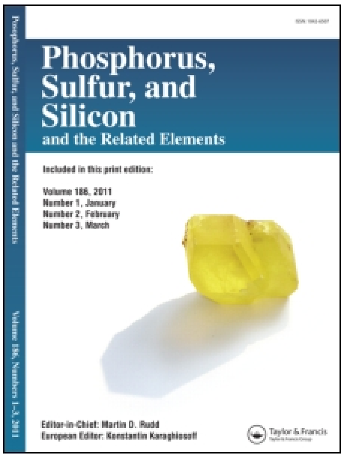

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REACTIONS OF PHOSPHORUS SULFIDES (P_4S_5, P_4S_7 AND P_4S_{10}) AND 2,4-BIS(ALKYLTHIO)-2,4-DITHIOXO-1,3,2λ^5,4λ^5-DITHIADIPHOSPHETANES WITH DIALKYLDISULFIDES AND THIOACETALS IN THE PRESENCE OF IODINE

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REACTIONS OF PHOSPHORUS SULFIDES (P_4S_5, P_4S_7 AND P_4S_{10}) AND 2,4-BIS(ALKYLTHIO)-2,4-DITHIOXO-1,3,2λ^5,4λ^5-DITHIADIPHOSPHETANES WITH DIALKYLDISULFIDES AND THIOACETALS IN THE PRESENCE OF IODINE

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The reactions of P_4S_5 and P_4S_7 with dialkyl disulfides and thioacetals were studied. The use of iodine results in the reactivity enhancement of P_4S_5, P_4S_7, P_4S_{10}, homologues of Davy's reagent, and red phosphorus in the presence of elemental sulfur in the reactions with disulfides and thioacetals.

Key words: Phosphorus sulfides, 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes, red phosphorus, elemental sulfur, disulfides, thioacetals, organothiophosphorus compounds.

INTRODUCTION

We have previously shown that the reactions of anhydrides of thiophosphorus and thiophosphoric acids such as phosphorus sulfides (P_4S_3 and P_4S_{10}) and 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with dialkyl disulfides and thioacetals result in some novel organothiophosphorus compounds.[1,2,3,4] However, the reactions of lower phosphorus sulfides such as tetraphosphorus pentasulfide, P_4S_5, and tetraphosphorus heptatasulfide, P_4S_7, with the same disulfides and thioacetals remained unknown. It seemed of interest to elucidate what kind of products may be formed.

We have previously developed efficient methods to facilitate the reactions of P_4S_3 with disulfides and thioacetals by involvement of organic amines and benzoyl peroxide,[1] elemental iodine,[5] and of the reactions of P_4S_{10} with disulfides and thioacetals by the use of UV irradiation[2] and ultrasound.[6] In order to increase the reactivity of lower (P_4S_5, P_4S_7) and higher (P_4S_{10}) phosphorus sulfides and the homologues of Davy's reagent and to decrease the reaction temperature of their reactions with disulfides and thioacetals, and for increase of the yields of final organothiophosphorus products we involved crystalline iodine in these interactions. Furthermore the substitution of phosphorous sulfides with a mixture of red phosphorus and elemental sulfur in the reaction with disulfides may result in organothiophosphorus compounds. The last reaction may be also facilitated by iodine.

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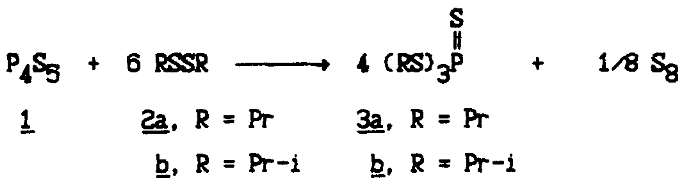
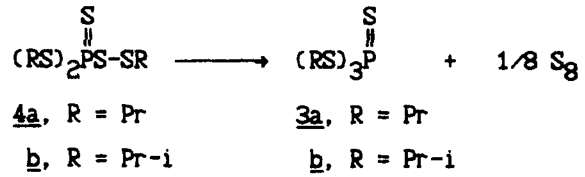
RESULTS AND DISCUSSION

We have found that tetraphosphorus pentasulfide 1 reacts with dialkyl disulfides 2a,b in anhydrous toluene at 50–110°C for 2.5–4 h to form trialkyl tetrathiophosphates 3a,b (Equation (1), and Table I).



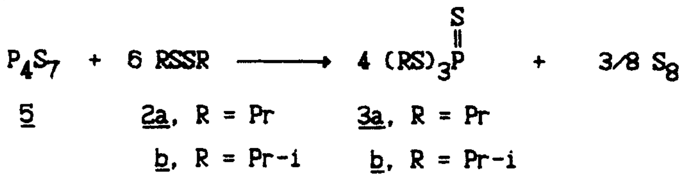
$$\begin{array}{cccccccc} P_4S_5 & + & 6\ RSSR & \longrightarrow & 4\ (RS)_3\overset{S}{\overset{\|}{P}} & + & 1/8\ S_8 & \\ \underline{1} & & \underline{2a},\ R = Pr & & \underline{3a},\ R = Pr & & & \\ & & \underline{b},\ R = Pr\text{-}i & & \underline{b},\ R = Pr\text{-}i & & & \end{array} \qquad (1)$$

