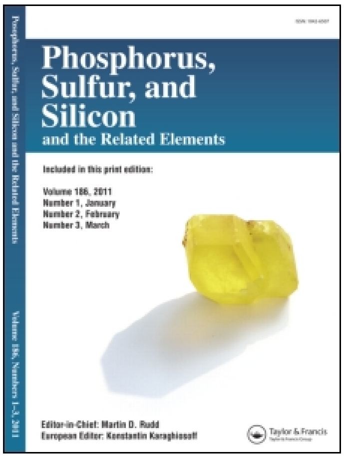

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TETRAPHOSPHORUS TRISULFIDE IN REACTIONS WITH THIOACETALS, AMINALS, SULFENAMIDES AND DISULFIDES. INFLUENCE OF AMINES AND BENZOYL PEROXIDE

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TETRAPHOSPHORUS TRISULFIDE IN REACTIONS WITH THIOACETALS, AMINALS, SULFENAMIDES AND DISULFIDES. INFLUENCE OF AMINES AND BENZOYL PEROXIDE

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The reactions of tetraphosphorus trisulfide with thioacetals, aminals, sulfenamides and disulfides were studied. The reactions were found to give organothiophosphorus compounds and to be facilitated by organic amines and benzoyl peroxide.

Key words: Tetraphosphorus trisulfide; thioacetals; aminals; sulfenamides; disulfides; organothiophosphorus compounds.

INTRODUCTION

Phosphorus sulfides used in organic synthesis hold a prominent place among mineral phosphorus derivatives. They serve as raw material for the synthesis of useful organothiophosphorus compounds.[1] However, the lower phosphorus sulfides had not been given due consideration. Thus organic synthesis based on phosphorus sesquisulfide dealt with reactions of alcohols,[2,3] amines,[4,5] alkyl and aryl halides,[6–8] Grignard reagents,[9] dialkyl sulfides,[10] disulfides,[11,12] sulfenyl halides,[13] thiobisamines[14] and sulfurization reactions.[15–17] For the synthesis of organothiophosphorus compounds we have now introduced compounds with mobile alkylthio and dialkylamino groups (thioacetals, aminals, sulfenamides and dialkyl disulfides) into the reactions with tetraphosphorus trisulfide.

RESULTS AND DISCUSSION

We have found that tetraphosphorus trisulfide **1** reacts with phenylbis(alkylthio)methanes **2a,b** in the molar ratios of 1:6 in sealed tubes at 200°C to form *S,S'*-dialkyl-1-(alkylthio)benzyl trithiophosphonates **3a,b** and *S*-(1-alkylthiobenzyl)-1-(alkylthio)benzyl alkyldithiophosphinates **4a,b** (Equation 1).

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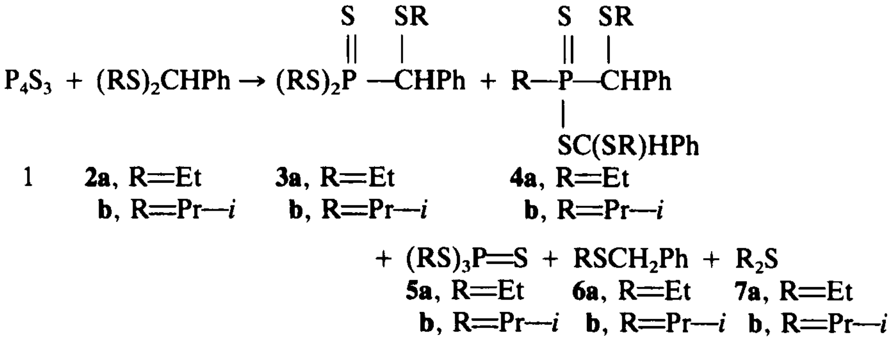
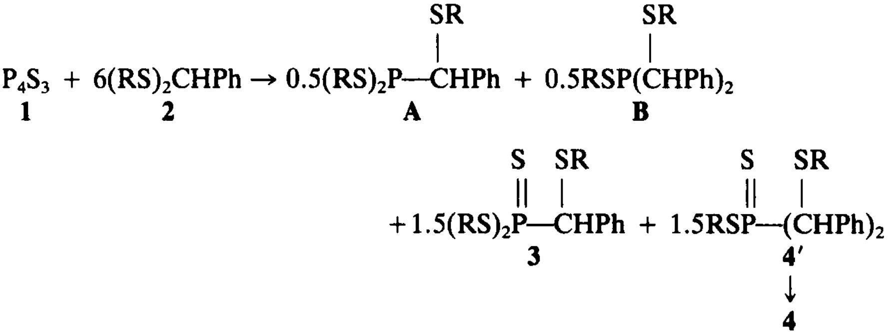


$$\begin{array}{lllll}
P_4S_3 + (RS)_2CHPh \rightarrow & (RS)_2\overset{S}{\overset{\|}{P}}-\overset{SR}{\overset{|}{C}}HPh & + & R-\underset{SC(SR)HPh}{\underset{|}{\overset{S}{\overset{\|}{P}}}}-\overset{SR}{\overset{|}{C}}HPh & \\
\mathbf{1} \quad \mathbf{2a}, R{=}Et & \mathbf{3a}, R{=}Et & & \mathbf{4a}, R{=}Et & \\
\qquad\ \ \mathbf{b}, R{=}Pr{-}i & \mathbf{b}, R{=}Pr{-}i & & \mathbf{b}, R{=}Pr{-}i & \\
 & + (RS)_3P{=}S & + RSCH_2Ph & + R_2S & \\
 & \mathbf{5a}, R{=}Et & \mathbf{6a}, R{=}Et & \mathbf{7a}, R{=}Et & \\
 & \mathbf{b}, R{=}Pr{-}i & \mathbf{b}, R{=}Pr{-}i & \mathbf{b}, R{=}Pr{-}i &
\end{array} \qquad (1)$$

