Heteroatom Chemistry
Volume 5, Number 5/6, 1994

1,3,4-Thia(selena)azaphospholines and Phospholidines

R. M. Kamalov,* G. S. Stepanov, I. A. Litvinov, and M. A. Pudovik

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420083, Kazan, Arbuzov str., 8, Russia

Received 20 May 1994

ABSTRACT

O-Phenyl chloromethyldithio- and chloromethylselenothiophosphonic acids, formed by the reaction of O-phenyl chloromethyl-(chloro)thiophosphonate with hydrogen sulfide or hydrogen selenide, respectively, in the presence of Et_3N, react in situ with alkyl thiocyanates and bis(thiocyanato)methane, yielding 2-alkylthio-4,5-dihydro-4-thioxo-4-phenoxy-1,3,4-thia(selena)azaphospholes and 2,4-dithioxo-4-phenoxy-1,3,4-thia(selena)azaphospholidines, respectively.

INTRODUCTION

The predominant products of the reaction between dithiophosphoric acids **1** with heterocyanides (cyanates, thiocyanates, cyanamides, etc.) of general formula **2** are *N*-thiophosphoryl thio- [1], dithiocarbamates [2], and thioureas [3,4] **4**, which are formed via a phosphorotropic rearrangement of the adducts **3** (Scheme 1).

Due to the presence of the labile proton in the P–NH–C fragment, compounds **4** can enter into heterocyclization processes. Thus, when in the reaction with dithiophosphoric acids **1**, heterocyanides **5** containing facile leaving groups are involved, a cyclization of intermediary dithiocarbamates or thioureas 6 into *N*-thiophosphoryl thiazacyclanes is observed (Scheme 2) in some cases.

The length of chain Y defines the size of the heterocyclic ring. Four-, five-, and six-membered rings are found to be formed in such reactions [4–6]. As the leaving group, *Z*, the chlorine atom [5] or the 10-phenothiazinyl group [4,6] was used. Due to the ambident character of the thiocarbamoyl triad in **6**, ring formation including both the sulfur atom (**7**) and the nitrogen atom (**8**) of this triad is possible [4–6].

Developing this idea, we have supposed that the reactions of dithiophosphonic acids of type **9**, bearing facile leaving groups at phosphorus, with heterocyanides **2** could lead to a new synthetic route to S,N,P-containing heterocycles (Scheme 3).

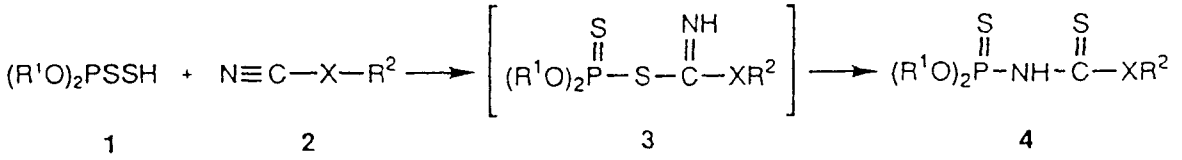
When the length of chain *Y* in **9** is short enough and the heteroatom X bears no protons (X ≠ NH), predominant formation of heterocycles of type **12** is expected. It results from a ring-closure reaction at the sulfur atom of thiocarbamoyl derivatives **11**, formed via rearrangement of the original addition products **10**. Recently [7,8], we have found that *N*-(thio)phosphonyl thioureas and dithiocarbamates of type **11**, formed by the reactions of isothiocyanato(chloromethyl)thiophosphonates with amines and thiols, respectively, do undergo such cyclization.

RESULTS AND DISCUSSION

In order to obtain a functionally substituted dithiophosphonic acid, which could be used as a precursor in the synthesis of heterocycles of type **12**, we attempted to synthesize O-phenyl chloromethylthiophosphonic acid **14a** (Scheme 4). For this purpose, a solution of triethylamine in benzene or ether was added dropwise at 5°C to a solution of O-phenyl chloromethyl(chloro)thiophosphonate **13** in anhydrous diethyl ether, [8] and simultaneously hydrogen sulfide was passed through the reaction

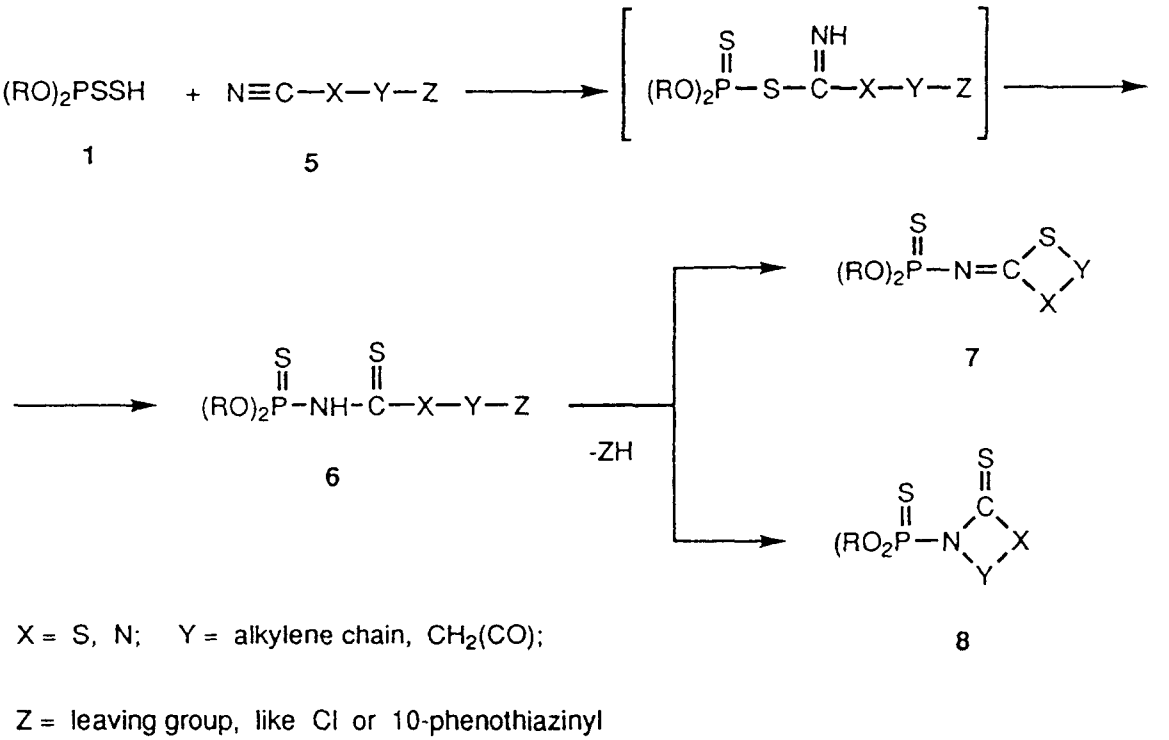
*To whom correspondence should be addressed.

