Heteroatom Chemistry
Volume 3, Number 2, 1992

Synthesis of N,P,S,Se-Containing Mono- and Bicyclic Compounds in Reactions of Isothiocyanato- and Diisothiocyanato(di)chloromethyl(thio)phosphonates with Hydrosulfur(seleno) Compounds

R. M. Kamalov,* G. S. Stepanov, L. F. Chertanova, A. A. Gazikasheva, M. A. Pudovik, and A. N. Pudovik

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Centre of the USSR Academy of Sciences, 420083, Kazan, Arbuzov str., 8, USSR

Received 27 May 1991.

ABSTRACT

Reactions of phenyl isothiocyanato(di)chloromethyl(thio)phosphonates (**1**) *with thiols in the presence of a base give rise to 2-alkylthio-4,5-dihydro-4-oxo(thioxo)-4-phenoxy-1,3,4-thiazaphospholes* (**5**). *Some of these compounds can also be obtained by alkylation of 2,4-dithioxo-4-phenoxy-1,3,4-thiazaphospholidine* (**4**), *which is formed in the reaction of phenyl isothiocyanatochloromethylthiophosphonate* (**1a**) *with sodium hydrosulfide. The interaction of* **1a** *with H_2Se and triethylamine results in the formation of 2,4-dithioxo-4-phenoxy-1,3,4-selenazaphospholidine* (**8**), *which when alkylated affords 2-alkylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-selenazaphospholes* (**9**) *Diisothiocyanatodichloromethyl(thio)-phosphonates* (**11**) *react with α-toluenethiol in the presence of a base, giving rise to 3,7-bis(benzylthio)-1-oxo(thioxo)bicyclo[3.3.0]-4,6-dithia-2,8-diaza-1-phosphaocta-2,7-dienes* (**13**). *By the interaction of phenyl isothiocyanatotrichloromethylthiophosphonate* (**14**) *with ethanethiol and Et_3N,* S-*ethyl*-N-(O-*phenyl(trichloromethyl)thiophosphonyl)dithiocarbamate triethylammonium salt* (**15**) *has been formed. The molecular structures of some P,N,S,Se-containing heterocycles that we have synthesized have been studied by X-ray diffraction.*

INTRODUCTION

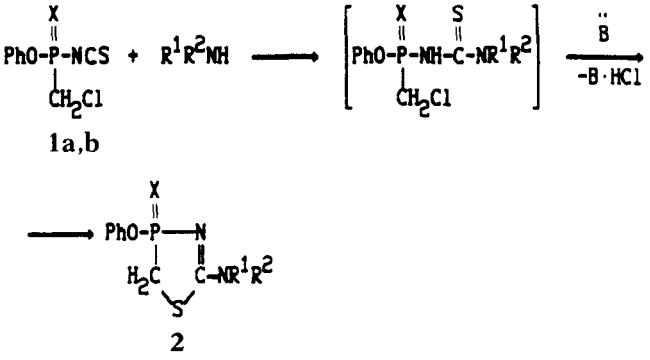
Addition of thiols to isothiocyanatophosphates results in the formation of *N*-phosphorylated dithiocarbamates [1]. Another synthetic route to these compounds is the alkylation of potassium *N*-(thio)phosphoryl dithiocarbamates, which are formed in reactions of isothiocyanato(thio)-phosphates with potassium hydrosulfide [2]. *S*-Alkyl *N*-(thio)phosphoryl dithiocarbamates are unstable and easily disintegrate into thiols and the corresponding isothiocyanato(thio)phosphates [3,4]. However, when alkylated, they yield stable *S,S'*-dialkyl *N*-(thio)phosphoryl iminodithiocarbonates [5]. Reactions of potassium *N*-(thio)phosphoryl dithiocarbamates with alkylene dihalides in the presence of a base give rise to *N*-(thio)phosphorylated 2-imino-1,3-dithietanes, dithiolanes, and dithianes [2,5]. Some of them are used as effective insecto-acaricides [6]. *N*-Dialkoxythiophosphoryl 2-imino-1,3-dithietanes, dithiolanes, and dithianes also result from intramolecular alkylation of *S*-(chloroalkyl) *N*-dialkoxythiophosphoryl dithiocarbamates, appearing in the course of reaction between dithiophosphoric acids and chloroalkyl thiocyanates [7].

In the present work, we have studied reactions

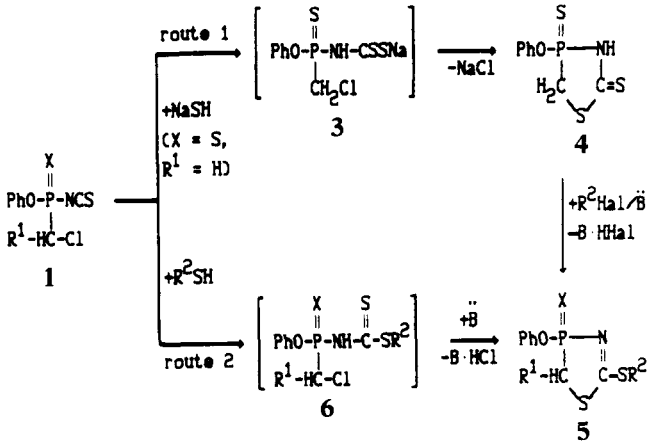
*To whom correspondence should be addressed.

1042-7163/92/$3.50 + .25

of isothiocyanato- and diisothiocyanatochloromethyl-, dichloromethyl-, and trichloromethyl(thio)phosphonates with hydrosulfur(seleno) compounds. *N*-(thio)phosphorylated dithiocarbamates and thioselenocarbamates, formed at the first stage, were expected to undergo intramolecular alkylation at the expense of the chloromethyl groups at the phosphorus atom and to bring about corresponding thiaza- or selenazaphosphaheterocycles. That this kind of cyclization might occur has recently been demonstrated on reactions of phenyl isothiocyanatochloromethyl(thio)phosphonates (**1a,b**) with amines, resulting in 2-amino-4,5-dihydro-4-oxo(thioxo)-4-phenoxy-1,3,4-thiazaphospholes (2) (Scheme 1) [8].



SCHEME 1



1: **a** R^1 = H, X = S; **b** R^1 = H, X = O;
c R^1 = Cl, X = S
5: **a** R^1 = H, R^2 = Me, X = S (route 1);
b R^1 = H, R^2 = CH_2Ph, X = S (routes 1, 2);
c R^1 = H, R^2 = Et, X = S (route 2);
d R^1 = H, R^2 = CH_2Ph, X = O (route 2);
e R^1 = Cl, R^2 = CH_2Ph, X = S (route 2)

SCHEME 2

RESULTS AND DISCUSSION

Reaction of phenyl isothiocyanatochloromethylthiophosphonate (**1a**) with sodium hydrosulfide readily proceeds with slight cooling to yield 2,4-dithioxo-4-phenoxy-1,3,4-thiazaphospholidine (**4**), presumably via cyclization of the intermediate sodium *N*-thiophosphonyldithiocarbamate (**3**) (Scheme 2, route 1). 2-Methylthio- or 2-benzylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphospholes (**5a,b**) are formed in good yield by treatment of the thiazaphospholidine (**4**) with methyl iodide or benzyl chloride in the presence of triethylamine. Compound **5b** has also been obtained by addition of α-toluenethiol to the isothiocyanatothiophosphonate (**1a**) in the presence of Et_3N (Scheme 2, route 2). In a similar way, 1,3,4-thiazaphospholines (**5c,d**) have been formed in reactions of phenyl isothiocyanatochloromethylthiophosphonate (**1a**) with ethanethiol and phenyl isothiocyanatochloromethylphosphonate (**1b**) with α-toluenethiol, respectively. Reaction of phenyl isothiocyanatodichloromethylthiophosphonate (**1c**) with α-toluenethiol proceeds in the same manner and is followed by the formation of 2-benzylthio-5-chloro-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**5e**). In contrast to crystalline products **5a–d** compound **5e** is a thick sticky noncrystallizable oil.