The structures of products **3a,b** and **4a,b** were confirmed by IR (Table II), ^1H NMR (Table III), ^{31}P and mass spectral and elemental analytical data (Table I). The constants of thiophosphonate **3a** correspond to those of authentic **3a**.[18] Trialkyl tetrathiophosphates **5a,b**, alkyl benzylsulfides **6a,b** and dialkyl sulfides **7a,b** have also been isolated from the reaction mixtures. In the ^{31}P NMR spectra a weak intensity signal with a chemical shift of δ 115 ppm was observed in the reaction mixture and in low boiling distillation fractions in the reaction of phosphorus sulfide **1** with thioacetal **2a**. This signal may be attributed to triethyl trithiophosphite.[19]

Some assumptions may be suggested concerning the scheme of formation of major products in this reaction. Products **3**, **4′**, **A**, and **B** may result in accordance with the stoichiometry of equation 2:



$$\begin{array}{lll}
\underset{\mathbf{1}}{P_4S_3} + \underset{\mathbf{2}}{6(RS)_2CHPh} \rightarrow & \underset{\mathbf{A}}{0.5(RS)_2P-\overset{SR}{\overset{|}{C}}HPh} & + \underset{\mathbf{B}}{0.5RSP(\overset{SR}{\overset{|}{C}}HPh)_2} \\
 & +1.5\underset{\mathbf{3}}{(RS)_2\overset{S}{\overset{\|}{P}}-\overset{SR}{\overset{|}{C}}HPh} & + 1.5\underset{\underset{\mathbf{4}}{\downarrow}}{\underset{\mathbf{4'}}{RS\overset{S}{\overset{\|}{P}}-(\overset{SR}{\overset{|}{C}}HPh)_2}}
\end{array} \qquad (2)$$

Perhaps, thionophosphinate **4′** is the precursor of thionophosphinate **4** isolated from the reaction mixture. The formation of thionophosphinate **4** can have occurred through R,S-migration of alkyl and alkylthio groups. We did not manage to record of trivalent phosphorus compounds **A** and **B**, perhaps, owing to their sulfurization in severe conditions with the formation of products **3** and **4**.

Gem-diamines have proved to be more reactive as regards tetraphosphorus trisulfide. Thus *N,N′*-tetraalkyl-1-*N″*-(dialkylamino)methyl diamidothionophosphonates **9a,b** (Tables I–III) were isolated from the reactions of phosphorus sulfide **1** with bis(alkylamino)methanes **8a,b** when heated in sealed tubes for 4–5 h at 130–140°C (Equation 3).

TABLE I

Physical properties, yields and analytical data of the compounds prepared

					^{31}P NMR	Molecular	Analytical data Found/Calc. (%)					M^{+} [M +
%	B.p. °C (mm)	R_f^c Value	d_4^{20}	n_D^{20}	δ, ppm	Formula	C	H	N	P	S	Found
1.2	220–225 (0.002)[b]			1.6419	85	$C_{20}H_{27}PS_4$	56.20	6.33		7.51	30.08	426.0
							56.30	6.38		7.26	30.06	426.0
8.6		0.73	1.1061	1.6031	92	$C_{16}H_{27}PS_4$	51.04	7.10		8.11	33.38	
							50.78	7.21		8.19	33.82	
3.1		0.74		1.6177	85	$C_{23}H_{33}PS_4$	57.90	6.95		7.01	27.68	468.1
							58.97	7.05		6.62	27.35	468.1
1.1	79–80 (0.04)		1.0235	1.5108	83	$C_7H_{20}N_3PS$	40.65	9.65	19.75	14.41	14.83	
							40.16	9.66	20.08	14.81	15.29	
5.6	113–115 (0.077)		0.9654	1.5041	77	$C_{13}H_{32}N_3PS$	53.28	10.88	14.80	10.67	11.17	294.2
							53.20	11.02	14.02	10.56	10.90	294.2
6.1		0.64		1.5302	93.8	$C_{10}H_{25}N_2PS_2$	44.56	9.70	10.41	11.49	24.37	269[e]
							44.75	9.42	10.44	11.55	23.84	269
8.4		0.82		1.5690	94.1	$C_8H_{20}NPS_3$	37.38	7.98	5.59	12.50	37.05	258[e]
							37.34	7.85	5.45	12.05	37.31	258
8.3		0.62	1.0017	1.5245	94	$C_{11}H_{27}N_2PS_2$	46.36	9.38	10.03	10.92	22.71	
							46.61	9.63	9.89	10.94	22.93	
5.6		0.65		1.5533	93	$C_{10}H_{24}NPS_3$	41.89	8.38	5.20	11.37	33.92	286.0
							42.09	8.50	4.91	10.86	33.64	286.0

absence of additives.

erature of the spiral of thermoelement of a molecular evaporator.

t: Benzene.

of molecular ion $M^{+\cdot}$ in electron impact mass spectrum.

of m/z of ion $[M + H]^{+}$ in chemical ionization mass spectrum.