1042-7163/94/$5.00 + .25



X = O, S, N-

SCHEME 1



X = S, N; Y = alkylene chain, $CH_2(CO)$;

Z = leaving group, like Cl or 10-phenothiazinyl

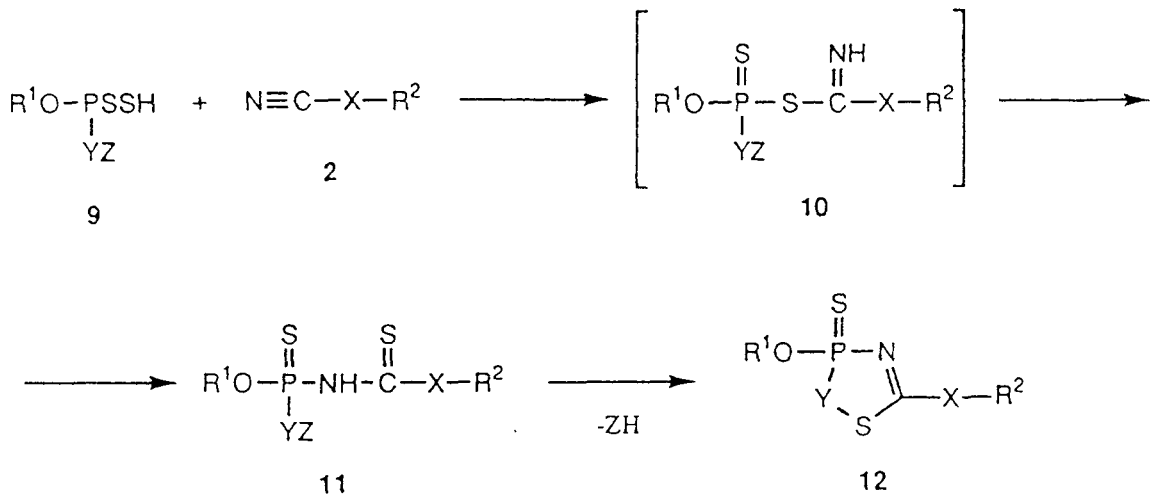
SCHEME 2

mixture. The solution obtained was worked up using a standard procedure for purification of dithiophosphoric and dithiophosphonic acids [9]. There was in the ^{31}P NMR spectrum predominantly one signal with $\delta_P \cong 105$. When distilled in vacuo, this compound decomposed with strong gas evolution.

A similar result was obtained by the reaction of chlorothiophosphonate **13** with sodium hydrosulfide in ether. Our attempts to isolate pure O-phenyl chloromethyldithiophosphonic acid **14a** failed. However, the quantitative precipitation of triethylamine hydrochloride and NaCl, respectively, in the preceding reactions indicated that the formation of the desired dithiophosphonic acid **14a**, at least as an intermediate, takes place. Therefore, we carried out the synthesis of the dithiophosphonic acid **14a** in situ in the reaction mixture containing an excess of alkyl thiocyanate **15**.

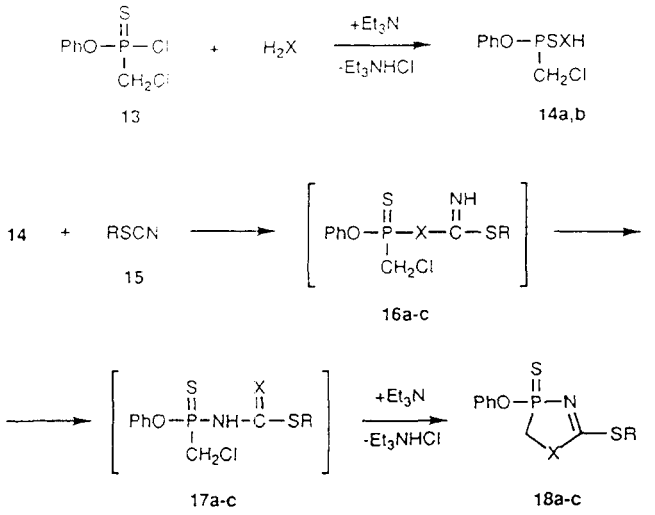
When dried hydrogen sulfide was passed through the solution of O-phenyl chloromethyl(chloro)thiophosphonate **13** and an 1.2–2 equivalent excess of methyl or benzyl thiocyanate **15a, b** in ether, with triethylamine simultaneously being added to the mixture, 2-methylthio- and 2-benzylthio-4, 5-dihydro-4-thioxo-4-phenoxy-1, 3, 4-thiazaphospholes **18a, b**, respectively, were obtained (Scheme 4). The structures of the products **18a, b** were confirmed by their IR, ^1H, and ^{31}P NMR spectra and by X-ray diffraction studies [10].