However, the yields of tetrathiophosphates 3a,b are not very high (7–24%). It should be noted that the yields of products 3a,b are dependent from the reaction temperature. Thus, the yield of product 3a was only 7% when the reaction of 1 with disulfide 2a was carried out 50–60°C for 5 h, while the yield of tetrathiophosphate 3b is increased to 24% when the reaction of 1 with disulfide 2b proceeds at 110°C for 2.5 h. The products 3a,b were identified by IR, ^{1}H NMR, ^{31}P NMR and mass spectral data, and by comparison of their physical constants with literature data (see Experimental). It should be emphasized that tetrathiophosphates 3 are secondary products which were obtained by the destruction of initial products—S,S′-dialkyl S″,S″-alkyltetrathiolothionophosphates 4 with an S—S bridge bond. These pentathiophosphates 4 were previously obtained in the reaction of P_4S_{10} with dialkyl disulfides.[2] Together with the signals of tetrathiophosphates 3a and 3b at δ_P 91.8 and 86.5[2] ppm, respectively the signals at δ_P 100.0 and 94.8[2] ppm were also observed in the ^{31}P NMR spectra of the crude reaction mixtures of 1 with disulfides 2a and 2b, which may be attributed to pentathiophosphates 4a and 4b,[2] respectively. The chemical ionization mass spectrum of the crude reaction mixture of the reaction of 1 with disulfide 2a shows the mass peak of molecular ion $[M + H]^+$ 331 (62%) of pentathiophosphate 4a. The pentathiophosphates 4a,b are unstable during distillation and tetrathiophosphates 3a,b were isolated in distilled form from the reaction mixture (Equation (2), see Reference 2).



$$\begin{array}{cccccc} (RS)_2\overset{S}{\overset{\|}{P}}S\text{-}SR & \longrightarrow & (RS)_3\overset{S}{\overset{\|}{P}} & + & 1/8\ S_8 & \\ \underline{4a},\ R = Pr & & \underline{3a},\ R = Pr & & & \\ \underline{b},\ R = Pr\text{-}i & & \underline{b},\ R = Pr\text{-}i & & & \end{array} \qquad (2)$$

The formation of the same pentathiophosphates 4 and tetrathiophosphates 3 was observed in the reaction of disulfides 2 with the next member of a series of phosphorus sulfides—tetraphosphorus heptasulfide at 140–160°C for 2.5–3 h (Equation (3), Table I).



$$\begin{array}{cccccccc} P_4S_7 & + & 6\ RSSR & \longrightarrow & 4\ (RS)_3\overset{S}{\overset{\|}{P}} & + & 3/8\ S_8 & \\ \underline{5} & & \underline{2a},\ R = Pr & & \underline{3a},\ R = Pr & & & \\ & & \underline{b},\ R = Pr\text{-}i & & \underline{b},\ R = Pr\text{-}i & & & \end{array} \qquad (3)$$

TABLE I

Experimental data and yields of the products obtained

Initial compounds				Reaction conditions		Yield
				temp., ^{o}C/time, h	solvent	Prod. (%)
1	2a			50-60/5	T^{c}	3a (7^{b})
1	2b			110/2.5	T^{c}	3b (24^{b})
5	2a			150-160/3		3a (91^{a}/47^{b})
5	2b			140-150/2.5		3b (23^{b})
1	2a	I_2		60-70/1	B^{d}	3a (61^{b})
5	2a	I_2		20/1	B^{d}	3a (74^{b})
7	2b			100/1^{e}		3b (10^{b})
7	2a	I_2^{g}		60/4	B^{d}	3a (25^{b})
7	2b	I_2		20/4	B^{d}	3b (27^{b})
8a	2c			90/1.5^{e}		3c (47^{b})
8b	2d			100/1^{e}		3d (42^{b})
8a	2c	I_2		20/7	B^{d}	3c (63^{b})
8b	2d	I_2^{g}		20/6	B^{d}	3d (24^{b})
P_{red}	2d	S_8		120-130/2^{f}		3d (6^{b})
P_{red}	2a	I_2	S_8	60/2	B^{d}	3a (54^{a}/32^{b})
P_{red}	2c	I_2	S_8	60-70/2	B^{d}	3c (23^{b})
PI_3	2a^{g}			60/1	B^{d}	3a (36^{b})
PI_3	2c^{g}			60/1	B^{d}	3c (45^{b})
1	10a			120-130/1	T^{c}	11a (50^{b}); 12a (27^{b})
1	10b			130-140/1	T^{c}	11b (86^{b}); 12b (14^{b})
5	10a			140-150/2.5		11a (41^{b})
5	10b			130-140/3		11b (35^{b}); 12b (14^{b})
1	10a	I_2		60-70/2	B^{d}	11a (53^{b})
5	10b	I_2		60-70/2	B^{d}	11b (37^{b})
14	10a			100/3^{e}		15a (86^{b}); 16a (8^{b})
14	10a	I_2^{g}		50-60/3	B^{d}	15a (84^{b})
14	10b	I_2^{g}		50-60/3	B^{d}	15b (71^{a}/56^{b})

[a] Yield of crude product.

[b] Yield of isolated product.

[c] Toluene.

[d] Benzene.

[e] See reference 2.

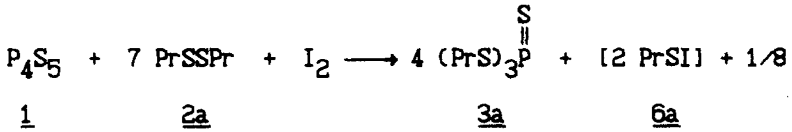
[f] See reference 10.

[g] With washing with an aqueous solution of sodium thiosulfate.

The initial formation of pentathiophosphates 4a,b in this case (Equation (3)) was also confirmed by the ^{31}P NMR spectra of the crude reaction mixtures indicating the signals at δ_P 100.0 and 94.8 ppm which correspond to pentathiophosphates 4a and 4b, respectively.