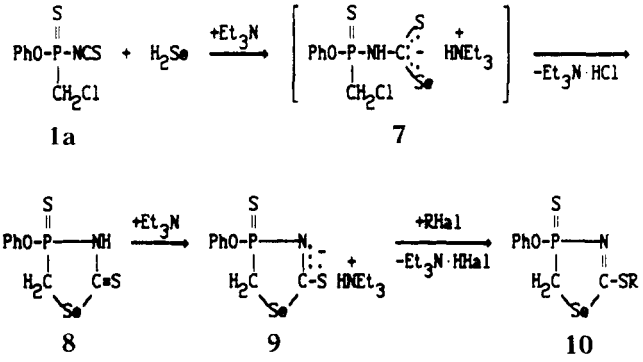
The structures of the thiazaphospholidine (**4**) and the thiazaphospholines (**5a–e**) have been confirmed by ^1H and ^{31}P NMR, IR, and mass spectroscopy and by X-ray diffraction [9]. The protons of the methylene group in the heterocycles are seen in the ^1H NMR spectra in the form of eight lines (AB part of ABX system) in the δ range 3.2–4.3. Two doublets at δ = 5.23 and 5.25 in the ^1H NMR spectrum of 5-chlorothiazaphospholine (**5e**), assigned to the methyne proton, result from the existence of two stereoisomers. Methylene protons of the benzyl group in **5b,d,e** are nonequivalent and appear as two doublets (AB system) at 250.13 MHz and as a singlet at 60 MHz in the δ range 4.2–4.4. The ^{31}P chemical shift of the 4-oxo-thiazaphospholine (**5d**), δ = 59.8 (CD_3CN), and that of thiazaphospholidine (**4**), δ = 87.2 (CCl_4), is more close to the δ_P value of 70.0 reported for the recently described (4-diethylamino-3-methyl-5-methylene-4-thioxo-1,3,4-thiazaphospholine-2-ilide) methylamine of similar structure [10], than the ^{31}P chemical shifts of the thiazaphospholines (**5a–d,e**) which are observed at much lower field at δ_P = 106–120. The absorption ν(C = N) in the IR spectra of the thiazaphospholines (**5a–e**) is shifted to lower frequencies as compared to the usual C = N bonds and appears in the 1505–1525 cm^{-1} range.

The products **5a–c** having a P = S group do not change on exposure to air and when standing for a

long period of time, whereas their oxygen analog **5d** degrades on exposure to air during a few days, probably through ring opening as a result of hydrolysis, similar to Ref. [8]. However, compound **5d** does not undergo any transformations when exposed to water for a short period of time.

N-(Thio)phosphonyl dithiocarabamates (**6**) can be assumed to be intermediates in the formation of **5** by route 2. The chlorine atom in chloromethylphosphonates is known [11] to have a low reactivity and cannot be substituted readily by nucleophiles. Therefore, the readiness of intramolecular alkylation of **6**, resulting in **5**, is noteworthy.

Hydrogen selenide can also be used in the reaction with isothiocyanatothiophosphonate (**1a**). In the presence of an equimolar amount of triethylamine, the reaction is characterized by quantitative isolation of Et_3NHCl and formation of 2,4-dithioxo-4-phenoxy-1,3,4-selenazaphospholidine (**8**) with δ_P = 89.8 (CCl_4). Because of the acidic nature of the selenathiocarbarmate fragment, this compound in reaction with excess triethylamine yields the salt **9** with δ_P = 122.4. When exposed to triethylamine, the thiazaphospholidine (**4**) undergoes a similar reaction, giving rise to a salt of type **9** with S instead of Se in the ring and with δ_P = 118.6. The alkylation of the salt **9** by methyl iodide or benzyl chloride produces the 2-alkylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-selenazaphospholes (**10a,b**) (Scheme 3). However, the one-pot synthesis of **10a,b** without isolation of **8** has been found to be more convenient.



10: **a** R = Me, **b** R = CH_2Ph

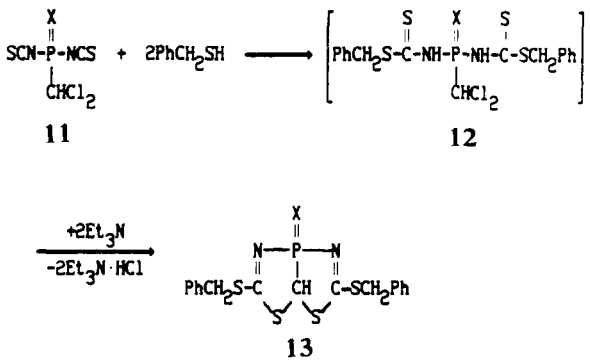
SCHEME 3

The ^1H, ^{31}P NMR, and IR spectra of selenazaphospholidine (**8**) and selenazaphospholines (**10a,b**) were found to be rather similar to those of their thia-analogs **4**, **5a**, and **5b**, respectively. The structures of the Se-containing products discussed were proved by mass spectra [9] and X-ray analysis of **10a** as well.

It is important to note that triethylammonium *N*-thiophosphonyl thioselenocarbamate (**7**), formed at the first stage, can undergo cyclization either at the selenium atom, or at the sulfur atom. The intramolecular alkylation prefers the Se atom as it is the softer nucleophile. It is also necessary to mention that, according to NMR and mass spectral data, the synthesis of **8** and **10a,b** is followed by the formation of small amounts of the corresponding *S*-containing heterocycles **4** and **5a,b**, respectively, probably because of some disproportionation reactions.

Reaction of isothiocyanatodichloromethylthiophosphonate (**1c**) with α-toluenethiol, yielding 1,3,4-thiazaphospholines (**5e**), has given evidence that substitution of one of the chlorine atoms in the dichloromethyl group of dithiocarbamate (**6e**) is possible. We assumed that the presence of another chlorine atom probably could be used for forming a second ring, annelated with the first one. This process was performed in the reaction of diisothiocyanatodichloromethylthiophosphonate (**11a**) with two equivalents of α-toluenethol in the presence of Et_3N. The above reaction resulted in the formation of 3,7-bis(benzylthio)-1-thioxobicyclo[3.3.0]-4,6-dithia-2,8-diaza-1-phosphaocta-2,7-diene (**13a**) (Scheme 4). The structure of **13a** was proved by X-ray analysis and characterized by IR, ^1H, ^{31}P NMR, and mass spectroscopy [9] as well. In particular, the signal in the ^{31}P NMR spectrum of **13a** is shifted further downfield (δ_P = 154.7 (CD_3CN) than that of heterocycles **5** and **10**. It must be noted that, in this reaction, some unidentified resinous product with δ_P = 82.5 has been formed as a byproduct of (**13a**).

The oxo-analog (**13b**) of the bicyclic product (**13a**) has been formed in the reaction of diisothiocyanatodichloromethylphosphonate (**11b**) with α-toluenethiol. The oxo-analog failed to be isolated in an analytically pure state, but its occurrence in the reaction mixture has been evidenced spectroscopically. Thus, in the ^{31}P NMR spectrum of the reaction mixture there is actually only one signal with δ_P = 107 (C_6H_6), which is ascribed to **13b**, and an intense peak of the **13b** molecular ion is observed in the electron impact mass spectrum.



11, 13: **a** X = S, **b** X = O

SCHEME 4

Reaction between phenyl isothiocyanatotrichloromethylthiophosphonate (**14**), ethanethiol, and triethylamine gives rise to triethylammonium *S*-ethyl *N*-[0-phenyl(trichloromethyl)thiophosphonyl] dithiocarbamate (**15**) (Scheme 5).

When the salt **15** was boiled in benzene for a few hours in the presence of an excess of Et_3N, an equimolar amount of triethylamine hydrochloride precipitated and a very complicated resinous mixture was also formed. By heating **15** under the same conditions with no additional amount of triethylamine, disintegration of this salt into its precursors occurs predominantly.

