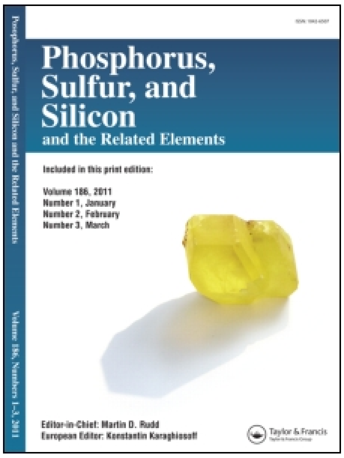

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REACTIONS OF AMINOPHOSPHINES WITH ALKYL THIOCYANATES. 1,2-BIS[(PHOSPHORANYLIDENE)-AMINO]TETRACYANOETHANES AND N^2-ALKYLDICYANOMETHYL-N^1-(HEXAETHYLTRIAMINOPHOSPHORANYLIDENE)-CYANOFORMAMIDINES

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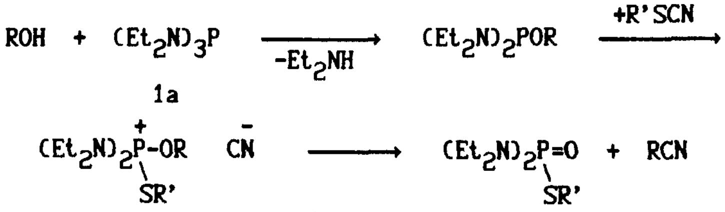
Reactions of hexaethyltriaminophosphine and tetraethyldiaminophenylphosphine with alkyl thiocyanates have been found to proceed in an unusual way and to give rise to the appropriate aminophosphine sulfides, alkyl cyanides, dialkyl sulfides and disulfides along with the formation of 1,2-bis[(phosphoranylidene)amino]tetracyanoethanes and N^2-alkyldicyanomethyl-N^1-(hexaethyltriaminophosphoranylidene)cyanoformamidines. These reactions were assumed to take both a heterolytic and a homolytic course. X-Ray and mass spectral studies of the polycyanides obtained have been carried out.

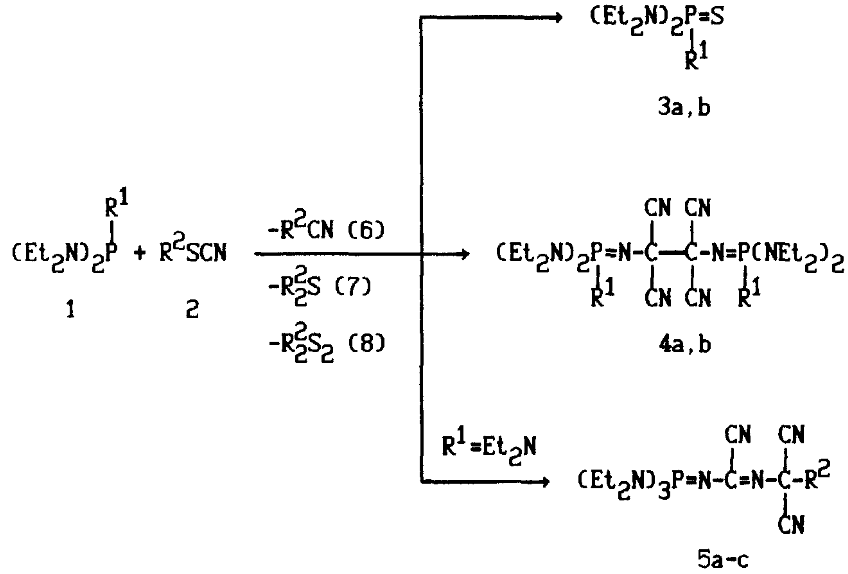
Key words: Aminophosphines; alkyl thiocyanates; 1,2-bis(phosphoranylideneamino)tetracyanoethanes; N^2-alkyldicyanomethyl-N^1-(phosphoranylidene)cyanoformamidines; Arbuzov reaction; homolytic pathways.

INTRODUCTION

The interaction of trialkyl phosphites,[1] dialkyl dialkylamidophosphites, alkyl tetraalkyldiamidophosphites,[2] trimethylsilyldialkyl phosphites and tetraalkyl pyrophosphites[3] with alkyl thiocyanates proceed according to the Arbuzov reaction scheme and are followed by the formation of the appropriate thiolphosphates and cyanides. In all these reactions the cyano group behaves as a pseudohalogen which makes it possible to use the reactions for the effective cyanation of various organic and organoelement compounds. In particular, the successive interaction of aliphatic alcohols, first with hexaethyltriaminophosphine **1a**, and then with alkyl thiocyanates, can be suggested as a synthetic method to convert the initial alcohols into cyanides (Scheme 1).



Scheme 1



$1, 3, 4$: $R^1 = Et_2N$ (a), Ph (b);

$2, 5\text{-}8$: R^2 = Me (a), Et (b), i-Pr (c), $MeOOCCH_2$ (d)

Scheme 2

We have recently briefly reported,[2] that the reactions of hexaethyltriaminophosphine **1a** and tetraethyldiaminophenylphosphine **1b** with alkyl thiocyanates **2a–c** are of a specific character and bring about hexaethyltriamidothiophosphate **3a**, tetraethyldiamidophenylthiophosphonate **3b**, 1,2-bis[(hexaethyltriaminophosphoranylidene)amino]- and 1,2-bis[(tetraethyldiaminophenylphosphoranylidene)amino]tetracyanoethanes **4**, N^2-alkyldicyanomethyl-N^1-(hexaethyltriaminophosphoranylidene)cyanoformamidines **5**, cyanides **6**, dialkyl sulfides **7** and disulfides **8** (Scheme 2). The structures of the reaction products formed indicate that, in this case, the cyano group exhibits properties both of a pseudohalogen and a multiple bond, i.e., it undergoes not only substitution, but also addition reactions. Earlier such behavior of the cyano group in reactions between thiocyanates and λ^3-P acid derivatives has not been considered characteristic. Experimental data obtained indicate that these reactions can take a pure heterolytic course via homolytic stages.

In this report the results of the investigation of the reactions between aminophosphines **1** and thiocyanates **2** are given and the structures of their products have been studied in greater detail.

RESULTS AND DISCUSSION

The predominant products of the interaction between aminophosphines **1a,b** and methyl, ethyl, isopropyl, methoxycarbonylmethyl thiocyanates **2a–d** are triamidothiophosphate **3a** (yield 65–70%) and diamidophenylthiophosphonate **3b** (yield

58–60%). These compounds have been isolated and identified by comparing their physical constants, IR, ^1H and ^{31}P NMR spectra with the data of species obtained by known methods.

The detection of cyanides **6**, dialkyl sulfides **7** and disulfides **8**, formed in the reactions, and the estimation of their yields have been carried out by gas-liquid chromatography. Thus, at the ratio **1a**:**2b** = 1:1, 1 mol of **2b** has been found to yield 0.067 mol of **6b** and 0.093 mol of **7b**; at the ratio **1a**:**2b** = 1:2 it gives rise to 0.11 mol of **6b**, 0.05 mol of **7b** and 0.19 mol of **8b**.

