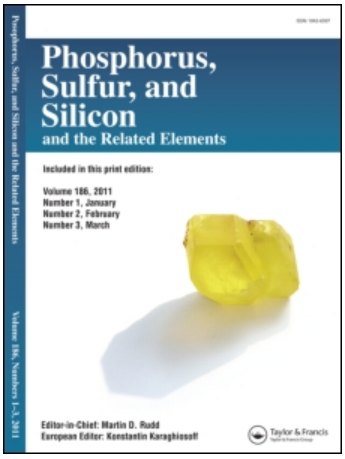

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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M. G. Zimin[a]; R. M. Kamalov[a]; R. A. Cherkasov[a]; A. N. Pudovik[a]
[a] V. I. Ul'yanov-Lenin State University, Kazan, USSR

To cite this Article Zimin, M. G. , Kamalov, R. M. , Cherkasov, R. A. and Pudovik, A. N.(1982) 'REACTIONS OF DIALKYL DITHIOPHOSPHORIC AND DIPHENYLDITHIOPHOSPHINIC ACIDS WITH THIOCYANATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 13: 3, 371 — 378
To link to this Article: DOI: 10.1080/03086648208081199
URL: http://dx.doi.org/10.1080/03086648208081199

Phosphorus and Sulfur, 1982, Vol. 13, pp. 371–378
0308-664X/82/1303-0371/$06.50/0

REACTIONS OF DIALKYL DITHIOPHOSPHORIC AND DIPHENYLDITHIOPHOSPHINIC ACIDS WITH THIOCYANATES

M. G. ZIMIN, R. M. KAMALOV, R. A. CHERKASOV and A. N. PUDOVIK

V. I. Ul'yanov-Lenin State University, Kazan, 420008, USSR

(*Received May 5, 1982*)

The interaction between phosphorus (IV) dithio acid partial esters and thiocyanates proceeds with initial formation of addition products to the C≡N bond. These adducts are either split by the second molecule of dithio acid to S-alkyl dithiocarbamates and tetraalkyl trithiopyrophosphates or rearrange into dialkyl *N*-thiophosphoryldithiocarbamates. The latter easily split off the thiols and convert to isothiocyanatothiophosphates. A number of thiophosphorylated and diphosphorylated thioureas were synthesized by the reaction of isothiocyanatothiophosphates with amines and α-aminoalkylphosphonates.