We assume that O-phenyl chloromethyldithiophosphonic acid **14a**, formed at the first stage, adds to the C≡N bond of the alkyl thiocyanates **15** to give rise to adducts **16a, b**, which rearrange rapidly into *N*-thiophosphonyl dithiocarbamates **17a, b**. The latter undergo a cyclization in the presence of triethylamine into thiazaphospholines **18a, b** [δ_P = 119.8 (**18a**) and 117.9 (**18b**) in CCl_4]. According to



X = O, S, N; Y = alkylene; Z = leaving group

SCHEME 3



14: a X = S, b X = Se; 15: a R = Me, b R = CH_2Ph;

16-18: a R = Me, X = S; b R = CH_2Ph, X = S; c R = Me, X = Se

SCHEME 4

^{31}P NMR spectral monitoring, the reaction is accompanied or followed by side reactions, and therefore the yield of thiazaphospholines **18a, b** is relatively low (25–28%).

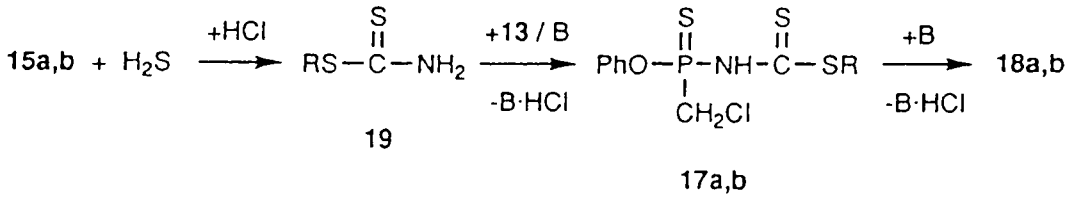
It could be assumed, as well, that another route leads to the thiazaphospholines **18a, b**. Thus, according to Scheme 5, thiocyanates **15** could add hydrogen sulfide with the formation of S-alkyl dithiocarbamates **19**. Such a reaction can be catalyzed by HCl, induced by the equilibrium reaction between chlorothiophosphonate **13** and H_2S. Dithiocarbamates **19** could react with chlorothiophosphonate **13** to give *N*-thiophosphonyl dithiocarbamates **17a, b**, these being cyclized further into 1,3,4-thiazaphospholines **18a, b**.

However, this scheme seems to be less probable than the former one, because, in a special experiment, when H_2S was passed through the ether solution of chlorothiophosphonate **13** and thiocyanate **15a** present in the same molar ratio, but in the absence of Et_3N, no reaction was detected by ^1H and ^{31}P NMR spectroscopy. By the addition of triethylamine, H_2S must preferentially react with chlorothiophosphonate **13** rather than with thiocyanate **15**.

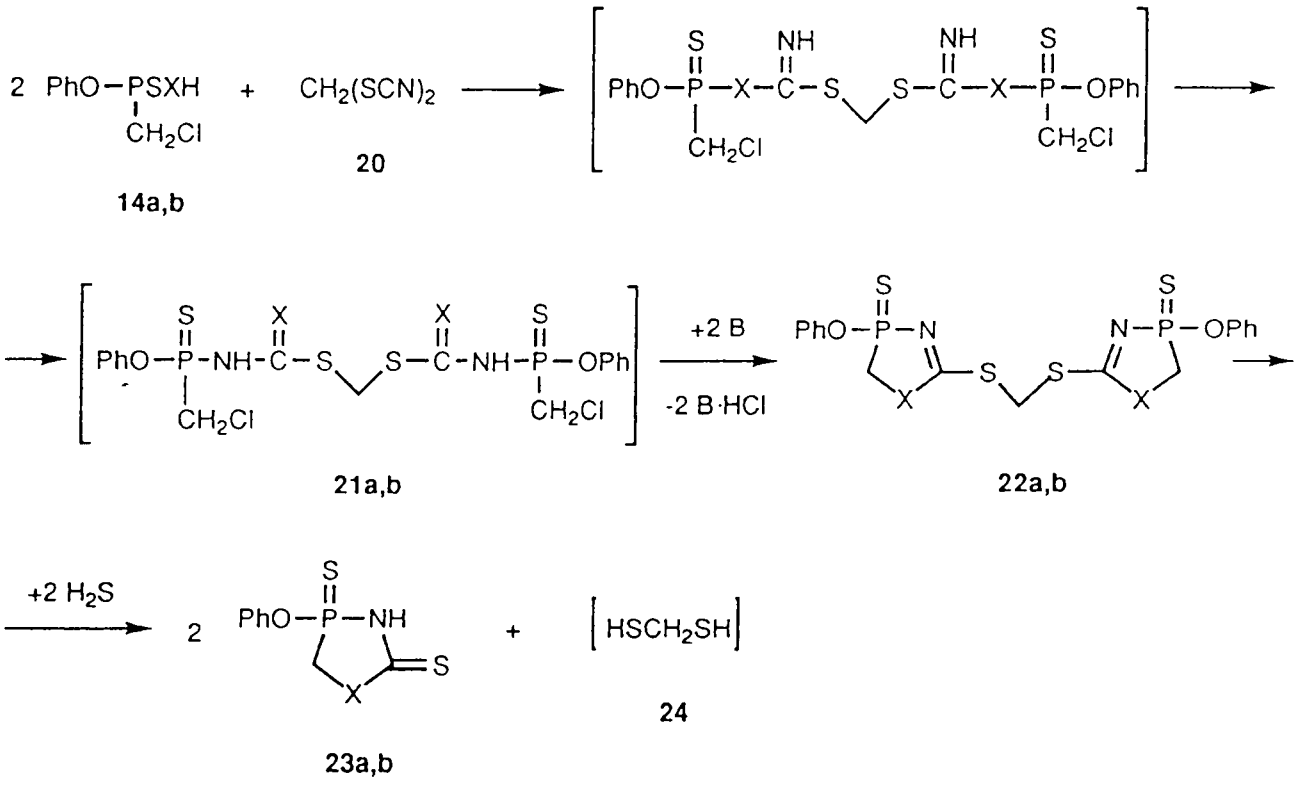
A reaction of O-phenyl chloromethyldithiophosphonic acid **14a** with bis(thiocyanato)methane **20** has been found to proceed in a manner contrary to expectations. When H_2S was passed through a benzene solution of compounds **13** and **20** (molar ratio 2:1) and, at the same time, triethylamine was added dropwise to the mixture, 2,4-dithioxo-4-phenoxy-1,3,4-thiazaphospholidine **23a** was isolated in a yield of 41% (Scheme 6).