The structures of products **4a,b** and **5b,c** have been proved by X-Ray analysis, IR, Raman, mass, ^1H and ^{31}P NMR spectra. When equimolar amounts of precursors are used, full expenditure of the aminophosphines **1a,b** cannot be reached in all reactions investigated. Therefore, mostly a twofold excess of thiocyanates **2** has been employed in the reactions with **1**. In this case the maximal yield of **4b** has been observed. The yields of amidines **5** are also about four times higher than those at the 1:1 ratio. On the contrary, the yield of tetracyanoethane **4a** decreases, when the precursors ratio changes from 1:1 to 1:2.

The reactivity of the thiocyanates **2** towards the aminophosphines **1** decreases in the following sequence: **2a** > **2b** ≅ **2d** > **2c**. The full disappearance of initial aminophosphine **1a** in its reaction with isopropyl thiocyanate **2c** can be attained only by heating the reaction mixture. Reactions of aminophosphines **1a,b** with thiocyanates **2a,d** easily proceed at room temperature with a small exothermic effect. The interaction between aminophosphine **1a** and methyl thiocyanate **2a** is followed by a strong exothermic effect and polymerization. Owing to the latter and to the low yield, the amidine **5a** was not isolated as such but was identified in the reaction mixture by means of ^{31}P NMR spectroscopy (δ_P 26.0 ppm).

By monitoring the course of the reaction between triaminophosphine **1a** and ethyl thiocyanate **2b** by ^{31}P NMR spectroscopy in the probe for 1–3 min after mixing the initial compounds (in a 1:1 ratio without solvent or in the presence of 20% benzene) ^{31}P chemically induced dynamic nuclear polarization (^{31}P CIDNP) has been observed. In these spectra the following polarized signals have been detected (δ_P, ppm): 18(A), 30(E), 37(E), 63(E), 78(E), 118(E) (magnetic field strength is 0.6T).[4] In 5 min there appear signals in the spectra, predominating in intensity, with δ_P 63 and 78 ppm and a few weak signals in the δ_P 18–32 ppm range, as well. During the following few days the signal with δ_P 63 ppm gradually disappears and the intensity of the signal with δ_P 78 ppm increases. Besides, during a few hours after mixing compounds **1a** and **2b** some nitrogen-containing radical particles were detected by ESR spectra in the reaction mixture. These data make it possible to suggest the formation of the reaction products to proceed by pathways, including homolytic stages.

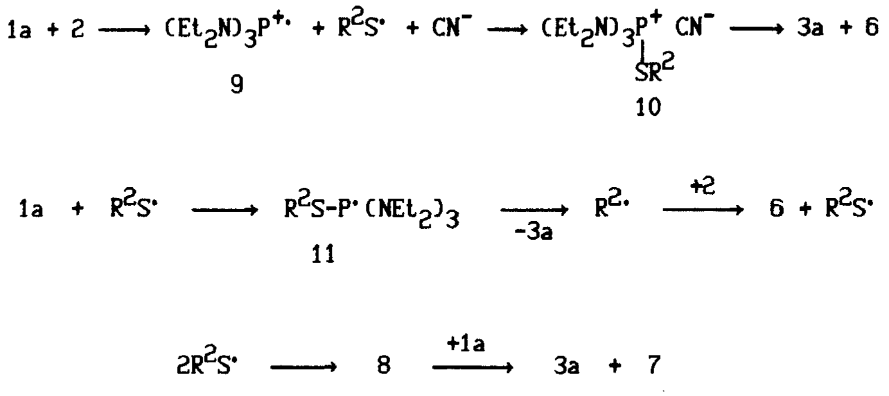
It can be assumed that the initiation of the homolytic reaction courses results from a single electron transfer (SET) from a lone electron pair of the aminophosphine **1a** to the vacant MO of the thiocyanates **2**. Aminophosphines of type **1** can exhibit electron donating properties in SET-reactions,[5] the low values of their first ionization energy (7.19 eV for **1a**[6]) promote such processes. In particular, aminophosphines can be donors in SET-reactions with bis(p-nitrophenyl) and bis(2,6-dimethylphenyl)methyl bromides, 2,7-dinitro-g-bromofluorene,[7] and quinones.[5,8] As a result of the SET-reaction between aminophosphine **1a** and thiocyanates **2** the triamidophosphite cation **9**, cyanide anion and alkylthio radicals can appear which subsequently form quasi-phosphonium salts **10**. The latter further disintegrate heterolytically into triamidothiophosphate **3a** and cyanides **6**, according to the course of the second stage of the Arbuzov reaction (Scheme 3).

Interaction of alkylthio radicals with the initial aminophosphine **1a** can produce alkylthio phosphoranyl radicals **11** which then disintegrate into thiophosphate **3a** and alkyl radicals. Similar processes have been noted to proceed in the reactions of λ^3-P acid derivatives with thiols and disulfides.[5] When exposed to alkyl radicals the initial thiocyanates **2** can give off cyanides **6** and regenerate alkylthio radicals. The recombination of the latter results in dialkyl disulfides **8** which can be desulfurized by aminophosphines **1a** into dialkyl sulfides **7**.

As an alternative route, leading to the formation of cation radicals **9**, alkylthio phosphoranyl radicals **11** and cyanide anion, quasi-phosphonium salts **10** may be assumed to function as acceptors in a SET-reaction with the aminophosphine **1a**. This salt is apparently formed mostly heterolytically (Scheme 4).

The cation radicals **9** may be assumed to produce the isocyanophosphoranyl radical **12** when exposed to cyanide anion. The radical **12** reacts further with **2** via the carbene **14** formation, giving rise either to phosphoranylideneamino(dicyano)methyl radical **15**, or to carbene **16**. Recombination of the former yields tetracyanoethane **4a**. As is shown by ESR spectra,[9] this process is reversible. The formation of tetracyanoethane **4b** in the appropriate reactions of the aminophosphine **1b** can proceed in a similar way.

The formation of the products **5** is probably due to the following stepwise interaction of intermediate **16** with thiocyanates **2** according to Scheme 5.

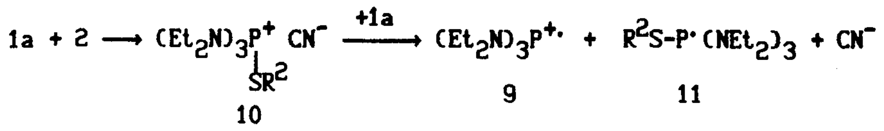


$$1a + 2 \longrightarrow \underset{9}{(Et_2N)_3P^{+\cdot}} + R^2S^\cdot + CN^- \longrightarrow \underset{10}{(Et_2N)_3\underset{SR^2}{P^+}\ CN^-} \longrightarrow 3a + 6$$

$$1a + R^2S^\cdot \longrightarrow \underset{11}{R^2S\text{-}P^\cdot(NEt_2)_3} \xrightarrow[-3a]{} R^{2\cdot} \xrightarrow{+2} 6 + R^2S^\cdot$$

