Russian Journal of General Chemistry, Vol. 74, No. 9, 2004, pp. 1335–1340. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 9, 2004, pp. 1441–1446.

Reaction of Chloromethyliso(thio)cyanato(thio)phosphonates-(-phosphinates) with Phenol, Ethanol, and Thiols

N. A. Khailova, R. Kh. Bagautdinova, A. A. Shaimardanova, N. E. Krepysheva, M. A. Pudovik, G. A. Chmutova, N. M. Azancheev, R. Z. Musin, and A. N. Pudovik

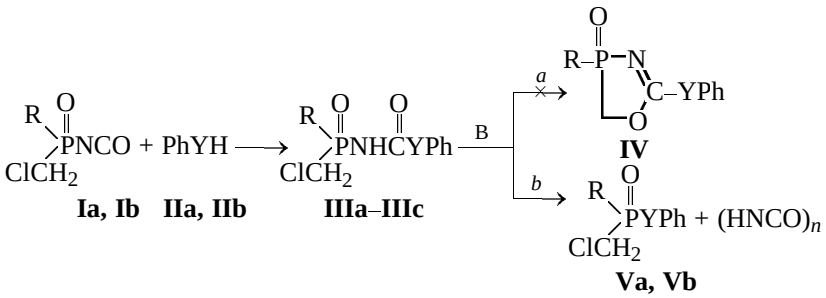
Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Received October 31, 2002

Abstract — (Chloromethyl)isocyanatophosphonates(-phosphinates) take up phenol to form carbamates whose β-cleavage gives rise to phenyl (chloromethyl)phosphonates(-phosphinates). (Chloromethyl)(thio)phosphinic-(phosphonic) isothiocyanates react with phenol at 20°C in the absence of catalyst to afford phenyl phosphinates(-phosphonates). (Alkylsulfanyl)carbamates formed by addition of thiols to (chloromethyl)iso(thio)cyanastophosphonates(-phosphinates) under the action of an equimolar amount of triethylamine undergo cyclization into 1,3,4-oxaza(thiaza)phospholines.

It is known that isocyanates of P(V) acids take up phenols and thiols by the C=N bond of the isocyanate group to give N-phosphorylated carbamates and thiocarbamates [1]. Previously we showed that phosphorylated carbamates in the presence of bases undergo heterocyclization due to intramolecular interaction of the chloromethyl and carbonyl groups to form unsaturated heterocycles, such as 1,3,2-oxazaphospholines [2]. Aiming at preparing new functionalyzed (chloromethyl)phosphonates and (chloromethyl)thiophosphonates capable of further transformations, we reacted (chloromethyl)iso(thio)cyanatophosphonates-(-phosphinates) with phenol, ethanol, and thiols. We expected that the presence on the phosphorus atom of several structural fragments capable of interacting with each other would enable us to synthesize new phosphorus-containing heteroatomic cyclic and acyclic compounds.

It was shown that isocyanatophosphonates(-phosphinates) **Ia** and **Ib** react with phenol (**IIa**) and benzenethiol (**IIb**) to form carbamates **IIIa**–**IIIc**. Their structure was confirmed by IR and ^{31}P and ^{1}H NMR spectroscopy. The IR spectra of N-phosphorylated carbamates **IIIa**–**IIIc** contain absorption bands the P=O (1260–1280 cm^{-1}), Ph (1590 cm^{-1}), C=O (1745 cm^{-1}), and NH groups (3150 cm^{-1}). In the ^{1}H NMR spectrum, PCH_2 protons give a doublet at 3.77–4.07 ppm and phenyl protons, a multiplet at 7.2–7.3 ppm.



I, R = PhO (**a**), $ClCH_2$ (**b**); **II**, Y = O (**a**), S (**b**); **III, V**, R = PhO, Y = O (**a**); R = $ClCH_2$, Y = O (**b**); **IIIc**, R = CH_2Cl, Y = S.