The structure of 2,4-dithioxo-4-phenoxy-1,3,4-thiazaphospholidine **23a** was established by means of ^1H, ^{31}P NMR (δ_P = 87.2 in CCl_4), and IR spectroscopy [10], elemental analyses, and was confirmed by X-ray diffraction studies.

One of the possible reaction schemes can include the stages of the addition of dithiophosphonic acid **14a** to both thiocyanato groups of bis(thiocyanato)methane **20**. A subsequent rearrangement and cyclization produce the product **22a**,



SCHEME 5



21-23 : a X = S, b X = Se

SCHEME 6

containing two thiazaphospholine rings. Additional hydrogen sulfide, present in the reaction mixture, cleaves compound **22a**, yielding thiazaphospholidine **23a** and dimercaptomethane **24**. The compound **24** is unstable and can react with other components of the reaction mixture or eliminate H_2S and polymerize into trithiane.

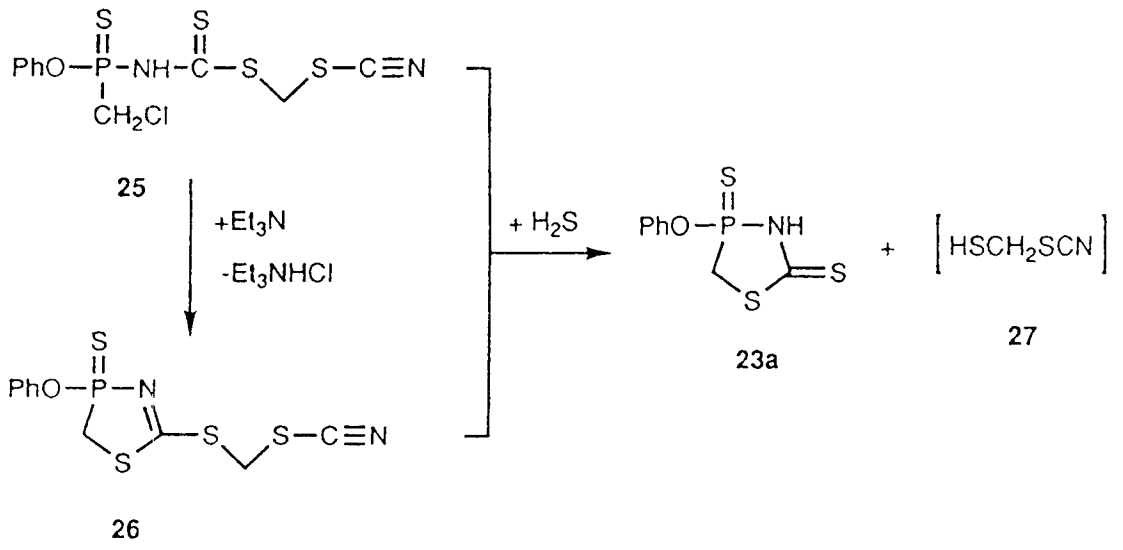
Hydrogen sulfide could interfere in the course of the reaction also at an earlier stage, e.g., it could cleave the product **21a**. Also, it was found that some of the starting chlorothiophosphonate **13** remained after the reaction. This fact provides possible evidence that only one thiocyanato group of bis(thiocyanato)methane **20** can enter into this reaction.

The dithiocarbamate **25**, formed in the initial stages, or the product of its cyclization **26** can also be cleaved by H_2S to give thiazaphospholidine **23a** and the unstable mercaptomethyl thiocyanate **27** (Scheme 7).

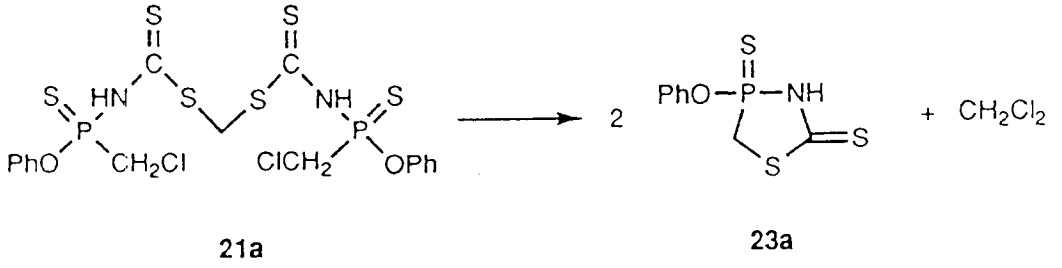
There is also a possibility for an intramolecular reaction, followed by the formation of methylene chloride according to Scheme 8. However, CH_2Cl_2 was detected only in small amounts by means of gas-liquid chromatography of the reaction mixture.

We regret that the data obtained do not allow us to conclude which scheme is most probable.

The reactions of chloromethyldithiophosphonic acid **14a** with thiocyanates **15a**, **b** and **20** result in the formation of S,N,P-containing heterocycles—thiazaphospholines **18a**, **b**, and thiaza-



SCHEME 7



SCHEME 8

phospholidine **23a**. To develop this approach, we studied the possibility of obtaining Se,N,P-containing heterocycles—selenazaphospholines and selenazaphospholidines by a similar reaction of O-phenyl chloromethylselenothiophosphonic acid **14b** with thiocyanates **15a** and **20**.