14 **15**

SCHEME 5

X-ray Structure Investigation of **5b**, **10a**, *and* **13a**

ORTEP drawings of the molecules **5b**, **10a**, and **13a** are shown in Figures 1, 2, and 3, respectively. Selected bond distances, bond angles, and torsion angles for **5b**, **10a**, and **13a** are summarized in Tables 1, 2, and 3.

A five-membered ring in molecule **5b** has an envelope conformation with the deviation of the C2 atom out of the P1–N1–C1–S2 plane equal to −0.323(4) Å. When the S2 atom is substituted by Se1, the five-membered ring becomes more planar and the deviation of the C2 atom out of this plane in **10a** does not exceed −0.130(11) Å.

When two thiazaphospholine rings are annelated along the P–C bond, the envelope conformation of the heterocycles is preserved. The bridge C2 atom is out of the P1–N1–C1–S2 and P1–N2–C4–S4 planes by 0.183(5) and 0.120(5) Å, respectively. The conformation of bicycle **13a** is defined by the P1–N1–C1–S2/P1–N2–C4–S4 and P1–C2–S2/P1–C2–S4 dihedral angles, equal to 111.0 and 123.4°, respectively.

The P=S bond in **5b** and **10a** is equatorial and the phenoxy group is axial relative to the heterocycles. Their orientation toward each other is synclinal (cs) in **5b**, and it is close to synperiplanar (sp)

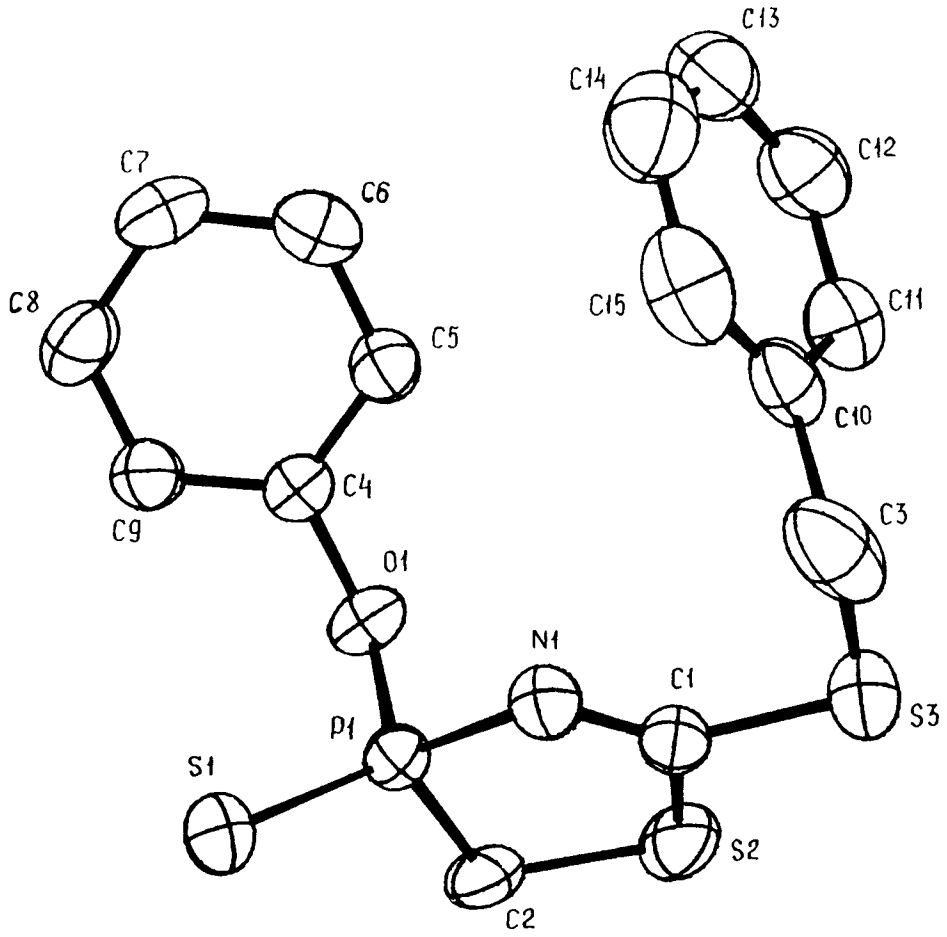


FIGURE 1 ORTEP Perspective Drawing of **5b**.

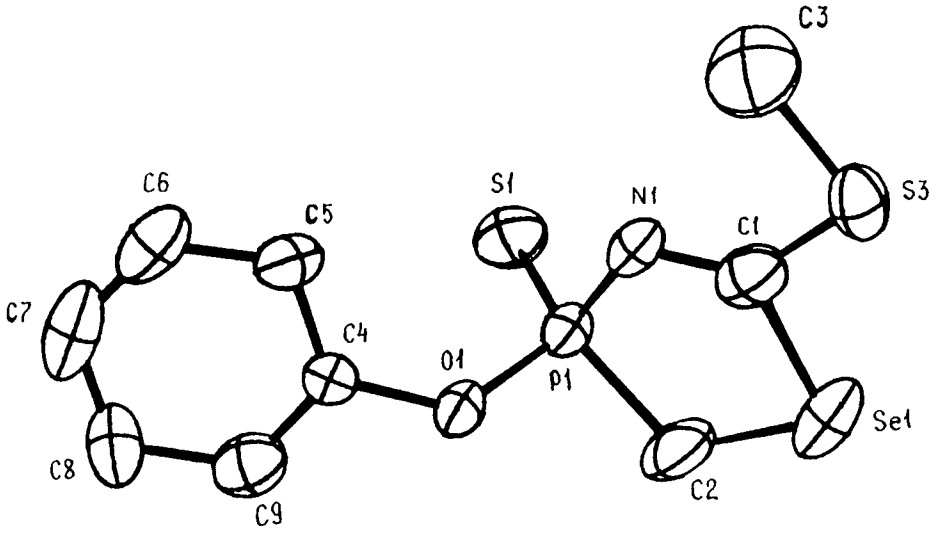


FIGURE 2 ORTEP Perspective Drawing of **10a**.

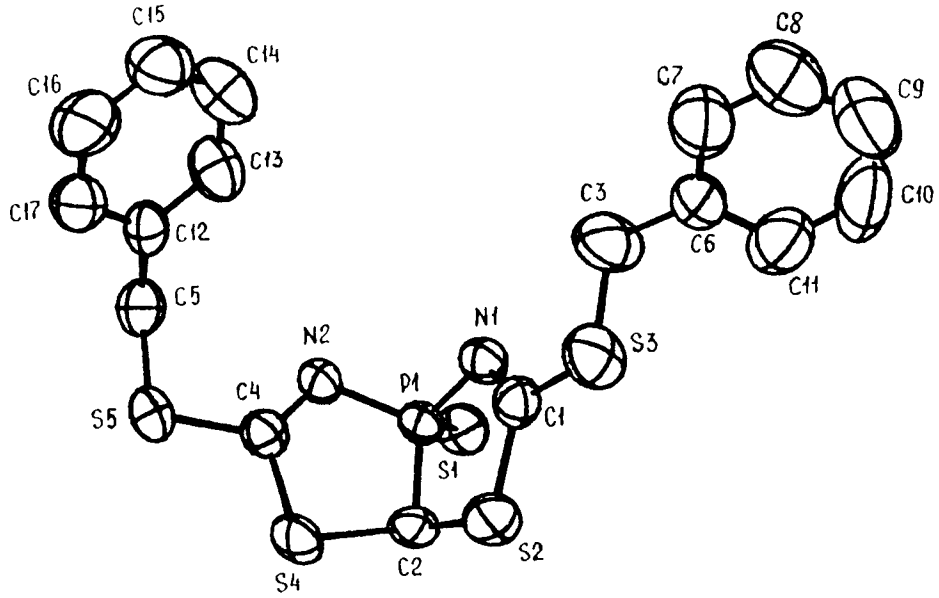


FIGURE 3 ORTEP Perspective Drawing of **13a**.

in **10a** (the S1–P1–O1–C4 torsion angles are 54.0 and −27.7°, respectively).