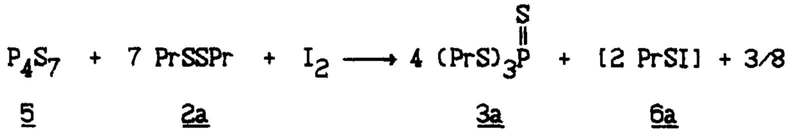
Thus, on the basis of the results of the reactions of dialkyl disulfides 2 with P_4S_3 (reaction conditions: 180–200°C, 4 h),[5] P_4S_5, P_4S_7, and P_4S_{10} (reaction conditions: 100–110°C, 1 h)[2] a series of reactivity of the phosphorus sulfides towards disulfides in the absence of any additives can be conceived: $P_4S_3 < P_4S_5 \sim P_4S_7 < P_4S_{10}$, i.e. the reactivity of phosphorus sulfides increases in accordance with the increase of the amount of the sulfur atoms in a molecule of phosphorus sulfide. In general, the reactivity of phosphorus sulfides is determined by their solubilities in liquid organic reagents or in organic solvent.[7]

Thus, the reactions of P_4S_5 and P_4S_7 with disulfides 2 proceed under severe conditions (100–160°C). However when an equimolar amount of elemental iodine was present the formation of tetrathiophosphate 3a occurred already at 60–70°C for 1 h in the reaction of P_4S_5 1 with disulfide 2a in anhydrous benzene (Equation (4), Table I).



$$\underset{\underline{1}}{P_4S_5} + 7\,\underset{\underline{2a}}{PrSSPr} + I_2 \longrightarrow 4\,\underset{\underline{3a}}{(PrS)_3\overset{S}{\overset{\|}{P}}} + [2\,\underset{\underline{6a}}{PrSI}] + 1/8\,S_8 \qquad (4)$$

Use of iodine in the reaction of P_4S_5 1 with disulfide 2a (Equation (4)) leads to significant improvement in yield of tetrathiophosphate 3a (61%, Table I). The similar increased yield of product 3a (74%) was obtained when the reaction of P_4S_7 5 with disulfide 2a was carried out in the presence of an equimolecular amount of elemental iodine (20°C, 1 h, benzene) (Equation (5), Table I).

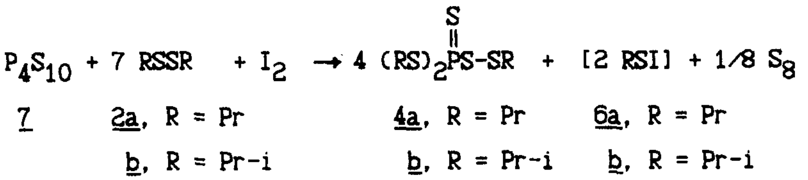


$$\underset{\underline{5}}{P_4S_7} + 7\,\underset{\underline{2a}}{PrSSPr} + I_2 \longrightarrow 4\,\underset{\underline{3a}}{(PrS)_3\overset{S}{\overset{\|}{P}}} + [2\,\underset{\underline{6a}}{PrSI}] + 3/8\,S_8 \qquad (5)$$

These reactions (Equations (4) and (5)) proceed via intermediate formation of pentathiophosphate 4a (δ_P (C_6H_6) 101.3 ppm). The formation of propylsulfenyl iodide 6a was confirmed by the chemical ionization mass spectral analysis of these reaction mixtures (Equations (4) and (5)) indicating the mass peak m/e 203 which corresponds to molecular ion $[PrSI + H]^+$ (40%). However, sulfenyl iodide 6a was not isolated as it decomposes under the reaction conditions.[8]

We have tried to find the range of application of this effective technique and extended it to higher phosphorus sulfides, homologues of Davy's reagent and the mixture of elemental phosphorus and sulfur with organic reagents.

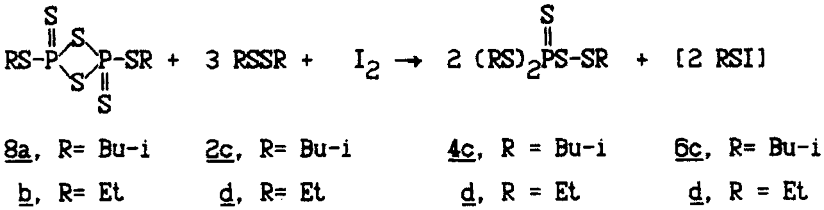
Use of iodine in the reaction of P_4S_{10} 7 with disulfides 2a,b (Equation (6)) leads to formation of pentathiophosphates 4a,b at 20–60°C and to increased yields of tetrathiophosphates 3a,b (25–27%) compared with 10% yield of 3b in the traditional technique[2] (Table I). The intermediate formation of sulfenyl iodides 6a,b was also observed in the chemical ionization mass spectra of the reaction mixture (m/e 203 [PrSI + H]$^+$ (60–88%).



$$P_4S_{10} + 7\ RSSR + I_2 \rightarrow 4\ (RS)_2\overset{S}{\overset{\|}{P}}S\text{-}SR + [2\ RSI] + 1/8\ S_8 \qquad (6)$$

7 2a, R = Pr
b, R = Pr-i
4a, R = Pr
b, R = Pr-i
6a, R = Pr
b, R = Pr-i

Pentathiophosphates 4 were also formed in the reaction of 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes 8a,b with disulfides 2 at 90–100°C for 1–1.5 h[2] whereas the iodine technique gave a decrease of the reaction temperature (to 20°C) and the yield of tetrathiophosphate 3c was increased by up to 63% (Equation (7), Table I).



(7)

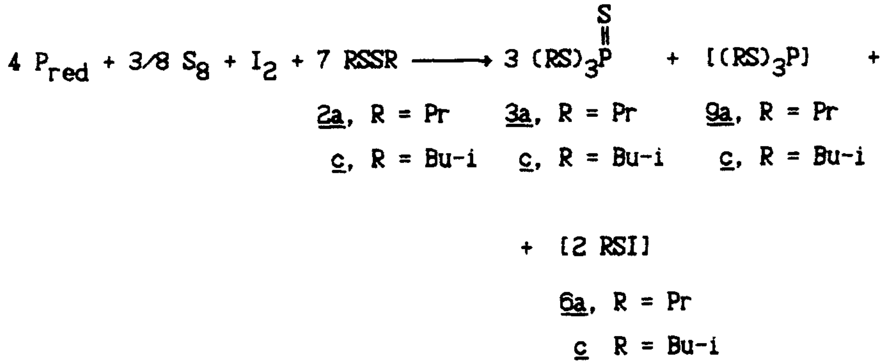
8a, R= Bu-i
b, R= Et
2c, R= Bu-i
d, R= Et
4c, R = Bu-i
d, R = Et
6c, R= Bu-i
d, R = Et

It should be noted that the course of the reactions studied of P_4S_5, P_4S_7, P_4S_{10} and dithiadiphosphetanes 8a,b with disulfides 2a–d in the presence of iodine (Equations (4)–(7)) does not depend upon the sequence of mixing of the reagents (see Experimental).