1070-3632/04/7409-1335

However, unlike structurally related alkylurethans whose cyclization under the action of bases gives rise to 1,3,4-oxazaphospholines **IV**, phenylurethans **IIIa** and **IIIb** under the same conditions provide β-elimination products, viz. phenyl (chloromethyl)phosphonates(-phosphinates) **Va** and **Vb**. Evidence for the preference of β-elimination (pathway *b*) over cyclization (pathway *a*) was also obtained by PM_3 semiempirical quantum-chemical calculations (MOPAC) for the reaction of isocyanate **Ia** with phenol [3]. Pathway *b* is 47.3 kJ mol^{-1} more favored over pathway *a* even for conformer **IIIa** that is best susceptible to cyclization. In the presence of a base (triethylamine), which favors cyclization, the β-elimination pathway still remains preferred ($\Delta\Delta H_f$ 11.7 kJ mol^{-1}). The calculated enthalpies of formation ΔH_f (kJ mol^{-1}) are as follows: **Ia** –516.9; **IIa** 90.7; **IIIa** 599.3; **IVa** –376.0; **Va** –471.7; HCl –85.7; and HNCO –64.0.

Attempted synthesis of phenylurethan **IIIb** by direct phosphorylation of phenylurethan with bis-(chloromethyl)phosphinic chlorides **VI**. However, here, too, the final product of this reaction is phenyl bis(chloromethyl)phosphinate (**Vb**).

$$\underset{\textbf{VI}}{(ClCH_2)_2P(O)Cl} + PhOC(O)NH_2 \xrightarrow[-HCl]{} \textbf{Vb} + (HNCO)_n.$$

Bezenethiol adds to isocyanate **Ib**, affording phosphorylated (phenylsulfanyl)urethan **IIIc**. When treated with base, the latter, urethans **IIIa** and **IIIb**, forms a series of products. The ^{31}P NMR spectrum of the reaction mixture contains no signal of *S*-phenyl bis-(chloromethyl)thiophosphinate (**Vc**) (δ_P 51.6 ppm) obtained in a special experiment by the reaction of phosphinic chloride **VI** with benzenethiol in the presence of triethylamine. From that it follows that the β-elimination pathway does not take place in the case of phosphorylated urethan **IIIc**.

$$\textbf{VI} + PhSH \xrightarrow[-Et_3N\cdot HCl]{-Et_3N} \underset{\textbf{Vc}}{(ClCH_2)_2P(O)SPh}.$$

Unlike phosphoric and phosphinic isocyanates that, according to published data, fail to react with phenol in the presence of catalyst and at elevated temperatures [4], (chloromethyl)thiophosphinic isocyanate reacts with phenol reacts with phenol at room temperature without catalyst. However, thiocarbamate **VIIIa** could not be detected spectrally. It can be proposed that adduct **VIIIa** is unstable and decomposes to form *O*-phenyl bis(chloromethyl)thiophosphinate (**IXa**), or nucleophilic substitution of the isocyanate group by phenoxyl in compound **VIIa** takes place to form the same product. According to PM3 calculations for structures **VIIb**–**IXb**, phenol addition to isothiocyanate **VIIb** is unfavorable (the endo effect of the addition stage is 101.6 kJ mol^{-1}) and, therefore, direct nucleophilic substitution is more probable. Phenyl bis(chloromethyl)isothiocyanatophosphinate (**VIIb**) reacts with phenol only at 80°C in the presence of a catalytic amount of triethylamine. The necessity of prolonged heating of the reaction mixture for the formation of product **Va** is explained by the fact that the whole process has an appreciable endo effect (70.7 kJ mol^{-1}). The calculated ΔH_f values (kJ mol^{-1}) are as follows: **VIIb** –286.5; **VIIIb** –275.2; **Va** –471.7, and HNCS 165.2.

$$\underset{\textbf{VIIa, VIIb}}{R(X)P(ClCH_2)NCS} + PhOH \longrightarrow \underset{\textbf{VIIIa, VIIIb}}{\left[R(X)P(S)(ClCH_2)NHCOPh\right]} \longrightarrow R(X)P(ClCH_2)OPh + (HNCS)_n,$$

Va, IXa, IXb

VII–**IX**, R = $ClCH_2$, X = S (**a**); R = PhO, X = O (**b**).