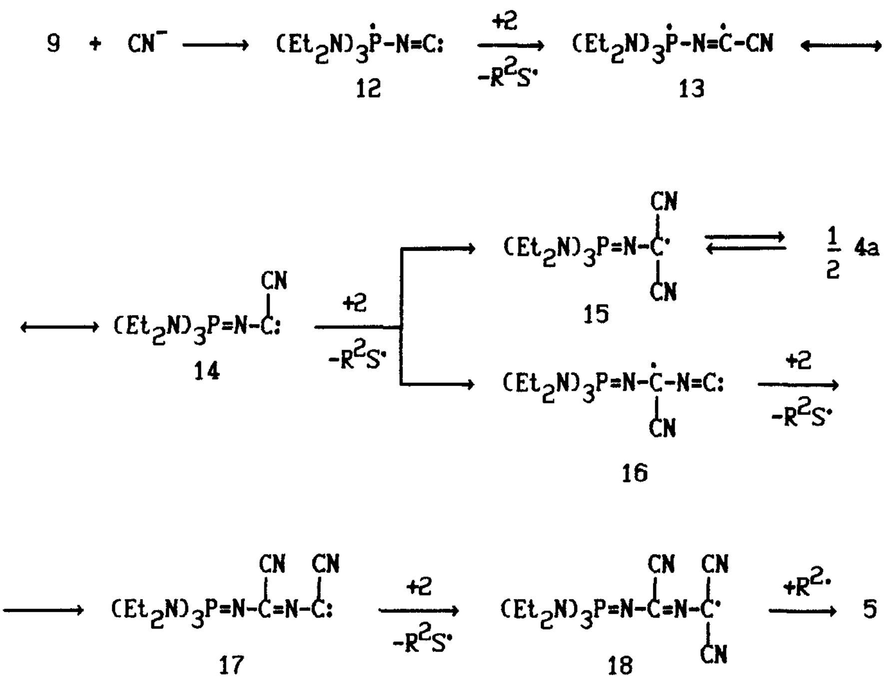
$$2R^2S^\cdot \longrightarrow 8 \xrightarrow{+1a} 3a + 7$$

Scheme 3



$$1a + 2 \longrightarrow \underset{10}{(Et_2N)_3\underset{SR^2}{P^+}\ CN^-} \xrightarrow{+1a} \underset{9}{(Et_2N)_3P^{+\cdot}} + \underset{11}{R^2S\text{-}P^\cdot(NEt_2)_3} + CN^-$$

Scheme 4



Scheme 5

X-RAY AND MASS-SPECTRAL STUDIES OF PRODUCTS **4a,b** AND **5b,c**

The molecular structure of 1,2-bis[(hexaethyltriaminophosphoranylidene)amino]-tetracyanoethane **4a** has been determined by means of X-ray analysis. A schematic drawing of the molecule **4a** is shown in Figure 1. The bond distances, bond angles and torsion angles are given in Tables I, II and III, respectively.

The molecule **4a** has been found to occupy a special position in a symmetry center, which is in the middle of the C(13)—C(13)′ single bond. The P=N(4) bond [1.557(3)Å] is significantly shorter than the single P—N bonds in **4a** [in the 1.630(3)–1.660(3)Å range], and is in agreement with the average value of the bond length for P=N bonds in phosphazenes [1.504(2)–1.64(1)Å].[10] The P—N(4)—(13) angle equals 129.9(2)°. The N(4)—C(13) bond distance [1.413(4)Å] is somewhat shorter than the usual C(sp^3)—N(sp^2) bonds (1.465Å).[11] The conformation around the N(4)—C(13) bond is antiperiplanar, the P—N(4)—C(13)—C(13)′ torsion angle equals 168.7°. The same conformation around the C(13)—C(13)′ bond is observed [the N(4)—C(13)—C(13)′—N(4)′ torsion angle is 180.0°]. Deviations of the atoms P and P′ from the N(4)—C(13)—C(13)′—N(4)′ least square plane are equal to ±0.125Å (the P—N(4)—C(13)—C(13)′—N(4)′—P′ fragment is planar in the 0.04Å range). The characteristic feature of structure **4a** is the significant lengthening of the C(13)—C(13)′ bond [1.609(6)Å], being essentially longer than the appropriate bond in 1,1,2,2-tetracyanoethane [1.561(3)Å].[12] Such lengthening of the C(13)—C(13)′ bond is probably the consequence, on the one hand, of steric interaction between

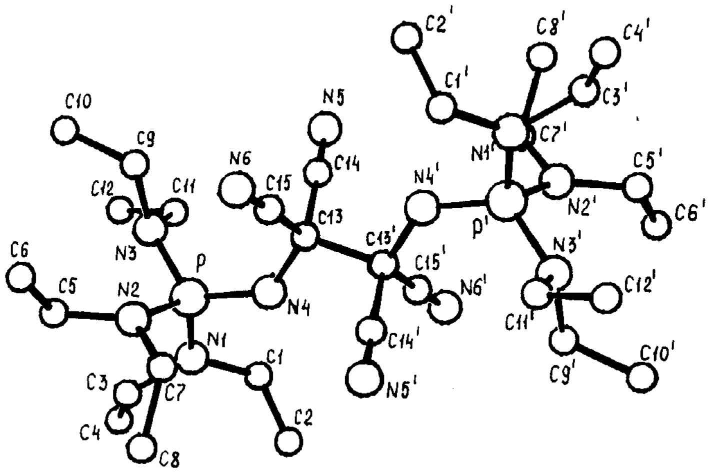


FIGURE 1 Perspective drawing of the molecule **4a**.

TABLE I

Bond distances (Å) for **4a** and **5b**, with estimated standard deviations (e.s.d.'s) in parentheses

Bond	**4a**	**5b**	Bond	**4a**	**5b**
P-N(1)	1.647(3)	1.621(4)	N(8)-C(17)	-	1.116(6)
P-N(2)	1.630(3)	1.629(3)	C(1)-C(2)	1.458(7)	1.501(7)
P-N(3)	1.660(3)	1.624(3)	C(3)-C(4)	1.291(7)	1.256(12)
P-N(4)	1.557(3)	1.617(4)	C(5)-C(6)	1.503(7)	1.489(8)
N(1)-C(1)	1.496(5)	1.504(6)	C(7)-C(8)	1.479(7)	1.504(6)
N(1)-C(3)	1.439(6)	1.428(8)	C(9)-C(10)	1.497(6)	1.474(7)
N(2)-C(5)	1.465(5)	1.477(6)	C(11)-C(12)	1.434(7)	1.434(9)
N(2)-C(7)	1.528(5)	1.458(5)	C(13)-C(13)'	1.609(6)	-
N(3)-C(9)	1.474(5)	1.489(5)	C(13)-C(14)	1.493(6)	-
N(3)-C(11)	1.482(6)	1.506(6)	C(13)-C(15)	1.490(6)	1.503(6)
N(4)-C(13)	1.413(4)	1.306(5)	C(14)-C(16)	-	1.485(7)
N(5)-C(13)	-	1.317(5)	C(14)-C(17)	-	1.507(7)
N(5)-C(14)	1.126(5)	1.465(5)	C(14)-C(18)	-	1.533(6)
N(6)-C(15)	1.135(5)	1.138(5)	C(18)-C(19)	-	1.510(7)
N(7)-C(16)	-	1.117(5)			