It indicates that these three component reactions under mild conditions (20–60°C) were started only after involvement of iodine in the reaction mixtures and lead to the thermodynamic stable final tetrathiophosphates 3. Perhaps, these reactions were initiated by the primary interaction of iodine with the phosphorus compounds (P_4S_5, P_4S_7, P_4S_{10} and dithiadiphosphetanes 8).

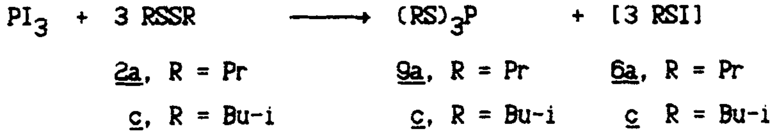
We have previously developed a one-pot synthesis of pentathiophosphate 3d directly from red phosphorus in its reaction with disulfide 2d in the presence of elemental sulfur (reaction conditions: 120–130°C, 5 h).[9]

Involvement of iodine in this reaction (Equation (8)) leads to increased yields of tetrathiophosphates 3a,c and reduction of the reaction temperature (to 60–70°C) (Table I). The ^{31}P NMR spectral control of the course of this reaction (Equation (8)) shows that trithiophosphite 9c (δ_P (C_6H_6) 118.0 ppm) is the only organothiophosphorus compound in the case of disulfide 2c at 20°C. Heating of the reaction mixture at 60–70°C for 2 h leads to a decrease of the intensity of the signal of trithophosphite 9c[5] and the appearance of an intensive signal of tetrathiophosphate 3c (δ_P (C_6H_6) 93.0 ppm).[2] The more reactive dipropyl disulfide 2a (Equation (8)) leads already at 20°C to tetrathiophosphate 3a.



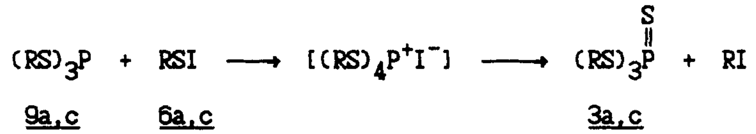
$$4\,P_{red} + 3/8\,S_8 + I_2 + 7\,\underset{\substack{\underline{2a},\ R = Pr\\ \underline{c},\ R = Bu\text{-}i}}{RSSR} \longrightarrow 3\,\underset{\substack{\underline{3a},\ R = Pr\\ \underline{c},\ R = Bu\text{-}i}}{(RS)_3\overset{S}{\overset{\|}{P}}} + \underset{\substack{\underline{9a},\ R = Pr\\ \underline{c},\ R = Bu\text{-}i}}{[(RS)_3P]} + \underset{\substack{\underline{6a},\ R = Pr\\ \underline{c}\ R = Bu\text{-}i}}{[2\,RSI]} \tag{8}$$

We assumed that this four component reaction (Equation (8)) may be started by both 1) initial interaction of iodine with red phosphorus with the formation of phosphorus triiodide, PI_3,[10] or 2) the three component interaction of the elements (phosphorus, sulfur and iodine) with the intermediate formation of β-diiodotetraphosphorus trisulfide, β-$P_3S_3I_2$.[12-14] In the first case the consequent substitution reaction of PI_3 with disulfides 2 may result in the formation of trithiophosphites 9a,c and sulfenyl iodides 6. To corroborate this assumption we carried out a model reaction of PI_3 with disulfides 2a,c (Equation (9)).

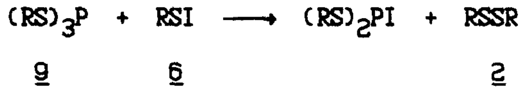


$$PI_3 + 3\,\underset{\substack{\underline{2a},\ R = Pr\\ \underline{c},\ R = Bu\text{-}i}}{RSSR} \longrightarrow \underset{\substack{\underline{9a},\ R = Pr\\ \underline{c},\ R = Bu\text{-}i}}{(RS)_3P} + \underset{\substack{\underline{6a},\ R = Pr\\ \underline{c}\ R = Bu\text{-}i}}{[3\,RSI]} \tag{9}$$

The consequent interaction of trithiophosphites 9 with alkylsulfenyl iodides, intermediates formed under the reaction conditions (Equation (9)), may proceed either via Arbuzov reaction with the formation of tetrathiophosphates 3a,c (Equation (10)) or via substitution reaction with the formation of dialkyliododithiophosphites and disulfides 2a,c (Equation (11)).



