6$	17.2(3)	$P^4N^3C^2S^1$	–2.3(4)
$N^3P^4O^4C^6$	–112.1(3)	$P^4N^3C^2O^2$	176.5(3)
$C^5P^4O^4C^6$	147.1(3)	$S^4P^4N^3H^3$	–48(8)
$S^4P^4N^3C^2$	136.0(3)	$O^4P^4N^3H^3$	80(8)
$O^4P^4N^3C^2$	–95.8(3)	$C^5P^4N^3H^3$	–175(8)
$C^5P^4N^3C^2$	9.2(3)	$H^3N^3C^2S^1$	–179(7)
$S^4P^4C^5S^1$	–137.72(15)	$H^3N^3C^2O^2$	0(8)
$O^4P^4C^5S^1$	94.5(2)		

includes nucleophilic attack of the carbamothioate sulfur on the chloromethyl carbon, yielding carbocation **X**. In the absence of base, chloride ion attacks the carbon atom of the alkoxy group to form alkyl halide and thiazaphospholidine **XI**. According to ^{31}P NMR, the reactions give phosphorylated carbamothioates **XIIa**–**XIId** along with the major product **XI**. The chemical shifts of compounds **XII** are 88–89 ppm. Carbamate **XIIa** (δ_P 88.12 ppm) was isolated pure by column chromatography. Its IR spectrum contains absorption bands at 1190 (PhO), 1590 (Ph), 1690 (C=O), 3080, 3310, and 3420 cm^{-1} (NH). In the ^1H NMR spectrum, protons of the PCH_2Cl group appear as a doublet in the range 3.6 ppm ($^2J_{PH}$ 10 Hz), which suggests that the methylene group is incorporated in the acyclic fragment of the molecule. Hence, together with the above-described cyclization, the thione–thiol isomerization of carbamothioate **IX** to alkyl [(chloromethyl)alkoxyphosphinothioyl]carbamodithioate **XII** takes place.

Addition of alcohols and their phosphorylated derivatives **VIII** to isothiocyanate **VII** in the presence of equimolar amount of base leads to other synthetic results. This reaction involves heat release and occurs by two concurrent pathways. The main pathway is the addition of alcohols by the C–N bond of isothiocyanate **VII** to form thiophosphorylated carbamothioates **IXa**–**IXf**. They undergo heterocyclization into 1,3,4-thiazaphospholes **XIVa**–**XIVf**. In this case, a scheme analogous to that we offered on the basis of theoretical studies on cyclization of chloromethylphosphorylated ureas and thioureas [3] is evidently realized. On the first stage, a complex between the base (triethylamine) and carbamothioate **IX** is formed, which results in weakening or even cleavage of the N–H bond and formation of the ion pair $\mathbf{IX}^- Et_3NH^+$. Subsequent nucleophilic attack of the carbamothioate sulfur on the chloromethyl carbon leads to liberation of chloride ion, ring closure, and triethylamine hydrochloride formation. The second reaction pathway involves nucleophilic substitution of the isothiocyanate group on phosphorus by alkoxyl. We failed to separate unsaturated phosphacyclanes **XIVa**–**XIVf** and (chloromethyl)phosphonothioates **XVa**–**XVf** by vacuum distillation because of the insufficient thermal stability of phosphacyclanes **XIVa**–**XIVf**. Chromatographic purification of the reaction mixture gave a mixture of organophosphorus products **XIV** and **XV** free of other admixtures, and it was characterized by spectral methods.



VIIIa–VIIIf

IXa–IXf

XIII

XIVa–XIVf

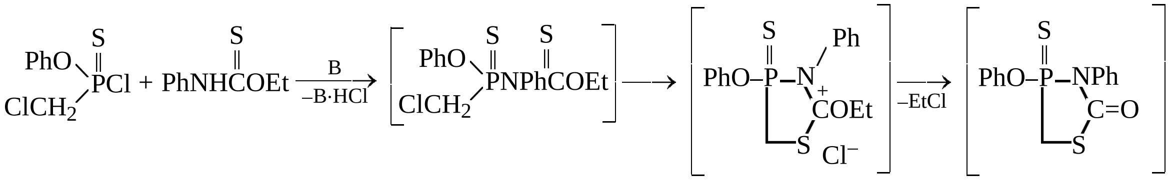
XVa–XVf

VIII, XIV, XV, R = Me (**a**), Et (**b**), Pr (**c**), Bu (**d**), $CH_2P(O)(OPr\text{-}i)_2$ (**e**), $CH(CH_3)P(O)(OPr\text{-}i)_2$ (**f**).