TABLE II

Bond angles (deg.) for **4a** and **5b**, with e.s.d.'s in parentheses

Angle	**4a**	5b
N(1)-P-N(2)	111.9(2)	109.7(2)
N(1)-P-N(3)	106.0(2)	107.5(2)
N(1)-P-N(4)	104.0(2)	105.7(2)
N(2)-P-N(3)	103.1(2)	110.7(2)
N(2)-P-N(4)	112.2(2)	110.3(2)
N(3)-P-N(4)	119.6(2)	112.7(2)
P-N(1)-C(1)	122.0(3)	117.2(3)
P-N(1)-C(3)	120.3(3)	124.4(4)
C(1)-N(1)-C(3)	117.8(3)	115.6(4)
P-N(2)-C(5)	125.9(3)	120.5(3)
P-N(2)-C(7)	118.0(3)	126.0(3)
C(5)-N(2)-C(7)	113.9(3)	113.5(3)
P-N(3)-C(9)	119.6(2)	125.8(3)
P-N(3)-C(11)	117.4(3)	118.8(3)
C(9)-N(3)-C(11)	112.4(3)	115.4(4)
P-N(4)-C(13)	129.9(2)	127.9(3)
C(13)-N(5)-C(14)	-	112.8(3)
N(1)-C(1)-C(2)	110.5(5)	112.0(4)
N(1)-C(3)-C(4)	128.0(6)	130.1(9)
N(2)-C(5)-C(6)	113.8(4)	113.4(4)
N(2)-C(7)-C(8)	113.2(4)	115.2(4)
N(3)-C(9)-C(10)	114.2(3)	114.7(4)
N(3)-C(11)-C(12)	114.4(5)	115.2(5)
N(4)-C(13)-N(5)	-	128.8(4)
N(4)-C(13)-C(13)'	108.9(3)	-
N(4)-C(13)-C(14)	113.4(3)	-
N(4)-C(13)-C(15)	116.1(3)	121.1(4)
C(13)'-C(13)-C(14)	105.2(3)	-
C(13)'-C(13)-C(15)	105.3(3)	-
C(14)-C(13)-C(15)	107.0(3)	-
N(5)-C(13)-C(15)	-	109.9(4)
N(5)-C(14)-C(13)	175.0(4)	-
N(5)-C(14)-C(16)	-	112.5(4)
N(5)-C(14)-C(17)	-	111.8(4)
N(5)-C(14)-C(18)	-	106.8(3)
C(16)-C(14)-C(17)	-	108.1(4)
C(16)-C(14)-C(18)	-	110.1(3)
C(17)-C(14)-C(18)	-	107.4(4)
N(6)-C(15)-C(13)	175.5(4)	177.8(7)
N(7)-C(16)-C(14)	-	172.6(5)
N(8)-C(17)-C(14)	-	175.0(5)
C(14)-C(18)-C(19)	-	113.8(4)

TABLE III

Torsion angles (deg.) for **4a** and **5b**, with e.s.d.'s in parentheses

Angle	**4a**	5b
N(2)-P-N(1)-C(1)	-141.2	-69.4
N(2)-P-N(1)-C(3)	38.7	90.9
N(3)-P-N(1)-C(1)	107.2	170.1
N(3)-P-N(1)-C(3)	-72.9	-29.6
N(4)-P-N(1)-C(1)	-19.8	49.5
N(4)-P-N(1)-C(3)	160.1	-150.2
N(1)-P-N(2)-C(5)	-78.5	-44.8
N(1)-P-N(2)-C(7)	84.0	133.7
N(3)-P-N(2)-C(5)	35.0	73.7
N(3)-P-N(2)-C(7)	-162.5	-107.8
N(4)-P-N(2)-C(5)	165.0	-160.8
N(4)-P-N(2)-C(7)	-32.5	17.7
N(1)-P-N(3)-C(9)	174.7	120.9
N(1)-P-N(3)-C(11)	-43.3	-58.7
N(2)-P-N(3)-C(9)	57.0	1.1
N(2)-P-N(3)-C(11)	-161.1	-178.5

TABLE III (*continued*)

Angle	4a	5b
N(4)-P-N(3)-C(9)	-68.3	-123.1
N(4)-P-N(3)-C(11)	73.6	57.3
N(1)-P-N(4)-C(13)	162.1	160.5
N(2)-P-N(4)-C(13)	-76.7	-81.0
N(3)-P-N(4)-C(13)	44.1	43.3
P-N(1)-C(1)-C(2)	100.4	-110.8
C(3)-N(1)-C(1)-C(2)	-79.5	87.2
P-N(1)-C(3)-C(4)	153.8	134.1
C(1)-N(1)-C(3)-C(4)	-26.3	-35.3
P-N(2)-C(5)-C(6)	-135.7	111.1
C(7)-N(2)-C(5)-C(6)	61.2	-67.6
P-N(2)-C(7)-C(8)	-98.3	115.1
C(5)-N(2)-C(7)-C(8)	66.2	-66.2
P-N(3)-C(9)-C(10)	-142.5	-115.6
C(11)-N(3)-C(9)-C(10)	73.8	64.0
P-N(3)-C(11)-C(12)	123.8	-116.2
C(9)-N(3)-C11)-C(12)	-91.7	64.1
P-N(4)-C(13)-N(5)	-	-176.1
P-N(4)-C(13)-C(14)	-74.5	-
P-N(4)-C(13)-C(15)	50.1	9.6
P-N(4)-C(13)-C(13)'	168.7	-
C(14)-N(5)-C(13)-N(4)	-	6.1
C(14)-N(5)-C(13)-C(15)	-	-179.1
C(13)-N(5)-C(14)-C(16)	-	-58.7
C(13)-N(5)-C(14)-C(17)	-	63.2
C(13)-N(5)-C(14)-C(18)	-	-179.6
N(4)-C(13)-C(14)-N(5)	1.6	-
C(15)-C(13)-C(14)-N(5)	-127.7	-
C(13)'-C(13)-C(14)-N(5)	120.6	-
N(4)-C(13)-C(15)-N(6)	-16.1	-89.0
N(5)-C(13)-C(15)-N(6)	-	95.7
C(14)-C(13)-C(15)-N(6)	111.7	-
C(13)'-C(13)-C(15)-N(6)	-136.7	-
N(4)-C(13)-C(13)'-N(4)'	-180.0	-
N(5)-C(14)-C(16)-N(7)	-	-117.1
C(17)-C(14)-C(16)-N(7)	-	119.0
C(18)-C(14)-C(16)-N(7)	-	1.9
N(5)-C(14)-C(17)-N(8)	-	71.3
C(16)-C(14)-C(17)-N(8)	-	-164.3
C(18)-C(14)-C(17)-N(8)	-	-45.5
N(5)-C(14)-C(18)-C(19)	-	62.0
C(16)-C(14)-C(18)-C(19)	-	-60.4
C(17)-C(14)-C(18)-C(19)	-	-177.9

two phosphoranylidene groups and four cyano groups and, on the other hand, it results from the strong electron withdrawing influence of the latter. This gives rise to the facile cleavage of the =NC—CN= bond in **4a** and **4b**[9] which is reflected in the electron impact (EI) mass spectra of the compounds **4a,b**.

There are no peaks in the mass spectra of **4a,b**, corresponding to molecular ions ($M^{+\cdot}$). This is due to the disintegration of **4a,b** into two equal halves with the conservation of the charge on one of them. This process is evidenced by the appearance in the mass spectra of peaks at m/z 325 for **4a** ($[M_1/2]^+$) and at 330 for **4b** ($[M_2/2]^+$) (see Experimental section).

A peak at m/z 608 has been observed in the mass spectra of **4b** which corresponds to the $[M-(CN)_2]^+$ ion. The generation of the latter is probably favored by the formation of a system of conjugated π-bonds when two cyano groups are abstracted from the $M^{+\cdot}$ ion.