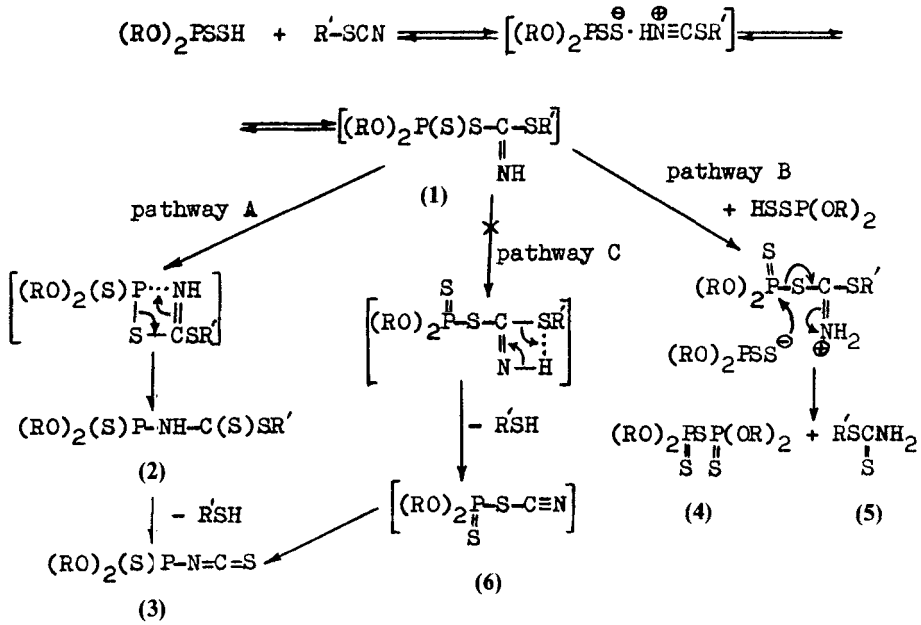
INTRODUCTION

The formation of various substances in the reactions of dialkyl dithiophosphoric acids with cyanogen-containing compounds is usually assigned to the transformations of addition products containing a >P(S)SC=NH fragment.[1-13] These addition compounds undergo breaking of the P—S bond by the second molecule of dithiophosphoric acid,[1-3] hydrogen chloride,[7] water,[8] or methanol.[10] In addition, they can rearrange into dialkyl *N*-thiophosphorylthioamides.[2,3,5,11] If the adduct contains a facile leaving group, the splitting of this group and formation of thiophosphorylthiocyanates isomerizing into isothiocyanatothiophosphates[6,10] can be supposed to be an alternative to the rearrangement process. It was found that the latter[9,11] are formed also as a result of *N*-thiophosphoryldithiocarbamate decomposition. The interaction between phosphorodithionic acids and chlorosubstituted acetonitriles results in a combination of addition reactions on the CN group, substitution of chlorine atoms, the rearrangement of addition products, and splitting of the P—S bond under the action of hydrogen chloride.[5] In the presence of a carbonyl group in the nitrile molecule, this carbonyl group also participates in the addition reactions; quite a number of processes result in the formation of bis(dialkyl thiophosphoryl) disulfide.[4]

RESULTS AND DISCUSSION

Reactions of phenyl- and alkylthiocyanates with O,O-dialkyl dithiophosphoric acids are accompanied by an exothermic effect and terminate at room temperature after 2–14 days. The reaction yields S-phenyl and S-alkyl dialkyl *N*-thiophosphoryldithiocarbamates (**2**), isothiocyanatothiophosphoric acid dialkyl esters (**3**), tetraalkyl trithiopyrophosphates (**4**) and S-phenyl or S-alkyl dithiocarbamates (**5**). The results obtained can be interpreted on the basis of the following reaction. At the first stage, dialkyl dithiophosphoric acids add to the C≡N bond to form the adducts of imidoyl

structure (**1**), which however, were neither isolated nor identified. The appearance of (**1**) in the course of the reaction is confirmed by the formation of thiophosphoryldithiocarbamates (**2**) isomeric to these adducts.



It seems that the above illustrates the initial protonation of the CN group, however, the cyclic mechanism suggested in Ref. 13 is also possible. At any rate, the interactions between methyl- and propylthiocyanates and diethyl dithiophosphoric acid potassium salt, when protonation is completely impossible, give rise to the other course of the reaction than that which occurs in the presence of acid. The only phosphorus-containing products in this case appear to be O,O-diethyl S-alkyl dithiophosphates (**7**).

(**7**)

These reactions indicate the importance of the protonation. It is quite interesting also that the thiocyanate group behaves in this reactions as a pseudohaloid.

Since they are capable of phosphorylating to a great extent,[14] the compounds of type (**1**) phosphorylate the initial molecule of dithio acid in the course of interaction which yields tetraalkyl trithiopyrophosphates (**4**) and S-alkyl dithiocarbamates (**5**) (pathway B) which were isolated from the reaction mixture and identified. The easy isomerization of the compounds of type (**1**) into type (**2**) is also indicative of their instability (pathway A). Such isomerization into type (**2**) can be considered as an intramolecular phosphorylation.[11,15] *N*-thiophosphoryldithiocarbamates (**2**) appear to be weak acids ($pK_a \sim 7.5$[16]) and therefore they can be isolated from the reaction mixture. However, the compounds of type (**2**) are also unstable and, when standing at room temperature or in the course of distillation in vacuum, they smoothly split off the thiols and transform into isothiocyanatothiophosphates (**3**), which has been demonstrated in special experiments. Such a reaction makes it possible to avoid the formation of the compounds of type (**4**) and type (**5**) due to the splitting of

dithiocarbamates (**2**) by the second molecule of dithiophosphoric acid. The model reactions of S-alkyl *N*-thiophosphoryldithiocarbamates (**2**) with dialkyl dithiophosphoric acids, in fact, did not exhibit even slight traces of pyrophosphates (**4**) and dithiocarbamates (**5**), either at room temperature (on standing for two months) or on boiling in benzene (for 3 hours). Only isothiocyanates (**3**) and mercaptans were identified.