Analysis of the structure of compounds **XIVa**–**XIVXIVf** and **XVa**–**XVXVf** was carried out by ^1H, ^{21}P, ^{31}P–{^1H}, ^{13}C, ^{13}C–{^1H}, and 2D COSY NMR spectroscopy. The ^{31}P NMR spectra of the mixtures contain signals at 112–113 (**XIVa**–**XIVf**) and 81–84 ppm (**XVa**–**XVf**). Pure compound **XVa** was obtained by independent synthesis by the reaction of *O*-phenyl (chloromethyl)phosphonothioate with methanol. Its chemical shift is δ_P 83.5 ppm. Further evidence for the presence of the two types of compounds in the mixture is also confirmed by different multiplicities of their signals. The downfield signal is a broadened doublet (see Experimental) with the coupling constant J_{PH} 13 Hz that points to stronger interaction with one of endocyclic CH_2 protons and does not alter with changing alkyl radical length. The upfield signal is a broadened quintet (J_{PH} 8–9 Hz) for compounds **XIVb**–**XIVd** and a nine-line multiplet (J_{PH} 7 Hz) for compund **XIVa**. The latter is connected with the almost twofold difference in the $^2J_{PCH}$ and $^3J_{POCH}$ constants, as a result of which only 9 lines are observed instead of 12 (quartet of triplets). Furthermore, the signal at 112 ppm in the $^{31}P–\{^{1}H\}$ NMR spectra in all the cases is slightly broader that the upfield one, which is evidently connected with the effect of the quadrupole ^{14}N nucleus in compounds **XIVa**–**XIVf**. The **XIVa**–**XIVd**:**XVa**–**Vd** ratio in the mixtures, according to the integral intensities in the ^{31}P NMR spectra, increases in favor of the cyclic product with elongation of alkyl radical R: 1:2.9 (**a**), 1:1.9 (**b**), 1:0.9 (**c**), and 1:07 (**d**). The **XIVe, XIVf**:**XVe, XVf** ratio is much dependent on the starting (α-hydroxyalkyl)phosphonate. With C-phosphorylated methanol **VIIId**, the ratio of thiazaphosphole **XIVe** and phosphonothioate **XVf** is 3:1, whereas the **XIVf**:**XVf** ratio is 10:1. This result evidently reflects the enhancing steric congestion in going from hydroxyphosphonate **VIIIf** to its analog **VIIIf**. According the ^{31}P NMR spectrum, compound **XIVf** is formed as a 1:1 mixture of two diastereomers, which is caused by the presence of two asymmetric centers, phosphorus and carbon (δ_P 111.7 and 111.4, 15.2 and 15.0 ppm), in the molecule. We took account of this circumstance when considered the ^{1}H and ^{13}C NMR spectra. Their parameters confirm the structures of compounds **XIVa**–**XIVf** and **XVa**–**XVf**. Using 2D COSY data, we could identify in the one-dimensional ^{1}H NMR spectra of the mixtures spin systems formed by protons of substituents R in compounds **XIVa**–**XIVf** and **XVa**–**XVf**. Moreover, the 2D COSY spectra contain an additional cross peak that allowed us to assign two multiplets at ~3.9 and 3.7 ppm to ring CH_2 protons of compounds **XIVa**–**XIVf**. These signals form the *AB* part of the *ABX* spectrum (X=P) with the following parameters for compound **XIVc**: δ_A 3.865 ppm, δ_A 3.68 ppm, J_{AB} 13.3 Hz, J_{AB} 13.8 Hz, and J_{BX} 5.4 Hz. Compounds **XIVa**–**XIVf** have close spectral characteristics. The resulting values agree with the described shape of the downfield signal in the ^{31}P NMR spectrum in which the doublet lines are additionally broadened by coupling with phenyl protons (J_{BX} constant). The nonequivalence of protons of the ring methylene group in phosphacyclanes **XIVa**–**XIVd** is also reflected in the ^{13}C NMR spectra. The signal of the corresponding carbon atom is registered as two doublets of doublets and not as two triplets due to certain difference in the values of the direct $J_{C–H_A}$ and $J_{C–H_B}$ constants. In the ^{1}H NMR spectra of compounds **XVb**–**XVd**, the signals of CH_2Cl protons, too, form the *AB* part of the *ABX* spectrum, but the nonequivalence of these protons is much less significant (with phosphonate **XVa**, broadening of the corresponding lines is only observed: δ_A 3.854 ppm, δ_A 3.841 ppm, $^{3}J_{AX}$ 8.0 Hz, and $^{3}J_{BX}$ 7.5 Hz). Note that these parameters are almost independent of the size of substituent R. The O–CH_2 protons of the alkyl radical in compounds **XIVb**–**XIVd** are nonequivalent and form the *AB* part of the ABM_3 [M_3=CH_3 (**XIVb**)] or ABM_2 spectra [M_2 = CH_2 (**XIVc, XIVd**)] with close constants for all the three compounds: δ_A 4.52 ppm, δ_A 4.50 ppm, J_{AB} ~10.6, and $^{3}J_{AM} \approx J_{BM}$ ~7.2 Hz. For the analogous group in compounds **XVb**–**XVd**, additional splitting due to the coupling with the ^{31}P nucleus is characteristic. Its analysis allows spectral parameters for compound **XVb** to be estimated: δ_A 4.28 ppm, δ_A 4.23 ppm, J_{AB} 10.2 Hz, and $^{3}J_{AM} \approx {}^{3}J_{BM}$ 7.2 Hz. The constants are almost equal for all the three compounds. Hence, protons of the P–CH_2Cl and O–CH_2 groups in compounds **XVb**–**XVd** have close $^{2}J_{PH}$ and $^{3}J_{PH}$ constants equal to 7.5-11 Hz, which explains the shape of the upfield multiplet in the ^{31}P NMR spectrum. The integral intensity ratios of the fairly resolved multiplets of compounds **XIVa**–**XIVd** and **XVa**–**XVd** lead to values close to those estimated from the ^{31}P NMR spectra.

The structures of the reaction products are confirmed by EI mass spectrometry. Its data show that the reaction products are mixtures of thiazaphospholes **XIVa**–**XIVd** and phosphonothioates **XVa**–**XVd**. The mass spectra contain molecular ion peaks $[M]^+$ of **XIVa**–**XIVd** with *m/z* 259, 273, 287, and 301. There are also molecular ion peaks $[M]^+$ of compounds **XVa**–**XVd** with *m/z* 236, 250, 264, and 278. This conclusion is drawn from a comparison of the mass spectra measured in series over the course of 3 min. In the initial moment of measurements (in Experimental, the mass spectra measured after 1.5 min are given), the mass spectra of the products contain primarily peaks of ions formed from more volatile esters **XVa**–**XVd** and then from cyclic molecules **XIVa**–**XIVd**. This result suggests fractionation in the course of the mass spectral experiment, as a result of which the mixture is enriched with less volatile compounds **XIVa**–**XIVd**. The mass spectra of **XIVa**–**XIVd** contain ions formed by ring cleavage: $[PhOPS]^+$, *m/z* 156; $[CH_2PS_2]^+$, *m/z* 109; $[CH_2PS]^+$, *m/z* 77; and $[PS]^+$, *m/z* 63. The fragmentation of **XIVa**–**XIVd** characteristically involves loss of the PhO and PhS groups. Evidence for the proposed fragmentation pattern under electron impact was obtained from the high-resolution mass spectrum of phosphacyclane **XIVd**. The fragmentation of esters **XVa**–**XVd** proceeds with generation of $[M - PhO]^+$ and $[M - CH_2Cl]^+$ cations. The $[M - PhS]^+$ and $[PhS]^+$ ions are evidently formed by a rearrangement including sulfur–oxygen exchange in the M^+ ion. Hence, the EI mass spectra provide unambiguous evidence for the formation of a mixture of cyclic and acyclic compounds in the course of the reaction.

To simulate the cyclization process including dealkylation of the intermediate carbocation, we reacted *O*-ethyl *N*-phenylcarbamothioate (**XVII**) with *O*-phenyl (chloromethyl)phosphonochloridothioate (**XVI**). Phoshorylated carbamothioate that should form in this reaction contains no secondary amino group and, therefore, can transform in a single direction to form a saturated heterocyclic product. The reaction occurs under prolonged heating and actually provides thiazaphospholidine **XX** (δ_P 79.9 ppm).


XVI **XVII** **XVIII** **XIX** **XX**

The structure of compound **XX** was established by means of IR and ^1H and ^{31}P NMR spectroscopy, and high-resolution mass spectrometry. The IR spectrum of compound **XX** contains absorption bands at 1590 cm^{-1} (Ph) and 1705 cm^{-1} (C=O), but the absorption band of the secondary amino group is absent. In the ^1H NMR spectra, PCH_2 protons give eight lines (*ABX* system) in the range 4.02–4.22 ppm, which points to an endocyclic character of the methylene group. The mass spectrum of product **XX** (see Experimental) contains an intense M^+ ion peak at *m/z* 321 and fragment ions formed by P–N and C–S bond cleavage in the five-membered heteroring. When the charge is localized on the phosphorus-containing fragment, this process leads to formation of *m/z* 202 ions. The ions with *m/z* 156 are generated by P–N and P–C bond cleavage in the ring with the charge localized on the phosphorus-containing fragment. The resulting data show that phosphorylated carbamothioate **XVIII** under the reaction conditions undergoes cyclization via intramolecular alkylation of the thiocarbonyl sulfur atom with the chloromethyl group followed by elimination of ethyl chloride.