Thiols **Xa** and **Xb** easily add to (chloromethyl)isocyanatophosphonates(-phosphinates) **Ia** and **Ib** to form alkyl thiocarbamates **XIa**–**XIc**. The reaction proceeds without catalyst and is complete within 30 min, whereas dialkylphosphinic isocyanates react slowly (several days) [1].

$$\textbf{Ia, Ib} + R'SH \longrightarrow \underset{\textbf{XIa–XIc}}{R(O)P(ClCH_2)NHC(O)SR'}$$

Xa, Xb

$$\xrightarrow[-B\cdot HCl]{B} R{-}P(=O){-}N{=}C{-}SR'$$

XIIa–**XIIc**

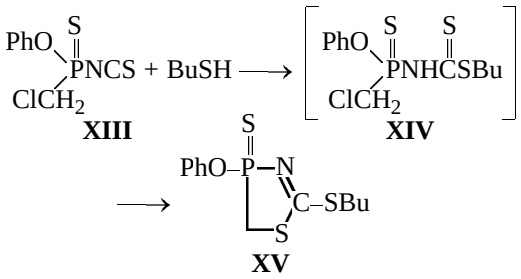
X, R' = Bu (**a**), *t*-Bu (**b**); **XI, XII**, R = PhO, R' = *t*-Bu (**a**); R = PhO, R' = Bu (**b**); R = $ClCH_2$, R' = Bu (**c**).

Carbamates **XIa**–**XIc** are crystalline substances. Their structure was confirmed by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and their composition, by elemantal analysis. Under the action of equimolar amount of triethylamine, compounds **XIa**–**XIc** undergo intramolecular cyclization via alkylation of the carbonyl oxygen with the chloromethyl group to give

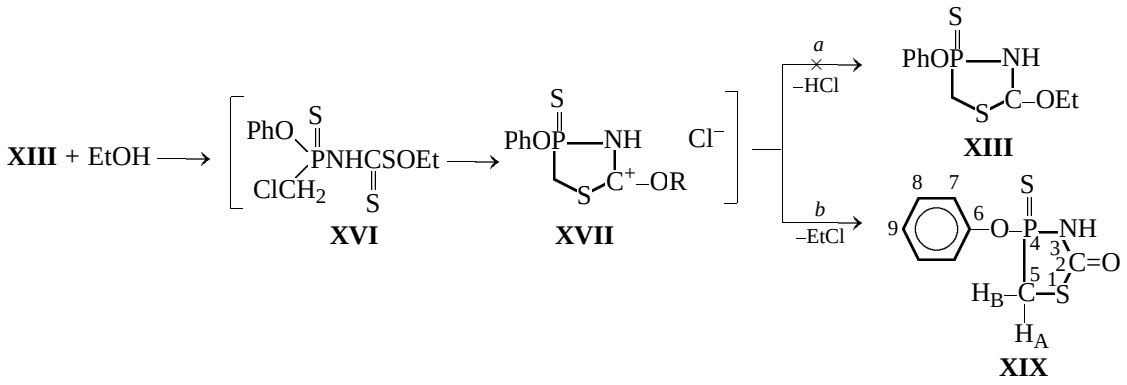
oxazaphospholines **XIIa**–**XIIc**. The IR spectra of phosphorylated carbamates **XIa**–**XIc** contain characteristic absorption bands of the carbonyl (1670–1680 cm^{-1}) and NH groups (3060–3070 cm^{-1}), whereas the spectra of compounds **XIIa**–**XIIc** lack such bands. Instead, a new absorption band appears at 1545 cm^{-1}, due to the endocyclic C=N bond. Evidence for the formation of phospholines **XIIa**–**XIIc** is also provided by the downfield shift of signals in the ^{31}P NMR spectra [δ_P 48.9 (**XIc**) and 61.8 ppm (**XIIc**)]. In the ^1H NMR spectrum, PCH_2 protons appear in as an octet (ABX system) in the range 4.02–4.22 ppm, implying an endocyclic position of the methylene group. The methylene group of carbamates **XIa**–**XIc** gives a doublet at 3.7–3.8 ppm ($^2J_{HP}$ 11–13 Hz). Compounds **XIIa**–**XIIc** were characterized crude, since they are unstable and disproportionate when purified to form a series of products.