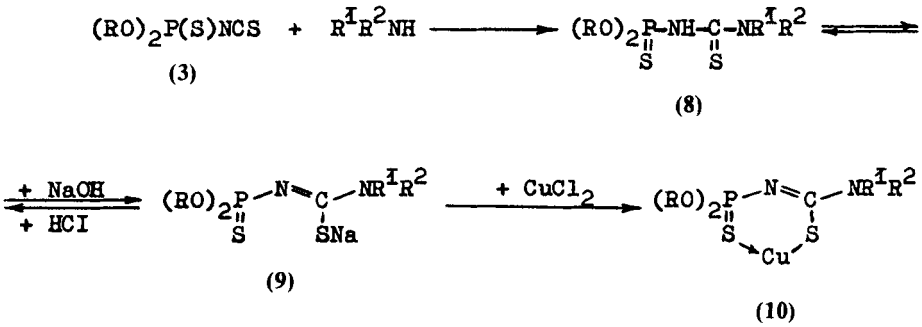
It is the facile decomposition of phosphorylated dithiocarbamates (**2**) that we suppose to be responsible for the formation of isothiocyanates (**3**) in the reactions of dialkyl dithiophosphoric acids with thiocyanates (pathway A). Pathway (C) for this process was proposed in Ref. 6. According to Ref. 17, it is unlikely that thiocyanatophosphates can appear as intermediates in the reactions which directly yield phosphorylisothiocyanates. IR and NMR ^{31}P spectra recorded in the course of the reaction of diisopropyl dithiophosphoric acid with methylthiocyanate fail to identify intermediates (**6**). The experiments described herein (see Figure 1) show that firstly there occurs a parallel formation of thiophosphoryldithiocarbamates (**2**) (δp 54 p.p.m.), tetraalkyl trithiopyrophosphates (**4**) (δp 74 p.p.m.) and S-alkyl dithiocarbamates (**5**). The accumulation of isothiocyanates (**3**) (δp 42 p.p.m.) in the reaction mixture becomes noticeable only at 3–4 weeks after the beginning of the reaction or on 1–2 hours heating of the starting reagents at 60–100°C. The integration of the ^{31}P NMR signals in the course of interaction shows that the reaction preferably proceeds by pathway (A) (to the extent of 60–70%).

The process in fact proceeds by pathway (A) only when the reaction of dialkyl dithiophosphoric acids with thiocyanates is carried out at 80–100°C in an excess of the latter. In this case, isothiocyanatothiophosphates (**3**) are isolated with yields of 90–95%, and the procedure becomes a suitable method for synthesizing the latter.[18]

An additional result was also found in the reaction of methylthiocyanate with dimethyl dithiophosphoric acid. Under mild conditions in an ether medium, it is possible to obtain S-methyl dimethyl *N*-thiophosphoryldithiocarbamate in a good yield and small quantities of O,O,S-trimethyl dithiophosphate. In the absence of a solvent, a vigorous exothermic reaction mainly results in O,O,S-trimethyl dithiophosphate (65–70%) due to a dealkylation reaction.[19]

The interaction between methylthiocyanate and diphenyldithiophosphinic acid, as well as nitriles,[1,12] proceeds exclusively by pathway (B) giving tetraphenyltrithiopyrophosphinate and S-methyl dithiocarbamate. In this case the process, does not proceed by pathway (A) since the substitution of alkoxyl groups at the phosphorus atom in compounds of type (**1**) by alkyl[20] or phenyl[15] radicals deprives them of their capability for rearranging.

Dialkyl esters of isothiocyanatothiophosphoric acid (**3**) were identified by their ability to add amines, including α-aminophosphonates, yielding thiophosphorylthioureas (**8**) which are readily identified (see Table III).