Selenothiophosphonic acid **14b** was obtained in situ when hydrogen selenide was passed through an ether solution of O-phenyl chloromethyl(chloro)thiophosphonate **13** in the presence of triethylamine and an excess of methyl thiocyanate **15a**. This reaction yielded 2-methylthio-4,5-dihydro-4-thioxo-4-phenoxy-1,3,4-selenazaphosphole **18c**, identified by means of X-ray, IR, ^{1}H, and ^{31}P NMR studies [10] (Scheme 4).

Selenazaphospholine **18c** is likely formed in the same way as its thia-analogs **18a**, **b**. Probably ambident selenothiophosphonic acid **14b** adds to the C≡N bond of thiocyanate **15a** at the selenium atom, the softest nucleophilic center of the S–P–Se triad.

After the hydrogen selenide had been passed into the reaction mixture, the predominant signals with δ_P = 123.7, 119.8, and 72.2 appeared together with other relatively minor signals in the ^{31}P NMR spectra. When an additional amount of triethylamine had been added to the mixture, the intensity of the signal with δ_P = 123.7 was increased and the signal with δ_P = 72.2 had fully disappeared. Perhaps, the signal with δ_P = 72.2 belongs to selenothiocarbamate **17c**, which undergoes cyclization under treatment with base into selenazaphospholine **18c** (δ_P = 123.7). The signal with δ_P = 119.8 belongs to the compound **18a**, which was identified by the addition of an authentic sample to the reaction mixture. Probably, the formation of thiazaphospholine **18a** in this reaction results from a disproportionation process.

Bis(thiocyanato)methane **20** reacts with O-phenyl chloromethylselenothiophosphonic acid **14b** in a similar way as with its thio-analog **14a** and produces 2,4-dithioxo-4-phenoxy-1,3,4-selenazaphospholidine **23b** (Scheme 6).

Identification of selenazaphospholidine **23b** was carried out by means of IR, ^{1}H, and ^{31}P NMR (δ_P = 89.8 in CCl_4) spectra [10], and the structure was confirmed by X-ray diffraction analysis. In the pure state, the compound **23b** is a crystalline solid, slowly oxidizing in air with formation of elemental sele-

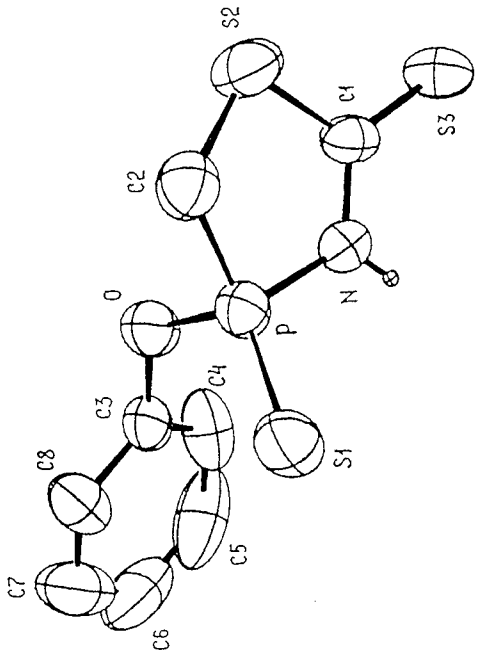


FIGURE 1 ORTEP perspective drawing of **23a**.

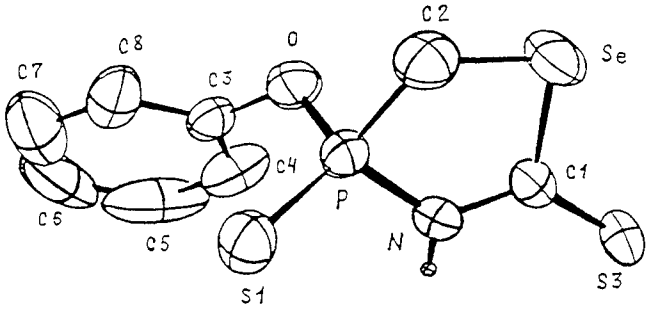


FIGURE 2 ORTEP perspective drawing of **23b**.

TABLE 1 Bond Distances (Å) for **23a**, **b** with Estimated Standard Deviations (ESDs) in Parentheses

Bond	**23a**	**23b**	*Bond*	**23a**	**23b**
S1–P	1.900(1)	1.901(2)	N–C1	1.342(4)	1.341(6)
S3–C1	1.646(3)	1.663(5)	C3–C4	1.356(5)	1.374(8)
S2[a]–C1	1.743(3)	1.882(5)	C4–C5	1.409(8)	1.403(15)
S2[a]–C2	1.806(4)	1.924(7)	C5–C6	1.362(9)	1.39(2)
P–O	1.594(2)	1.594(4)	C6–C7	1.348(7)	1.32(2)
P–N	1.679(3)	1.679(5)	C7–C8	1.362(6)	1.353(11)
P–C2	1.788(4)	1.788(6)	C3–C8	1.352(5)	1.337(8)
O–C3	1.416(4)	1.411(6)			

[a]In structure **23b**, atom Se is replaced by atom S2.