The appearance of characteristic ions by dissociation ionization of **4a,b** results from the following fragmentation of the $[M_1/2]^+$ and $[M_2/2]^+$ ions. The loss of the

H_3C_2' and H_4C_2 particles gives rise to the $[M_1/2—C_2H_3]^+$ ion with m/z 298 for **4a** and to the $[M_2/2—C_2H_4]^+$ ion with m/z 302 for **4b**.

The cleavage of the P—N bond with the migration of the hydrogen atom to the charged fragment results in the appearance of the $[M/2—N(C_2H_4)C_2H_5]^+$ ions with m/z 254 for **4a** and 259 for **4b**. These ions undergo further changes, with the cleavage of another P—N bond, involving the formation of ions with m/z 183 (**4a**) and 188 (**4b**).

The intense peak at m/z 175 present in the mass spectrum of **4a**, corresponding to the $[(Et_2N)_2P]^+$ ion, can be accounted for by the decomposition of the ion with m/z 254 at the P=N bond with the migration of the hydrogen atom onto the neutral fragment. The cleavage of the P—N bond in $[(Et_2N)_2P]^+$ ion produces the $[Et_2NPH]^+$ ion with m/z 104. A similar sequence of disintegration of the ion with m/z 259 for **4b** results in the appearance of the $[Et_2NPPh]^+$ and $[PhPH]^+$ ions with m/z 180 and 109, respectively. The intense peak at m/z 72, present in mass spectra of **4a,b**, corresponds to the $[Et_2N]^+$ ion.

The X-ray analysis of the amidine **5b** has been carried out. Figure 2 shows a schematic drawing of the molecule **5b**. The bond distances, bond angles and torsion angles are given in Tables I–III, respectively.

The molecule of **5b** was found to have Z-configuration around the "double" C(13)=N(5) bond, the C(14)—N(5)—C(13)—N(4) torsion angle is 6.1°. The P=N(4) bond distance, 1.617(4)Å, is close to the single P—N bond lengths (1.621–1.629Å) in **5b**. Significant shortening of the N(4)—C(13) bond [1.306(5)Å] has been observed. It is even shorter than the N(5)=C(13) "double" bond [1.317(5)Å]. Such redistribution of bond distances in the molecule **5b** may result from a strong conjugation along the P=N(4)—C(13)=N(5) chain, favored by the flat conformation of this fragment [the P—N(4)—C(13)=N(5) torsion angle is −176.1°]. Perhaps, the resonance form B significantly contributes to the structure of the molecule **5b**.

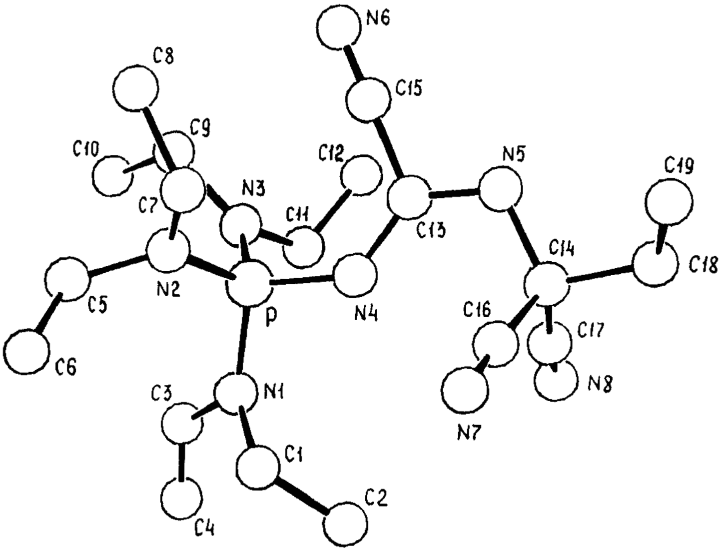
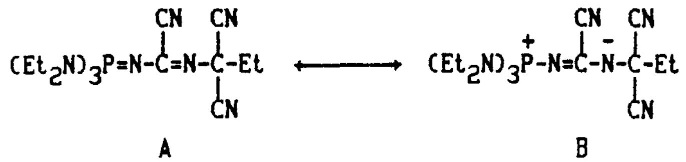


FIGURE 2 Perspective drawing of the molecule **5b**.



$(Et_2N)_3P{=}N{-}C(CN){=}N{-}C(CN)_2{-}Et \longleftrightarrow (Et_2N)_3\overset{+}{P}{-}N{=}C(CN){-}\overset{-}{N}{-}C(CN)_2{-}Et$

A **B**

In the EI mass spectrum of **5c** the peak at m/z 420 corresponds to the molecular ion ($M^{+\cdot}$). The electron-impact dissociation ionization of **5c** is connected with successive elimination of various hydrocarbon particles both from the $(C_2H_5)_2N$ and i—C_3H_7 groups. The formation of the $[M—CH_3]^+$ ion with m/z 405 is probably due to the cleavage of the C—C bond in the i—C_3H_7 group.

The elimination of the C_2H_5 group and of the C_2H_4 molecule from the M^+ ion leads to the appearance of the $[M—C_2H_5]^+$ ion with m/z 391 and $[M—C_2H_4]^+$ ion with m/z 392. The loss of the C_3H_6 molecule by the i—C_3H_7 group, present in **5c**, and the elimination of this group itself produces the $[M—C_3H_6]^+$ and $[M—C_3H_7]^+$ ions with m/z 378 and 377, respectively. In turn, these ions, having readily split off the C_2H_5 group, decompose into the $[M—C_3H_6—C_2H_5]^+$ ion with m/z 349 and the $[M—C_3H_7—C_2H_5]^+$ ion with m/z 348.

The formation of the ion with m/z 350 by dissociation ionization probably results from the loss of the C_2H_4 molecule by the ion with m/z 378. Ions with m/z 349 and 350 undergo a fragmentation with the loss of the CH_3 group, giving rise to the $[M—C_3H_6—C_2H_5—CH_3]^+$ ion with m/z 334 and the $[M—C_3H_6—C_2H_4—CH_3]^+$ ion with m/z 335.

Another course of fragmentation for the ion with m/z 349 is the elimination of the $(C_2H_5)_2N$ group, forming the $[M—C_3H_6—C_2H_5—N(C_2H_5)_2]^+$ ion with m/z 277.

It should be noted that the abstraction of the CN group, yielding the $[M—CN]^+$ ion with m/z 394, is characteristic of **5c**. The subsequent elimination of the C_2H_4 molecule from this ion accounts for the appearance of another characteristic ion, $[M—CN—C_2H_4]^+$ with m/z 366.

The cleavage of the C—N bond in the $M^{+\cdot}$ ion results in the formation of an ion with m/z 313 of maximum peak intensity. In the range of lower values of m/z the intense peaks due to the ions $[\{(C_2H_5)_2N\}_2P]^+$ with m/z 175, $[(C_2H_5)_2NPH]^+$ with m/z 104, $[(C_2H_5)_2N]^+$ with m/z 72, $[C_4H_{10}]^+$ with m/z 58 and $[C_3H_7]^+$ with m/z 43 were found.

SUMMARY

The structures of the phosphorus containing polycyanides **4** and **5** can be considered as providing indirect evidence of homolytic pathways of their formation in reactions between aminophosphines **1** and thiocyanates **2**. On the one hand, one can hardly imagine such structures could be formed in these reactions exclusively by a heterolytical pathway. On the other hand, compounds **4** possess structural features due to which they themselves can serve as a source of radicals. In combination with the ^{31}P CIDNP and ESR evidence this makes it possible to conclude that in the reactions discussed some radical processes are involved, yielding products **4** and **5**.