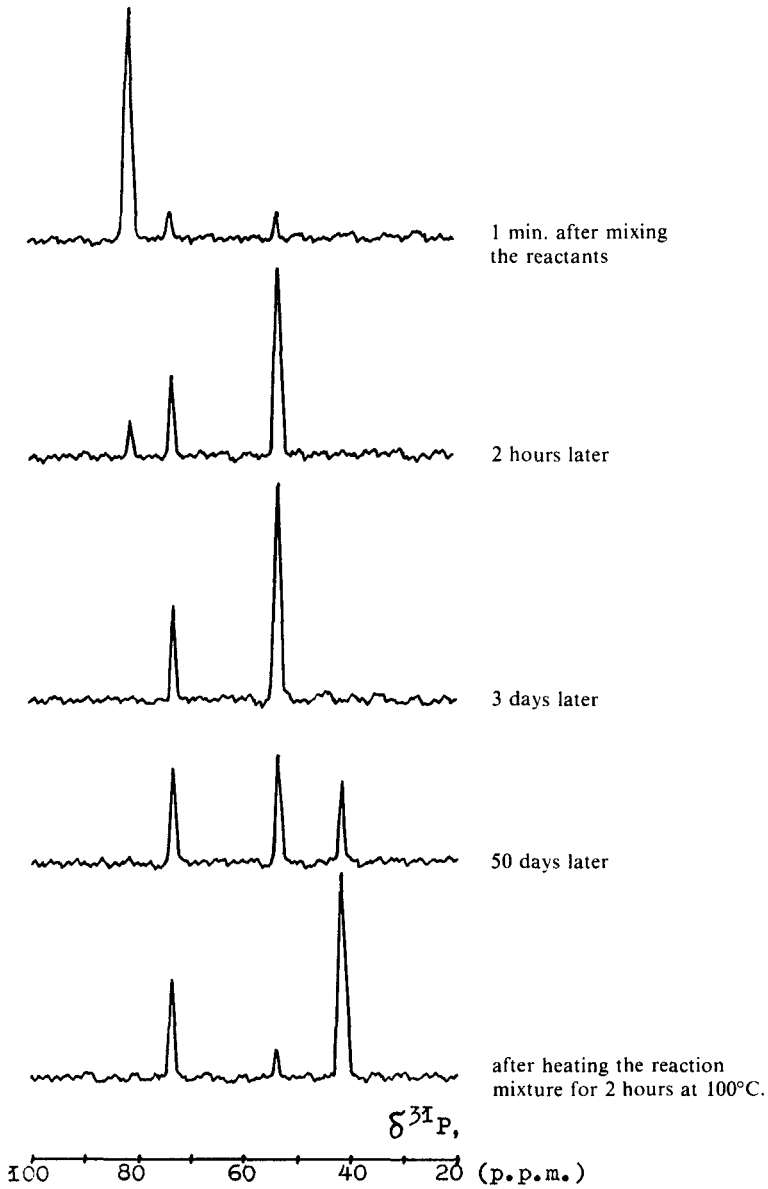


FIGURE 1 NMR ^{31}P spectra in the course of the interaction between CH_3SCN and $HSSP(OC_3H_7\text{-iso})_2$ (δp 82 p.p.m.).

The compounds of type (**8**) are much more stable than thiophosphoryldithiocarbamates (**2**) though they also decompose into the initial components on fractionation in vacuum. When Cu (II) ions are added to sodium derivatives of the thiophosphorylthioureas (**9**), very stable chelates of structure (**10**) are formed, with copper being reduced to the univalent state.

EXPERIMENTAL

IR spectra were determined on UR-10 and UR-20 instruments in the range of 400–3650 cm^{-1}. The samples were studied in the form of films or weighed suspensions in vaseline oil. NMR ^{31}P spectra were obtained on a nonserial KGU-4 instrument at 10.2 mHz with 85% H_3PO_4 as the external standard. Positive shifts are those downfield of the standard. NMR ^1H spectra were recorded on a HA-100 D Varian spectrometer using tetramethylsilane (TMS) as an internal standard. Melting points were taken in open capillary tubes and are uncorrected.