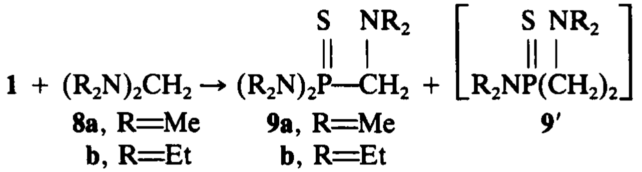
TABLE II

IR spectral data (cm^{-1}) of the compounds prepared

Cpd.	C—H[a], Ph	C=C[a], Ph	C—N—C as[b]	P—N—C as[b]	P=S[a]	PS,[a] PCS[a]
4a	3090, 3064, 3032	1600, 1494			645	515
3b	3088, 3064, 3030	1600, 1490			654	545, 513
4b	3090, 3064, 3030	1600, 1490			652	515
9a			1191	990, 960	590	
9b			1210, 1183	1030	597	
11a			1180, 1165	1030	625	530
12a			1170	1028	658	535
11b			1180, 1165	1025	620	535
12b			1171	1028	661	543

[a] Valent vibrations.

[b] Antisymmetrical vibrations.



$$1 + (R_2N)_2CH_2 \rightarrow (R_2N)_2\overset{\overset{\large S}{\|}}{P}\text{—}\overset{\overset{\large NR_2}{|}}{C}H_2 + \left[R_2N\overset{\overset{\large S}{\|}}{P}(\overset{\overset{\large NR_2}{|}}{C}H_2)_2\right] \qquad (3)$$

8a, R=Me **9a**, R=Me **9′**

b, R=Et **b**, R=Et

Two weak ^{31}P-NMR signals with chemical shifts of δ 43 and 71 ppm in the case of the reaction with aminal **8a** and of 42 and 68 ppm in the case of substance **8b** were observed in the reaction mixtures. The structure of non-isolated thionophosphinate **9′** may be ascribed to one of the signals. Small quantities of non-identified powders insoluble in organic solvents have also been isolated.

TABLE III

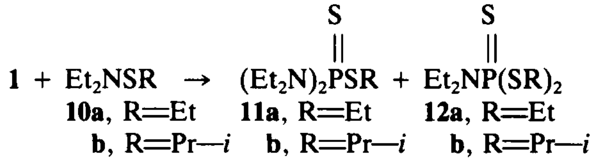
^{1}H NMR spectral data of the compounds prepared

Cpd.	δ, ppm, J, Hz
4a[+]	0.84 (dt, 3H, $\underline{\mathrm{CH}}_3$C—P, $^3J_{H-H}$ 7.5, $^2J_{P-H}$ 25.0); 1.20 (t, 6H, $\underline{\mathrm{CH}}_3$C—S, $^3J_{H-H}$ 7.0); 1.53–3.00 (m, 6H, $\underline{\mathrm{CH}}_2$S); δ_1 4.00, δ_2 4.10 (two d, 1H, C$\underline{\mathrm{H}}$P, $^2J_{P-H}$ 12.0 and 11.5); δ_1 4.92, δ_2 4.95 (two d, 1H, $\underline{\mathrm{CH}}$SP, $^3J_{P-H}$ 15.0 and 13.0).
3b	1.17 (d, 6H, $\underline{\mathrm{CH}}_3$CSC, $^3J_{H-H}$ 7.0); 1.33 (d, 12H, $\underline{\mathrm{CH}}_3$CSP, $^3J_{H-H}$ 7.0); 2.85 (q, 1H, $\underline{\mathrm{CH}}$SC, $^3J_{H-H}$ 7.0); 3.34 (dq, 2H, $\underline{\mathrm{CH}}$SP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 14.0); 4.20 (d, 1H, $\underline{\mathrm{CH}}$P, $^2J_{P-H}$ 13.0); 6.90–7.57 (m, 5H, C_6H_5).
4b[+]	0.71 (dd, 6H, $\underline{\mathrm{CH}}_3$CP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 25.0); 1.17 (d, 6H, $\underline{\mathrm{CH}}_3$CSCP, $^3J_{H-H}$ 7.0); 1.28 (d, 6H, $\underline{\mathrm{CH}}_3$CSCSP, $^3J_{H-H}$ 7.0); 2.23–3.68 (m, 3H, C$\underline{\mathrm{H}}$P, $\underline{\mathrm{CH}}$SC); δ_1 4.00, δ_2 4.10 (two d, 1H, C$\underline{\mathrm{H}}$P, $^2J_{P-H}$ 13.0 and 12.0); δ_1 4.92, δ_2 4.98 (two d, 1H, $\underline{\mathrm{CH}}$SP, $^3J_{P-H}$ 14.0 and 13.0).
9a	2.41 (d, 12H, $\underline{\mathrm{CH}}_3$NP, $^3J_{P-H}$ 6.5); 2.65 (s, 6H, $\underline{\mathrm{CH}}_3$NC); 2.88 (d, 2H, $\underline{\mathrm{CH}}_2$P, $^2J_{P-H}$ 6.0).
9b	0.99 (t, 12H, $\underline{\mathrm{CH}}_3$CNP, $^3J_{H-H}$ 7.0); 1.10 (t, 6H, $\underline{\mathrm{CH}}_3$CNC, $^3J_{H-H}$ 7.0); 2.85 (dq, 8H, $\underline{\mathrm{CH}}_2$NP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 26.0); 3.05 (q, 4H, $\underline{\mathrm{CH}}_2$NC, $^3J_{H-H}$ 7.0); 3.29 (d, 2H, $\underline{\mathrm{CH}}_2$P, $^2J_{P-H}$ 7.0).
11a	1.12 (t, 12H, $\underline{\mathrm{CH}}_3$CN, $^3J_{HH}$ 7.0); 1.29 (t, 3H, $\underline{\mathrm{CH}}_3$CS, $^3J_{H-H}$ 7.5); 2.80 (dq, 2H, $\underline{\mathrm{CH}}_2$SP, $^3J_{P-H}$ 15.0); 3.16 (dq, 8H, $\underline{\mathrm{CH}}_2$NP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 14.0).
12a	1.13 (t, 6H, $\underline{\mathrm{CH}}_3$CN, $^3J_{H-H}$ 7.0); 1.33 (t, 6H, CH_3CS, $^3J_{H-H}$ 7.5); 2.86 dq (4H, $\underline{\mathrm{CH}}_2$SP, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 15.0); 3.33 (dq, 4H, $\underline{\mathrm{CH}}_2$NP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 14.0).
11b	1.13 (t, 12H, $\underline{\mathrm{CH}}_3$CN, $^3J_{H-H}$ 7.0); 1.35 (d, 6H, $\underline{\mathrm{CH}}_3$SP, $^3J_{H-H}$ 7.0); 3.15 (dq, 8H, $\underline{\mathrm{CH}}_2$NP, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 14.0); 2.85–3.45 (m, 1H, $\underline{\mathrm{CH}}$SP).
12b	1.13 (t, 6H, $\underline{\mathrm{CH}}_3$CN, $^3J_{H-H}$ 7.0); 1.37 (d, 12H, $\underline{\mathrm{CH}}_3$CS, $^3J_{H-H}$ 7.0); 2.92–3.63 (m, 2H, $\underline{\mathrm{CH}}$SP, 4H, $\underline{\mathrm{CH}}_2$NP).