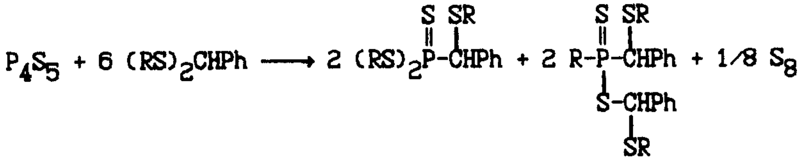
$$\underset{\underline{9a,c}}{(RS)_3P} + \underset{\underline{6a,c}}{RSI} \longrightarrow [(RS)_4P^+I^-] \longrightarrow \underset{\underline{3a,c}}{(RS)_3\overset{S}{\overset{\|}{P}}} + RI \tag{10}$$



$$\underset{\underline{9}}{(RS)_3P} + \underset{\underline{6}}{RSI} \longrightarrow (RS)_2PI + \underset{\underline{2}}{RSSR} \tag{11}$$

The reaction according to Equation (11) may be excluded as we do not observe the signals of dialkyliododithiophosphites in the ^{31}P NMR spectra. On the other hand, we cannot rule out that the reaction of phosphorus, sulfur, iodine and disulfides 2a,c (Equation (8)) proceeds via the intermediate formation of β-$P_3S_3I_2$ and its consequent interaction with disulfides 2a,c (the second possibility). We have previously shown that β-$P_3S_3I_2$ reacts with disulfides 2 to form the same tetrathiophosphates 3 at 20°C.[5]

We carried out the reaction of P_4S_5 1 with thioacetals 10a,b in anhydrous toluene at 120–140°C for 1 h and obtained S,S'-dialkyl-1-(alkylthio)benzyl trithiophosphonates 11a,b and S-(1-alkylthiobenzyl)-1-(alkylthio)benzyl alkyldithiophosphinates 12a,b (Equation (12), Table I) like in the reaction with P_4S_3.[1]



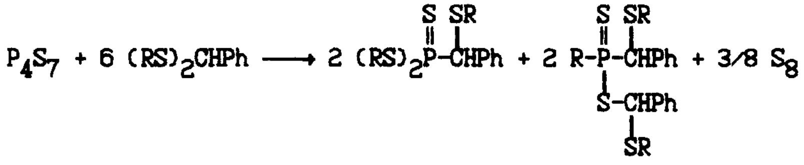
$$P_4S_5 + 6\ (RS)_2CHPh \longrightarrow 2\ (RS)_2\overset{\overset{S}{\|}}{P}-\overset{\overset{SR}{|}}{C}HPh + 2\ R-\underset{\underset{\underset{\underset{SR}{|}}{S-CHPh}}{|}}{\overset{\overset{S}{\|}}{P}}-\overset{\overset{SR}{|}}{C}HPh + 1/8\ S_8 \qquad (12)$$

1 10a, R = Et 11a, R = Et 12a, R = Et

b, R = Pr-i b, R = Pr-i b, R = Pr-i

It is interesting that in this case the reaction (Equation (12)) leads to the formation of thionophosphinates 12a,b and not to the isomeric thiophosphinates 12'a,b (Drawing I); this was established by their ^{31}P and ^{1}H NMR spectra (see Experimental) and comparison of their physical constants with authentic samples of thionophosphinates 12a,b.

The same products 11a,b and 12a,b were also isolated in the reaction of P_4S_7 5 with thioacetals 10a,b at 130–150°C for 2.5–3 h (Equation (13), Table I).



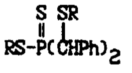
$$P_4S_7 + 6\ (RS)_2CHPh \longrightarrow 2\ (RS)_2\overset{\overset{S}{\|}}{P}-\overset{\overset{SR}{|}}{C}HPh + 2\ R-\underset{\underset{\underset{\underset{SR}{|}}{S-CHPh}}{|}}{\overset{\overset{S}{\|}}{P}}-\overset{\overset{SR}{|}}{C}HPh + 3/8\ S_8 \qquad (13)$$

5 10a, R = Et 11a, R = Et 12a, R = Et

b, R = Pr-i b, R = Pr-i b, R = Pr-i

It is remarkable that the reactivity of phosphorus sulfides [P_4S_3 (reaction conditions: 200°C)[1]; P_4S_5 (120–140°C); P_4S_7 (130–150°C); P_4S_{10} (100°C)[2]] and the homologues of Davy's reagent, DR (20°C)[2] towards thioacetals increases in the series: $P_4S_3 < P_4S_5 \sim P_4S_7 < P_4S_{10} <$ DR like in the reactions with disulfides.

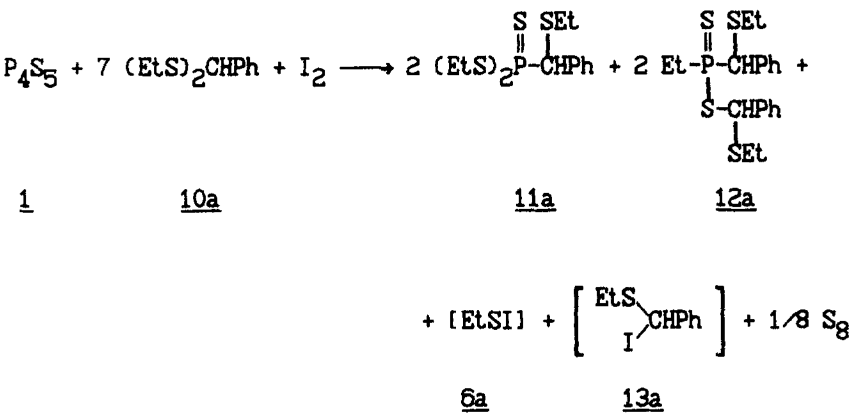
The reaction of P_4S_5 1 with thioacetal 10a and P_4S_7 5 with thioacetal 10b in the presence of an equimolecular amount of elemental iodine occurs in anhydrous benzene at 60–70°C for 2 h (Equations (14) and (15), Table I).