Reactions of Dialkyl Dithiophosphoric Acids with Thiocyanates. Equimolar quantities (of 0.1 mol each) of diethyl, dipropyl, diisopropyl, and dibutyl dithiophosphoric acids and methyl, propyl, phenylthiocyanates were stored in a sealed ampul at room temperature for 2–14 days. The mixtures were fractionated in vacuum after the reaction was completed, monitoring being carried out by the NMR ^{31}P spectra.

Low-boiling fractions yielded crystalline S-alkyl dithiocarbamates identified by IR spectra (νNH_2, doublet, 3130–3280, 3425–3480 cm^{-1}, δNH 1600–1630 cm^{-1}) as well as by the mixture melting point with pure samples.

S-methyl dithiocarbamate, 38% yield, m.p. 42°C (from benzene), (Lit.[21]: m.p. 42°C). $C_2H_5NS_2$ (107) Calculated %: C, 22.43; H, 4.67; N, 13.08; S 59.81. Found %: C, 22.08; H, 4.69; N, 12.73; S, 59.78.

S-propyl dithiocarbamate, 40% yield, m.p. 58°C (reprecipitation by hexane from benzene), (Lit.[21]: m.p. 58°C). $C_4H_9NS_2$ (135) Calculated %: C, 35.56; H, 6.67; N, 10.37; S, 47.41. Found %: C, 36.01; H, 6.86; N, 10.31; S, 47.90.

S-phenyl dithiocarbamate, 42% yield, m.p. 113–114°C (from ether-hexane mixture, 1 : 1). $C_7H_7NS_2$ (169) Calculated %: C, 49.70; H, 4.14; N, 8.28; S, 37.87. Found %: C, 49.75; H, 4.16; N, 8.27; S, 37.81.

The following compounds were obtained from the higher-boiling fractions:

Dialkyl esters of isothiocyanatothiophosphoric acid, their structures were confirmed by IR (625–670 cm^{-1}, $\nu P{=}S$; 2010–2030 cm^{-1} νNCS) and NMR ^{31}P spectra as well as by the transformation into *N*-thiophosphorylated thioureas. Characteristic data of dialkyl esters of isothiocyanatothiophosphoric acid are given in Table I.

Tetraisopropyl trithiopyrophosphate, 20% yield, b.p. 118–120°C (0.04 mm of Hg), n_D^{20} 1.5098, δp 74 p.p.m. (Lit.[22]: b.p. 126–129°C (0.25 mm), n_D^{20} 1.5128). IR spectra (ν, cm^{-1}): 640 (P=S), 985, 1020 (POC), 1150, 1185 (POAlk).

Tetraethyl, tetrapropyl, and tetrabutyl trithiopyrophosphates were identified by NMR ^{31}P spectra in the reaction mixtures (δp 78, 77, 79 p.p.m., respectively).

S-alkyl dialkyl *N*-thiophosphoryldithiocarbamates were identified by means of spectroscopy in the reaction mixture prior to fractional distillation and isolated in special tests.

Alkanethiols were condensed in a trap, cooled by liquid nitrogen, and identified by means of gas–liquid chromatography.

Reaction of Diphenyldithiophosphinic Acid with Methylthiocyanate. The reaction of diphenyldithiophosphinic acid (0.02 mol) with methylthiocyanate (0.02 mol) was carried out in 30 ml anhydrous ether at room temperature. The formation of tetraphenyltrithiopyrophosphinate crystals was complete after one day. Yield 88%, m.p. 120.5–121.5°C (from benzene), (Lit.[24]: m.p. 121.5°C), δp 60 p.p.m. $C_{24}H_{20}P_2S_3$ (466) Calculated %: C, 61.81; H, 4.29; P, 13.30; S, 20.60. Found %: C, 61.91; H, 4.17; P, 13.10; S, 20.85.

After the ether was removed, S-methyl dithiocarbamate was isolated from the residue, yield 65%, m.p. 42°C (from benzene), and confirmed by mixture melting point.