The sulfur atoms of the benzylthio fragments are in the planes of the appropriate heterocycles, and the N=C–S–R fragment (R=CH_2Ph in **5b** and **13a**; R = Me in **10a**) possesses a synperiplanar (sp) conformation (the N=C–S–R torsion angles are −9.2 in **5b**, 1.6 in **10a**, and −2.4, −0.5° in **13a**). The orientation of the phenyl group is synclinal (sc) in **5b** (the C1–S3–C3–C10 torsion angle is −76.9°), and in structure **13a** rotations of the phenyl groups are essentially different for the right and left parts of the molecule (the C1–S3–C3–C6 and C4–S5–C5–C12 torsion angles are −158.1 and −91.3°, respectively).

In all three structures that have been investigated, the phosphorus atom has essentially a distorted tetrahedral coordination: Endocyclic N–P–C angles as well as external N1–P1–O1, O1–P1–C2 angles in **5b** and **10a** and the N1–P1–N2 angle in **13a** are reduced, whereas the S=P–N and S=P–C angles as well as the S=P–O angles in **5b** and **10a** are extended as compared to the standard value, 109.5°.

The angle values at the phosphorus atom in all three molecules investigated are in good agreement with each other in the esd range. However, there are some differences between bond angles in the rings; thus, in the selenium-containing heterocycle (**10a**) the endocyclic P–N–C angle is increased and the Se–C–N angle is decreased by 4° as compared to the *S*-containing heterocycles, **5b** and **13a**. Values of the appropriate bond angles in the latter are in

Table 1 Selected Bond Distances (Å) for **5b**, **10a**, and **13a** with Estimated Standard Deviations (esd's) in Parentheses

Bond	**5b**	**10a**	**13a**
S1–P1	1.924(1)	1.916(2)	1.912(2)
S2[a]–C1	1.785(6)	1.940(5)	1.781(5)
S2[a]–C2	1.786(5)	1.891(7)	1.780(5)
S3–C1	1.728(4)	1.711(6)	1.720(5)
S3–C3	1.810(9)	1.802(7)	1.822(7)
S4–C2	—	—	1.818(5)
S4–C4	—	—	1.777(5)
S5–C4	—	—	1.717(5)
S5–C5	—	—	1.824(5)
P1–O1	1.610(4)	1.603(4)	—
P1–N1	1.671(4)	1.646(5)	1.672(4)
P1–N2	—	—	1.669(4)
P1–C2	1.803(6)	1.817(5)	1.860(4)
O1–C4	1.404(6)	1.408(6)	—
N1–C1	1.274(7)	1.287(7)	1.258(6)
N2–C4	—	—	1.295(5)
C3–C6	—	—	1.500(8)
C3–C10	1.516(9)	—	—
C5–C12	—	—	1.469(7)

[a] In structure **10a** atom Se1 is replaced by atom S2.

Table 2 Selected Bond Angles (deg) for **5b**, **10a**, and **13a**, with esd's in Parentheses

Angle	**5b**	**10a**	**13a**
C1–S2[a]–C2	94.0(2)	91.4(3)	94.9(2)
C1–S3–C3	102.4(3)	100.1(3)	100.3(3)
C2–S4–C4	—	—	95.6(2)
C4–S5–C5	—	—	102.1(2)
S1–P1–O1	116.1(1)	115.5(2)	—
S1–P1–N1	115.2(2)	114.9(2)	115.5(1)
S1–P1–N2	—	—	115.0(1)
O1–P1–N1	104.9(2)	104.1(3)	—
N1–P1–N2	—	—	104.9(2)
O1–P1–C2	99.6(2)	100.1(3)	—
N1–P1–C2	101.9(2)	102.9(3)	99.9(2)
N2–P1–C2	—	—	102.0(2)
P1–O1–C4	123.1(3)	125.5(3)	—
P1–N1–C1	112.3(4)	118.3(4)	115.0(3)
P1–N2–C4	—	—	114.1(3)
S2[a]–C1–S3	110.7(3)	112.5(3)	111.8(3)
S2[a]–C1–N1	122.6(4)	118.6(5)	122.5(4)
S3–C1–N1	126.7(5)	128.9(4)	125.7(4)
S2–C2–S4	—	—	115.5(3)
S2[a]–C2–P1	106.3(3)	108.3(3)	106.8(2)
S4–C2–P1	—	—	105.5(2)
S3–C3–C6	—	—	109.4(5)
S3–C3–C10	117.1(5)	—	—
S4–C4–S5	—	—	112.3(2)
S4–C4–N2	—	—	122.4(4)
S5–C4–N2	—	—	125.3(4)
S5–C5–C12	—	—	114.6(4)

[a] In structure **10a** atom Se1 is replaced by atom S2.

Table 3 Selected Torsion Angles (deg) for **5b**, **10a**, and **13a**, with esd's in Parentheses

Torsion Angle	**5b**	**10a**	**13a**
C2–S2[a]–C1–S3	172.4	177.8	177.6
C2–S2[a]–C1–N1	−7.8	−3.1	−3.2
C1–S2[a]–C2–P1	14.2	5.6	7.6
C3–S3–C1–S2[a]	170.5	−179.3	176.7
C3–S3–C1–N1	−9.2	1.6	−2.4
C1–S3–C3–C6	—	—	−158.1
C1–S3–C3–C10	−76.9	—	—
C4–S4–C2–S2	—	—	112.6
C4–S4–C2–P1	—	—	−5.0
C2–S4–C4–S5	—	—	−179.9
C2–S4–C4–N2	—	—	2.8
C5–S5–C4–S4	—	—	−177.7
C5–S5–C4–N2	—	—	−0.5
C4–S5–C5–C12	—	—	−91.3
S1–P1–O1–C4	54.0	−27.7	—
N1–P1–O1–C4	−74.4	99.2	—
C2–P1–O1–C4	−179.6	−154.6	—
S1–P1–N1–C1	140.6	−123.4	−118.6
O1–P1–N1–C1	−90.5	109.3	—
N2–P1–N1–C1	—	—	113.6
C2–P1–N1–C1	13.0	5.2	8.3
S1–P1–N2–C4	—	—	123.4
N1–P1–N2–C4	—	—	−108.5
C2–P1–N2–C4	—	—	−4.7
S1–P1–C2–S2[a]	−143.6	120.3	116.0
S1–P1–C2–S4	—	—	−120.6
O1–P1–C2–S2[a]	90.5	−114.0	—
N1–P1–C2–S2[a]	−17.1	−6.8	−9.7
N1–P1–C2–S4	—	—	113.7
N2–P1–C2–S2	—	—	−117.3
N2–P1–C2–S4	—	—	6.0
P1–O1–C4–C5	94.7	−57.3	—
P1–N1–C1–S2[a]	−3.5	−1.3	−3.7
P1–N1–C1–S3	176.2	177.7	175.4
P1–N2–C4–S4	—	—	1.4
P1–N2–C4–S5	—	—	−175.6
S3–C3–C6–C7	—	—	−120.0
S3–C3–C10–C11	−33.5	—	—
S5–C5–C12–C13	—	—	115.7

[a] In structure **10a** atom Se1 is replaced by atom S2.

good agreement with those found in 2-amino-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole [8].

The P–N bond distances in the sulfur-containing heterocycles **5b** and **13a** (average value 1.671 Å) somewhat exceed the length of the P–N bond in selenazaphospholine (**10a**), which equals 1.646(5) Å. There are essential differences between P–C bonds in the structures investigated. Thus, in **5b** it equals 1.803(6) Å, in **10a** this bond is lengthened to 1.817(5) Å, and, by annellation of two thiazaphospholine rings in **13a**, the bridge P–C bond reaches a value of 1.860(4) Å.

The lengths of formally double N=C bonds in **5b**, **10a**, and **13a** change from 1.258(6) to 1.295(5)

Å. The chemically equivalent bonds in the bicyclic structure (**13a**) essentially differ from each other.