[+] The mixture of diastereoisomers.

The formation of mixed amidothiophosphates and phosphites should be expected in the reactions of tetraphosphorus trisulfide with compounds containing both alkylthio and dialkylamino groups in one molecule e.g. with sulfenamides.

In fact alkylsulfendiethylamides **10a**,**b** were found to react with phosphorus sulfide **1** to give *S*-alkyl-*N*,*N*′-bis(diethylamido) dithiophosphates **11a**,**b** and *S*,*S*′-dialkyl-*N*-diethylamido trithiophosphates **12a**,**b** (Tables I–III) when heated in sealed tubes for 3–8 h at 175°C (Equation 4).

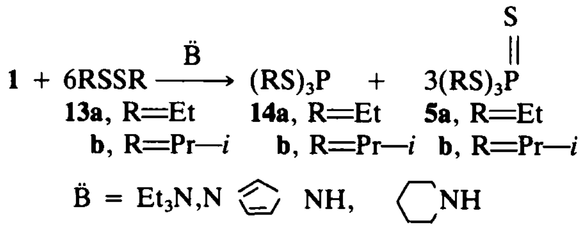


$$\begin{array}{llll} \mathbf{1} + Et_2NSR & \rightarrow (Et_2N)_2\overset{\overset{S}{\|}}{P}SR & + \ Et_2N\overset{\overset{S}{\|}}{P}(SR)_2 & \\ \quad \mathbf{10a}, R{=}Et & \quad \mathbf{11a}, R{=}Et & \quad \mathbf{12a}, R{=}Et & \\ \quad \mathbf{b}, R{=}Pr{-}i & \quad \mathbf{b}, R{=}Pr{-}i & \quad \mathbf{b}, R{=}Pr{-}i & \end{array} \qquad (4)$$

Thionophosphate esters **11a**,**b** and **12a**,**b** are liquid mixtures which are difficult to separate by distillation. Individual substances **11a**,**b** and **12a**,**b** were isolated by column chromatography. Weak intensity signals in the range of δ 106–115 ppm were also observed in ^{31}P NMR spectra of reaction mixtures and low boiling distillation fractions. They may be attributed to products of amidophosphite structure.

All the reactions studied proceed at high temperatures (130–200°C) and are accompanied by considerable polymerization. In order to decrease the reaction temperatures we searched for catalysts for these transformations. Organic amines have proved the most effective catalysts of the reactions of phosphorus sesquisulfide with thioacetals **2**, aminals **8** and sulfenamides **10**. Primary, secondary and tertiary amines of different structure and basicity were used. Thus the reaction of phosphorus sulfide **1** with thioacetal **2a** proceeds at 130–140°C in the presence of 20% of triethylamine, diethylamine, pyridine or imidazole. However, the formation of thionophosphonate esters **9** occurred already at 85–110°C in the interaction of tetraphosphorus trisulfide **1** with aminals **8a**,**b** in the presence of 30% of imidazole or triethylamine. Twenty per cent of pyridine or 30% of piperidine when used in the interactions of phosphorus sulfide **1** with sulfenamides **10a**,**b** in flasks stirred at 85°C made it possible to obtain mixtures of thiophosphate esters **11a**,**b** and **12a**,**b**. The latter reaction is also influenced by imidazole, triethylamine and diethylamine.

Phosphorus sesquisulfide is known to be photochemically oxidized by organic disulfides under UV irradiation to give trithiophosphite esters and tetrathiophosphate esters.[11,12] Considering the fact that the reaction of tetraphosphorus trisulfide with organic substances can be catalyzed by amines we extended this technique to the reactions of phosphorus sulfide **1** with disulfides too. Thus the addition of 20% of triethylamine, 27% of imidazole or up to 50% of piperidine made it possible to carry out the reactions of tetraphosphorus trisulfide **1** with dialkyl disulfides **13a**,**b** at 85°C both in sealed tubes and in the flasks with stirring (Equation 5).