TABLE I

Dialkyl Thiophosphorylisothiocyanates[a]

	$(RO)_2P(S)NCS$, R	b.p. (°C/mm Hg)	n_D^{20}	$\delta^{31}P$ (p.p.m.)	Yield (%)	P, %	
3a.	C_2H_5	79–81/9	1.5200	44	45	Calc.	14.69
						Fd.	14.79
3b.	*n*-C_3H_7	90–93/3	1.5091	46	40	Calc.	12.97
						Fd.	12.86
3c.	*i*-C_3H_7	82–83/3	1.5084	42	50	Calc.	12.97
						Fd.	12.93
3d.	C_4H_9	121–122/3	1.5033	46	48	Calc.	11.61
						Fd.	11.53

[a] Cf. Ref. 23.

Reaction of Dimethyl Dithiophosphoric Acid with Methylthiocyanate. On mixing 0.18 mol dimethyl dithiophosphoric acid with 0.18 mol of methylthiocyanate during one hour, a strong exothermic effect was observed. O,O,S-trimethyl dithiophosphate (δp 100 p.p.m.), S-methyl dimethyl *N*-thiophosphoryldithiocarbamate (δp 63 p.p.m.), and the dimethyl ester of isothiocyanatothiophosphoric acid (δp 49 p.p.m., νNCS 1995 cm^{-1}) were identified in the reaction mixture prior to fractional distillation. O,O,S-trimethyl dithiophosphate (68% yield) was isolated by fractionating the mixture in vacuum, b.p. 61–63°C (3 mm), n_D^{20} 1.5267, δp 100 p.p.m. (Lit.[25]: b.p. 55°C (2 mm), n_D^{20} 1.5290, δp 99.5 p.p.m.). IR spectra (ν, cm^{-1}): 530 (P—S), 665 (P=S), 1020, 1170 ($POCH_3$). $C_3H_9O_2PS_2$ (172) Calculated %: P, 18.02. Found %: P, 17.87.

S-alkyl Dialkyl N-thiophosphoryldithiocarbamates. Equimolar quantities (0.05 mol each) of diethyl, dipropyl, and diisopropyl dithiophosphoric acids and methyl-, ethyl-, iso-butyl-thiocyanates were stored at room temperature for 2–5 weeks. Then the reaction mass was treated with a 1N solution of NaOH (50–100 ml) and impurities were extracted by benzene. The aqueous solution was acidified by a 1N solution of HCl to pH 2–3 (litmus). Yellow oils were isolated which soon became crystalline in case of S-methyl and S-ethyl diisopropyl *N*-thiophosphoryldithiocarbamates. The product was separated from water by extraction with benzene or by filtration. Benzene extracts were dried over $MgSO_4$, the solvent was removed in vacuum, the residue were stored in vacuum for 1.5–2 hours at 0.05 mm of mercury until a constant refractive index was achieved. If necessary, the products were again treated with alkali and then acid. IR spectra of the compounds of type (**2**) show the absorption bands (ν, cm^{-1}): 645–660 (P=S), 960–975, 1030–1040 (POC), 1150–1180 (POAlk), 1250–1270, 1320–1340 (N—C=S bands), 1560–1610, 3200–3250 (NH). The constants of the S-alkyl *N*-thiophosphoryldithiocarbamates are given in Table II.

The reaction between methylthiocyanate and dimethyl dithiophosphoric acid was carried out in 60 ml anhydrous ether. After standing at room temperature for 5–7 days, the solvent was removed from the reaction mixture in vacuum, S-methyl dimethyl *N*-thiophosphoryldithiocarbamate was isolated from the residue according to the procedure described above (see the constants in Table II). NMR ^1H (δ, p.p.m.): SCH_3, singlet 2.57 (3H), $POCH_3$, doublet with the center 3.80, $^3J(PH)$ 15.6 Hz (6H), NH, doublet with the center 7.91, J(PNH) 13.9 Hz (1H).

Dialkyl Esters of Isothiocyanatothiophosphoric Acid. Dialkyl dithiophosphoric acids (0.1 mol) were added dropwise on stirring to methylthiocyanate (0.3 mol) heated to 80–100°C, then the mixture was heated at 100°C for 2–3 hours. The following compounds were obtained by fractionation in vacuum: (**3a**)–88% yield, (**3b**)–95% yield, (**3c**)–95% yield. Their physical constants are similar to those reported in the literature.[23]

5 g of S-ethyl diisopropyl *N*-thiophosphoryldithiocarbamate was fractionated in vacuum. 3.7 g (95%) of (**3c**) with b.p. 83°C (3 mm Hg), n_D^{20} 1.5080 was isolated, 0.8 g (80%) of ethyl mercaptan was condensed in the trap.