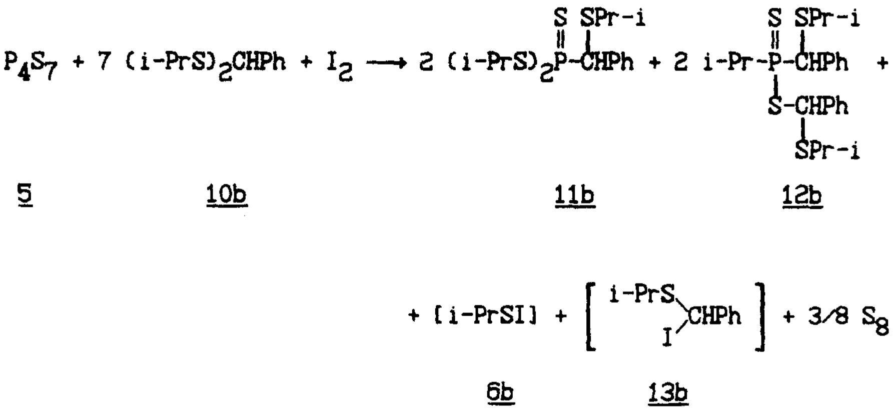
$$RS-\overset{\overset{S}{\|}}{P}(\overset{\overset{SR}{|}}{C}HPh)_2$$

12'a,b

DRAWING I



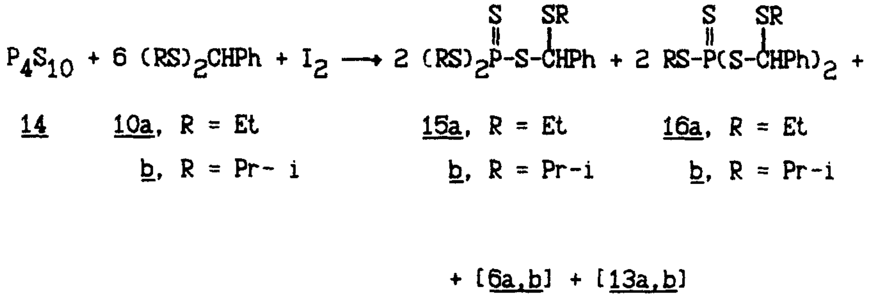
(14)



(15)

Sulfenyl iodides 6a,b and phenyl(alkylthio)methyl iodides 13a,b were not isolated owing to their instability under the reaction conditions (Equations (14) and (15)).

We have also shown that the reaction temperature of the reaction of tetraphosphorus decasulfide, P_4S_{10}, 14 with thioacetals 10a,b which leads to S,S′-dialkyl S″-(1-alkylthio)benzyl tetrathiophosphates 15a,b and S-alkyl S′,S′-bis(1-alkylthiobenzyl) tetrathiophosphates 16a,b is reduced from 100°C (3 h in the traditional method[2]) to 50–60°C (3 h) in the presence of an equimolecular amount of elemental iodine (Equation (16), Table I).



(16)

Thus, the use of iodine has been shown to be an effective means of promoting the reactions of lower and higher phosphorus sulfides and their organic derivatives (homologues of Davy's reagent), and red phosphorus in the presence of sulfur with dialkyl disulfides and thioacetals. The application of elemental iodine in these reactions has resulted in an enhanced chemical reactivity of phosphorus sulfides, reduction in reaction temperature and in most cases increased yields of organothiophosphorus products.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded with a Bruker MSL-400 (162 MHz) spectrometer and a Bruker CXP-100 (36.5 MHz) spectrometer in C_6H_6, reference external H_3PO_4 (85%). The ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4, reference internal $(Me_3Si)_2O$. IR spectra were obtained in a KBr pellet with UR-20 infrared spectrometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were obtained on a M 80 B Hithachi chromato mass spectrometer.

Reaction of Tetraphosphorus Pentasulfide 1 *with Di-i-propyl Disulfide* 2b: *Typical Procedure.* The mixture of 1 (7.3 g, 48.6 mmol) and 2b (2.3 g, 8.1 mmol) in 5 mL of anhydrous toluene was stirred at 110°C for 2.5 h then filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mm Hg) at 40°C for 2 h. Distillation of the residue gave tri-i-propyl tetrathiophosphate 3b (2.2 g, 24%), b.p. 110–112°C (0.06 mm Hg), n_D^{20} 1.5668. The ^{31}P NMR spectrum (C_6H_6) δ_P: 87.0 ppm. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 288 $[M]^+$ (25) (Reference 14: b.p. 123–125°C (0.3 mm Hg); Reference 1: n_D^{20} 1.5653, the ^{31}P NMR spectrum δ_P: 85.5 ppm).

Similarly 1 (2.1 g, 7.4 mmol) and 2a (6.7 g, 44.6 mmol) (reaction conditions: 50–60°C, 5 h, 10 mL toluene) gave distilled tripropyl tetrathiophosphate 3a (0.6 g, 7%), b.p. 124–125°C (0.04 mm Hg), n_D^{20} 1.5892. The ^{31}P NMR spectrum (C_6H_6) δ_P: 91.8 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 289 $[M + H]^+$ (55) (Reference 14: b.p. 131–132°C (0.5 mm Hg), n_D^{20} 1.5885, the ^{31}P NMR spectrum δ_P: 92.5 ppm).

Similarly 5 (1.3 g, 3.7 mmol) and 2a (3.4 g, 22.7 mmol) (reaction conditions: 150–160°C, 3 h, absence of a solvent) gave distilled 3a (2.0 g, 47%).

Similarly 5 (3.6 g, 10.4 mmol) and 2b (9.3 g, 62.0 mmol) (reaction conditions: 140–150°C, 2.5 h, absence of a solvent) gave distilled 3b (2.7 g, 23%).

Reaction of Tetraphosphorus Pentasulfide 1 *with Dipropyl Disulfide* 2a *in the Presence of Iodine: Typical Procedure.* The solution of iodine (1.8 g, 14.2 mg-atom) in 3 mL of anhydrous benzene was added dropwise to a stirred suspension of 1 (2.0 g, 7.0 mmol) in 5 mL of benzene at 20°C. Disulfide 2a (7.4 g, 49.3 mmol) was added dropwise with stirring at 20°C to the mixture. The mixture was stirred at 60–70°C for 1 h then filtered. The filtrate was evaporated under vacuum (10 and 0.03 mm Hg) at 50°C for 2 h. Distillation of the residue gave pure 3a (4.9 g, 61%).