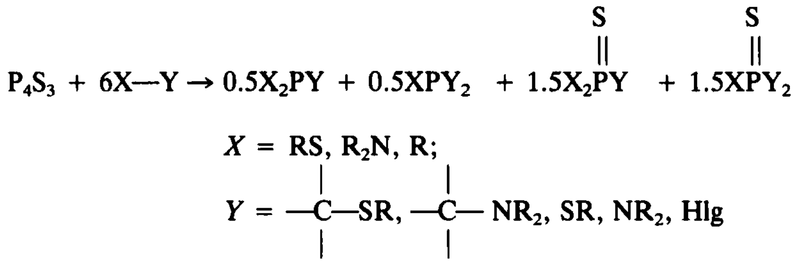
$$\begin{array}{llll} \mathbf{1} + 6RSSR & \xrightarrow{\ddot{B}} (RS)_3P & + \ 3(RS)_3\overset{\overset{S}{\|}}{P} & \\ \quad \mathbf{13a}, R{=}Et & \quad \mathbf{14a}, R{=}Et & \quad \mathbf{5a}, R{=}Et & \\ \quad \mathbf{b}, R{=}Pr{-}i & \quad \mathbf{b}, R{=}Pr{-}i & \quad \mathbf{b}, R{=}Pr{-}i & \end{array} \qquad (5)$$

$\ddot{B}$ = Et_3N, N⬠NH, ⬡NH

Taking into account the fact that the reaction of tetraphosphorus trisulfide with disulfides proceeds under free radical[11,12] conditions with UV irradiation, we have assumed that this reaction can be carried out when exposed to other radical initiators as well.

Actually we have shown that phosphorus sulfide **1** reacts with disulfides **13a** in the presence of 7.6% of benzoyl peroxide at the temperature of decomposition of the latter (100–110°C). The influence of organic peroxides on the reactions described is of a rather general character. Thus benzoyl peroxide in the amount of 8–12% initiates the reactions of the phosphorus sesquisulfide **1** with aminals **8a** and sulfenamide **10a** at 100–110°C.

Thus on the basis of the results of the reactions of tetraphosphorus trisulfide with thioacetals, $RS{-}\overset{|}{\underset{|}{C}}{-}SR$, aminals, $R_2N{-}\overset{|}{\underset{|}{C}}{-}NR_2$, disulfides, $RS{-}SR$, sulfenamides, $RS{-}NR_2$, as well as with alkyl and aryl halides, $R{-}Hlg$[6-8] and sulfenyl halides, $RS{-}Hlg$,[13] a general scheme of these transformations can be conceived (Equation 6).

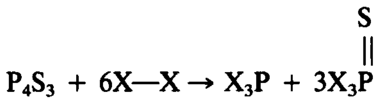


$$P_4S_3 + 6X{-}Y \rightarrow 0.5X_2PY + 0.5XPY_2 + 1.5X_2\overset{\overset{S}{\|}}{P}Y + 1.5X\overset{\overset{S}{\|}}{P}Y_2 \qquad (6)$$

$$X = RS, R_2N, R;$$

$$Y = {-}\overset{|}{\underset{|}{C}}{-}SR, {-}\overset{|}{\underset{|}{C}}{-}NR_2, SR, NR_2, Hlg$$

When $X \neq Y$ the formation of four types of organophosphorus compounds with trivalent and pentavalent phosphorus atoms is most likely. When $X = Y$ the reactions resolve into two types of products as in the case of disulfides (Equation 7).



$$P_4S_3 + 6X{-}X \rightarrow X_3P + 3X_3\overset{\overset{S}{\|}}{P} \qquad (7)$$

However, even when $X \neq Y$ the reactions have resulted mainly in the formation of two or three organothiophosphorus compounds; this appears to be connected with the sulfurization of trivalent phosphorus products under the reaction conditions.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker WM 250 or non-serial NMR KGU-4 (10.2 MHz) spectrometers relative to external H_3PO_4 (85%). ^1H NMR spectra were run on Varian T-60 spectrometer (60 MHz) in CCl_4 using TMS as an internal reference. IR spectra were obtained in KBr with a UR-20 infrared spectrophotometer. Masses of compounds **3a** and **4a,b** were defined from electron impact mass spectra on a MKH-1310 instrument (70 eV). Masses $[M + H]^+$ of products **9b,11b** and **12a,b** were determined on the basis of their chemical ionization mass spectra using a Finnigan MAT 212 spectrometer. Column chromatography was performed on Al_2O_3 consequently eluted with solvents.

Physical constants of novel and known compounds are presented at first description. At the following descriptions their constants corresponded to the ones mentioned above.

Reaction of Tetraphosphorus Trisulfide **1** *with Phenylbis(ethylthio)methane* **2a**. The mixture of **1** (5.4 g, 24.5 mmol) and **2a** (31.2 g, 147.2 mmol) was heated (bath temperature 200°C) in a sealed tube for 12 h. The crystals which separated were recrystallized from benzene to recover tetraphosphorus trisulfide **1** (0.36 g, 6.7%, m.p. 169–171°C (Lit.:[1] m.p. 171°C)). Repeated distillations of the filtrate gave S,S′-diethyl-1-(ethylthio)benzyl trithiophosphonate **3a** (5.5 g, 44.4%) b.p. 130–150°C (0.002 mmHg), n_D^{20} 1.6315, ^{31}P NMR δ 94 ppm; Found: $M^{+\cdot}$ 336.02707. $C_{13}H_{21}PS_4$. Calc.: M. Wt. 336.02638 (Lit.:[18] b.p. 225°C (0.007 mmHg, n_D^{20} 1.6305, ^{31}P NMR δ 94 ppm)). *S*-(1-Ethylthiobenzyl)-1-(ethylthio)benzyl ethyldithiophosphonate **4a** (4.9 g), diethyl sulfide **7a** of 2.2 g, b.p. 92–92.5°C, n_D^{20} 1.4437 (Lit.:[20] b.p. 92.1°C, n_D^{20} 1.4430), ethyl benzylsulfide **6a** (2.0 g, b.p. 98–99°C (10 mmHg, n_D^{20} 1.5518 (Lit.:[21] b.p. 97°C (10 mmHg, n_D^{20} 1.5513)) and triethyl tetrathiophosphate **5a** (1.7 g, b.p. 160°C (10 mmHg, n_D^{20} 1.6207, ^{31}P NMR δ 92 ppm (Lit.:[22] b.p. 124–125°C (1.5 mmHg, n_D^{20} 1.6201, ^{31}P NMR δ 91.7 ppm) were also obtained.