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrophotometer in the range 400-3600 cm^{-1} in mineral oil or in thin layer. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer at 400.13, 100.62, and 162.98 MHz, respectively. The mass spectra were measured on a Finnigan MAT TRACE MS spectrometer, ionizing energy 70 eV, ion source temperature 200°C. Direct sample injection into the ion source was applied. The injector ampule was heated from 35 to 150°C at a step of 35 deg min^{-1}. The mass spectra were treated using the Xcalibur program. The mass spectrum of product **XIVd** was obtained on an MX-1310 instrument, ionizing energy 70 eV, collector current 30 μA; the sample was injected directly into the ion source at 120°C. The exact mass numbers were measured automatically against perfluorokerosene.

The X-ray data were obtained on an Enraft–Nonius automatic four-circle diffractometer (CuK_α radiation, λ 1.54184 Å, graphite monochromator, ω/2θ scanning, θ < 69.88°). Monoclinic crystal ($C_8H_8NO_2PS_2$), *M* 245.24, 0.8 × 0.3 × 0.3 mm, space group $P2_1/c$, *a* 6.570(4) Å, *b* 8.520(5) Å, *c* 18,550(10) Å, *V* 1037.7 Å^3, d_{calc} 1.570 g cm^{-3}, *Z* 4. The unit cell parameters and the intensities of 2116 reflections, among which 1936 with $I > 2\sigma$, were measured at 20°C. Final divergence factors: R_1 0.0849 and wR_2 0.2097.

No intensity decay of control reflections was observed in the course of the experiment. The MolEN and AlphaStation-200 programs [4] were used for X-ray analysis, and the SHELXL program [5], for refinement. Analysis of intermolecular contacts, including hydrogen bonds, in crystals was carried out using the PLATON program [6].

Ethyl *N*-[bis(chloromethyl)phosphinoyl]carbamate (II). Anhydrous methanol, 4.6 g, was added dropwise to 2 g of isocyanate **Ia**. Crystals formed and were washed with methanol to obtain 1.40 g (56%) of compound **II**, mp 126–128°C. IR spectrum (KBr), ν, cm^{-1}: 1190 (P=O), 1725 (C=O), 3100 (NH). ^1H NMR spectrum (CD_3CN), δ, ppm (J, Hz): 1.03 t (3H, CH_3C, $^2J_{HH}$ 7.0), 3.77 d (4H, CH_2P, $^2J_{PH}$ 8.0), 3.90 m (2H, OCH_2), 10.76 br.s (H, NH). ^{31}P NMR spectrum: δ_P 28.34 ppm. Found, %: C 24.83; H 4.16; N 5.74; P 13.18. $C_5H_{10}Cl_2NO_3P$. Calculated, %: C 25.65; H 4.30; N 5.98; P 13.23.

4-(Chloromethyl)-2-ethoxy-4,5-dihydro-1,3,4λ^5-

oxazaphosphol-4-one (III). A solution of 1 g of urethane **II** and 0.43 g of triethylamine in 15 ml of anhydrous benzene was kept for 1 day at 20°C. Triethylamine hydrochloride was removed, the filtrate was evaporated, and the crystalline product was washed with hexane to obtain 0.65 g (77%) of compound **III**, mp 147°C. IR spectrum (KBr), ν, cm^{-1}: 1630 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.60 t (3H, CH_3C, J_{HH} 7.1). 3.92 m (2H, OCH_2), 4.00 m (4H, CH_2P). ^{31}P NMR spectrum: δ_P 60.23 ppm. Found, %: C 31.09; H 5.04; N 6.88; P 14.97. $C_5H_9ClNO_3P$. Calculated, %: C 30.39; H 4.59; N 7.09; P 15.69.

(Diisopropoxyphosphinoyl)methyl *N*-[bis(chloromethyl)phosphinoyl]carbamate (Va). To a solution of 1.5 g of α-hydroxyphosphonate **IVa** in 5 ml of anhydrous benzene, 1.44 g of isocyanate **Ia** was added dropwise. The precipitate that formed was filtered off and washed with ether to give 2.7 g (92%) of compound **Va**, mp 106-108°C. IR spectrum (KBr), ν, cm^{-1}: 1220, 1250 (P=O), 1720 (C=O), 3060 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.22 d (12H, CH_3C, $^2J_{HH}$ 7.2); 3.94 d (4H, PCH_2Cl, $^2J_{PH}$ 9.3); 4.26 d (2H, CH_2P, $^2J_{PH}$ 8.4); 4.63 m (2H, CHO); 9.46 br.s (1H, NH). ^{31}P NMR spectrum, δ_P, ppm: 16.76, 30.31. Found, %: C 31.17; H 5.68; Cl 17.94; N 3.50; P 16.22. $C_{10}H_{21}Cl_2NO_6P_2$. Calculated, %: C 31.26; H 5.52; Cl 18.45; N 3.65; P 16.13.

1-(Diisopropoxyphosphinoyl)ethyl *N*-[bis(chloromethyl)phosphinoyl]carbamate (Vb) was obtained analogously from 1.42 g of α-hydroxyphosphonate **IVb** and 1.27 g of isocyanate **Ia**. Yield 2.6 g (97%), mp 88-91°C. IR spectrum (KBr), ν, cm^{-1}: 1232, 1264 (P=O), 1718 (C=O), 3065 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.35 m (15 H, CH_3C, $^2J_{HH}$ 7.2), 3.94 d (4H, PCH_2Cl, $^2J_{PH}$ 8.5), 4.66 m (3H, CHO, CHP), 10.08 br.s (1H, NH). ^{31}P NMR spectrum, δ_P, ppm:18.51; 29.73. Found, %: C 33.06; H 5.69; Cl 18.19; N 3.53; P 15.29. $C_{11}H_{23}Cl_2NO_6P_2$. Calculated, %: C 33.18; H 5.83; Cl 17.80; N 3.52; P 15.56.

1-(Diisopropoxyphosphinoyl)ethyl *N*-[(chloromethyl)phenoxyphosphinoyl]carbamate (Vc) was prepared analgously from 1.45 g of α-hydroxyphosphonate **IVb** and 1.6 g of isocyanate **Ib**. Yield 2.25 g (74%), mp 95-97°C. IR spectrum (KBr), ν, cm^{-1}: 1220, 1250 (P=O), 1735 (C=O), 3060 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.47 m (15H, CH_3C, $^2J_{HH}$ 7.2), 4.14 d (2H, PCH_2Cl, $^2J_{PH}$ 12.4), 4.95 m (3H, CHO, CHP), 7.3 m (5H, Ph). ^{31}P NMR spectrum, δ_P: 18.33 and 20.33 ppm. Found, %: C 43.25; H 5.93; Cl 8.00; N 3.21; P 13.76. $C_{16}H_{26}Cl \cdot NO_7P_2$. Calculated, %: C 43.49; H 5.94; Cl 8.02; N 3.17; P 14.02.