TABLE 2 Bond Angles (Deg) for **23a**, **b** with ESD's in Parentheses

Angle	**23a**	**23b**	*Angle*	**23a**	**23b**
C1–S2[a]–C2	98.0(2)	93.3(2)	S2[a]–C1–N	113.3(2)	112.8(4)
S1–P–O	115.89(9)	116.0(2)	S3–C1–N	126.2(2)	126.2(4)
S1–P–N	114.0(1)	113.4(2)	O–C3–C4	119.4(3)	118.0(6)
S1–P–C2	121.0(2)	120.7(3)	O–C3–C8	117.4(3)	119.5(5)
O–P–N	106.2(1)	105.8(2)	C4–C3–C8	123.2(4)	122.4(7)
O–P–C2	100.1(2)	100.2(3)	C3–C4–C5	116.0(5)	116.(1)
N–P–C2	96.8(2)	98.2(3)	C4–C5–C6	120.1(5)	120.(1)
P–O–C3	120.9(2)	120.9(3)	C5–C6–C7	121.9(5)	121.5(9)
P–N–C1	121.1(2)	123.1(4)	C6–C7–C8	118.4(5)	119.0(9)
S2[a]–C2–P	107.8(2)	108.0(3)	C3–C8–C7	120.3(4)	121.4(8)
S2[a]–C1–S3	120.4(2)	121.0(3)			

[a]In structure **23b**, atom Se is replaced by atom S2.

nium. In a sealed tube, it can be stored without change for a long time.

X-RAY STRUCTURE INVESTIGATION OF COMPOUNDS **23a, b**

ORTEP drawings and atom numbering schemes for the molecules **23a**, **b** are shown in Figures 1 and 2, respectively.

Heterocyclic rings of the molecules **23a**, **b** have an envelope conformation. The fragments P–N–C1–X (X = S2, Se) are planar in the ranges 0.015(3) (**23a**) and 0.010(5) Å (**23b**), the deviations of the C2 atoms out of these planes being equal to −0.321(4) (**23a**) and −0.412(7) Å (**23b**). Dihedral angles between the planes of the heterocycle feet and the envelope valves are equal to 17.7° (**23a**) and 22.3° (**23b**). Thus, the ring of the molecule **23a** is more planar than that of the molecule **23b**. In contrast, the Se-containing ring is more planar than its S-containing analog in the recently studied 1,3,4-thiaza- and 1,3,4-selenazaphospholines [8].

The phenoxy group at the phosphorus atom in **23a**, **b** is in an axial position. The plane of the Ph substituent is practically orthogonal to the plane of the bonds of oxygen, and the dihedral angles between appropriate planar fragments are equal to 95.8° (**23a**) and 93.6° (**23b**) that is characteristic of phosphorylated phenols [11]. Axial orientation of the P–O bond can be due to an anomeric effect—interaction of the lone electron pair of the endocyclic nitrogen atom with the antibonding orbital of the P–O bond ($n-\sigma^*$ interaction). The nitrogen atoms in the molecules **23a** and **23b** have a planar coordination. The conformation along the N–P bond is most favorable for such interaction.

The lengths of the P–N and P–O bonds in the molecules **23a** and **23b** are equal (Table 1). The endocyclic N–P–C2 bond angle in **23a** [96.8(2)°] is essentially smaller than that in **23b** [98.2(3)°] (Table 2). On the contrary, the bond angles āt the endocyclic chalcogen atoms X decrease in the reverse

TABLE 3 Structure Determination Summary for **23a**, **b** at 20°C

Compound	**23a**	**23b**
Empirical formula	$C_8H_8NOPS_3$	$C_8H_8NOPS_2Se$
Color	yellow	
Crystal size (mm)	0.15 × 0.3 × 0.4	0.2 × 0.4 × 0.5
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions (from 25 high angle reflections)		
a(Å)	9.529(2)	9.600(3)
b(Å)	6.413(2)	6.512(3)
c(Å)	19.260(4)	19.101(6)
β(deg)	93.67(2)	93.68(2)
Volume V(Å^3)	1175	1192
Z	4	4
Formula weight	261.33	308.22
Density (calcd) (g · cm^{-3})	1.478	1.718
Absorption coefficient (cm^{-1})	7.09	35.56
F(000)	536	608
Diffractometer used	Enraf–Nonius CAD-4	
Radiation	Mo K_α (λ = 0.71073 Å) graphite monochromator	
2θ range (deg)	3–60	4–60
Scan mode	$\omega/(5/3\theta)$	$\omega/2\theta$
Scan speed	variable: 1–20° min^{-1} in $\sigma(I)$	
Scan range	variable: $\omega = (1.2 + 0.35 \cdot tg\theta)°$	
Standard reflections	two intensity and two orientation control reflections measured every 200 reflections	
Index ranges	$-13 \le h \le 13$ $0 \le k \le 9$ $0 \le l \le 27$	
Reflections collected	2220	2220
Observed reflections ($F^2 \ge 3\sigma$)	1404	1227
Absorption correction	not applied	empirical
System	SDP-PLUS, PDP 11/23	
Solution	heavy atom	crystal of **23b** is isostructural to crystal **23a**
Refinement method	full-matrix least squares (on F's)	
Quantity minimized	$\Sigma\, w(\|F_O\| - \|F_C\|)^2$	
Hydrogen atoms	from difference Fourier were refined isotropically	
Weighting scheme	$w = 4\|F_O\|^2/[(\sigma(I))^2 + (0.07\ \|F_O\|^2)^2]$	
R	0.036	0.040
R_W	0.051	0.054
Goodness of fit	1.222	1.344
Largest Δ/σ	0.53	0.67
Data to parameter ratio	8.83	7.72
Largest difference peak ($e \cdot$ Å^{-3})	0.31	0.68

order: in **23a**, it is equal to 98.0(2)°, and, in **23b**, this angle is significantly smaller—93.3(2)°. Such differences in bond angles are probably due to the increase of the bond distances Se–C compared to the bond lengths S–C.

The molecules in the crystals are assembled via H bonds in centrosymmetric dimers: in **23a**, N–H···S3′ (2-x, 1-y, 1-z); N···S3′ 3.347(2) Å, N–H 0.83 Å, H···S3′ 2.52 Å, angle N–H···S3′ equals 171°; in **23b**, N–H···S3′ (1-x, 1-y, 1-z); N···S3′ 3.369(2) Å, N–H 0.72 Å, H···S3′ 2.66 Å, angle N–H···S3′ equals 167°.