N-alkyl- and N-arylsubstituted Dialkyl N'-thiophosphorylthioureas. Equimolar quantity of amine in 50 ml ether was added to 0.05 mol of dialkyl ester of isothiocyanatothiophosphoric acid in 50 ml ether. On the following day, ether was removed in vacuum, the residue underwent crystallization. *N*-phosphorylated thioureas are weak acids.[26] For purification, they were dissolved in a 1N solution of NaOH and

TABLE II

S-Alkyl Dialkyl *N*-Thiophosphoryldithiocarbamates

	$(RO)_2P(S)-NH-C(=S)-SR'$ R	R'	n_D^{20} or m.p. (°C)	d_4^{20}	$\delta^{31}P$ (p.p.m.)	Yield (%)	Elem. analysis Calcd./Found C	H	P
2a.	CH_3	CH_3	1.6206		63	60	20.77 21.34	4.32 4.54	13.41 13.35
2b.	C_2H_5	CH_3	1.5901	1.2670	57	48	27.79 28.34	5.40 5.40	11.96 11.64
2c.	C_2H_5	*i*-C_4H_9	1.5596	1.1811	58	45	35.88 35.60	6.64 6.53	10.30 10.01
2d.	*n*-C_3H_7	CH_3	1.5700	1.2030	57	60	33.44 33.51	6.27 6.15	10.80 10.59
2e.	*i*-C_3H_7	CH_3	m.p. 49–50 (d.)		55	49	33.44 33.56	6.27 6.60	10.80 11.34
2f.	*i*-C_3H_7	C_2H_5	m.p. 43–44 (d.)		56	60	35.88 36.13	6.64 6.85	10.30 10.10
2g.	*i*-C_3H_7	*i*-C_4H_9	1.5448	1.1244	54	55	40.12 40.29	7.29 7.02	9.42 9.25

TABLE III

N-Dialkyl Thiophosphorylthioureas $(R^1O)_2P(S)NHC(S)NR^2R^3$

	R^1	R^2	R^3	m.p. (°C) (solv.) and ref.	$\delta^{31}P$ (p.p.m.)	Yield (%)	Elem. analysis Calcd.	Found
8a.	C_2H_5	H	C_6H_5	90[6] (benzene)	56	80	C 43.42 H 5.59 N 9.21 P 10.20	43.61 5.69 9.32 10.50
8b.	*i*-C_3H_7	H	C_6H_5	85 (benzene)	54	80	C 46.99 H 6.33 N 8.43 P 9.34	46.69 6.21 8.19 9.44
8c.	*i*-C_3H_7	H	*t*-C_4H_9	111–111.5 (hexane)	52	92	C 42.31 H 8.01 N 8.97 P 9.94	42.25 7.94 9.33 9.96
8d.	*n*-C_3H_7	H	C_6H_5	67.5–68.5[6] (benzene)	58	80	C 46.99 H 6.33 N 8.43 P 9.34	46.74 6.37 8.32 9.66
8e.	*n*-C_3H_7	H	*t*-C_4H_9	40–41 (ether)	58	80	C 42.31 H 8.01 N 8.97 P 9.94	42.32 8.00 8.80 9.74
8f.	C_3H_7	H	$CH_2C_6H_5$	67–67.5 (*i*-PrOH/H_2O, 5:1)	62	71	C 48.55 H 6.65 N 8.09 P 8.96	49.00 6.58 8.40 9.30
8g.	C_3H_7	H	NHC_6H_5	117–118 (dec.) (hexane/benzene, 1:1)	64	70	C 44.96 H 6.34 N 12.10 P 8.93	45.15 6.30 12.03 8.63
8h.	C_4H_9	H	C_6H_5	40.5–41.5 (hexane)	60	60	C 50.00 H 6.94 N 7.78 P 8.61	49.90 6.96 7.81 8.77
8i.	C_3H_7	CH_3	$CHP(O)(OC_3H_7\text{-}i)_2$ C_6H_5	84–84.5 (*i*-PrOH)	64.19	60	C 48.09 H 7.25 P 11.83 S 12.21	48.21 7.13 11.89 12.40