4-Phenoxy-4-thioxo-1,3,4λ^5-thiazaphospholidin-2-one (XI). *a*. Isothiocyanate **VII**, 0.23 g, was treated with 0.03 g of methanol. After 30 days, the precipitate that formed was filtered off and washed with benzene to give 0.07 g (64%) of compound **XI**, mp 163–165°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.22 m (1H, PCH_A, $^2J_{PH_A}$ 17.2, $^2J_{H_AH_B}$ 14.3); 4.02 m (1H, PCH_B, $^2J_{PH_B}$ 5.1, $^2J_{H_AH_B}$ 14.3), 7.22 m (2H^7, $J_{H^7H^8}$ 7.7, $^4J_{H^7H^8}$ 1.4), 7.44 m (2H^8, $^3J_{H^8H^9}$ 7.4, $^3J_{H^7H^8}$ 7.7), 7.27 (1H^9), 10.02 (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 169.54 d (C^2, $^2J_{PNC}$ 23.4), 32.43 m (C^5, $^2J_{PC^5H}$ 81.2, $^1J_{CH}$ 148.0), 149.68 m (C^6, $^2J_{POC}$ 10.5), 121.36 m (C^7, $^3J_{POC^6C^7}$ 4.8, $^1J_{CH}$ 166.9, $^3J_{C^7C^8C^9H^9}$ 8.6, $^3J_{C^7C^6C^{7'}H^7}$ 3.3), 128.80 m (C^8, $^4J_{POC^6C^7C^8}$ 1.4, $^3J_{C^8C^7C^{8'}H^{8'}}$ 8.0), 125.64 m (C^9, $^4J_{POC^6C^7C^8C^9}$ 1.9, $^3J_{C^9C^8C^7H^7}$ 5.2). ^{31}P NMR spectrum (DMSO-d_6), δ_P: 81.66 ppm. Mass spectrum, *m/z* (I_{rel}, %): 245 $[M]^+$ (67.9); 202 $[M - NHCO]^+$ (2.1); 199 $[M - CH_2S]^+$ (2.4); 156 $[PhOPS]^+$ (100.0); 152 $[M - PhO]^+$ (3.7); 123 $[C_7H_8P]^+$ (70.4); 110 $[C_6H_6S\}^+$ (13.5); 94 $[C_6H_6O]^+$ (54.5); 78 $[PSNH\}^+$ (11.3); 77 $[C_6H_5]^+$ (19.6); 63 $[PS]^+$ (21.7); 47 $[PO]^+$ (1.2). Crystallization from tetrachloromethane gave 0.2 g (36%) of carbamate **XIIa**, mp 72–75°C. IR spectrum (KBr), ν, cm^{-1}: 1590 (Ph), 1690 (C=O), 3080, 3310, 3420 (NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.66 d (2H, $ClCH_2P$, $^2J_{PH}$ 6.0), 3.81 d (3H, CH_3–S), 5.89 br.s (1H, NH), 7.17 (5H, Ph). ^{31}P NMR spectrum: δ_P: 90.04 ppm.

b. From 2.0 g of isothiocyanate **VII** and 0.35 g of ethanol, 0.5 g (54%) of compound **XI**, was obtained, mp 163–165°C. ^{31}P NMR spectrum: δ_P 81.6 ppm.

c. From 1.8 g of isothiocyanate **VII** and 0.41 g of propanol, 0.3 g (36%) of compound **XI** was obtained, mp 163–165°C. ^{31}P NMR spectrum: δ_P 81.6 ppm.

d. From 1.35 g of isothiocyanate **VII** and 0.38 g of butanol, 0.23 g (37%) of compound **XI** was obtained, mp 163–165°C. ^{31}P NMR spectrum: δ_P 81.6 ppm.

Reaction of *O*-phenyl (chloromethyl)phosphonoisothiocyanatidothioate (VII) with alcohols in the presence of triethylamine. *a*. A solution of 1.2 g of isothiocyanate **VII** in 10 ml of anhydrous benzene was successively treated with stirring at 5°C with 0.5 g of Et_3N and 0.14 g of methanol. After 12 h, triethylamine hydrochloride was removed, the solvent was distilled off, and the residue was subjected to chromatography on Al_2O_3, eluent benzene, to obtain a mixture of **2-methoxy-4-phenoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole-4-thione (XIVa) and *O*-methyl *O*-phenyl (chloromethyl)phosphonothioate**

(XVa) was obtained. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm (J, Hz): **XIVa**: 4.07 br. s (3H, CH$_3$O), 3.70 m, 3.88 m (2H, CH$_2$P), 7.27 m (5H, Ph); **XVa**: 3.86 t (3H, CH$_3$O, $^{3}J_{\mathrm{PH}}$ 13.9), 3.86 d (2H, ClCH$_2$P, $^{2}J_{\mathrm{PH}}$ 7.2), 7.27 m (5H, Ph). ^{13}C NMR spectrum (CDCl$_3$), δ$_\mathrm{C}$, ppm (J, Hz): **XIVa**: 36.88 m (PCH$_2$, $^{1}J_{\mathrm{PC}}$ 59.7, $^{1}J_{\mathrm{CH}_A}$ 148.6, $^{1}J_{\mathrm{CH}}$ 144.6), 59.67 m (OCH$_3$, $^{1}J_{\mathrm{CH}}$ 149.5), 150.26 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 10), 121.29 m (C$_o$, $^{3}J_{\mathrm{PC}}$ 4.6, $^{1}J_{\mathrm{CH}}$ 164.5), 129.49 m (C$_m$, $^{4}J_{\mathrm{PC}}$ 1.3, $^{1}J_{\mathrm{CH}}$ 163.2, $^{3}J_{\mathrm{CH}}$ 8.6), 125.22 m (C$_p$, $^{5}J_{\mathrm{CP}}$ 1.3, $^{1}J_{\mathrm{CH}}$ 163.2, $^{3}J_{\mathrm{CH}}$ 6.7), 177.55 d (C=N, $^{2}J_{\mathrm{PNC}}$ 18.6); **XVa**: 40.06 m (PCH$_2$, $^{1}J_{\mathrm{CP}}$ 124.7, $^{1}J_{\mathrm{CH}}$ 150.6), 54.3 m (OCH$_3$, $^{1}J_{\mathrm{CH}}$ 149.3, $^{2}J_{\mathrm{PC}}$ 6.6), 149.9 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 8.9), 121.31 m ($^{5}J_{\mathrm{PC}}$ 2.0, $^{1}J_{\mathrm{CH}}$ 163.0, $^{3}J_{\mathrm{CH}}$ 7.5). ^{31}P NMR spectrum, δ$_\mathrm{P}$, ppm (J, Hz): 112.4 br.d ($^{2}J_{\mathrm{PH}}$ 13.6); 82.9 m ($^{2}J_{\mathrm{PH}}$ 6.3–7.3). Mass spectrum, m/z (I_rel, %): 259 $[M_{\mathbf{XIVa}}]^+$ (100), 236 $[M_{\mathbf{XVa}}]^+$ (51.0), 205 $[M_{\mathbf{XVa}} - \mathrm{CH_3}]^+$ (13.2), 187 $[M_{\mathbf{XVa}} - \mathrm{Cl}]^+$ (71.7), 166 $[M_{\mathbf{XIVa}} - \mathrm{PhO}]^+$ (51.1), 156 $[\mathrm{PhOPC}]^+$ (27.7), 150 $[M_{\mathbf{XIVa}} - \mathrm{PhS}]^+$ (61.0), 143 $[M_{\mathbf{XVa}} - \mathrm{PhO}]^+$ (8.6), 125 $[\mathrm{PhOPh}]^+$ (68.1), 109 $[\mathrm{CH_2PS_2}]^+$ (76.5), 77 $[\mathrm{C_6H_5}]^+$, $[\mathrm{CH_2PS}]^+$ (86.9), 63 $[\mathrm{PS}]^+$ (64.5), 47 $[\mathrm{PO}^+]$ (14.7).