When comparing the endocyclic geminal S–C bond distances, the lengths of the chemically nonequivalent C1–S2 (1.785(6) Å) and S2–C2 (1.786(5) Å) bonds in **5b** are seen to be equal. The same is observed in one of the rings in **13a**: The bond distances discussed are 1.781(5) and 1.780(5) Å. In another ring, the S–C(sp^2) and S–C(sp^3) bonds are essentially different, being equal to 1.777(5) and 1.818(5) Å, respectively. On the contrary, the Se1–C2 bond in **10a** (1.891(7) Å) is shorter than the Se1–C1 bond (1.940(5) Å). The exocyclic C–S bond distances in **5b**, **10a**, and **13a** are in good agreement with each other, and their average value is 1.719 Å.

When the values of P–N, S–C, Se–C, and N=C bonds in **5b**, **10a**, and **13a** are compared to the average lengths of P–N 1.75, S–C(sp^3) 1.82, S–C(sp^2) 1.75, Se–C(sp^3) 1.97, Se–C(sp^2) 1.89, N–C(sp^2) 1.42, and N=C(sp^2) 1.26 Å bonds [12], it can be noted that all of them actually have intermediate values between standard single and double bonds. Considering this, it can be concluded that there is probably some electron density delocalization in **5b**, **10a**, and **13a** involving lone electron pairs of the S or Se atoms and the π system of the C=N bond, although the character of this delocalization is different in all structures investigated.

EXPERIMENTAL

Spectral Studies

Infrared spectra were recorded on a UR-20 spectrophotometer, using films of liquid products and nujol mulls of solid products, and are reported in cm^{-1}. ^1H NMR spectra were obtained on a Varian T-60 (at 60 MHz) and a Bruker WM-250 (at 250.13 MHz) spectrometer (TMS as internal standard). ^{31}P NMR spectra were recorded at 10.2 MHz on a KGU-4 and at 101.26 MHz on a Bruker WM-250 spectrometer with 85% H_3PO_4 as an external standard. Chemical shifts are reported in ppm downfield from the reference, and coupling constants are given in Hz.

X-ray Diffraction Analysis

Crystallographic data for **5b**, **10a**, and **13a** were obtained at room temperature on an Enraf Nonius CAD-4 diffractometer with a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å), operating in the $\omega/(5/3)\theta$ scan mode. Intensities of reflections were measured according to the criterion $I \geq 3\sigma(I)$. A summary of the crystal data and experimental details are given in Table 4. The structures of **5b**, **10a**, and **13a** were each solved using a direct method employing MULTAN and refined by the full-matrix least-squares techniques.

No correction for absorption was applied to **5b** and **13a**. Because the value of μ is relatively high for **10a**, an empirical absorption correction was calculated for all observations using the program EAC [13] at the end of isotropic refinement. In structures **5b** and **13a**, all H atoms were located from a subsequent difference Fourier synthesis, and parameters for these atoms were refined in later cycles. In structure **10a**, all hydrogens were inserted into the chemically reasonable positions and their contributions were included in the structure factor calculations. The quantity minimized was $\Sigma\, W(F_o - F_c)^2$, where $W = |1/\sigma(F)|^2$.

Table 4 X-ray Crystal Data for **5b**, **10a**, and **13a**

Data	**5b**	**10a**	**13a**
Formula	$C_{15}H_{14}NOPS_3$	$C_9H_{10}NOPS_2Se$	$C_{17}H_{15}N_2PS_5$
Molecular weight	351.45	322.25	438.62
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$
a, Å	9.668(6)	7.381(4)	18.167(7)
b, Å	19.029(16)	12.771(3)	9.896(4)
c, Å	9.618(7)	26.419(7)	11.073(5)
β, deg	114.17(5)	90.0	92.58(3)
V, Å^3	1614.4	2490.4	1988.7
d_{calc}, g/cm^3	1.446	1.719	1.465
Z	4	8	4
Abs. coeff., cm^{-1}	5.35	34.06	6.43
F(000), *e*	728	1280	904
2θ range, deg	3–60	3–60	3–50
No. of unique data	4953	3628	3696
No. of data in refinement	1301	900	1887
Data/parameter ratio	5.3	6.6	8.6
Final dif. Four., eA^{-3}	0.144	0.292	0.283
R	0.031	0.045	0.042
R_w	0.032	0.048	0.045

All calculations were performed using SDP package [13] on a PDP-11/23. The final atomic coordinates and isotropic thermal parameters are given in Tables 5, 6, and 7.

Synthetic Procedures

Initial isothiocyanato(thio)phosphonates **1a–c**, **11a,b**, and **14** have been obtained by the reaction of appropriate chloroanhydrides (**16**) with KSCN in dry acetonitrile either at room temperature for 24 h (**1c**, **11a**) or by heating with reflux for 3 h (**14**). Preparation of **1a,b** has been described in Ref. [8]; **11b** is known as well [14]. The constants and spectral data for the isothiocyanates **1c**, **11a**, and **14** are given below:

1c, yield 62%, bp 116–118°C (0.05 Torr), n_D^{20} 1.6280, d_4^{20} 1.4331; results by ^{1}H NMR (CCl_4), δ = 5.83 (d, 1 H, CH, $^2J_{PH}$ 3), 6.91–7.34 (m, 5 H, C_6H_5); by ^{31}P NMR, δ = 54; by IR, 665 m (P=S), 945 s (P–N), 1165 m, 1190 s, 1590 m (P–O–Ph), 1970 vs,b (N=C=S), 2960 m (CCl_2–H), 3045 w, 3070 w (H–C_{ar}).

11a, yield 69%, bp 110–111°C (0.07 Torr), n_D^{20} 1.6893; results by ^{1}H NMR (CCl_4), δ = 5.84 (d, $^2J_{PH}$ 6); by ^{31}P NMR, δ = 29; by IR, 665 m (P=S), 950 w, 1050 s (P–N), 1970 vs,b (N=C=S), 2950 w (CCl_2–H).

14, yield 68%, bp 120°C (0.06 Torr), n_D^{20} 1.6298, d_4^{20} 1.4954, mp 32.5–33.5°C (recryst. from pentane); results by ^{31}P NMR, δ = 52; by IR, 690 shoulder (P=S), 705 vs (CCl_3), 955 s (P–N), 1165 m, 1190 s, 1590 m (P–O–Ph), 1970 vs,b (N=C=S), 3045 w, 3060 w,b (H–C_{ar}).

The chloroanhydrides **16a–f** [15] and **16i** [16] are known. Preparation of the phenyl esters **16g–h** was carried out by the reaction of the appropriate dichloroanhydrides with one equivalent of phenol in the presence of Et_3N.

Table 5 Final Atomic Parameters for **5b** with esd's in Parentheses

Atom	*x*	*y*	*z*	B_{iso} (Å^2)[a]
S1	0.46361(9)	0.17753(6)	0.6774(1)	4.19(2)
S2	0.0929(1)	0.33287(6)	0.4080(1)	4.70(3)
S3	−0.1478(1)	0.26161(8)	0.4561(2)	6.43(3)
P1	0.28909(8)	0.21287(5)	0.5081(1)	2.89(2)
O1	0.2626(2)	0.1824(1)	0.3429(3)	3.37(6)
N1	0.1234(3)	0.2015(2)	0.5211(4)	3.42(7)
C1	0.0362(3)	0.2544(3)	0.4719(4)	3.84(8)
C2	0.2858(4)	0.3057(2)	0.4695(5)	3.92(9)
C3	−0.1894(4)	0.1728(4)	0.4945(5)	6.1(1)
C4	0.2545(3)	0.1102(2)	0.3101(4)	2.81(7)
C5	0.1149(3)	0.0779(2)	0.2469(4)	3.34(8)
C6	0.1065(4)	0.0091(3)	0.2024(5)	4.14(9)
C7	0.2361(4)	−0.0288(2)	0.2233(5)	4.22(9)
C8	0.3756(4)	0.0057(3)	0.2892(5)	4.7(1)
C9	0.3845(3)	0.0738(2)	0.3308(5)	3.89(9)
C10	−0.2246(3)	0.1194(3)	0.3676(4)	3.84(9)
C11	−0.2998(4)	0.1381(3)	0.2149(5)	4.3(1)
C12	−0.3367(4)	0.0854(3)	0.1026(5)	4.7(1)
C13	−0.3016(4)	0.0177(3)	0.1384(5)	5.0(1)
C14	−0.2272(5)	−0.0010(3)	0.2909(6)	5.8(1)
C15	−0.1879(4)	0.0506(3)	0.4028(5)	5.2(1)