O-Phenyl (chloromethyl)isothiocyanatothiophosphonate (**XIII**) reacts with butanethiol to give 2-(butylsulfanyl)-4-phenoxy-1,3,4λ^5-thiazaphospholine 4-sulfide (**XV**). With equimolar amount of triethylamine, the reaction is considerably accelerated. Hence, in the absence of triethylamine the reaction is complete in two months, while in the presence, it occurs with heat release and is compete in 30 min. However, no linear reaction product, thiocarbamate **XIV**, was found in both cases. According to ^{31}P NMR, cycle **XV** is formed directly.

Quantum-chemical calculations reveal unfavourableness of thiocarbamate formation from compound **XIII** and ethanethiol: The heat effect of this stage is 30.9 kJ mol^{-1}. However, formation of cycle **XV** in the presence of triethylamine is favorable: The exothermic effect of this reaction is –101.2 kJ mol^{-1}.



Developing these studies, we turned to reaction of ethanol with isothiocyanatothiophosphonate **XIII**. It was expected that the initially formed carbamate **XVI** would undergo an intramolecular transformation involving nucleophilic attack of sulfur on the chloromethyl carbon atom and resulting in formation of intermediate **XVII**, followed by HCl evolution from the latter to give thiazaphospholine **XVIII** (pathway *a*). Theoretical consideration showed that this pathway is really energetically favorable (the exo effect is –116.7 kJ mol^{-1}). However, it was found that the most preferred is pathway *b* that involves the attack of the chloride ion on the alkoxyl carbon, yielding saturated thiazaphospholidine ring **XIX** ($\Delta\Delta H_f$ –134.7 kJ mol^{-1}). The calculated enthalpies of formation ΔH_f (kJ mol^{-1}) are as follows: **XIII** 29.4; EtSH –36.4; EtOH –237.5; thiocarbamate like **XIV** 18.0; **XV** –164.4; SEt analog of compound **XV** 1.7; **XVII** –162.3; and EtCl –92.4. It was found that isothiocyanate **XIII** readily reacts with ethanol at 20°C in the absence of base and actually provides 1,3,4-thiazaphospholidine **XIX**.



The structure of compound **XIX** was confirmed by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy and high-resolution mass spectrometry. The IR spectrum of 1,3,4-thiazaphospholidine **III** contains the following absorption bands, ν, cm^{-1}: 1190 (P–O–Ph), 1590 (Ph), 1680 (C=O), and 3150 (NH). In ^1H NMR spectrum, PCH_2 protons appear as eight lines (*ABX* system) in the range 4.02–4.22 ppm, implying an endocyclic

character of the methylene group. Phenyl protons give a multiplet (A_2B_2C system) in the range 7.22–7.44 ppm.

EXPERIMENTAL

The IR spectra of were measured on a UR-20 spectrometer in the range 400–3600 cm^{-1} in mineral oil or thin layer. The ^{31}P NMR spectra were obtained on a Bruker MSL-400 NMR Fourier spectrometer (161.97 MHz) and on a KGU-4 custom-made spectrometer (10.2 MHz) against internal 85% phosphoric acid. The ^1H NMR spectra were recorded on a Varian T-60 spectrometer (60 MHz) against internal TMS and on a Bruker WM-250 spectrometer (250.132 MHz). The ^{13}C NMR spectra were measured on a Bruker MSL-400 spectrometer (100.6 MHz). The electron impact mass spectra were obtained on an MX-1310 spectrometer (*R* 15000, direct inlet, 120°C).