b. A mixture of **2-ethoxy-4-phenoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole-4-thione (XIVb) and *O*-ethyl *O*-phenyl (chloromethyl)phosphonothioate (XVb)**, 0.8 g, was obtained analogously from 1.68 g of isothiocyanate **VII**, 0.7 g of triethylamine, and 0.3 g of ethanol. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm (J, Hz); **XIVb**: 1.36 t (3H, CH$_3$C, $^{3}J_{\mathrm{HH}}$ 7.2), 4.52 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.6), 4.50 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.6), 3.67 m, 3.86 m (2H, CH$_2$P), 7.26 m (5H, Ph); **XVb**: 1.32 t.d (3H, CH$_3$C, $^{3}J_{\mathrm{HH}}$ 7.2, $^{4}J_{\mathrm{PH}}$ 0.5), 4.28 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.2, $^{2}J_{\mathrm{PH}}$ 11.2), 4.23 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.2, $^{2}J_{\mathrm{PH}}$ 10.2), 3.83 m (2H, ClCH$_2$P), 7.26 m (5H, Ph). ^{13}C NMR spectrum (CDCl$_3$), δ$_\mathrm{C}$, ppm (J, Hz): **XIVb**: 13.89 m (CCH$_3$, $^{1}J_{\mathrm{CH}}$ 127.7, $^{2}J_{\mathrm{CH}}$ 2.6), 36.48 m (PCH$_2$, $^{1}J_{\mathrm{PC}}$ 59.7, $^{1}J_{\mathrm{CH}_A}$ 148.3. $^{1}J_{\mathrm{CH}_B}$ 145.0), 69.9 m (OCH$_2$, $^{4}J_{\mathrm{PC}}$ 0.7, $^{1}J_{\mathrm{CH}_A}$ 150.5, $^{2}J_{\mathrm{CH}_B}$ 4.4), 150.25 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 9.6), 121.20 m (C$_m$, $^{3}J_{\mathrm{PC}}$ 4.6, $^{1}J_{\mathrm{CH}}$ 163.8), 129.34 m (C$_m$, $^{4}J_{\mathrm{PC}}$ 1.7, $^{1}J_{\mathrm{CH}}$ 162.5, $^{3}J_{\mathrm{CH}}$ 8.6), 125.08 m (C$_p$, $^{5}J_{\mathrm{PC}}$ 1.7, $^{1}J_{\mathrm{CH}}$ 2.66, $^{3}J_{\mathrm{CH}}$ 7.6), 176.69 d (C=N, $^{2}J_{\mathrm{PNC}}$ 17.7); **XVb**: 15.83 m (CCH$_3$, $^{1}J_{\mathrm{CH}}$ 127.4, $^{2}J_{\mathrm{CH}}$ 2.66, $^{3}J_{\mathrm{PC}}$ 6.6), 40.44 m (PCH$_2$, $^{1}J_{\mathrm{PC}}$ 124.7, $^{1}J_{\mathrm{CH}}$ 150.6), 64.44 m (OCH$_2$, $^{2}J_{\mathrm{PC}}$ 6.8, $^{1}J_{\mathrm{CH}}$ 148.6, $^{3}J_{\mathrm{CH}}$ 4.4), 149.89 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 9.6), 121.28 m (C$_o$, $^{3}J_{\mathrm{PC}}$ 4.3, $^{1}J_{\mathrm{CH}}$ 164.5), 129.34 m (C$_m$, $^{4}J_{\mathrm{PC}}$ 1.7, $^{1}J_{\mathrm{CH}}$ 162.5, $^{3}J_{\mathrm{CH}}$ 8.6), 125,31 m (C$_p$, $^{5}J_{\mathrm{PC}}$ 2.0, $^{1}J_{\mathrm{CH}}$ 162.5, $^{3}J_{\mathrm{CH}}$ 7.5). ^{31}P NMR spectrum, δ$_\mathrm{P}$, ppm (J, Hz): 113.1 br.d ($^{2}J_{\mathrm{PH}}$ 12.2), 80.9 m ($^{2}J_{\mathrm{PH}}$ 7.5–9.4). Mass spectrum, m/z (I_rel, %): 273 $[M_{\mathbf{XIVb}}]^+$ (75.4), 250 $[M_{\mathbf{XVb}}]^+$ (95.1), 245 $[M_{\mathbf{XIVb}} - \mathrm{C_2H_4}]^+$ (11.0), 222 $[M_{\mathbf{XVb}} - \mathrm{C_2H_4}]^+$ (26.2), 180 $[M_{\mathbf{XIVb}} - \mathrm{PhO}]^+$ (17.9), 173 $[M_{\mathbf{XVb}} - \mathrm{C_2H_4Cl}]^+$ (76.4), 164 $[M_{\mathbf{XIVb}} - \mathrm{SPh}]^+$ (47.1), 157 $[\mathrm{PhOPSH}]^+$ (75.8), 152 $[M_{\mathbf{XIVb}} - \mathrm{C_2H_4} - \mathrm{PhO}]^+$ (58.8), 109 $[\mathrm{CH_2PS_2}]^+$ (89.2), 77 $[\mathrm{C_6H_5}]^+$, $[\mathrm{CH_2PS}]^+$ (100.0), 63 $[\mathrm{PS}^+]$ (91.0), 47 $[\mathrm{PO}]^+$ (75.0).