Reaction of Tetraphosphorus Trisulfide **1** *with Phenylbis(i-propylthio)methane* **2b**. (*a*) The mixture of **1** (0.8 g, 3.6 mmol) and **2b** (5.2 g, 21.7 mmol) was heated at 200°C in a sealed tube for 2.5 h. The mixture was filtered. Tetraphosphorus trisulfide 1[1] (0.2 g, 25.0%) was recovered. The filtrate was chromatographed (3:1.6:1 *n*-hexane-benzene-CCl_4) and yielded S,S′-diipropyl-1-(*i*-propylthio)benzyl trithiophosphonate **3b** (0.6 g) and *S*-(1-*i*-propylthiobenzyl)-1-(*i*-propylthio)benzyl *i*-propyldithiophosphinate **4b** (1.9 g). The following distillation of chromatographic fractions (R_f 0.79–0.91) resulted in *i*-propyl benzylsulfide **6b** (0.6 g, b.p. 104–106°C (10 mmHg, n_D^{20} 1.5428), phenylbis(*i*-propylthio)methane **2b** (0.8 g, 15.4%, b.p. 138–139°C (0.02 mmHg, n_D^{20} 1.5515) and tri-*i*-propyl tetrathiophosphate **5b** (0.5 g, b.p. 124°C (0.02 mmHg, n_D^{20} 1.5653, ^{31}P NMR δ 86.5 ppm (Lit.:[22] b.p. 123–125°C (0.3 mm)).

(*b*) *In the presence of amines.* The mixtures of **1** (0.2 g, 0.9 mmol) and **2b** (1.3 g, 5.4 mmol) in the presence of triethylamine (0.03 g, 0.3 mmol, 20.0%) or diethylamine (0.01 g, 0.4 mmol, 20.0%), or pyridine (0.02 g, 0.4 mmol, 20.0%), or imidazole (0.01 g, 0.1 mmol, 20.0%) were heated in sealed tubes for 12 h at 130–140°C. The signals with δ 92 and 85 ppm were observed in the ^{31}P NMR spectra and corresponded to thionophosphonate **3b** and thionophosphinate **4b** respectively.

Reaction of Tetraphosphorus Trisulfide **1** *with Bis(diethylamino)methane* **8b**. (*a*) The mixture of **1** (6.5 g, 29.5 mmol) and **8b** (30.2 g, 206.9 mmol) was heated in a sealed tube at 140°C for 5 h. The mixture was filtered. A non-identified powder (1.2 g) was obtained. *N*,*N*′-Tetraethyl-1-*N*″-(diethylamino)methyl diamidothionophosphonate **9b** (4.6 g) was isolated from the filtrate by means of a vacuum evaporator (temperature of spiral of thermoelement was 110–120°C (0.03 mmHg). Tetraphosphorus trisulfide **1**[1] (0.7 g, 10.8%) and bis(diethylamino)methane **8b** (3.4 g, 11.3%, b.p. 62–63°C (18 mm), n_D^{20} 1.4246) were recovered as well.

(*b*) *In the presence of imidazole*. Similarly **1** (6.0 g, 27.3 mmol), **8b** (27.9 g, 191.1 mmol) and imidazole (0.57 g, 8.4 mmol, 30.0%) (reaction conditions: 85°C, 13 h) yielded thionophosphonate **9b** (5.4 g, 45.0%) and a non-identified powder (1.5 g). Bis(diethylamino)methane **8b** (2.9 g, 10.4%) was recovered.

(*c*) *In the presence of benzoyl peroxide*. The mixture of **1** (6.0 g, 27.3 mmol), **8b** (23.9 g, 163.7 mmol) and benzoyl peroxide (0.5 g, 2.1 mmol, 7.6%) was heated in a sealed tube for 28 h at 100–110°C. Thionophosphonate **9b** (5.3 g, 44.2%) was obtained. Tetraphosphorus trisulfide **1**[1] (0.5 g, 8.3%) and **8b** (8.1 g, 33.9%) were recovered.

Reaction of Tetraphosphorus Trisulfide **1** *with Bis(dimethylamino)methane* **8a**. (*a*) Similarly to the preparation of compound **9b** (item *a*) **1** (6.3 g, 28.6 mmol) and **8a** (20.4 g, 199.7 mmol) (reaction conditions: 130°C, 4 h) gave *N*,*N*′-tetramethyl-1-*N*″-(dimethylamino)methyl diamidothionophosphonate **9a** (5.5 g) b.p. 70–90°C (0.03 mmHg). Bis(dimethylamino)methane **8a** (5.4 g, 26.5%, b.p. 82–84°C, n_D^{20} 1.4018 (Lit.:[23] b.p. 82–84°C)) was recovered.

(*b*) *In the presence of triethylamine*. Similarly **1** (6.0 g, 27.3 mmol), **8a** (13.6 g, 133.2 mmol) and triethylamine (0.56 g, 5.6 mmol, 20.0%) (reaction conditions: 110°C, 6 h) yielded phosphonate **9a** (5.2 g, 60.5%).