Similarly 5 (2.0 g, 5.8 mmol), 2a (6.0 g, 40.0 mmol) and iodine (1.5 g, 11.8 mg-atom) (reaction conditions: 20°C, 1 h, 7 mL of benzene) gave pure 3a (4.9 g, 74%).

Reaction of Tetraphosphorus Decasulfide 7 *with Dipropyl Disulfide* 2a *in the Presence of Iodine.* Iodine (1.5 g, 11.8 mg-atom) was added portionwise to a stirred solution of 2a (6.4 g, 42.6 mmol) in 10 mL of benzene. Phosphorus sulfide 7 (2.7 g, 6.1 mmol) was added portionwise with stirring at 20°C to the mixture and stirring was continued for 4 h at 60°C. The mixture was filtered. The filtrate was diluted by 30 mL of benzene and washed by a saturated aqueous solution of sodium thiosulfate until the mixture was colourless, and then washed by water. The benzene layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mm Hg). Distillation of the residue gave pure 3a (1.7 g, 25%).

Similarly 7 (3.0 g, 6.8 mmol), 2b (7.1 g, 47.3 mmol) and iodine (1.7 g, 13.4 mg-atom) (reaction conditions: 20°C, 4 h, 10 mL of benzene) gave crude reaction mixture (not washed by a solution of sodium thiosulfate). Distillation of the reaction mixture gave pure 3b (2.1 g, 27%).

Reaction of 2,4-Bis(ethylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane 8b *with Diethyl Disulfide* 2d *in the Presence of Iodine.* Disulfide 2d (7.2 g, 58.9 mmol) was added dropwise to a stirred suspension of 8b (6.1 g, 19.6 mmol) in 10 mL of benzene at 20°C. Iodine (5.0 g, 39.4 mg-atom) was added portionwise with stirring at 20°C to the mixture and stirring was continued for 5 h at 20°C. The mixture was filtered. The filtrate was diluted by 30 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then washed with water. The benzene layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (10 and 0.03 mm Hg) at 50°C for 2 h. Distillation of the residue gave pure 3d (2.3 g, 24%), b.p. 110°C (0.03 mm Hg), n_D^{20} 1.6235. The ^{31}P NMR spectrum (C_6H_6) δ_P: 90.4 ppm. Mass spectrum (electron impact, 70 eV), m/e (I_{rel}, %): 246 $[M]^{+\cdot}$ (33%) (Reference 14: b.p. 124–125°C (1.5 mm Hg), n_D^{20} 1.6201, the ^{31}P NMR spectrum δ_P: 91.7 ppm).

Similarly 8a (3.5 g, 9.5 mmol, 2c (5.1 g, 28.6 mmol) and iodine (2.4 g, 18.9 mg-atom) gave a crude reaction mixture (not washed with a solution of sodium thiosulfate). Distillation of reaction mixture gave pure 3c (4.0 g, 63%), b.p. 130°C (0.03 mm Hg), n_D^{20} 1.5558. The ^{31}P NMR spectrum (C_6H_6) δ_P: 92.9 ppm. (Reference 2: b.p. 136–137°C (0.02 mm Hg), n_D^{20} 1.5549, the ^{31}P NMR spectrum (C_6H_6) δ_P: 92.8 ppm).

Reaction of Red Phosphorus, Sulfur and Dipropyl Disulfide 2a in the Presence of Iodine. Disulfide 2a (16.1 g, 107.3 mmol) was added dropwise to a stirred suspension of red phosphorus (1.9 g, 61.2 mg-atom) and sulfur (1.5 g, 46.2 mg-atom) in 10 mL of benzene. Iodine (3.9 g, 15.4 mg-atom) was added with stirring at 20°C to the mixture obtained. The mixture was stirred at 60°C for 2 h then filtered. The filtrate was diluted by 30 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then washed with water. The benzene layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (10 and 0.02 mm Hg) at 40–50°C for 2 h and gave crude 3a (7.1 g, 54%). Distillation of the residue gave pure 3a (4.2 g, 32%).

Similarly disulfide 2c (15.1 g, 84.8 mmol), red phosphorus (1.5 g, 48.4 mg-atom), sulfur (1.2 g, 37.5 mg-atom) and iodine (3.1 g, 24.4 mg-atom) gave distilled 3c (2.8 g, 23%).

Reaction of Phosphorus Triiodide with Dipropyl Disulfide 2a. Disulfide 2a (10.0 g, 66.6 mmol) was added dropwise to a stirred solution of PI_3 (9.1 g, 22.1 mmol) in 10 mL of benzene at 20°C. The mixture was stirred at 60°C for 1 h. The mixture was diluted with 50 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then water. The benzene layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (10 mm Hg) at 50°C for 2 h. Distillation of the residue gave pure 3a (2.3 g, 36%). The crystalline iodine (6.1 g) which had formed in the aqueous layer was filtered and dried.

Similarly PI_3 (7.7 g, 18.7 mmol) and 2c (10.0 g, 56.1 mmol) gave 3c (2.8 g, 45%).

Reaction of Tetraphosphorus Pentasulfide 1 with Phenylbis(ethylthio)methane 10a. The mixture of 1 (2.0 g, 7.0 mmol) and 10a (9.0 g, 42.5 mmol) in 10 mL of toluene was stirred at 120–130°C for 1 h. The mixture was filtered. The filtrate was evaporated under vacuum (0.1 and 0.02 mm Hg) at 50°C for 2 h. Multiple distillation of the residue on a thin layer distillatiom apparatus gave trithiophosphonate 11a (3.2 g, 50%) at 130°C (0.02 mm Hg), n_D^{20} 1.6323. ^{31}P NMR spectrum (C_6H_6) δ_P: 93.6 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 337 $[M + H]^+$ (10), 247 $[M + H - SEt - Et]^+$ (70) (Reference 1: b.p. 130–150°C (0.002 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6315, ^{31}P NMR spectrum (neat) δ_P: 94 ppm). Dithiophosphinate 12a (1.6 g, 27%) was also isolated, b.p. 200°C (0.02 mm Hg), (thin layer distillation apparatus), n_D^{20} 1.6428. ^{31}P NMR spectrum (C_6H_6) δ_P: 84.3 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 427 $[M + H]^+$ (47) (Reference 1: b.p. 220–225°C (0.002 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6419, the ^{31}P NMR spectrum (neat) δ_P: 85 ppm).