impurities were extracted by benzene. The aqueous solution was acidified with 1N HCl to pH 2–3 and the oil formed was extracted by benzene. Benzene extracts were dried over $MgSO_4$, and after the solvent was removed, the products were purified by recrystallization and dried in vacuum. The constants of *N*-substituted dialkyl *N'*-thiophosphorylthioureas are given in Table III. IR spectra (ν, cm^{-1}): 640–660 (P=S), 970–1000, 1020–1040 (POC), 1170–1180 (POAlk), 1500–1510, 1600–1605, 3070–3080 (C_6H_5), 1540–1560, 3150–3400 (NH).

N-phenyl dipropyl *N'*-thiophosphorylthiourea (15 g) was placed into an Arbuzov test tube, melted and subjected to vacuum fractionation. The only fraction, b.p. 54–60°C (0.085 mm Hg), appeared to be an azeotropic mixture of aniline and dipropyl thiophosphorylisothiocyanate (δp, 46 p.p.m., νNCS 2010 cm^{-1}). On standing, the mixture again undergoes a reaction which yields the initial thiourea with m.p. 68°C, δp 58 p.p.m.

N-phenyl Diisopropyl N'-thiophosphorylisothiourea Chelate Salt of Copper (I). Sodium (0.2 g) was dissolved in 35 ml of *n*-propanol. 2.9. g of *N*-phenyl diisopropyl *N'*-thiophosphorylthiourea was added to the solution which was then mixed with 100 ml of an aqueous solution containing 1.45 g of $CuCl_2 \cdot 2H_2O$. The chelate was isolated by extraction with chloroform, then the chloroform solution was

dried over $MgSO_4$ and evaporated in vacuum. The resulting crystalline substance was washed several times with pentane and dried in vacuum. M.p. 145–145.5°C (with decomp.), δp 49 p.p.m. IR spectra (ν, cm^{-1}): 625 (P=S), 1000, 1010 (POC), 1150 (POC_3H_7), 1530 (S—C=N), 1605, 3070 (C_6H_5), 3340 (NH). $C_{13}H_{21}CuN_2O_2PS_2$ (395.5) Calcd. %: C, 39.44; H, 5.31; P, 7.84; Cu, 16.07. Found %: C, 39.57; H, 5.25; P, 7.71; Cu, 15.86.

Reaction of Potassium Diethyl Dithiophosphate with Thiocyanate. A mixture of 7.33 g of potassium diethyl dithiophosphate and 7.17 g of methylthiocyanate was heated with reflux at 100–130°C for 3 hours, then 30 ml of water and 30 ml of benzene were added. The benzene extract was dried over $MgSO_4$ and the solvent was removed in vacuum. On fractionating the residue, 6.1 g (93%) of O,O-diethyl S-methyl dithiophosphate was obtained, b.p. 81°C (3.5 mm), n_D^{20} 1.5089, δp 96 p.p.m. (Lit.[25]: b.p. 48°C (0.01 mm), n_D^{20} 1.5100). $C_5H_{13}O_2PS_2$ (200) Calcd. %: C, 30.00; H, 6.50; P, 15.50. Found %: C, 29.91; H, 6.48; P, 15.62. The thiocyanate anion was identified in aqueous solution by means of $FeCl_3$.

Under the conditions of the experiment described above, 4.20 g (90%) of O,O-diethyl S-propyl dithiophosphate (b.p. 70–72°C (2 mm), n_D^{20} 1.5013, δp 94 p.p.m.) was obtained from 4.58 g of potassium diethyl dithiophosphate and 6.21 g of propylthiocyanate. $C_7H_{17}O_2PS_2$ (228) Calcd. %: C, 36.84; H, 7.46; P, 13.60. Found %: C, 36.13; H, 7.53; P, 13.44.

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