Phenyl [(chloromethyl)phenoxyphosphinoyl]-carbamate (IIIa). To a solution of 2.3 g of phosphonate **Ia** in 30 ml of anhydrous ether, 0.33 g of phenol was added. After 24 h, the precipitate that formed was filtered off to obtain 2.0 g (65%) of compound **IIIa**, mp 117–119°C. IR spectrum (KBr), ν, cm^{-1}: 1195 (OPh), 1280 (P=O), 1590 (Ph), 1745 (C=O), 3100 (NH). ^1H NMR spectrum (CD_3CN), δ, ppm: 4.07 d (2H, CH_2P, $^2J_{PH}$ 10 Hz), 7.2 m (10H, Ph), 8.17 br.s (H, NH). ^{31}P NMR spectrum: δ_P 15.28 ppm. Found, %: C 53.97; Cl 11.55; N 4.45; P 9.72. $C_{14}H_{13}ClNO_3P$. Calculated, %: C 54.29; Cl 11.45; N 4.52; P 10.0.

Phenyl [bis(chloromethyl)phosphinoyl]carbamate (IIIb). To a solution of 2.1 g of phosphinate **Ib** in 30 ml of anhydrous ether, 1.05 g of phenol was added. After 24 h, the precipitate that formed was filtered off to obtain 2.4 g (77%) of compound **IIIb**, mp 106°C. IR spectrum (KBr), ν, cm^{-1}: 1260 (P=O), 1600 (Ph), 1745 (C=O), 3100 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.0 d (4H, CH_2P, $^2J_{HP}$ 8 Hz), 7.2 m (5H, Ph), 8.0.3 br.s (H, NH). ^{31}P NMR spectrum: δ_P 27.61 ppm. Found, %: C 38.37; H 3.52; N 5.21; P 10.91. $C_9H_{10}Cl_2NO_3P$. Calculated, %: C 38.32; H 3.58; N 4.97; P 10.98.

***N*-Bis(chloromethyl)phosphinoyl-*S*-phenylcarbamate (IIIc).** To a solution of 2.9 g of phosphinate **Ib** in 15 ml of anhydrous benzene, a solution of 1.7 g of benzenethiol in 7 ml of anhydrous benzene was added dropwise. After 24 h, the precipitate that formed was filtered off to give 3.4 g (73%) of compound **IIIc**, mp 130–132°C. IR spectrum (KBr), ν, cm^{-1}: 1240 (P=O), 1580 (Ph), 1680 (C–O), 3060 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.77 d (4H, CH_2P, $^2J_{PH}$ 9 Hz), 7.3 m (5H, Ph), 10.7 br.s (1H, NH). ^{31}P NMR spectrum: δ_P 26.5 ppm. Found, %: C 36.07; H 3.11; Cl 24.29; N 4.87; P 10.47; S 10.46. $C_9H_{10}Cl_2$ NO2PS. Calculated, %: C 36.26; H 3.12; Cl 23.78; N 4.70; P 10.39; S 10.75.