c. A mixture of **4-phenoxy-2-propoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole-4-thione (XIVc) and *O*-propyl *O*-phenyl (chloromethyl)phosphonothioate (XVc),** 1.1 g, was prepared analogously from 1.7 g of isothiocyanate **VII**, 0.7 g of triethylamine, and 0.38 g of propanol. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm (J, Hz): **XIVc**: 0.97 t (3H, CH$_3$C, $^{3}J_{\mathrm{HH}}$ 7.4), 1.76 sextet (2H, CH_2CH$_3$, $^{3}J_{\mathrm{CH}}$ 7.1 Hz), 4.45 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.4, $^{2}J_{\mathrm{HH}}$ 6.7), 4.42 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.4, $^{3}J_{\mathrm{HH}}$ 6.7), 3.865 m (1H, CH$_2$P, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 13.3, $^{2}J_{\mathrm{PHA}}$ 13.8), 3.68 m (H, CH$_2$P, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 13.3, $^{2}J_{\mathrm{PH}_B}$ 5.4), 7.47 m (5H, Ph); compound **XVb**: 0.96 t (3H, CH$_3$C, $^{3}J_{\mathrm{HH}}$ 7.4), 1.72 m (2H, CH$_2$CH$_3$, $^{3}J_{\mathrm{CH}}$ 7.1, $^{4}J_{\mathrm{PH}}$ 0.5), 4.19 m (1H, OCH$_A$, $^{3}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.1, $^{3}J_{\mathrm{HH}}$ 6.6, $^{3}J_{\mathrm{PH}_A}$ 10.1), 4.13 m (1H, OCH$_A$, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 10.1, $^{3}J_{\mathrm{HH}}$ 6.6, $^{3}J_{\mathrm{PH}_B}$ 9.3), 3.854 m (H, CH$_2$P, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 13.8, $^{2}J_{\mathrm{PH}_A}$ 8.0), 3.841 m (H, CH$_2$P, $^{2}J_{\mathrm{H}_A\mathrm{H}_B}$ 13.8, $^{2}J_{\mathrm{PH}_B}$ 7.5), 7.26 m (5H, Ph). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm (J, Hz): compound **XIVc**: 9.75 m (CCH$_3$, $^{1}J_{\mathrm{CH}}$ 126.0), 36.29 m (PCH$_2$, $^{1}J_{\mathrm{PC}}$ 58.7, $^{1}J_{\mathrm{CH}_A}$ 148.5, $^{1}J_{\mathrm{CH}_B}$ 145.5), 21.48 m (CH$_2$CH$_3$, $^{1}J_{\mathrm{CH}}$ 127.7), 74.92 m (OCH$_2$, $^{4}J_{\mathrm{PC}}$ 0.7, $^{1}J_{\mathrm{CH}}$ 149.4, $^{2}J_{\mathrm{CH}} = {}^{3}J_{\mathrm{CH}}$ 5.3), 149.97 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 10.0), 121.05 m (C$_o$, $^{3}J_{\mathrm{PC}}$ 4.7, $^{1}J_{\mathrm{CH}}$ 163.2), 129.19 m (C$_m$, $^{4}J_{\mathrm{PC}}$ 1.5, $^{1}J_{\mathrm{CH}}$ 162.2, $^{3}J_{\mathrm{CH}}$ 8.8), 124.94 m (C$_p$, $^{5}J_{\mathrm{PC}}$ 1.8, $^{1}J_{\mathrm{CH}}$ 163.8, $^{3}J_{\mathrm{CH}}$ 7.6), 176.73 d (C=N, $^{2}J_{\mathrm{PNC}}$ 17.9); compound **XVb**: 9.67 m (CCH$_3$, $^{1}J_{\mathrm{CH}}$ 126.2), 40.18 m (PCH$_2$, $^{1}J_{\mathrm{PC}}$ 124.6, $^{1}J_{\mathrm{CH}}$ 150.8), 23.16 m (CH$_2$CH$_3$, $^{3}J_{\mathrm{PC}}$ 6.9, $^{1}J_{\mathrm{CH}}$ 126.3), 69.63 m (OCH$_2$, $^{2}J_{\mathrm{PC}}$ 7.0, $^{1}J_{\mathrm{CH}}$ 148.2), 149.61 d (C$_i$, $^{2}J_{\mathrm{PC}}$ 9.4), 121.13 m (C$_o$, $^{3}J_{\mathrm{PC}}$ 4.4, $^{1}J_{\mathrm{CH}}$ 163.2), 129.19 m (C$_m$, $^{4}J_{\mathrm{PC}}$ 1.5, $^{1}J_{\mathrm{CH}}$ 162.2, $^{3}J_{\mathrm{CH}}$ 8.8), 125.16 m (C$_p$, $^{5}J_{\mathrm{PC}}$ 1.9, $^{1}J_{\mathrm{CH}}$ 162.8, $^{3}J_{\mathrm{CH}}$ 7.6). ^{31}P NMR spectrum, δ$_\mathrm{P}$, ppm (J, Hz): 112.8 br.d.d ($^{2}J_{\mathrm{PH}}$ 13.6 and 4.6), 80.9 m ($^{2}J_{\mathrm{PH}}$ 7.5–9.4). Mass spectrum, m/z (I_rel, %): 287 $[M_{\mathbf{XIVc}}]^+$ (36.5), 264 $[M_{\mathbf{XVc}}]^+$ (26.5), 245 $[M_{\mathbf{XIVc}} - \mathrm{C_3H_6}]^+$ (26.2), 222 $[M_{\mathbf{XVc}} - \mathrm{C_3H_6}]^+$ (86.2), 205 $[M_{\mathbf{XVc}} - \mathrm{OC_3H_7}]^+$ (19.8), 178 $[M_{\mathbf{XIVc}} - \mathrm{SPh}]^+$ (33.0), 156 $[\mathrm{PhOPS}]^+$ (43.0), 109 $[\mathrm{CH_2PS_2}]^+$ (71.0), 77 $[\mathrm{C_6H_5}]^+$, $[\mathrm{CH_2PS}]^+$ (78.2), 63 $[\mathrm{PS}]^+$ (68.1), 47 $[\mathrm{PO}]^+$ (44.0).

d. A mixture of **2-butoxy-4-phenoxy-4,5-dihydro-1,3,4λ^5-thiazaphosphole-4-thione (XIVb)** and ***O*-butyl *O*-phenyl (chloromethyl)phosphonothioate (XVb),** 0.3 g, was prepared analogously from 0.55 g of isothiocyanate **VII**, 0.21 g of triethylamine, and