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

Table 6 Final Atomic Parameters for **10a** with esd's in Parentheses

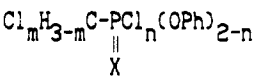
Atom	*x*	*y*	*z*	B_{iso} (Å^2)[a]
Se1	0.8268(2)	0.21239(7)	0.19036(5)	6.04(3)
S1	0.6620(4)	−0.0511(2)	0.0886(1)	4.59(5)
S3	0.8341(4)	0.0700(2)	0.28247(8)	4.00(5)
P1	0.8492(3)	0.0192(2)	0.12563(9)	3.39(4)
O1	1.0521(8)	−0.0047(4)	0.1074(2)	4.3(1)
N1	0.852(1)	−0.0057(4)	0.1867(3)	3.6(1)
C1	0.841(1)	0.0717(6)	0.2177(4)	4.1(2)
C2	0.851(2)	0.1614(6)	0.1235(4)	5.5(2)
C3	0.853(2)	−0.0686(8)	0.2937(4)	7.1(3)
C4	1.111(1)	−0.0976(6)	0.0837(3)	2.9(2)
C5	1.086(1)	−0.1935(6)	0.1075(4)	4.2(2)
C6	1.161(2)	−0.2794(6)	0.0825(4)	5.1(2)
C7	1.246(2)	−0.2712(7)	0.0394(4)	5.7(2)
C8	1.272(1)	−0.1772(7)	0.0159(4)	5.2(2)
C9	1.197(1)	−0.0884(7)	0.0402(4)	4.4(2)

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

Table 7 Final Atomic Parameters for **13a** with esd's in Parentheses

Atom	*x*	*y*	*z*	B_{iso} (Å^2)[a]
S1	0.52571(8)	0.0556(2)	1.3481(1)	4.79(3)
S2	0.64748(9)	0.3365(2)	1.1306(2)	5.59(4)
S3	0.7765(1)	0.3425(2)	1.2944(2)	6.39(4)
S4	0.58498(9)	0.1108(2)	0.9700(1)	4.85(3)
S5	0.62526(9)	−0.1699(2)	0.9354(1)	5.11(3)
P1	0.59992(8)	0.0806(1)	1.2331(1)	3.56(3)
N1	0.6807(2)	0.1393(4)	1.2892(4)	4.01(9)
N2	0.6211(2)	−0.0575(4)	1.1554(3)	3.94(9)
C1	0.6998(3)	0.2515(6)	1.2474(5)	4.2(1)
C2	0.5809(3)	0.2056(5)	1.1102(4)	3.9(1)
C3	0.8127(4)	0.2346(7)	1.4165(7)	7.5(2)
C4	0.6135(3)	−0.0437(5)	1.0392(4)	4.0(1)
C5	0.6501(3)	−0.3137(6)	1.0319(5)	5.1(1)
C6	0.8615(3)	0.3164(6)	1.5014(6)	5.8(2)
C7	0.9316(4)	0.2828(9)	1.5198(9)	10.8(2)
C8	0.9787(5)	0.353(1)	1.599(1)	15.9(3)
C9	0.9519(6)	0.456(1)	1.6603(9)	13.7(3)
C10	0.8817(6)	0.4902(8)	1.6448(8)	11.3(3)
C11	0.8342(4)	0.4218(8)	1.5659(7)	7.7(2)
C12	0.7297(3)	−0.3308(5)	1.0570(5)	4.4(1)
C13	0.7606(4)	−0.3181(7)	1.1736(5)	6.2(2)
C14	0.8324(4)	−0.3385(8)	1.2009(6)	7.2(2)
C15	0.8793(4)	−0.3725(7)	1.1133(7)	7.1(2)
C16	0.8508(4)	−0.3896(8)	0.9967(7)	7.8(2)
C17	0.7771(4)	−0.3712(7)	0.9701(5)	6.1(2)

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



16

16: a X = O, m = 1, n = 2; **b** X = S, m = 1, n = 2; **c** X = O, m = n = 2; **d** X = S, m = n = 2; **e** X = S, m = 3, n = 2; **f** X = O, m = n = 1; **g** X = S, m = n = 1; **h** X = S, m = 2, n = 1; **i** X = S, m = 3, n = 1

16g, yield 76%, bp 105°C (0.08 Torr), n_D^{20} 1.5858; results by ^1H NMR (CCl_4), δ = 4.01 (d, 2 H, CH_2, $^2J_{PH}$ 5.5), 6.99–7.26 (m, 5 H, C_6H_5); by ^{31}P NMR, δ = 84.

16h, yield 62.6%; bp 103–105°C (0.04 Torr), n_D^{20} 1.5875; results by ^1H NMR (CCl_4), δ = 5.93 (d, 1 H, CH, $^2J_{PH}$ 5), 7.04–7.23 (m, 5 H, C_6H_5); by ^{31}P NMR, δ = 79.

Elemental analyses (C, H, Cl, N, P, S) for **1c**, **11a**, **14**, and **16g–h** are in good agreement with the calculated values.

2,4-Dithioxo-4-phenoxy-1,3,4-thiazaphospholidine (**4**). A solution of 35.50 g (134.62 mmol) of **1a** in 75 mL of dry acetonitrile was added dropwise at 20°C with stirring to a suspension of 7.55 g (134.68 mmol) of NaSH in 250 mL of acetonitrile. The next day, the precipitate of NaCl was removed by filtration, and the solvent was evaporated in vacuo. The solid residue was recrystallized from benzene and 25.3 g (yield 72%) of **4** was obtained, mp 122–122.5°C; results by ^1H NMR ($(CD_3)_2C{=}O$), δ = 3.50–4.27 (o, 2 H, CH_2), 6.75–7.43 (m, 5 H, C_6H_5), 10.72 (broadened s, 1 H, NH); by IR, 675 s (P=S), 925 vs (P–N), 905 vs, 1030 vs, 1170 s, 1190 s, 1585 m (P–O–Ph), 2900–3500 s, broad (NH). Anal. Calcd. for $C_8H_8NOPS_3$: C, 36.77; H, 3.09; N, 5.36; P, 11.85; S, 36.81%. Found: C, 36.56; H, 2.96; N, 5.38; P, 11.63; S, 37.21%.

2-Methylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**5a**). A solution of 3.97 g (27.97 mmol) of methyl iodide in 20 mL of dry benzene was added dropwise with stirring at 7–10°C to a mixture containing 7.30 g (27.94 mmol) of **4**, 2.83 g (27.96 mmol) of triethylamine, and 150 mL of benzene. After completion of the addition, the stirring of the reaction mixture was continued for 1 h at room temperature. The next day, the mixture was washed with 150 mL of water and dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. The precipitated solid was recrystallized from CCl_4 and yielded 6.12 g (79.6%) of **5a**, mp 99–99.5°C; results by ^1H NMR ($(CD_3)_2C{=}O$), δ = 2.62 (s, 3 H, CH_3), 3.40–4.20 (o, 2 H, CH_2), 7.15–7.28 (m, 5 H, C_6H_5); by ^{31}P NMR (CCl_4), δ = 119.8; by IR, 660 s (P=S), 950 vs (P–N), 910 vs, 1170 m, 1195 vs, 1590 m (P–O–Ph), 1505 s, 1515 s (C=N, doublet). 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, 39.03; H, 3.56; N, 4.79; P, 11.63; S, 35.07%.