Diphenyl (chloromethyl)phosphonate (Va). *a*. To a solution of 1 g of carbamate **IIIa** in 20 ml of anhydrous benzene, 0.4 g of triethylamine was added dropwise, and the resulting mixture allowed to stand for 12 h at 20°C. After removal of the solvent, 0.6 g (70%) of phosphonate **Va** was obtained. IR spectrum (KBr), ν, cm^{-1}: 1285 (P=O), 1595 (Ph). ^1H NMR spectrum (CCl_4), δ, ppm: 3.63 d (2H, CH_2P, $^2J_{PH}$ 8Hz), 7.13 m (10H, Ph). ^{31}P NMR spectrum: δ_P 10.2 ppm.

b. To a solution of 3.05 g of isothiocyanate **VIb** in 20 ml of anhydrous benzene, a solution of 1.16 g of phenol in 5 ml of anhydrous benzene was added dropwise. One drop of triethylamine was then added, and the resulting mixture was heated for 12 h at 80°C. The solvent was removed in a vacuum, and the residue was fractionated to give 0.9 g (26%) of phosphonate **Va**, bp 130–131°C (0.03 mm Hg). ^1H NMR spectrum (CCl_4), δ, ppm: 3.72 d (2H, CH_2P, $^2J_{PH}$ 9 Hz), 7.2 m (10H, Ph). ^{31}P NMR spectrum: δ_P 10.8 ppm [4].

Phenyl bis(chloromethyl)phosphinate (Vb). *a*. A mixture of 4.04 g of phenylurethan and 5.35 g of bis-(chloromethyl)phosphinic chloride was heated for 8 h at 125°C, the solvent was removed in a vacuum, and the residue was fractionated to give 3.4 g (48%) of phosphinate **Vb**, bp 118–118 (0.02 mm Hg), n_D^{20} 1.5510. ^{31}P NMR spectrum: δ_P 38.0 ppm [5].

b. To a solution of 1 g of carbamate **IIIb** in 30 ml of anhydrous benzene, 1.0 g of triethylamine was added dropwise with stirring, and the resulting mixture was kept for 12 h at 20°C. After removal of the solvent, 0.65 g (76%) of phosphinate **Vb** was obtained. IR spectrum (KBr), ν, cm^{-1}: 1270 (P=O), 1590 (Ph). ^1H NMR spectrum (CCl_4), δ, ppm: 3.77 d (4H, CH_2P, $^2J_{PH}$ 9 Hz), 7.13 m (5H, Ph). ^{31}P NMR spectrum: δ_P 36.7 ppm.

***S*-Phenyl bis(chloromethyl)thiophosphinate (Vc).** To a solution of 5.8 g of bis(chloromethyl)phosphinic chloride in 20 ml of anhydrous benzene, a solution of 3.56 g of benzenethiol and 3.25 g of triethylamine in 10 ml of anhydrous benzene was added dropwise with stirring. The resulting mixture was heated for 2 h at 80°C. The triethylamine hydrochloride was filtered off, the filtrate was evaporated, and the residue was distilled in a vacuum to obtain 4.5 g (55%) of phosphinate **Vc**, bp 130–132°C

(0.05 mm Hg), mp 61–65°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 3.93 d (4H, CH_2P, $^2J_{PH}$ 6 Hz), 7.46 m (5H, Ph). ^{31}P NMR spectrum, δ_P, ppm: 51.6. Found, %: C 38.07; H 3.54; Cl 27.45; P 12.61; S 13.17. $C_8H_9Cl_2OPS$. Calculated, %: C 37.65; H 3.56; Cl 27.79; P 12.14; S 12.56.

Phenyl bis(chloromethyl)thiophosphinate (IXa). To a solution of 1.85 g of isothiocyanate **VIa** in 20 ml of anhydrous ether, a solution of 0.8 g of phenol in 5 ml of anhydrous ether was added dropwise with stirring. After 1 day, the solvent was removed, and the residue was recrystallized from ether to obtain 1.4 g (76%) of phosphinate **IXa**, mp 55–57°C. ^{31}P NMR spectrum: δ_P 85 ppm [4].