EXPERIMENTAL

X-Ray Structure Determination for **23a, b**

A summary of the structure determination carried out at room temperature is given in Table 3. Final atomic parameters for the molecules **23a**, **b** are listed in Tables 4 and 5, respectively.

TABLE 4 Final Atomic Parameters for **23a** with ESD's in Parentheses

Atom	*x*	*y*	*z*	$B_{iso}(Å^2)^a$
S1	1.0130(1)	−0.1003(2)	0.39075(5)	5.60(2)
S2	0.61921(8)	0.2266(2)	0.46028(6)	5.57(2)
S3	0.78011(8)	0.5628(1)	0.53235(5)	4.79(2)
P	0.86116(8)	0.0923(1)	0.38741(4)	4.04(2)
O	0.8213(2)	0.1952(4)	0.3134(1)	4.87(5)
N	0.8831(2)	0.2905(4)	0.4440(1)	3.93(5)
C1	0.7751(3)	0.3643(5)	0.4781(2)	3.70(6)
C2	0.6904(4)	0.0155(7)	0.4114(2)	5.15(8)
C3	0.9266(3)	0.2448(5)	0.2675(2)	3.89(6)
C4	0.9937(5)	0.4309(6)	0.2739(2)	6.4(1)
C5	1.0981(5)	0.4679(8)	0.2267(3)	9.1(1)
C6	1.1226(4)	0.3242(9)	0.1768(2)	8.0(1)
C7	1.0494(4)	0.1447(7)	0.1706(2)	7.0(1)
C8	0.9508(4)	0.1051(6)	0.2171(2)	5.13(8)
H(N)	0.964(3)	0.337(5)	0.453(2)	6.0(8)
H2, 1	0.637(3)	−0.019(7)	0.374(2)	7(1)
H2, 2	0.705(4)	−0.089(6)	0.444(3)	10(1)
H4	0.978(4)	0.519(7)	0.308(2)	9(1)
H5	1.125(4)	0.585(5)	0.239(2)	7(1)
H6	1.201(4)	0.368(6)	0.144(2)	8(1)
H7	1.082(3)	0.031(6)	0.134(2)	6.8(9)
H8	0.896(4)	−0.015(6)	0.221(2)	7.2(9)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE 5 Final Atomic Parameters for **23b** with ESDs in Parentheses

Atom	*x*	*y*	*z*	$B_{iso}(Å^2)^a$
Se	0.10493(6)	0.2282(1)	0.45706(4)	5.40(2)
S1	0.5168(2)	−0.0889(3)	0.39128(8)	5.05(4)
S3	0.2827(1)	0.5648(2)	0.53350(8)	3.91(3)
P	0.3618(1)	0.0933(2)	0.38767(7)	3.54(3)
O	0.3216(4)	0.1958(7)	0.3133(2)	4.04(8)
N	0.3807(4)	0.2886(7)	0.4448(2)	3.44(9)
C1	0.2743(5)	0.3669(9)	0.4784(3)	3.3(1)
C2	0.1937(6)	0.007(1)	0.4103(3)	4.8(1)
C3	0.4258(5)	0.2528(8)	0.2682(3)	3.5(1)
C4	0.4841(7)	0.445(1)	0.2764(3)	5.7(2)
C5	0.5884(7)	0.493(2)	0.2309(5)	9.2(2)
C6	0.6240(7)	0.352(2)	0.1807(4)	8.7(2)
C7	0.5615(8)	0.171(1)	0.1743(4)	7.1(2)
C8	0.4620(7)	0.122(1)	0.2185(3)	5.1(1)
H(N)	0.450(5)	0.326(9)	0.456(3)	4(1)
H2, 1	0.135(5)	−0.054(9)	0.375(3)	5(1)
H2, 2	0.211(5)	−0.095(8)	0.444(3)	5(1)
H4	0.469(5)	0.516(9)	0.307(3)	5(1)
H5	0.614(5)	0.579(8)	0.242(3)	5(1)
H6	0.683(6)	0.39(1)	0.163(3)	7(1)
H7	0.586(8)	0.08(2)	0.139(5)	9(2)
H8	0.436(7)	0.01(1)	0.217(4)	8(2)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

SYNTHETIC PROCEDURES

2-Methylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3-4-thiazaphosphole (**18a**)

Hydrogen sulfide was bubbled slowly through a solution of 12.50 g (51.9 mmol) of chloroanhydride **13** and 7.58 g (103.7 mmol) of methyl thiocyanate **15a** in 200 mL of dry ether at room temperature, with intense stirring, during 1 hour. Simultaneously, 5.78 g (57.1 mmol) of triethylamine was added dropwise to the reaction mixture. After 4 days, the solvent and the excess of thiocyanate **15a** were evaporated in vacuo, and a solution of 5.78 g (57.1 mmol) of triethylamine in 100 mL of ether was added to the reaction mixture. The next day, the precipitate of triethylamine hydrochloride was filtered off. The filtrate was washed with water and dried over anhydrous $MgSO_4$. After concentration of the reaction mixture in vacuo, the residue partially crystallized. The crystalline product was filtered off and recrystallized from CCl_4. This resulted in 3.6 g (yield 25%) of thiazaphospholine **18a**, mp 99°C. Anal. calcd for $C_9H_{10}NOPS_3$: C, 39.25; H, 3.67; N, 5.09; P, 11.25; S, 34.93%; found, C, 39.44; H, 3.48; N, 4.95; P, 11.59; S, 34.81%.