2-Benzylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**5b**): *Route 1.* A solution of 0.97 g (7.66 mmol) of benzyl chloride in 20 mL of dry benzene was added dropwise at room temperature with stirring to a mixture of 2.00 g (7.65 mmol) of **4**, 0.78 g (7.71 mmol) of triethylamine, and 50 mL of benzene. After this was completed, the mixture was stirred for 1 h and allowed to stand overnight. Then the reaction mixture was washed with 150 mL of water and dried over anhydrous $MgSO_4$, and the solvent was evaporated in vacuo. The solid obtained was recrystallized from CCl_4 and 2.60 g (yield 96.7%) of **5b** was obtained, mp 106.5–107°C; results by ^1H NMR (C_6D_6), δ = 3.16–3.36 (o, 2 H, PCH_2), 4.19, 4.39 (two d, 2 H, SCH_2, $^2J_{HH}$ 14.5), 7.12–7.46 (m, 10 H, C_6H_5); by ^{31}P NMR (CCl_4), δ = 117.9; by IR, 660 m (P=S), 950 vs (P–N), 1160 m, 1190 s, 1590 m (P–O–Ph), 1505 s (C=N). 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, 50.84; H, 3.85; N, 3.95; P, 8.52; S, 27.29%.

Route 2. To a solution of 18.27 g (69.28 mmol) of **1a** and 8.61 g (69.32 mmol) of α-toluenethiol in 150 mL of dry ether was added dropwise with stirring at 5–10°C 7.71 g (76.17 mmol) of triethylamine. After the weak exothermic reaction, the mixture was stirred for another hour at room temperature. The next day, 150 mL of water was added to the reaction mixture and a water insoluble substance was extracted by CCl_4. The extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. The precipitated solid was recrystallized from CCl_4, and 18.5 g (yield 76%) of **5b** with mp 107°C was isolated.

2-Ethylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**5c**). The procedure described for **5b** (route 2) was used to prepare 8.4 g (yield 82.8%) of **5c** from 9.25 g (35.08 mmol) of **1a**, 2.18 g (35.08 mmol) of ethanethiol, and 3.91 g (38.63 mmol) of triethylamine. The product was purified by recrystallization from a benzene–hexane (1:5) mixture, mp 59–60°C; results by ^1H NMR ($(CD_3)_2C{=}O$), δ = 1.35 (t, 3 H, CH_3, $^3J_{HH}$ 7), 3.25 (q, 2 H, CCH_2), 3.45–4.23 (o, 2 H, PCH_2), 7.05–7.50 (m, 5 H, C_6H_5); by ^{31}P NMR (CCl_4), δ = 119.9; by IR, 645 m (P=S), 950 vs (P–N), 905 vs, 1200 s, 1590 m (P–O–Ph), 1515 vs (C=N). Anal. Calcd. for $C_{10}H_{12}NOPS_3$: C, 41.50; H, 4.19; N, 4.84; P, 10.70; S, 33.24%. Found: C, 41.44; H, 4.07; N, 5.10; P, 10.83; S, 33.68%.

2-Benzylthio-4,5-dihydro-4-oxo-4-phenoxy-1,3,4-thiazaphosphole (**5d**). A solution of 2.64 g (21.25 mmol) of α-toluenethiol and 2.37 g (23.41 mmol) of triethylamine in 50 mL of dry ether was added

dropwise at 20°C with stirring to a solution of 5.27 g (21.28 mmol) of **1b** in 150 mL of ether in an anhydrous argon atmosphere. The mixture was stirred for about 1 h and allowed to stand overnight. Then the precipitate of Et_3NHCl was filtered off and washed with hot benzene. The filtrate was worked up with water as described above. The solid obtained was recrystallized, first from benzene, then from acetone, and 6.65 g (yield 93%) of **5d** was isolated, mp 87–88°C; results by ^1H NMR ($(CD_3)_2C=O$), δ = 3.35–3.62 (q, 2 H, PCH_2), 4.52 (s, 2 H, CCH_2), 7.07–7.40 (m, 10 H, C_6H_5); by IR, 950 s (P–N), 1170 m, 1210 s, 1590 m (P–O–Ph), 1245 s (P=O), 1520 s (C=N). Anal. Calcd. for $C_{15}H_{14}NO_2PS_2$: C, 53.71; H, 4.22; N, 4.18; P, 9.23; S, 19.12%. Found: C, 53.50; H, 4.56; N, 4.17; P, 9.50; S, 18.74%.

2-Benzylthio-5-chloro-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-thiazaphosphole (**5e**). To a solution of 5.75 g (19.29 mmol) of **1c** and 2.40 g (19.32 mmol) of α-toluenethiol in 100 mL of anhydrous ether was added dropwise at room temperature with stirring 2.15 g (21.24 mmol) of triethylamine. After the weak exothermic reaction the mixture was stirred for another hour and allowed to stand for 48 h. Then the precipitate of triethylamine hydrochloride was filtered off, and the solvent was removed in vacuo. The residue was dissolved in 100 mL of benzene, washed with water, and dried over anhydrous $MgSO_4$, yellow oil, left after solvent evaporation in vacuo, was chromatographed with benzene on silica gel (100/160 μ). This gave rise to 5.1 g (yield 68.6%) of **5e** as a very thick, sticky oil; results by ^1H NMR (C_6D_6), δ = 4.00 (s, 2 H, CH_2), 5.23 and 5.25 (two d with the ratio about 4:1, 1 H, PCH, $^2J_{PH}$ 3 and 2.5), 6.55–7.13 (m, 10 H, C_6H_5); by ^{31}P NMR, δ = 108; by IR 675 m (P=S), 945 s (P–N), 1165 m, 1195 m, 1590 w (P–O–Ph), 1525 s (C=N). Anal. Calcd. for $C_{15}H_{13}ClNOPS_3$: C, 46.68; H, 3.40; Cl, 9.19; N, 3.63; P, 8.03; S, 24.92%. Found: C, 46.33; H, 3.15; Cl, 9.02; N, 3.43; P, 7.88; S, 25.40%.

2,4-Dithioxo-4-phenoxy-1,3,4-selenazaphospholidine (**8**). Hydrogen selenide was bubbled through a solution of 5.29g (20.01 mmol) of **1a** and 2.03 g (20.01 mmol) of triethylamine in 50 mL of dry CCl_4 in an anhydrous argon atmosphere at room temperature with stirring until the end of the weak exothermic reaction (about 1 h) and then for 15 min. The next day, the precipitate of Et_3NHCl was filtered off and washed with hot benzene. The combined filtrate was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The solid residue that remained was recrystallized from benzene, and 3.1 g (yield 50%) of **8** was obtained, mp 126–127°C; results by ^1H NMR ((CD3)2C = O), δ = 4.20(o,AB part of ABX system, 2 H, CH_2), 7.15–7.39 (m, 5 H, C_6H_5), 11.46 (s, 1 H, NH); by IR, 675 m (P=S), 920 m (P–N), 905 vs, 1160 m, 1195 s, 1590 w (P–O–Ph), 3030 broad (NH). Anal. Calcd. for $C_8H_8NOPS_2Se$: C, 31.17; H, 2.62; N, 4.55; P, 10.05; S, 20.80%. Found: C, 31.02; H, 2.40; N, 4.29; P, 9.82; S, 20.61%.