***S*-*tert*-Butyl [(chloromethyl)phenoxyphosphinoyl]thiocarbamate (XIa).** *tert*-Butanethiol, 1.2 g, was added to 3.1 g of phosphinate **Ia**. After 1 day, the reaction mixture crystallized and was washed with ether to obtain 3.9 g (92%) of compound **XIa**, mp 94–99°C. IR spectrum (KBr), ν, cm^{-1}: 1260 (P=O), 1590 (Ph), 1680 (C=O), 3060 (NH). ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.47 s (9H, CH_3), 3.88 d (2H, CH_2P, $^2J_{PH}$ 10 Hz), 7.1 m (5H, Ph), 9.47 br.s (H, NH). ^{31}P NMR spectrum: δ_P 16.7 ppm. Found, %: C 44.42; H 4.88; Cl 11.34; N 4.26; P 9.76; S 9.47. $C_{12}H_{17}Cl\cdot NO_3PS$. Calculated, %: C 44.79; H 5.34; Cl 11.00; N 4.35; P 9.62; S 9.96.

***S*-Butyl [(chloromethyl)phenoxyphosphinoyl]thiocarbamate (XIb).** A mixture of 1.3 g of isocyanate **Ia** and 0.5 g of butanethiol was allowed to stand for 24 h at 20°C. Recrystallization from diethyl ether gave 0.8 g (44%) of compound **XIb**, mp 67–69°C. IR spectrum (KBr), ν, cm^{-1}: 1260 (P=O), 1685(C=O), 3070 (NH). ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 0.89 t (3H, CH_3CH_2, $^2J_{HH}$ 7.5 Hz), 1.36 m (2H, CH_3CH_2, 1.54 m (2H, SCH_2CH_2), 2.86 t (2H, SCH_2, $^2J_{HH}$ 7 Hz), 4.2 d (2H, CH_2P, $^2J_{PH}$ 10.7 Hz, 7.32 m (5H, Ph), 10.6 br.s (H, NH). ^{31}P NMR spectrum: δ_P 16.71 ppm. Found, %: C 44.48; H 5.46; Cl 10.49; N 4.28; P 8.56; S 10.01. $C_7H_{14}Cl_2NO_2PS$. Calculated, %: C 44.79; H 5.34; Cl 11.01; N 4.35; P 9.63; S 9.96.

***S*-Butyl [bis(chloromethyl)phosphinoyl]thiocarbamate (XIc).** Butanethiol, 1.2 g, was added to 2.5 g of isocyanate **Ib**. After 30 min, the crystals that formed were washed with ether to obtain 3.4 g (93%) of compound **XIc**, mp 111–114°C. IR spectrum (KBr), ν, cm^{-1}: 1240 (P=O), 1670 (C=O), 3070 (NH). ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 0.54 t (3H, CH_3CH_2, $^2J_{HH}$ 7 Hz), 1.04 m (2H, CH_3CH_2), 1.20 m (2H, SCH_2CH_2, 2.31 t (2H, SCH_2, $^2J_{HH}$ 7 Hz), 3.21, 3.71 2d, (4H, CH_2P, $^2J_{PH}$ 13.4 and 11.9 Hz), 6.9, 10.35 br.s (1H, NH). ^{13}C NMR spectrum [$(CD_3)_2SO$], δ_C, ppm: 13.20 (CH_3CH_2), 20.82 (CH_3CH_2), 30.61 (SCH_2CH_2), 37.82 (SCH_2), 35.82 d (CH_2P, $^1J_{PC}$ 99.8 Hz), 175.2 (O–C=O). ^{31}P NMR spectrum: δ_P 27.0 ppm. Found, %: C 30.42; H 5.02; Cl 25.64; N 5.07; P 11.24; S 11.54. $C_7H_{14}Cl_2NO_2PS$. Calculated, %: C 30.22; H 5.08; Cl 25.49; N 5.04; P 11.13; S 11.53.