EXPERIMENTAL

Spectral studies. Infrared spectra were recorded on a UR-20 spectrophotometer, using films of liquid products and nujol mulls of solid compounds. Raman spectra were determined on a CODERG PHO-82 spectrometer, equipped with a LG-38 He-Ne laser (λ = 6328Å). ^{1}H NMR spectra were obtained on a Varian T-60 (at 60 MHz) and a Bruker WM-250 (at 250.13 MHz) spectrometer (TMS as an internal standard). ^{31}P NMR spectra were recorded at 10.2 MHz on a KGU-4 nonserial spectrometer and at 101.26 MHz on a Bruker WM-250 instrument with 85% H_3PO_4 as an external standard. Mass spectra were obtained at 50 eV and 0.1 mA on an MX-1310 instrument operating on a SM-4 computer. The direct inlet was made into the ion source at 40°C (**5b**) and 150°C (**4a,b**). Precise values of m/z were determined automatically using reference peaks of perfluorokerosene; errors did not exceed 5 × 10^{-6} amu.

X-ray structure determination of **4a** *and* **5b**. Crystal data for **4a**: monoclinic, a = 0.049(6), b = 16.404(3), c = 13.117(4)Å, β = 101.57(4)°, V = 1907.3Å^3, d_{calc} = 1.13 g/cm^3, Z = 2, space group P2$_1$/c, μ = 1.46 cm^{-1}, F(000) = 708.

Crystal data for **5b**: orthorhombic, a = g.215(2), b = 15.229(8), c = 17.432(4)Å, V = 2446.3Å^3, d_{calc} = 1.10 g/cm^3, Z = 4, space group P2$_1$2$_1$2$_1$, μ = 1.27 cm^{-1}, F(000) = 880.

Crystallographic measurements were carried out at room temperature using an Enraf-Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ (**4a**) and $\omega/(5/3)\theta$ (**5b**) scan modes. The intensity data were collected within the $2 \leq \theta \leq 25°$ range using graphite monochromated Mo—K$_\alpha$ radiation (λ = 0.71073Å). Intensities of 3473 (**4a**) and 2418 (**5b**) unique reflections were measured, 1454, (**4a**) and 1207 (**5b**) reflections with $I \geq 3\sigma(I)$ of them were used in the structure solution by direct methods employing MULTAN. Corrections were applied for Lp, but not for absorption or extinction. Positional and thermal parameters were refined by full-matrix least squares minimizing the function $\Sigma w(F_0 - F_c)^2$ with $w = 1/\sigma^2(F)$ for the observed reflections and w = 0 for unobserved reflections. All the hydrogen atoms

TABLE IV

Atomic coordinates for **4a**, with e.s.d.'s in parentheses

Atom	x	y	z	B_{iso}(Å^2)[a]
P	0.7574(2)	0.0580(1)	0.7031(1)	3.34(3)
N(1)	0.9063(5)	0.1077(3)	0.6817(4)	4.4(1)
N(2)	0.6668(5)	0.1092(3)	0.7776(4)	4.1(1)
N(3)	0.8235(5)	-0.0217(3)	0.7762(4)	3.9(1)
N(4)	0.6602(5)	0.0439(3)	0.5923(4)	3.7(1)
N(5)	0.6427(8)	-0.1603(4)	0.5497(5)	6.7(2)
N(6)	0.3323(6)	-0.0114(4)	0.6711(5)	6.4(2)
C(1)	0.9509(8)	0.1069(5)	0.5779(6)	5.9(2)
C(2)	0.902(1)	0.1816(6)	0.5208(9)	10.4(3)
C(3)	0.998(1)	0.1540(7)	0.7639(7)	9.8(3)
C(4)	1.139(1)	0.1723(8)	0.7747(8)	11.4(3)
C(5)	0.7103(8)	0.1167(5)	0.8910(5)	5.3(2)
C(6)	0.581(1)	0.1068(6)	0.9462(6)	8.6(3)
C(7)	0.5526(8)	0.1732(5)	0.7268(5)	5.5(2)
C(8)	0.614(1)	0.2571(5)	0.7358(8)	8.9(3)
C(9)	0.7180(8)	-0.0752(4)	0.8170(5)	5.0(2)
C(10)	0.7772(9)	-0.1061(6)	0.9249(6)	6.8(2)
C(11)	0.9504(8)	-0.0675(5)	0.7475(6)	6.7(2)
C(12)	1.081(1)	-0.0741(7)	0.8293(8)	8.5(3)
C(13)	0.5412(6)	-0.0117(7)	0.5584(4)	3.4(1)
C(14)	0.5932(7)	-0.0975(4)	0.5519(5)	4.1(1)
C(15)	0.4191(6)	-0.0130(3)	0.6195(5)	4.1(1)

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

TABLE V

Atomic coordinates of **5b**, with e.s.d.'s in parentheses

Atom	x	y	z	$B_{iso}(\mathring{A}^2)^a$
P	0.5254(2)	0.1618(1)	0.3078(1)	3.66(3)
N(1)	0.6577(6)	0.1207(4)	0.2589(3)	4.3(1)
N(2)	0.5782(6)	0.2516(4)	0.3502(3)	4.1(1)
N(3)	0.4760(7)	0.0888(4)	0.3705(3)	4.9(1)
N(4)	0.3996(6)	0.1832(4)	0.2459(3)	4.0(1)
N(5)	0.1563(6)	0.2081(4)	0.2088(3)	4.6(1)
N(6)	0.1592(8)	0.2073(6)	0.3998(4)	8.2(2)
N(7)	0.4024(8)	0.3122(5)	0.0896(4)	7.1(2)
N(8)	0.2856(9)	0.0379(5)	0.0993(5)	7.9(2)
C(1)	0.7065(8)	0.1702(5)	0.1888(5)	5.4(2)
C(2)	0.6704(9)	0.1221(6)	0.1161(5)	6.6(2)
C(3)	0.760(1)	0.0582(8)	0.2881(7)	10.0(3)
C(4)	0.848(2)	0.009(1)	0.253(1)	19.4(7)
C(5)	0.7193(9)	0.2551(6)	0.3903(4)	5.9(2)
C(6)	0.828(1)	0.3124(6)	0.3515(6)	7.8(3)
C(7)	0.4992(8)	0.3345(5)	0.3520(4)	4.7(2)
C(8)	0.448(1)	0.3632(5)	0.4301(5)	6.7(2)
C(9)	0.4752(9)	0.1008(5)	0.4553(4)	5.4(2)
C(10)	0.577(1)	0.0434(6)	0.4973(5)	7.2(2)
C(11)	0.427(1)	0.0001(6)	0.3426(5)	6.4(2)
C(12)	0.278(1)	-0.0212(9)	0.3589(7)	11.0(3)
C(13)	0.2614(8)	0.1952(5)	0.2587(3)	4.0(2)
C(14)	0.2048(7)	0.1993(4)	0.1291(4)	3.5(2)
C(15)	0.2036(9)	0.2037(6)	0.3389(4)	5.8(2)
C(16)	0.3233(9)	0.2615(5)	0.1097(4)	4.5(2)
C(17)	0.2570(8)	0.1076(5)	0.1118(4)	4.9(2)
C(18)	0.0721(8)	0.2167(5)	0.0783(4)	5.1(2)
C(19)	0.010(1)	0.3079(6)	0.0870(5)	7.5(2)

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

were revealed in difference Fourier maps, but their positional and isotropic thermal parameters were not refined ($B_{iso} = 5$ Å^2). Convergence was obtained at $R = 0.071$, $R_w = 0.086$ (**4a**) and $R = 0.056$, $R_w = 0.065$ (**5b**). The absolute configuration of **5b** has been not determined.