Reaction of Tetraphosphorus Trisulfide **1** *with Ethylsulfendiethylamide* **10a**. (*a*) The mixture of **1** (6.4 g, 29.1 mmol) and **10a** (11.6 g, 87.2 mmol) was heated in a sealed tube at 175°C for 4 h. The mixture was filtered. The filtrate was distilled. The fraction (9.4 g, b.p. 88–96°C (0.05 mmHg, n_D^{20} 1.5480, ^{31}P NMR δ 94.1 and 93.8 ppm) was chromatographed (1:1 pet. ether-benzene) and gave *S*-ethyl-*N*,*N*′-bis(diethylamido) dithiophosphate **11a** (0.71 g) and *S*,*S*′-diethyl-*N*-diethylamido trithiophosphate **12a** (0.94 g). Tetraphosphorus trisulfide **1**[1] (3.0 g, 46.9%) and **10a** (0.7 g, 6.0%, b.p. 63°C (57 mmHg), n_D^{20} 1.4522 (Lit.:[24] b.p. 61°C (38 mmHg, n_D^{26} 1.4500)) were recovered.

(*b*) *In the presence of pyridine*. The mixture of **1** (6.0 g, 27.3 mmol), **10a** (10.9 g, 82.0 mmol) and pyridine (0.43 g, 5.4 mmol, 20.0%) was stirred for 13 h at 85°C. The mixture was filtered. The filtrate was distilled. A mixture (5.0 g) of thionophosphates **11a** and **12a** (b.p. 93–114°C, (0.06 mmHg, n_D^{20} 1.5655, ^{31}P NMR δ 94.1 and 93.8 ppm) was obtained. Tetraphosphorus trisulfide **1'** (2.5 g, 41.7%) was recovered.

Reaction of Tetraphosphorus Trisulfide **1** *with i-Propylsulfendiethylamide* **10b**. (*a*) Similarly to the reaction of sulfenamide **10a** (item *a*) **1** (7.4 g, 33.6 mmol) and **10b** (39.6 g, 269.2 mmol) (reaction conditions: 175°C, 8 h) yielded a fraction (9.4 g), b.p. 80–113°C (0.05 mmHg), ^{31}P NMR δ 94 and 93 ppm. This fraction was chromatographed (1.6:1 *n*-hexane-benzene) and gave *S*-*i*-propyl-*N*,*N'*-bis(diethylamido) dithiophosphate **11b** (1.2 g) and *S*,*S'*-di-*i*-propyl-*N*-diethylamido trithiophosphate **12b** (0.8 g). Tetraphosphorus trisulfide **1'** (4.7 g, 63.5%) was recovered.

(*b*) *In the presence of piperidine*. Similarly to the reaction of sulfenamide **10a** (item *b*) **1** (6.0 g, 27.3 mmol), **10b** (12.0 g, 81.6 mmol) and piperidine (0.69 g, 8,1 mmol, 30.0%) gave a mixture of thionophosphates **11b** and **12b** (3.0 g, b.p. 95–97°C (0.02 mmHg, n_D^{20} 1.5498, ^{31}P NMR δ 94 and 93 ppm). Tetraphosphorus trisulfide **1'** (3.0 g, 50.0%) was recovered.

(*c*) *In the presence of benzoyl peroxide*. The mixture of **1** (3.8 g, 17.3 mmol), **10b** (15.2 g, 103.4 mmol) and benzoyl peroxide (0.5 g, 2.1 mmol, 11.9%) was stirred for 23 h at 110°C. A mixture of thionophosphates **11b** and **12b** (5.1 g, b.p. 90–116°C (0.03 mmHg, n_D^{20} 1.5607, ^{31}P NMR δ 94 and 93 ppm) was obtained. Tetraphosphorus trisulfide **1'** (1.2 g, 31.6%) was recovered.

Reaction of Tetraphosphorus Trisulfide **1** *with Diethyl Disulfide* **13a**. (*a*) *In the presence of imidazole*. The mixture of **1** (6.0 g, 27.3 mmol), **13a** (20.0 g, 163.6 mmol) and imidazole (0.5 g, 7.4 mmol, 26.9%) was stirred for 20 h at 85°C. Triethyl tetrathiophosphate **5a**[22] (10.3 g, 51.2%) and triethyl trithiophosphite **14a** (0.5 g, 8.6%, b.p. 77–78.5°C (0.06 mmHg), n_D^{20} 1.5750, ^{31}P NMR δ 115 ppm (Lit.:[25] b.p. 140–143°C (18 mmHg),[19] ^{31}P NMR δ 116.6 ppm)) were obtained. Tetraphosphorus trisulfide **1'** (0.9 g, 15.0%) and diethyl disulfide **13a** (8.6 g, 43.0%, b.p. 38–39°C (10 mmHg), n_D^{20} 1.5075 (Lit.:[20] b.p. 40°C (10 mmHg), n_D^{20} 1.5073)) were recovered.

(*b*) *In the presence of triethylamine*. The mixture of **1** (5.0 g, 22.7 mmol), **13a** (16.7 g, 136.6 mmol) and triethylamine (0.46 g, 4.5 mmol, 20.0%) was heated in a sealed tube for 20 h at 85°C. Triethyl tetrathiophosphate **5a**[22] (3.6 g, 21.4%) and triethyl trithiophosphite **14a**[25,19] (1.2 g, 24.5%) were isolated. Tetraphosphorus trisulfide **1'** (2.1 g, 42.0%) and diethyl disulfide **13a**[20] (3.5 g, 21.0%) were recovered.