2-Benzylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**18b**)

Hydrogen sulfide was passed slowly through a solution of 16.45 g (68.2 mmol) of **13** and 12.22 g (81.9 mmol) of benzyl thiocyanate **15b** in 200 mL of dry ether with intense stirring, and a solution of 7.60 g (75.1 mmol) of triethylamine was added dropwise to the mixture during 1 hour. The reaction mixture was left to stand at room temperature during 3 days, and then a solution of an additional 7.60 g (75.1 mmol) of triethylamine in 100 mL of ether was added to it. The day after, the precipitate of Et_3NHCl was filtered off. The filtrate was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the substance that remained crystallized partially. The solid product was collected by filtration and recrystallized from CCl_4. This resulted in 6.72 g of thiazaphospholine **18b** (yield 28%) mp 106°C. Anal. calcd for $C_{15}H_{14}NOPS_3$: C, 51.26; H, 4.02; N, 3.99; P, 8.81; S, 27.37%; found, C, 51.08; H, 3.98; N, 3.87; P, 8.49; S, 27.51%.

2,4-Dithioxo-4-phenoxy-1,3,4-thiazaphospholidine (**23a**)

Hydrogen sulfide was bubbled through a solution of 6.21 g (47.7 mmol) of bis(thiocyanato)methane **20** and 23.00 g (95.4 mmol) of **13** in 250 mL of dry benzene and a solution of 21.24 g (209.8 mmol) of triethylamine in 50 mL of benzene were added dropwise to the mixture with intense stirring. The next day, the precipitate of triethylamine hydro-

chloride was filtered off, and the solvent from the filtrate was removed in vacuo. After having been allowed to stand for 2 days, the residue crystallized partially. The crystalline solid was separated by filtration and recrystallized from CCl_4. This gave 10.23 g (yield 41%) of thiazaphospholidine **23a**, mp 122°C. Anal. calcd for $C_8H_8NOPS_3$: C, 36.77; H, 3.09; N, 5.36; P, 11.85; S, 36.81; found, C, 36.60; H, 3.15; N, 5.49; P, 11.42; S, 37.30%.

2-Methylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-selenazaphosphole (**18c**)

Hydrogen selenide was passed slowly through a solution of 5.35 g (22.2 mmol) of **13** and 3.25 g (44.4 mmol) of **15a** in 100 mL of dry ether, and simultaneously 2.47 g (24.4 mmol) of triethylamine was added dropwise to the mixture, with intense stirring, during 1 hour. After 7 days, a solution of 2.47 g (24.4 mmol) of triethylamine in 50 mL of ether was added to the mixture. The next day, a precipitate of Et_3NHCl was filtered off, and the filtrate was evaporated in vacuo. When left to stand during 2 days, the residue crystallized. Recrystallization of the crystalline substance from CCl_4 produced 2.5 g (yield 35%) of selenazaphospholine **18c**, mp 91°C. Anal. calcd for $C_9H_{10}NOPS_2Se$: C, 33.54; H, 3.13; N, 4.35; P, 9.61; S, 19.90%; found, C, 33.23; H, 3.02; N, 4.49; P, 9.85; S, 19.48%.

2,4-Dithioxo-4-phenoxy-1,3,4-selenazaphospholidine (**23b**)

Hydrogen selenide was slowly passed through a solution of 2.01 g (13.5 mmol) of bis(thiocyanato)methane **20** and 6.51 g (27.0 mmol) of **13** in 100 mL of dry ether, and simultaneously a solution of 3.00 g (29.6 mmol) of triethylamine in 25 mL of ether was added dropwise to the reaction mixture with stirring during 1 hour. After 2 days, another 3.00 g (29.6 mmol) of triethylamine was added to the mixture. A day after a precipitate of Et_3NHCl had been filtered off, the solvent was removed in vacuo. When left to stand during 2 days, the residue partially became crystalline. After separation by filtration and recrystallization of the crystalline solid from benzene, 2.6 g (yield 31%) of selenazaphospholidine **23b** was obtained, mp 126°C. Anal. calcd for $C_8H_8NOPS_2Se$: C, 31.17; H, 2.62; N, 4.55; P, 10.05; S, 20.80%; found, C, 31.43; H, 2.49; N, 4.81; P, 10.40; S, 20.58%.

REFERENCES

[1] M. G. Zimin, R. M. Kamalov, R. A. Cherkasov, A. N. Pudovik, *Zh. Obshch. Khim. 52*, 1982, 482; *J. Gen. Chem. USSR, 52*, 1982, 423.

[2] M. G. Zimin, R. M. Kamalov, R. A. Cherkasov, A. N. Pudovik, *Phosphorus Sulfur, 13*, 1982, 371.

[3] H. Fedgenhäuer, R. Moll, *Z. Chem., 20*, 1980, 141.

[4] R. M. Kamalov, G. M. Makarov, I. A. Litvinov, O. N. Kataeva, M. A. Pudovik, R. A. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 451.

[5] R. M. Kamalov, G. M. Makarov, M. A. Pudovik, R. A. Cherkasov, A. N. Pudovik, *Zh. Obshch. Khim., 60*, 1990, 2220; *J. Gen. Chem. USSR, 60*, 1990, 1984.

[6] R. M. Kamalov, G. M. Makarov, O. N. Kataeva, R. Z. Musin, I. A. Litvinov, H. Al'-Akra, M. A. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 460.

[7] R. M. Kamalov, N. A. Khailova, A. A. Gazikasheva, L. F. Chertanova, M. A. Pudovik, A. N. Pudovik, *Dokl. Akad. Nauk SSSR, 316*, 1991, 1406.

[8] R. M. Kamalov, G. S. Stepanov, L. F. Chertanova, A. A. Gazikasheva, M. A. Pudovik, A. N. Pudovik, *Heteroatom Chem., 3*, 1992, 115.

[9] W. E. Bacon, W. M. Le Suer, *J. Am. Chem. Soc., 76*, 1954, 670.

[10] The data of ^1H and IR spectra of compounds **18a–c** and **23a**, **b**, as well as the results of X-ray study of heterocycles **18b**, **c**, were described in Ref. [8].

[11] R. P. Arshinova, *Zh. Obshch. Khim., 51*, 1981, 1007.