All calculations were performed on a PDP 11/23 computer, using the SDP package. The atomic positional parameters for **4a** and **5b** are given in Tables IV and V, respectively.

Synthetic procedures. Reaction of hexaethyltriaminophosphine **1a** *with ethyl thiocyanate* **2b**. A solution of 37.34 g (428.46 mmol) of **2b** in 20 ml of anhydrous benzene was added dropwise while stirring to 53.00 g (214.21 mmol) of **1a** in 70 ml of benzene at room temperature. A weak exothermic reaction started after a short induction period and the reaction mixture became deep brown in color and separated into two layers. After 5 days the solvent was removed under reduced pressure, and a thick viscous liquid remained. After standing for 2 days there appeared crystals of **4a**, which were separated by filtration. The filtrate was then distilled in vacuo. Two main fractions were obtained: 70–75 and 75–100°C (0.04 torr). After 2 days an additional amount crystals of **4a** appeared in the first fraction. Both portions of crystals were combined and recrystallized first from benzene and then from ethyl acetate, 2.8 g (4.30 mmol) of **4a** was obtained, mp 179°C. IR: (cm^{-1}): 960 (ν_{N-C-C}), 1030 (ν_{P-N-C}), 1285 ($\nu_{P=N}$), 2240 ($\nu_{C\equiv N}$, weak); Raman (cm^{-1}): 2220 ($\nu_{C\equiv N}$, very strong). ^{1}H NMR (CCl_4, δ, ppm): 1.08 (36H, *t*, CH_3, $^3J_{HH}$ 7 Hz), 2.98 (24H, d.q., CH_2, $^3J_{PH}$ 10 Hz). ^{31}P NMR (C_6D_6, δ, ppm): 22.2. Mass spectrum, m/z (relative intensity, %): 327(1.8), 326(20), 325(100) $[C_{15}H_{30}N_6P]^+$, 298(0.80), 255(9.1), 254(74) $[C_{11}H_{21}N_5P]^+$, 199(0.90), 183(6.7) $[C_7H_{12}N_4P]^+$, 181(13) $[C_7H_{10}N_4P]^+$, 176(5.2), 175(66) $[C_8H_{20}N_2P]^+$, 172(2.8), 158(2.9), 156(3.1), 147(2.1) $[C_6H_{16}N_2P]^+$, 129(2.3), 119(0.90), 116(0.90), 110(2.6), 105(3.0), 104(73) $[C_4H_{11}NP]^+$, 103(3.7), 102(8.5), 78(5.5), 75(6.4), 74(31), 73(9.5), 72(81) $[C_4H_{10}N]^+$. Anal. Calcd. for $C_{30}H_{60}N_{12}P_2$ (651.0): C, 55.35; H, 9.31; N, 25.83; P 9.51%. Found: C, 55.26; H, 9.56; N, 25.60; P, 9.54%.

Both main fractions were combined and refractionated which resulted in 38.9 g (yield 65%) of **3a**, bp 100–105°C (0.04 torr), n_D^{20} 1.5020, δ_P 78 ppm (Lit.[13]: bp 104°C(0.025 torr), n_D^{23} 1.5040, δ_P 77.8 ppm). IR and ^{31}P NMR spectral data of **3a** and of an authentic sample appeared identical.

The resinous residue left after the first fractionation was chromatographed (Silicagel 1 100/160μ, Chemapol, Czechoslovakia) with benzene. This produced 13.10 g (32.22 mmol) of **5b**, after recrystallization from hexane; mp 79–80°C. IR (cm^{-1}): 970 (ν_{N-C-C}), 1030, 1045 (ν_{P-N-C}), 1355 ($\nu_{P=N}$), 1550, 1560 ($\nu_{C=N}$), 2235, 2245 ($\nu_{C\equiv N}$, two weak absorptions). ^1H NMR (CCl_4, δ, ppm): 1.19 (18H, *t*, CH_3—C—N, $^3J_{HH}$ 7 Hz), 1.23 (3H, *t*, CH_3—C—C, $^3J_{HH}$ 7 Hz), 2.15 (2H, C—CH_2—C), 3.15 (12H, d.q., CH_2—N, $^3J_{PH}$ 11 Hz). ^{31}P NMR (C_6D_6, δ, ppm): 25.8. Anal. Calcd. for $C_{19}H_{35}N_8P$ (406.6): C, 56.12; H, 8.69; N, 27.57; P, 7.62%. Found: C, 55.92; H, 8.97; N, 27.48; P, 7.57%.

Reaction of hexaethyltriaminophosphine **1a** *with isopropyl thiocyanate* **2c**. A mixture of 29.50 g (119.23 mmol) of **1a** and 24.12 g (238.29 mmol) of **2c** was heated for 4 h at 140°C in an atmosphere of dry argon. Subsequent distillation of the reaction mixture in vacuo yielded 23.3 g (70%) of **3a**, bp 105°C (0.04 torr), n_D^{20} 1.5023. After recrystallisation of the residue first from hexane and then from petroleum ether (40–70°C) 6.52 g (15.50 mmol) of **5c** was obtained; mp 79.5°C. IR (cm^{-1}): 970 (ν_{N-C-C}), 1025 (ν_{P-N-C}), 1365, 1375 ($\nu_{P=N}$, doublet), 1570 ($\nu_{C=N}$), 2235, 2245 ($\nu_{C\equiv N}$, two weak absorptions). ^1H NMR (CCl_4, δ, ppm): 0.90 (18H, *t*, CH_3—C—N, $^3J_{HH}$ 7.1 Hz), 1.25 (6H, *d*, CH_3—C—C, $^3J_{HH}$ 6.7 Hz), 2.31 (1H, sept., CH), 2.92 (12H, d.q., CH_2—N, $^3J_{PH}$ 10.5 Hz). ^{31}P NMR (C_6H_6, δ, ppm): 25.9. Mass spectrum, m/z (relative intensity, %): 421(3.7), 420(14) $[C_{20}H_{37}N_8P]^+$, 406(1.5), 405(5.4) $[C_{19}H_{34}N_8P]^+$, 394(1.7) $[C_{19}H_{37}NP]^+$, 392(0.37) $[C_{18}H_{33}N_8P]^+$, 391(1.5) $[C_{18}H_{33}N_8P]^+$, 380(0.50), 379(1.3), 378(12) $[C_{17}H_{31}N_8P]^+$, 377(38) $[C_{17}H_{30}N_8P]^+$, 366(1.0) $[C_{17}H_{33}N_7P]^+$, 351(0.50), 350(2.2) $[C_{15}H_{27}N_8P]^+$, 349(11) $[C_{15}H_{26}N_8P]^+$, 335(0.90) $[C_{14}H_{24}N_8P]^+$, 334(5.0) $[C_{14}H_{23}N_8P]^+$, 315(1.7), 314(21), 313(100) $[C_{14}H_{30}N_6P]^+$, 278(2.5), 277(14) $[C_{13}H_{14}N_7P]^+$, 177(0.53), 176(1.8), 175(14) $[C_8H_{20}N_2P]^+$, 105(1.0), 104(24) $[C_4H_{11}NP]^+$, 73(1.0), 72(50) $[C_4H_{10}N]^+$, 59(0.44), 58(16) $[C_4H_{10}]^+$, 44(1.1), 43(8.3) $[C_3H_7]^+$, 29(7.1) $[C_2H_5]^+$. Anal. Calcd. for $C_{20}H_{37}H_8P$ (420.6): C, 57.11; H, 8.88; N, 26.65; P, 7.36%. Found: C, 56.92; H, 9.14; N, 26.35; P, 7.53%.