0.14 g of butanol. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (*J*, Hz): **XIVd**: 0.95 t (3H, $\mathrm{CH_3C}$, $^3J_{\mathrm{HH}}$ 7.4), 1.41 m (2H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.73 m (2H, $\mathrm{OCH_2C}H_2\mathrm{CH_2}$), 4.50 m (1H, OCH_A, $^2J_{\mathrm{H}_A\mathrm{H}_B}$ 10.5, $^3J_{\mathrm{HH}}$ 6.6), 4.48 m (1H, OCH_A, $^2J_{\mathrm{H}_A\mathrm{H}_B}$ 10.5, $^3J_{\mathrm{HH}}$ 6.6), 3.88, 3.69 m (2H, $\mathrm{CH_2P}$), 7.27 m (5H, Ph); **XVd**: 0.94 t (3H, $\mathrm{CH_3C}$, $^3J_{\mathrm{HH}}$ 7.3), 1.42 m (2H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.69 m (2H, $\mathrm{OCH_2C}H_2\mathrm{CH_2}$), 4.24 m (1H, OCH_A, $^2J_{\mathrm{H}_A\mathrm{H}_B}$ 10.1, $^3J_{\mathrm{PH}_A}$ 10.1, $^3J_{\mathrm{HH}}$ 6.6), 4.175 m (1H, OCH_A, $^2J_{\mathrm{H}_A\mathrm{H}_B}$ 10.1, $^3J_{\mathrm{PH}_B}$ 9.25, $^3J_{\mathrm{HH}}$ 6.6), 3.85 m (2H, $\mathrm{CH_2P}$), 7.27 m (5H, Ph). ^{13}C NMR spectrum ($\mathrm{CDCl_3}$), δ_{C}, ppm (*J*, Hz): **XIVd**: 13.46 m ($\mathrm{CCH_3}$, $^1J_{\mathrm{CH}}$ 125.4, $^1J_{\mathrm{CH}}$ = $^4J_{\mathrm{CH}}$ 4.0), 36.229 m ($\mathrm{PCH_2}$, $^1J_{\mathrm{PC}}$ 59.4, $^1J_{\mathrm{CH}_A}$ 148.6, $^1J_{\mathrm{CH}_B}$ 145.6), 18.76 m ($C\mathrm{H_2CH_3}$, $^1J_{\mathrm{CH}}$ 125.7, $^2J_{\mathrm{CH}}$ 4.2), 30.43 m ($\mathrm{OCH_2}C\mathrm{H_2CH_2}$, $^1J_{\mathrm{CH}}$ 126.5), 73.69 m ($\mathrm{OCH_2}$, $^4J_{\mathrm{PC}}$ 1.0, $^1J_{\mathrm{CH}}$ 149.3, $^2J_{\mathrm{CH}}$ = $^3J_{\mathrm{CH}}$ 4.3), 150.43 d (C_i, $^2J_{\mathrm{PC}}$ 10.6), 121.39 m (C_o, $^3J_{\mathrm{OPC}}$ 4.6, $^1J_{\mathrm{CH}}$ 163.9), 129.49 m (C_m, $^4J_{\mathrm{PC}}$ 1.7, $^1J_{\mathrm{CH}}$ 162.5, $^3J_{\mathrm{CH}}$ 8.0), 125.24 m (C_p, $^4J_{\mathrm{PC}}$ 1.7, $^1J_{\mathrm{CH}}$ 163.2, $^3J_{\mathrm{CH}}$ 7.5), 177 d (C=N, $^2J_{\mathrm{PCN}}$ 17.9); compound **XVd**: 13.42 m ($\mathrm{CCH_3}$, $^1J_{\mathrm{CH}}$ 125.4, $^2J_{\mathrm{CH}}$ = $^3J_{\mathrm{CH}}$ 4.0), 40.45 m ($\mathrm{PCH_2}$, $^1J_{\mathrm{PC}}$ 150.6), 18.60 m ($C\mathrm{H_2CH_3}$, $^1J_{\mathrm{CH}}$ 125.7, $^2J_{\mathrm{CH}}$ = $^3J_{\mathrm{CH}}$ 4.3), 32.12 m ($\mathrm{OCH_2}C\mathrm{H_2CH_2}$, $^1J_{\mathrm{CH}}$ 126.7, $^3J_{\mathrm{PC}}$ 6.3), 68.25 m ($\mathrm{OCH_2}$, $^2J_{\mathrm{PC}}$ 7.0, $^1J_{\mathrm{CH}}$ 147.9), 150.10 d (C_i, $^2J_{\mathrm{PC}}$ 9.3), 121.48 m (C_o, $^3J_{\mathrm{PC}}$ 4.3, $^1J_{\mathrm{CH}}$ 164.5), 129.19 m (C_m, $^4J_{\mathrm{PC}}$ 1.5, $^1J_{\mathrm{CH}}$ 162.2, $^3J_{\mathrm{CH}}$ 8.8), 125.45 m (C_p, $^5J_{\mathrm{PC}}$ 2.0, $^1J_{\mathrm{CH}}$ 162.5, $^3J_{\mathrm{CH}}$ 7.3). ^{31}P NMR spectrum, δ_{P}, ppm (*J*, Hz): 113.1 br.d ($^2J_{\mathrm{PH}}$ 13.2), 80.9 m ($^2J_{\mathrm{PH}}$ 7.5–9.4). Mass spectrum, *m/z* (I_{rel}, %): 301 $[M_{\mathbf{XIVd}}]^+$ (1.9), 245 $[M_{\mathbf{XIVd}} - \mathrm{C_4H_8}]^+$ (53.0), 222 $[M_{\mathbf{XVd}} - \mathrm{C_4H_8}]^+$ (45.9), 208 $[M_{\mathbf{XIVd}} - \mathrm{PhO}]^+$ (11.0), 192 $[M_{\mathbf{XIVd}} - \mathrm{SPh}]^+$ (19.7), 156 $[\mathrm{PhOPS}]^+$ (26.2), 109 $[\mathrm{CH_2PS_2}]^+$ (67.1), 94 $[\mathrm{C_6H_5OH}]$ (100), 77 $[\mathrm{C_6H_5}]^+$, $[\mathrm{CH_2PS}]^+$ (86.3), 63 $[\mathrm{PS}]^+$ (72.5), 47 $[\mathrm{PO}]^+$ (36.0).