(*c*) *In the presence of benzoyl peroxide*. The mixture of **1** (6.0 g, 27.3 mmol), **13a** (20.0 g, 163.7 mmol) and benzoyl peroxide (0.5 g, 2.1 mmol, 7.6%) was heated in a sealed tube for 29 h at 100–115°C. Triethyl tetrathiophosphate **5a**[22] (9.7 g, 48.3%) and triethyl trithiophosphite **14a**[25,19] (2.6 g, 44.8%) were obtained. Tetraphosphorus trisulfide **1'** (0.9 g, 15.0%) and diethyl disulfide **13a**[20] (4.4 g, 22.0%) were recovered.

Reaction of Tetraphosphorus Trisulfide **1** *with Di-i-propyl Disulfide* **13b**. (*a*) *In the presence of triethylamine*. Similarly to the reaction of disulfide **13a** (item *a*) **1** (6.0 g, 27.3 mmol), **13b** (24.6 g, 163.3 mmol) and triethylamine (0.55 g, 5.4 mmol, 20.0%) (reaction conditions: 85°C, 28 h) gave tri-*i*-propyl tetrathiophosphate **5b**[22] (3.0 g, 12.7%). Tetraphosphorus trisulfide **1'** (2.0 g, 33.3%) and di-*i*-propyl disulfide **13b** (8.5 g, 34.6%, b.p. 56–57°C (10 mmHg, n_D^{20} 1.4922 (Lit.:[20] 56.8°C (10 mmHg, n_D^{20} 1.4916)) were recovered.

(*b*) *In the presence of piperidine*. Similarly to the reaction of disulfide **13a** (item *b*) 1 (6.0 g, 27.3 mmol), **13b** (24.6 g, 163.7 mmol) and piperidine (1.16 g, 13.6 mmol, 50.0%) (reaction conditions: 85°C, 42 h) yielded tri-*i*-propyl tetrathiophosphate **5b**[22] (4.2 g, 17.8%). Tetraphosphorus trisulfide **1'** (2.0 g, 33.3%) and di-*i*-propyl disulfide **13b**[20] (7.3 g, 29.7%) were recovered.

REFERENCES

1. E. J. Griffith and M. Grayson, *Topics in Phosphorus Chemistry* (John Wiley and Sons, Inc., New York; London; Sydney; Toronto, 1976), Vol. 8, pp. 193–271.
2. W. N. Moulton and C. G. Wade, *J. Org. Chem.*, **26**, 2528 (1961).
3. K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, **25**, 683 (1963).
4. E. Fluck and H. Binder, *Z. Anorg. Allg. Chem.*, **359**, 102 (1968).
5. M. Becke-Goehring and H. Hoffman, *Z. Anorg. Allg. Chem.*, **369**, 73 (1969).
6. V. K. Unterberger, M. N. Yurlova, P. S. Khokhlov, L. I. Markova, O. V. Klimov, Z. W. Kvasha, L. D. Protasova, Yu. N. Fadeev, N. K. Blisnyuk et al., *Ger. Offen. Pat.*, **2,** 063, 182 (1970); C.A., **77,** 126839p (1972).
7. A. D. F. Toy and E. H. Uhing, *US Pat.*, **4,** 076, 746 (1974).
8. I. V. Murav'yov and R. R. Myshko, *Vestn. L'vov. Univ. Ser., Khim.*, 63 (1985).
9. L. Malatesta, *Gazz. Chim. Ital.*, **77,** 509 (1947); C.A., **42,** 5413i (1948).

10. E. H. Uhing and A. D. F. Toy, *US Pat.*, **4,** 130, 583 (1978); C.A., **90,** 152352n (1979).
11. F. H. Musa, B. W. Tattershall and W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1517 (1984).
12. B. W. Tattershall, *J. Chem. Soc., Dalton Trans.*, 1707 (1985).
13. G. H. Birum, *US Pat.*, **2,** 836, 534 (1958); C.A., **52,** 20056a (1958).
14. E. Fluck, G. Gonzalez, K. Peters and H.-G. Schnering, *Z. Anorg. Allg. Chem.*, **473,** 51 (1981).
15. R. Adams, *Organic Reactions* (John Wiley and Sons, Inc., 1951), Vol. 6.
16. M. R. Le Geyt and N. L. Paddock, *Can. Sulfur Symp.*, **B,** 1974 (Univ. Calgary, Dep. Chem.: Calgary, Canada); C.A., **82,** 67592f (1975).
17. V. K. Khairullin and M. A. Vasyanina, *US Pat.*, **3,** 933, 856 (1976); C.A., **84,** 164 597k (1976).
18. V. A. Al'fonsov, I. S. Nizamov, S. A. Katzyuba, E. S. Batyeva and A. N. Pudovik, *Zh. Obshch. Khim.*, **58,** 1273 (1988).
19. M. Grayson and E. J. Griffith, *Topics in Phosphorus Chemistry*; *P^{31} Nuclear Magnetic Resonance* (John Wiley, New York, 1967), Vol. 5, p. 492.
20. A. A. Potekhin, *Svoistva Organicheskikh Soedineniy. Spravochnik* (Khimiya, Leningrad, 1984), p. 520.
21. R. D. Obolentzev and N. G. Marina, *Khimiya Seraorganicheskikh Soedineniy, Soderzhashchikhsya v Neftyakh i Nefteproduktakh* (Vysshaya Shkola, Moskva, 1970), Vol. 8, pp. 103–107.
22. G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compounds* (John Wiley and Sons, Inc., New York; London; Sydney; Toronto, 1976), Vol. 7, p. 791.
23. J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22,** 355 (1957).
24. R. J. Major and L. H. Peterson, *J. Am. Chem. Soc.*, **78,** 6181 (1956).
25. A. Lippert and E. E. Reid, *J. Am. Chem. Soc.*, **60,** 2370 (1938).