Similarly 1 (3.0 g, 10.6 mmol) and 10b (15.2 g, 63.3 mmol) (reaction conditions: 130–140°C, 1 h, toluene) gave pure trithiophosphonate 11b (6.9 g, 86%), b.p. 150°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6042. ^{31}P NMR spectrum (C_6H_6) δ_P: 93.0 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 379 $[M + H]^+$ (70) (Reference 1: n_D^{20} 1.6031, the ^{31}P NMR spectrum (neat) δ_P: 92 ppm). Dithiophosphinate 12b (1.4 g, 14%) was also isolated, b.p. 200°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6183. ^{31}P NMR spectrum (C_6H_6) δ_P: 85.7 ppm. Mass spectrum (chemical ionization, 100 eV), m/e (I_{rel}, %): 469 $[M + H]^+$ (40) (Reference 1: n_D^{20} 1.6177, the ^{31}P NMR spectrum (neat) δ_P: 85 ppm).

Similarly 5 (3.5 g, 10.1 mmol) and 10a (12.8 g, 60.4 mmol) (reaction conditions: 140–150°C, 2 h, absence of a solvent) gave distilled 11a (2.8 g, 41%).

Similarly 5 (2.6 g, 7.5 mmol) and 10b (8.0 g, 45.0 mmol) (reaction conditions: 130–140°C, 3 h, absence of a solvent) gave distilled 11b (2.0 g, 35%) and 12b (1.0 g, 14%).

Reaction of Tetraphosphorus Pentasulfide 1 with Phenylbis(ethylthio)methane 10a in the Presence of Iodine: Typical Procedure. Iodine (0.7 g, 5.5 mg-atom) was added portionwise to a stirred suspension of 1 (0.8 g, 2.8 mmol) in 10 mL of benzene at 20°C. Thioacetal 10a (4.2 g, 19.8 mmol) was added dropwise with stirring at 20°C to the mixture and stirring was continued for 1 h at 60–70°C. The mixture was filtered. The filtrate was evaporated under vacuum (10 and 0.03 mm Hg) at 50°C for 2 h. Multiple distillation of the residue on a thin layer distillation apparatus gave 11a (1.0 g, 53%).

Similarly 5 (2.0 g, 5.8 mmol), 10b (9.7 g, 40.4 mmol) and iodine (1.5 g, 11.8 mg-atom) gave distilled 11b (1.6 g, 37%).

Reaction of Tetraphosphorus Decasulfide 14 *with Phenylbis(ethylthio)methane* 10a *in the Presence of Iodine.* Phosphorus sulfide 14 (2.6 g, 5.9 mmol) was added portionwise to a stirred solution of 10a (8.7 g, 41.0 mmol) in 10 mL of benzene at 20°C. Iodine (1.5 g, 11.8 mg-atom) was added portionwise with stirring at 20°C to the mixture and stirring was continued for 3 h at 50–60°C. The mixture was filtered. The filtrate was diluted by 50 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then water. The benzene layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (0.1 and 0.02 mm Hg) at 50°C for 2 h. Distillation of the residue on a thin layer distillation apparatus gave tetrathiophosphate 15a (3.6 g, 84%) at 150°C (0.02 mm Hg), n_D^{20} 1.6265. ^{31}P NMR spectrum (C_6H_6) δ_P: 89.6 ppm (Reference 2: b.p. 130–140°C (0.02 mm Hg) (thin layer distillation apparatus), n_D^{20} 1.6258, ^{31}P NMR spectrum (CCl_4) δ_P: 88.4 ppm).

Similarly 14 (2.2 g, 5.0 mmol), 10b (8.3 g, 34.6 mmol) and iodine (1.3 g, 10.3 mg-atom) gave crude tetrathiophosphate 15b (2.9 g, 71%). Distillation of the crude 15b on a thin layer distillation apparatus gave pure 15b (2.3 g, 56%) at 150°C (0.02 mm Hg), n_D^{20} 1.6062. ^{31}P NMR spectrum (C_6H_6) δ_P: 88.1 ppm. ^1H NMR spectrum (CCl_4, δ, ppm, J, Hz): 1.20 (d, 6H, $\underline{CH}_3CHSC$, $^3J_{H-H}$ 7.0); 1.42 (d, 12H, $\underline{CH}_3CHSP$, $^3J_{H-H}$ 7.0); 2.99–3.27 (m, 1H, $CH_3\underline{CH}SCS$); 3.66–4.02 (m, 2H, $CH_3\underline{CH}SP$); 5.33 (d, 1H, $\underline{CH}SP$, $^3J_{P-H}$ 12.0); 6.91–7.29 (m, 5H, $C_6\underline{H}_5$). IR spectrum (ν, cm^{-1}): 3070, 3035 ν (=C—H, Ar); 2970, 2930, 2870 ν (CH_3 as, s; CH_2 as, s); 1608, 1498 ν (C=C, Ar); 1390, 1370 δ [$(CH_3)_2C$ gem s], 1251 ω, τ (CH_2); 705, 693 ν (P=S), ν (PS_2 as); 560, 540 ν (PS_2 s), ν (P—SC). Found, %: C 46.44; H 6.78; P 7.23; S 39.40. $C_{16}H_{27}PS_5$. Calc., %: C 46.82; H 6.64; P 7.55; S 38.98.

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