e. A mixture of **disopropyl [4-phenoxy-4-thioxo-4,5-dihydro-1,3,4λ^5-thiazaphosphol-2-yl)oxymethyl]phosphonate (XIVe)** and **diisopropyl [[(chloromethyl)(phenoxy)phosphinothioyl]oxymethyl]-phosphonate (XVe),** 1.8 g, was prepared analogously from 1.7 g of isothiocyanate **VII**, 1 ml of triethylamine, and 1.25 g of α-hydroxyphosphonate **IVa**. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (*J*, Hz): **XIVd**: 1.38 m (12H, $\mathrm{CH_3C}$), 3.89 m (2H, $\mathrm{SCH_2P}$), 4.8 m (4H, POCH), 7.3 m (5H, Ph); **XVd**: 1.38 m (12H, $\mathrm{CH_3C}$), 3.98 (2H, $\mathrm{ClCH_2P}$), 4.4 m (2H, $\mathrm{OCH_2P}$, $^2J_{\mathrm{PH}}$ 23), 4.8 m (2H, POCH), 7.3 m (5H, Ph). ^{13}C NMR spectrum ($\mathrm{CDCl_3}$), δ_{C}, ppm (*J*, Hz): **XIVd**: 23.5 m ($\mathrm{CH_3}$), 36.8 d ($\mathrm{PCH_2S}$, $^1J_{\mathrm{PC}}$ 61), 65.2 d ($\mathrm{OCH_2P}$, $^1J_{\mathrm{PC}}$ 170), 71.68 d (OCH, $^2J_{\mathrm{PC}}$ 6.7), 71.65 d (OCH, $^2J_{\mathrm{PC}}$ 6.4), 149.7 d (C_i, $^2J_{\mathrm{PC}}$ 9.8), 121.93 d (C_o, $^3J_{\mathrm{PC}}$ 4.6), 129.06 d (C_m, $^4J_{\mathrm{PC}}$ 1.2), 124.9 d (C_p, $^5J_{\mathrm{PC}}$ 1.8), 176.6 d.d (C=N, $^2J_{\mathrm{PNC}}$ 20, $^3J_{\mathrm{PCOC}}$ 9.7); **XVd**: 23.4 m ($\mathrm{CH_3}$), 39.4 d ($\mathrm{PCH_2Cl}$, $^1J_{\mathrm{PC}}$ 124.5), 60.48 d.d ($\mathrm{POCH_2P}$, $^1J_{\mathrm{PC}}$ 172, $^2J_{\mathrm{POC}}$ 7.8), 71.49 d (OCH, $^2J_{\mathrm{PC}}$ 6.4), 149.25 d (C_i, $^2J_{\mathrm{PC}}$ 9.7), 120.96 d (C_o, $^3J_{\mathrm{PC}}$ 4.5), 129.11 d (C_m, $^4J_{\mathrm{PC}}$ 1.6), 125.22 d (C_p, $^5J_{\mathrm{PC}}$ 2.0). ^{31}P NMR spectrum, δ_{P}, ppm (*J*, Hz): **XIVd**: 111.0 m ($^4J_{\mathrm{PP}}$ 3.1, $^2J_{\mathrm{PH}}$ 13.1), 12.5 m ($^4J_{\mathrm{PP}}$ 3.1, $^2J_{\mathrm{PH}}$ 7.6); compound **XVd**: 84.8 m ($^3J_{\mathrm{PP}}$ 33, $^2J_{\mathrm{PH}}$ 8), 14.1 m ($^3J_{\mathrm{PP}}$ 33, $^2J_{\mathrm{PH}}$ 8).

f. A mixture of **disopropyl [1-[4-phenoxy-4-thioxo-4,5-dihydro-1,3,4λ^5-thiazaphosphol-2-yl)oxy]-ethyl]phosphonate (XIVf)** and **diisopropyl [1-[(chloromethyl)(phenoxy)phosphinothioyloxy]ethyl]phosphonate (XVf),** 1.4 g, was prepared analogously from 1.75 g of isothiocyanate **VII**, 1 ml of triethylamine, and 1.39 g of α-hydroxyphosphonate **IVb**. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm (*J*, Hz): 1.31 m (12H, $\mathrm{CH_3C}$), 1.52 and 1.59 d.d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{PCCH}}$ 9, $^3J_{\mathrm{HH}}$ 7), 3.8 m (2H, $\mathrm{SCH_2P}$), 4.75 m (2H, POCH), 4.75 d.q (1H, OCHP, $^2J_{\mathrm{PCH}}$ 25, $^3J_{\mathrm{HH}}$ 7), 7.25 m (5H, Ph). ^{13}C NMR spectrum ($\mathrm{CDCl_3}$), δ_{C}, ppm (*J*, Hz): **XIVf**: 14.68 d ($\mathrm{CH}C\mathrm{H_2}$, $^2J_{\mathrm{PC}}$, $^2J_{\mathrm{PC}}$), 23.7 m [$\mathrm{(CH_3)_2CHOP}$], 36.73 d ($\mathrm{PCH_2S}$, $^1J_{\mathrm{PC}}$ 60), 36.62 d ($\mathrm{PCH_2S}$, $^1J_{\mathrm{PC}}$ 60), 74.6 d (OCHP, $^1J_{\mathrm{PC}}$ 170), 71.78 d (POCH, $^2J_{\mathrm{PC}}$ 7), 71.72 d (POCH, $^2J_{\mathrm{PC}}$ 7), 71.62 d (POCH, $^2J_{\mathrm{PC}}$ 7), 71.48 d (POCH, $^2J_{\mathrm{PC}}$), 149.8 d (C_i, $^2J_{\mathrm{PC}}$ 10), 121.9 d (C_o, $^3J_{\mathrm{PC}}$ 5), 129.2 (C_m), 125.06 (C_p), 176.4 m (C=N); **XVf**: 14.68 d ($\mathrm{CH}C\mathrm{H_3}$, $^2J_{\mathrm{PC}}$ 20), 40.2 d ($\mathrm{PCH_2Cl}$, $^1J_{\mathrm{PC}}$ 120), 71.3 d (POCH, $^2J_{\mathrm{PC}}$ 7), 150.0 d (C_i, $^2J_{\mathrm{PC}}$ 10), 122.1 d (C_o, $^3J_{\mathrm{PC}}$ 5), 129.3 (C_m), 125.12 (C_p). ^{31}P NMR spectrum, δ_{P}, ppm (*J*, Hz): **XIVf**: 111.7 and 111.4 br.d ($^2J_{\mathrm{PH}}$ 13.8, $^2J_{\mathrm{PH}}$ 13.2), 15.2 and 15.0 m; **XVe**: 85.0 and 84.8 m, 16.5 and 16.3 m.

4-Phenoxy-3-phenyl-4-thioxo-1,3,4λ^5-thiazaphospholidin-2-one (XX). To a solution of 3.3 g of *O*-ethyl *N*-phenylcarbamothioate **XVII** in 50 ml of anhydrous benzene, 1.84 g of triethylamine and 4.39 g of acid chloride **XVI** were added in succession with stirring. The reaction mixture was heated fot 16 h at 100°C. Triethylamine hydrochloride was filtered off, the solvent was evaporated, and theresidue, a dark brown viscous material, was subjected to chromatography on $\mathrm{Al_2O_3}$, eluent benzene–hexane (5 : 1) to obtain 0.9 g (15%) of compound **XX**, n_{D}^{20} 1.6202. IR spectrum, (KBr), ν, cm^{-1}: 1590 (Ph), 1705 (C=O). ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm: 360 m (2H, $\mathrm{CH_2P}$), 7.17 (10H, Ph). ^{31}P NMR spectrum, δ_{P} 79.9 ppm. Mass spectrum, *m/z* (I_{rel}, %): 321 $[M]^+$ (100), 293 $[M - \mathrm{CO}]^+$ (12.6), 261 $[M - \mathrm{CSO}]^+$ (4.3), 228 $[M - \mathrm{PhO}]^+$ (5.9), 202 $[M - \mathrm{PhNCO}]^+$ (15.7), 156 $[\mathrm{PhOPS}]^+$ (95.2), 109 $[\mathrm{CH_2PS_2}]^+$ (41.0), 91 $[\mathrm{PhN}]^+$ (21.0), 77

$[C_6H_5]^+$, $CH_2PS]^+$ (97.8), 63 $[PS]^+$(64.0), 47 $[PO]^+$ (8.0).

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