2-(Butylsulfanyl)-4-phenoxy-1,3,4λ^5-thiazaphospholine 4-sulfide (XV). To a solution of 1.8 g of *O*-phenyl (chloromethyl)isothiocyanatothiophosphonate and 0.7 g of triethylamine in 20 ml of anhydrous benzene, 0.6 g of butanethiol was added dropwise with stirring at 5°C. The resulting mixture was kept for 12 h, the triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was subjected to chromatography on neutral aluminum oxide (Brockmann II), eluent chloroform to obtain 1.4 g (65%) of thiazaphospholine **XV** as a light yellow transparent oil, n_D^{20} 1.5340. IR spectrum (KBr), ν, cm^{-1}: 1515 (C=N), 1590 (Ph). ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 0.98 t (3H, CH_3CH_2, $^2J_{HH}$ 7 Hz), 1.48 m (2H, CH_3CH_2), 3.33 m (2H, SCH_2), 3.92 m (2H, CH_2P), 7.33 m (5H, Ph). ^{31}P NMR spectrum: δ_P 120.0 ppm. Found, %: P 9.65; S 30.43. $C_{12}H_{16}NOPS_3$. Calculated, %: P 9.76; S 30.30.

4-Phenoxy-1,3,4λ^5-thiazaphospholidin-2-one 4-sulfide (XIX). A mixture of 2.0 of isothiocyanatothiophosphonate **XIII** and 0.35 g of ethanol was allowed to stand for 1 months at 20°C. The precipitate that formed was filtered off and washed with benzene to obtain 0.5 g (27%) of compound **XIX**, mp 163–165°C. ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 4.22 m [1H, PC^1H_A, $^2J(PH_A)$ 17.2, $^2J(H_AH_B)$ 14.3], 4.02 m [1H, PCH_B, $^2J(PH_B)$ 5.1). 7.22 m (H^7, $^3J(H^7H^8)$ 7.7, $^4J(H^7H^9)$ 1.4], 7.44 m [1H, H^8, $^3J(H^8H^9)$ 7.4], 7.27 m (H, H^9 7.4), 10.02 br.s (1H, NH). ^{13}C NMR spectrum [$(CD_3)_2SO$], δ_C, ppm (*J*, Hz): 169.54 d (C=O, $^2J_{NC}$ 23.4), 32.43 m [C^5, $^2J(PC^5H^8)$ 1.2, J_{CH} 148.0], 149.68 m (C^6, $^2J_{POC}$ 10.5), 121.36 m [C^7, $^3J(POC^6C^7)$ 4.8, J_{CH} 166.9, $^3J(C^7C^8C^9H^9)$ 8.6, $^3J(C^7C^7C^{7'}H^7)$ 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, $^5J(POC^6C^7C^8C^9)$ 1.9, $^3J(C^9C^8C^7H^7)$ 5.2]. ^{31}P NMR spectrum: δ_P 81.66 ppm. Mass spectrum, *m/z* (I_{rel}, %):

(electron impact, 70 eV): 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 $[C_6H_6O]^+$ 954.5), 78 $[PSNH]^+$ (11.3), 77 $[C_6H_5]^+$ (19.6), 63 $[PS]^+$ (21.7), 47 $[PO]^+$ (1.2). Found, %: C 39.84; H 3.17; N 5.80; P 12.66; S 26.70. $C_8H_8NO_2PS_2$. Calculated, %: C 39.17; H 3.29; N 5.71; P 12.63; S 26.15.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32837).

REFERENCES

1. Shokol, V.A. and Kozhushko, B.N., *Izotsianaty fosfora* (Phosphorus Isocyanates), Kiev: Naukova Dumka, 1992.
2. Pudovik, M.A., Saakyan, G.M., Khairullin, V.K., Khailova, N.A., and Pudovik, A.N., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, no. 4, p. 810.
3. Tomaschewski, G. and Zanke, D., *Z. Chem.*, 1970, vol. 10, no. 3, p. 117.
4. Edmundson, R.S., *Dictionary of Organophosphorus Compounds*, London: Chapman and Hall, 1988, pp. 50, 152.
5. Kosolapoff, G.M. and Maier, L., *Organic Phosphorus Compounds*, New York: Wiley, 1975.