2-Methylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-selenazaphosphole (**10a**). Hydrogen selenide was passed through a solution of 6.85 g (25.98 mmol) of **1a** and 2.89 g (28.55 mmol) of triethylamine in 50 mL of dry benzene at 20°C with stirring in an inert atmosphere until the end of the weak exothermic reaction (about 1 h) and then for 15 min. A day after, the precipitate of Et_3NHCl was filtered off, and 3.69 g (26.00 mmol) of MeI was added dropwise at 15–20°C with stirring to the filtrate, mixed with 2.63 g (25.98 mmol) of triethylamine. The mixture was stirred for 1 h and allowed to stand for 48 h. Then the precipitate of Et_3NHI was removed by filtration. The filtrate was washed with water and dried over anhydrous $MgSO_4$, and the solvent was evaporated in vacuo. The remaining solid was recrystallized, first from the benzene–hexane mixture (1 : 10), then from ethyl acetate, and 3.0 g (yield 36%) of **10a** was obtained, mp 92–93°C; results by ^1H NMR (CCl_4), δ = 2.01 (s, 3 H, CH_3), 3.19–3.43 (o, 2 H, CH_2), 6.80–7.08 (m, 5 H, C_6H_5); by ^{31}P NMR (CCl_4), δ = 123.7; by IR, 660 m (P=S), 920 s (P–N), 905 s, 1200 s, 1590 m (P–O–Ph), 1520 m (C=N). 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, 33.02; H, 3.10; N, 4.29; P, 9.62; S, 19.61%.

2-Benzylthio-4,5-dihydro-4-phenoxy-4-thioxo-1,3,4-selenazaphosphole (**10b**). The procedure described for **10a** was used to obtain 4.4 g (yield 42.5%) of **10b** from 6.85 g (25.98 mmol) of **1a**, 5.78 g (57.10 mmol) of triethylamine, and 3.29 g (25.99 mmol) of benzyl chloride. After being washed with water and dried, the product (**10b**) was a very thick oil, which crystallized in about 6 months. The solid **10b** was recrystallized from ethyl acetate, mp 68–70°C; results by ^1H NMR (CCl_4), δ = 3.63–3.92 (o, 2 H, PCH_2), 4.38, 4.49 (two d, AB system, 2 H, SCH_2, $^2J_{HH}$ 13.5), 7.09–7.31 (m, 10 H, C_6H_5); by ^{31}P NMR (CCl_4), δ = 122.9; by IR, 655 m (P=S), 925 s (P–N), 900s, 1165 m, 1195 s, 1590 m (P–O–Ph), 1520 s (C=N). Anal. Calcd. for $C_{15}H_{14}NOPS_2Se$: C, 45.22; H, 3.55; N, 3.52; P, 7.77; S, 16.10%. Found: C, 45.19; H, 3.31; N, 3.72; P, 7.58; S, 16.45%.

3,7-Bis(benzylthio)-1-thioxobicyclo[3.3.0]-4,6-dithia-2,8-diaza-1-phosphaocta-2,7-diene (**13a**). A solution of 5.06 g (49.99 mmol) of triethylamine in 20 mL of dry ether was added dropwise at 0°C with stirring to a mixture containing 5.99 g (22.77 mmol) of **11a**, 5.66 g (45.56 mmol) of α-toluenethiol, and 100 mL of dry ether. After the exothermic reaction, the mixture was stirred for 1 h at room temperature and allowed to stand for 8 days. Then the precipitate of Et_3NHCl (3.5 g, 56%) was filtered off, and

5.06 g (49.99 mmol) of triethylamine was added to the filtrate. After 10 days the solvent was evaporated in vacuo, and the residue was washed with water as described above. The oil obtained was chromatographed on silica gel (100/160 μ), first with benzene, then with acetonitrile. The second fraction after evaporation of the solvent was a dark-red noncrystallizable thick, sticky oil (there was only one signal with δ_P = 82.5 in its ^{31}P NMR spectrum), which could not be identified. The removal of the solvent in vacuo from the benzene fraction and subsequent recrystallization of the solid that remained from CCl_4 yielded 1.9 g (19%) of **13a**, mp 140°C; results by ^1H NMR (C_6D_6), δ = 4.22, 4.40 (two d, AB system, 4 H, CH_2, $^2J_{HH}$ 14.1), 4.93 (d, 1 H, CH, $^2J_{PH}$ 3.8), 7.15–7.30 (m, 10 H, C_6H_5); by IR, 695 s (P=S), 930 s, 950 s (P–N), 1530 s (C=N), 1600 w (Ph). Anal. Calcd. for $C_{17}H_{15}N_2PS_5$: C, 46.55; H, 3.45; N, 6.39; P, 7.06; S, 36.55%. Found: C, 46.66; H, 3.29; N, 6.80; P, 7.55; S, 36.08%.

Triethylammonium S-ethyl N-[O-phenyl-trichloromethyl)thiophosphonyl dithiocarbamate (**15**). To a solution of 13.90 g (41.79 mmol) of **14** and 2.60 g (41.84 mmol) of ethanethiol in 100 mL of dry ether was added at room temperature with stirring 12.69 g (125.37 mmol) of triethylamine. The next day the precipitate of **15** was filtered off and washed with ether. After recrystallization from benzene, 18.5 g (yield 89%) of **15** was obtained, mp 75–76°C; results by ^1H NMR ($(CD_3)_2C$=O), δ = 1.22 (t, 3 H, CH_3–C–S, $^3J_{HH}$ 7), 1.27 (t, 9 H, CH_3–C–N, $^3J_{HH}$ 8), 2.85 (q, 2 H, SCH_2), 3.18 (q, 6 H, NCH_2), 6.43 (broadened s, 1 H, NH), 7.00–7.50 (m, 5 H, C_6H_5); by ^{31}P NMR (CH_3CN), δ = 64.0; by IR, 655 s (P=S), 695 s (CCl_3), 955 s (P–N), 1040 m, 1165 m, 1205 s, 1590 w (P–O–Ph), 2480 m, 2675 m, 2740 m (NH^+). Anal. Calcd. for $C_{16}H_{26}Cl_3N_2OPS_3$: C, 38.75; H, 5.30; Cl, 21.44; N, 5.65; P, 6.24; S, 19.39%. Found: C, 39.25; H, 5.20; Cl, 20.84; N, 5.80; P, 6.70; S, 19.76%.

REFERENCES AND NOTES

[1] D. T. Elmore, J. R. Ogle, *J. Chem. Soc.*, 1959, 2286.

[2] R. W. Addor, *J. Heterocycl. Chem., 7,* 1970, 381.

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

[4] M. G. Zimin, N. G. Zabirov, R. M. Kamalov, A. N. Pudovik, *Zh. Obshch. Khim. 56,* 1986, 2660; *J. Gen. Chem. USSR, 56,* 1986, 2353.

[5] R. M. Kamalov, M. G. Zimin, A. N. Pudovik, *Uspekhi Khimii, 54,* 1985, 2044; *Russ. Chem. Rev., 54,* 1985, 1210.

[6] C. Fest, K. J. Schmidt: *The Chemistry of Organophosphorus Pesticides,* Springer Verlag, Berlin, Heidelberg, New York, 1982.

[7] 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.

[8] R. M. Kamalov, N. A. Hailova, A. A. Gazikasheva, L. F. Chertanova, M. A. Pudovik, A. N. Pudovik, *Doklady AN SSSR, 316,* 1991, 1406.

[9] Results of the mass spectral investigation of heterocycles described in this paper as well as of the X-ray diffraction study of thiazaphospholidine (**4**) will be published in a special communications.

[10] E. Fluck, P. Kuhm, *Phosphorus, Sulfur, and Silicon, 42,* 1989, 123.

[11] A. N. Yarkevich, S. E. Tkachenko, E. N. Tsvetkov, *Zh. Obshch. Khim., 56,* 1986, 1614; *J. Gen. Chem. USSR, 56,* 1986, 1430.

[12] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. II,* 1987, Nr. 12, S1–S19.

[13] B. A. Frenz & Associates, Inc. SDP-1982 (**4**): Structure Determination Package, College Station, Texas 77840, USA, and Enraf-Nonius, Delft, Netherlands, 1982.

[14] G. I. Derkatsch, S. M. Ivanova, *Z. Chem., 9,* 1969, 369.

[15] R. S. Edmundson: *Dictionary of Organophosphorus Compounds,* Chapman and Hall, London, New York, 1988.

[16] M. Corallo, Y. Pietrasanta, *Phosphorus and Sulfur, 4,* 1978, 19.