Reaction of tetraethyldiaminophenylphosphine **1b** *with ethyl thiocyanate* **2b**. A mixture of 9.47 g (37.52 mmol) of **1b** and 6.54 g (75.04 mmol) of **2b** was left to stay at room temperature for 12 days. Then the precipitate of **4b** formed was collected by filtration. After recrystallization from ethyl acetate 1.24 g (1.88 mmol) of **4b** was isolated, mp 172–173°C. IR (cm^{-1}): 965 (ν_{N-C-C}), 1030, 1045 (ν_{P-N-C}), 1285 ($\nu_{P=N}$), 2240 ($\nu_{C\equiv N}$, very weak). ^{31}P NMR (C_6H_6, δ, ppm): 24.3. Mass spectrum, m/z (relative intensity, %): 609(0.50), 608(1.2) $[C_{32}H_{50}N_8P_2]^+$, 332(2.1), 331(16), 330(60) $[C_{17}H_{25}N_5P]^+$, 302(0.83) $[C_{15}H_{21}N_5P]^+$, 286(0.90), 278(1.0), 277(0.66), 261(0.63), 260(11), 259(54) $[C_{13}H_{16}N_4P]^+$, 258(4.0), 257(0.63), 252(2.4), 251(0.90), 243(2.2), 235(2.8), 229(1.4), 223(1.0), 215(1.5), 207(1.6), 206(10) $[C_{11}H_{15}N_2P]^+$, 205(2.3), 204(2.4), 196(0.53), 195(2.3), 192(1.0), 191(9.8), 188(4.2) $[C_9H_7N_3P]^+$, 187(1.0), 186(10), 182(0.68), 181(12), 180(89) $[C_{10}H_{15}NP]^+$, 179(1.6), 178(1.9), 175(0.88), 167(0.80), 166(2.4), 165(0.86), 164(1.5), 163(1.7), 161(0.84), 152(2.6), 149(3.2), 148(1.7), 147(1.0), 141(2.5), 138(0.54), 135(1.7), 134(14) $[C_7H_5NP]^+$, 124(1.8), 123(1.6), 122(4.9), 121(0.44), 120(1.0), 119(1.0), 118(1.0), 117(1.3), 116(0.50), 112(0.30), 110(5.1), 109(61) $[C_6H_6P]^+$, 108(4.3), 107(7.9), 106(0.70), 105(2.7), 104(4.8), 103(1.6), 102(1.7), 97(0.45), 92, (0.56), 83(2.1), 81(2.5), 78(2.5), 77(3.3) $[C_6H_5]^+$, 74(0.40), 73(10), 72(100) $[C_4H_{10}N]^+$. Anal. Calcd. for $C_{34}H_{50}N_{10}P_2$ (660.9): C, 61.79; H, 7.64; N, 21.20; P, 9.37%. Found, %: C, 62.02; H, 7.82; N, 21.15; P, 9.01%.

The filtrate was concentrated in vacuo and fractionated; 6.4 g (yield 60%) of **3b** was obtained, bp 134°C (0.08 torr), n_D^{20} 1.5585. ^1H NMR (CCl_4, δ, ppm): 0.98 (12H, *t*, CH_3, $^3J_{HH}$ 7Hz), 3.02 (8H, d.q., CH_2, $^3J_{PH}$ 12 Hz), 7.07–7.90 (5H, *m*, C_6H_5). ^{31}P NMR (C_6H_6, δ, ppm): 76.5. **3b** was also identified by comparing with the sample, synthesized by sulfurization of **1b**, bp 133–135°C (0.08 torr), n_D^{20} 1.5582, δ_P 76 ppm. Diethyl disulfide (1.60 g, 13.09 mmol) was condensed in a trap, cooled by liquid nitrogen, and identified by gas-liquid chromatography.

Reaction of tetraethyldiaminophenylphosphine **1b** *with methoxycarbonylmethyl thiocyanate* **2d**. To a solution of 7.54 g (57.49 mmol) of **2d** in 40 ml of anhydrous benzene was added dropwise with stirring at room temperature 14.50 g (57.45 mmol) of **2d**. After 5 days 1.20 g (1.82 mmol) of solid **4b** was isolated by filtration from the reaction mixture, mp 171.5–172.5°C (recryst. from ethyl acetate). Fractionation of the filtrate in vacuo yielded 9.48 g (58%) of **3b**, bp 130–134°C (0.08 torr), n_D^{20} 1.5576, δ_P 76 ppm.

REFERENCES AND NOTES

1. J. Michalski and J. Wieczorkowski, *Roczn. Chem.*, **33,** 105 (1959).
2. R. M. Kamalov, G. S. Stepanov, E. I. Gol'dfarb, D. V. Rygikov, M. A. Pudovik and A. N. Pudovik, *Doklady AN SSSR*, **308,** 1383 (1989).
3. R. M. Kamalov, G. S. Stepanov, M. A. Pudovik and A. N. Pudovik, *Zh. Obshch. Khim.*, **60,** 476 (1990).
4. The ^{31}P chemical shift of **1a** is 118 ppm, for **3a** it is 78 ppm. We consider the signal with δ_P 63 ppm to be due to the quasiphosphonium salt **10** [cf., e.g.: M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, P^{31} Nuclear Magnetic Resonance. Topics in Phosphorus Chemistry. New York, London, Sydney: Interscience Publishers, 1967, vol. 5, p. 413.].
5. Y. A. Levin and E. I. Vorkunova, *Homolytic Chemistry of Phosphorus*, Moscow: Nauka, 1978.
6. J. Hargis and S. D. Worley, *Inorg. Chem.*, **16,** 1686 (1977).
7. G. Boekestein and H. M. Buck, *Rec. Trav. Chim.*, **92,** 1095 (1973).
8. A. A. Kutyrev and V. V. Moskva, *Uspekhi Khimii*, **56,** 1798 (1987).
9. M. K. Kadirov, V. I. Morozov, R. M. Kamalov, G. S. Stepanov, A. V. Il'yasov and M. A. Pudovik, *Phosphorus, Sulfur and Silicon*, following paper in this issue.
10. V. A. Naumov and L. V. Vilkov, *Molecular Structures of Organo-phosphorus Compounds*, Moscow; Nauka, 1986, pp. 122–126.
11. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, **S1,** (1987).
12. C. Piccinni-Leopardi, B. Tinant, J. P. Declercq and G. Germain, *Bull. Soc. Chim. Belg.*, **92,** 311 (1983).
13. G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds*, New York, London, Sydney, Toronto: Wiley Interscience, 1973, vol. 6, p. 754.